

Two-dimensional material composites for thermal management and energy storage

IMPERIAL

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I would like to dedicate this thesis to my loving parents.

Declaration

Declaration of Originality

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this or any other university. This dissertation represents my own individual work, carried out from 2020 to 2024 at Imperial College London, except as specified in the text and Acknowledgements. Collaborative work or instances where previously published material is incorporated are duly acknowledged and correctly referenced. This dissertation contains fewer than 50,000 words, including appendices, bibliography, tables and equations and has 102 figures.

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Abstract

Energy transition from fossil fuels to renewable energy sources using energy storage devices is a continuing trend and contributes to global CO₂ reduction. However, existing energy storage technologies suffer from insufficient energy/power densities, energy loss and thermal issues during operation. 2D materials, with their exceptional electrical, thermal, and electrochemical properties, offer promising solutions as dielectric, electrode, and thermal interface materials to enhance energy and power densities and optimise energy efficiency. Despite their potential, the production of 2D materials remains largely confined to laboratory scales, necessitating the development of scalable manufacturing for industrial applications. This work aims to develop scalable processing of 2D materials, specifically h-BN and MXenes, and their composites using liquid phase exfoliation, to develop better energy storage devices. Using h-BN as dielectric additives for capacitors, the dielectric constant can achieve up to 17 compared to other printed nanomaterials (~ 3 -4), which could reduce the risk of devices being short-circuited and improve the device's reliability. To maximise the energy efficiency of devices, h-BN is studied as a thermal filler for thermal interface materials to control device temperatures effectively. The addition of few-layer h-BN into cellulose increases the thermal conductivity of the composites at one order of magnitude higher, reaching $\sim 21.7 \text{ W m}^{-1} \text{ K}^{-1}$ and favouring more efficient heat transfer. Compared to insulating h-BN, MXenes show high electrical conductivity as promising electrode candidates for energy storage devices. Ti₃C₂T_x exhibits a metallic behaviour while Ti₂CT_x reveals a variable range hopping transport mechanism. The addition of electrically conducting Ti₃C₂T_x into the carbon-based electrode materials for supercapacitors enhances the device capacitance by 120 %. Through these investigations, the work demonstrates a foundation for deploying 2D materials in critical applications that can contribute to CO₂ reduction by improving device reliability, energy efficiency and renewable energy storage capabilities.

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Nomenclature

Roman Symbols

F complex function

Greek Symbols

μ electron mobility

ε infrared emissivity

η dynamic viscosity

γ shear rate or surface tension

κ thermal conductivity

λ wavelength

ρ density or resistivity

σ_T Stefan Boltzmann constant

σ_t tensile strength

τ shear stress

θ angle

ε dielectric constant or relative permittivity

α optical absorption coefficient

ω angular velocity

Superscripts

$+$ hydrated ions

Subscripts

0 initial index

buo buoyant

c contact

cen centrifugal

FE	field-effect
fri	frictional
PDT	photothermal deflection technique
p	constant pressure
r	relative
s	sheet
SSM	steady-state measurement
T	temperature
t	real time or tensile

Other Symbols

C	capacitance
C_A	areal capacitance
C_p	specific heat capacity under a constant pressure
C_s	specific capacitance
D	thermal diffusivity
E	Young's modulus
F	force or frequency
G_s	sheet conductance
I	current
n_0	charge carrier concentration
R_s	sheet resistance
V	voltage
$\oint_\gamma$	integration around a curve γ

Acronyms / Abbreviations

We	Weber number
2D	two dimensional
AC	activated carbon
ACC	acid activated carbon
AFM	atomic force microscopy
Ar/H ₂	Argon mixed with 5% hydrogen gas
Ar	Argon gas

BE	binding energy
Bh-BN	bulk h-BN
BNNS	boron nitride nanosheets
<i>c</i> -LP	<i>c</i> -lattice spacing
CCD	charge coupled device
CE	counter electrode
CMC	sodium carboxymethyl cellulose
CNTs	carbon nanotubes
CO ₂	carbon dioxide
CO	carbon oxide
CV	cyclic voltammetry
CVD	chemical vapour deposition
D ₂	deuterium
d-MXene	delaminated MXene
DFT	density functional theory
DI	deionised
DMSO	dimethyl sulphoxide
DSC	differentiate scanning calorimetry
EBL	electron beam lithography
EDLC	electric double layer capacitor
EIS	electrochemical impedance spectroscopy
EMA	effective medium approximation
EVA	ethylene-vinyl acetate
FET	field-effect transistor
FLh-BN	few-layer h-BN
G''	loss modulus
G'	storage modulus
GCD	galvanostatic charge and discharge
H ⁺	hydron
H ₂ O ₂	hydrogen peroxide
H ₂ SO ₄	sulfide acid

h-BN	hexagonal boron nitride
HCl	hydrochloric acid
HF	hydrofluoric acid
ICs	integrated circuits
IPA	iso-propanol
KE	kinetic energy
KF	potassium fluoride
KOH	potassium hydroxide
LED	light-emitting diode
LiF	lithium fluoride
LPE	liquid phase exfoliation
m-MXene	multilayer MXene
MAX	$M_{n+1}AX_n$ phases, the precursors of MXenes
MBE	molecular beam epitaxial
MILD	minimally intensive layer delamination
MIM	metal-insulator-metal
MoS ₂	molybdenum disulfide
MXene	two dimensional transition metal carbides, nitrides or carbonitrides
N ₂	nitrogen gas
NaF	sodium fluoride
NaOH	sodium hydroxide
NH ₄ Cl	ammonium chloride
NIR	near-infrared
OAS	optical absorption spectroscopy
PDT	photothermal deflection technique
PEDOT	poly(3,4-ethylenedioxythiophene)
PE	polyethylene
PF	Poole-Frenkel
PLD	pulsed layer deposition
PMMA	polymethyl methacrylate

PPMS	physical property measurement system
PTFE	polytetrafluoroethylene
PVA	polyvinyl acetate
PVP	polyvinylpyrrolidone
rcf	relative centrifugal force
RE	reference electrode
rGO	reduced graphene oxide
rpm	revolutions per minute
RT	room temperature
SDC	sodium deoxycholate
SDC	sodium dodecyl sulfate
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
SiO ₂	silicon dioxide, or silica
Si	silicon
SSM	steady-state measurement
TCB	trichlorobenzene
TEABF ₄	tetraethylammonium tetrafluoroborate
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
Ti ₂ CT _x	titanium two carbide MXene
Ti ₃ C ₂ T _x	titanium three carbide two MXene
TIMs	thermal interface materials
TiO ₂	titania
TMAOH	tetramethylammonium hydroxide
TTO	thermal transport option
UTS	ultimate tensile strength
UV-Vis-NIR	ultraviolet-visible-near infrared
WE	working electrode
WS ₂	tungsten disulfide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1

Introduction and Motivation

1.1 Research background

Continued high levels of CO₂ emissions contribute to the warming of the Earth's atmosphere, leading to increasingly frequent and severe extreme weather events such as droughts, floods, and heatwaves. Mitigating the impacts of anthropogenic climate change and achieving long-term environmental stability and sustainable development require both reducing CO₂ emissions and removing excess CO₂ from the atmosphere. Effective strategies for CO₂ removal include carbon capture, carbon storage, and afforestation, while emission reductions can be achieved through transitioning from fossil fuels to renewable energy sources such as solar, wind, and hydroelectric power, and improving energy efficiency.

The intermittent nature of renewable energy necessitates the development of efficient energy storage systems, such as capacitors, batteries, and supercapacitors, to store and deliver energy as needed. To advance these energy storage devices, improvements in power density, energy density, cycle life, reliability, and energy efficiency are essential. Material innovation represents one of the most direct pathways to achieving these goals. Two-dimensional (2D) materials have demonstrated exceptional potential due to their superior electrical, thermal, and electrochemical properties. They can serve as electrode materials, dielectric layers, or thermal interface materials, enabling higher-performance energy storage devices with greater efficiency and durability. These advancements could reduce the need for frequent device replacements, thereby lowering the energy footprint associated with the production, disposal, and recycling of energy storage systems.

1.1.1 Introduction of 2D materials

2D materials have revolutionised the field of materials science since the groundbreaking discovery of graphene in 2004 by Andre Geim and Konstantin Novoselov [1]. Upon decades of studies and discoveries, the family of 2D materials has expanded beyond graphene to include various transition metal dichalcogenides (TMDs), hexagonal boron nitride (h-BN), MXenes, and others. These materials are characterised by their atomic-scale thickness and extensive lateral dimensions, providing unique properties that distinguish them from their bulk counterparts. Their planar structure significantly influences their physical and chemical properties. Graphene, for example, consists of a single layer of carbon atoms arranged in a hexagonal lattice, which endows it with high mechanical strength, superior electrical conductivity, and excellent thermal conductivity (κ). h-BN, often called "white graphene", has a similar hexagonal structure but consists of alternating boron and nitrogen atoms [2]. This arrangement makes h-BN an excellent electrical insulator with high κ , thermal stability and chemical resistance. The unique properties of 2D materials have led to their adoption in various applications, including electronics, sensors, electronic skin, composites, energy storage devices, and coatings [3].

1.1.2 Promising usage of 2D materials

The diversity within the 2D family and their superior properties open up many potential applications, for instance, energy storage devices which are one of the most important and promising applications for the global CO₂ reduction. Those devices vary from batteries, and supercapacitors to thermal management components like thermal interface materials (thermal pastes) [3], as shown in Figure 1.1. The 2D-materials embedded technologies are divided by technology readiness levels, a measurement system used to assess the maturity of a particular technology. The higher the technology readiness levels, the more mature the technology is. For instance, the technology at level 9 has been fully integrated into operational systems and has been proven to work as intended in real-life scenarios, including electrochemical sensors, conductive inks, lubricants, supercapacitors, and thermal pastes.

With this concept in mind, the work is motivated to the investigation and production of 2D-materials-based products which can be quickly transformed into the industry and the commercial market, with probability of large-scale production and a high technology readiness levels such as thermal pastes and supercapacitors. At the same time, using 2D materials for energy storage devices and their energy(thermal) management can improve the device performance, energy-efficiency and their lifetime, meaning fewer natural and artificial re-

sources are required for manufacturing over time, contributing to reduced CO₂ emissions in the manufacturing sector.

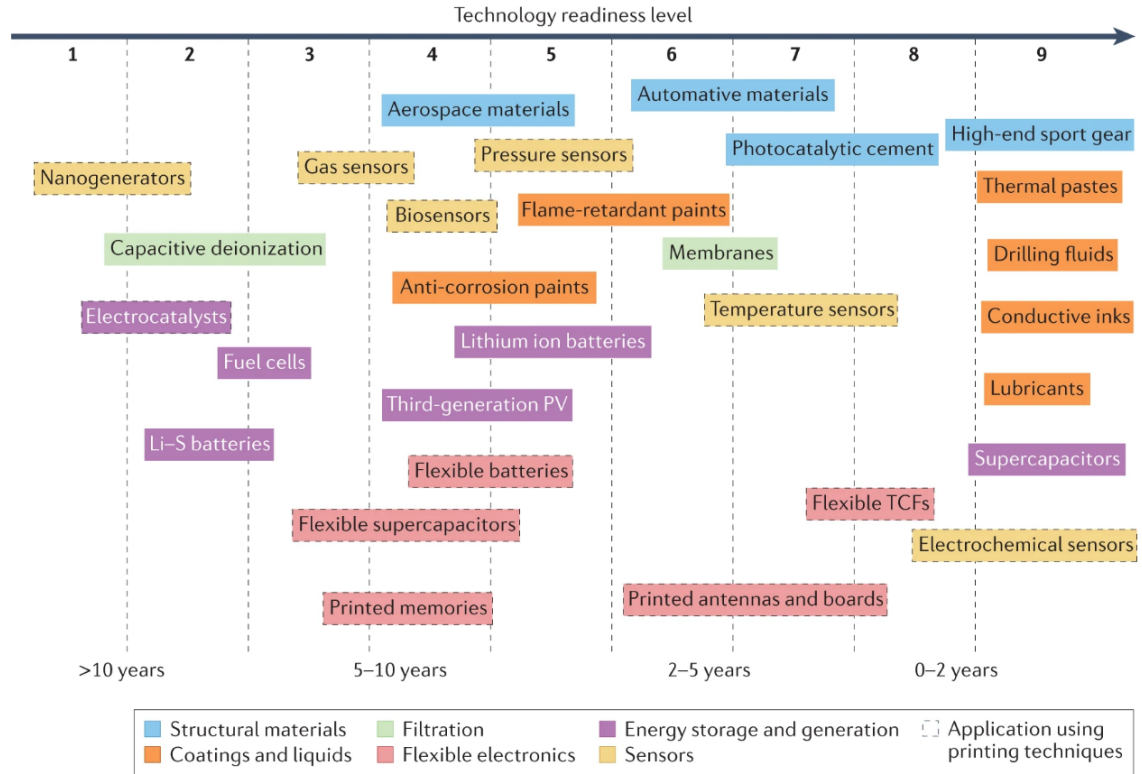


Fig. 1.1 Technology readiness level of applications using 2D materials. Image adapted with permission [3], © 2022, Springer Nature Limited.

1.2 Research motivation

Despite significant advancements in energy storage devices for renewable energy sources, the devices still face challenges, like pursuing higher energy and power densities, encountering power/energy loss during operation, running with thermal issues, and unsustainable fabrication [4]. Furthermore, the growing demand for miniaturised, low-power, flexible, and wearable energy storage solutions to enhance end-user experiences underscores the need for innovative approaches. One of the most sustainable and impactful strategies is to explore novel materials with superior inherent properties to transform the performance of existing device technologies, among which using 2D materials as alternative materials can be a promising way forward.

Among the various 2D materials, h-BN and MXenes stand out for their exceptional properties and promising applications, particularly in thermal management and energy storage. The focus on these materials is driven by the growing demand for miniaturised electronic devices and the pursuit of higher performance and energy efficiency of energy storage devices. The continuous miniaturisation of electronic devices, coupled with the demand for higher performance, has made thermal management a critical challenge. As devices shrink, the density of components increases, leading to higher heat generation locally within devices. Effective heat dissipation is essential to avoid accumulated heat and prevent overheating, which can degrade performance and reduce the lifespan of electronic components. In the thermal management system, thermal interface materials (TIMs), such as thermal pastes, are one of the key components that reduce the thermal contact resistance between two surfaces. The market for thermal pastes is expected to grow to an annual value of \$6.9 billion by 2030 [5]. As one of the thermal fillers for thermal pastes, 2D materials have raised huge interest and achieved the highest technology readiness level of 9 (Figure 1.1). Among the 2D family, h-BN is an ideal thermal interface material for efficient heat dissipation due to its high κ and electrical insulation. It can conduct heat effectively and reduce operating temperatures without interfering with electrical signals and causing short circuits. Besides, when exposed to the heat generated from electronics, h-BN is chemically stable without severe oxidation or decomposition apart from minor hydrolysis due to moisture. Therefore, the thermally conductive properties can be largely maintained.

The demand for higher energy and power density in energy storage devices has spurred the search for new materials with superior performance characteristics. MXenes have emerged as a promising class of materials for energy storage applications due to their high electrical conductivity, large surface area, and tunable surface chemistry. Their outstanding characteristics enable them to achieve high capacitance and energy density, making them ideal for use in batteries and supercapacitors.

Exploring 2D materials, particularly h-BN and MXenes, holds significant promise for developing better energy storage devices, by optimising heat dissipation, enhancing energy storage, and reducing energy loss. However, the production of 2D materials is limited to lab scales and large-scale production is challenging. The production of 2D materials with their structural and functional integrity requires sophisticated equipment and demanding synthesis conditions (i.e., high temperatures, high pressures and hazardous solvents), and the production yields are low in the order of milligrams which is away from the industrial scales.

1.3 Research aims and objectives

The work aims to advance the scalable processing of 2D materials, specifically h-BN and MXenes, and their composites and to demonstrate their potential in energy storage devices and thermal management applications, which eventually could support the global CO₂ reduction commitment. Specifically, the main objectives are explored and investigated:

1. To seek scalable and sustainable techniques to produce 2D h-BN, MXenes and their composites.
2. To explore ways of using 2D materials and their composites to enable high-performance energy storage devices with better energy density, power density, device durability, flexibility and wearability.
3. To develop a better thermal management system using 2D materials and their composites with higher thermal conductivities, enabling high-performance energy storage devices operating within the optimal temperature range for the best power rating and energy efficiency.

Through these objectives, the work could demonstrate a foundation for deploying 2D materials in critical applications that can contribute to CO₂ reduction by improving energy efficiency, thermal management, and renewable energy storage. The discussion will be provided in each chapter in detail.

1.4 Structure of the thesis

The PhD thesis consists of 8 chapters, with Chapter 1 describing the general background, research motivation, research aims and objectives.

Chapter 2 introduces the production, deposition and characterisation techniques used in this work for h-BN and MXenes. The chapter summarises (1) the main production methods of 2D materials, including shear exfoliation, microfluidisation, ultrasonication, stabilisation and purification of the exfoliated 2D flake dispersion, the selective-etching and soft delamination of MXenes; (2) the deposition techniques (spray coating and spin coating); (3) the various material characterisation methods; (4) physical property characterisation techniques (optical, electrical, rheological and thermal tests); and (5) electrochemical characterisation techniques. Each method discusses the underlying theory, the operation mechanism, and the advantages and disadvantages compared to the others.

Chapter 3 reviews the current application-based investigation of h-BN, especially (1) its use as an insulating layer in electronic devices due to its electrically insulating properties and (2) its use as thermal fillers for TIMs for thermal management of electronics.

Chapter 4 reviews the investigations on the chemical stability and factors that drive the oxidation of MXenes, with proposed strategies to improve the stability. Chapter 4 also reviews the charge transport mechanism between different types of MXenes. In the end, the promising application of MXenes (especially $\text{Ti}_3\text{C}_2\text{T}_x$) as electrode materials in energy storage devices like supercapacitors have been extensively reviewed, including the various types of electrode composites and the mechanism behind them.

Chapter 5 discusses the formulation and fabrication of the few-layer h-BN (FLh-BN) inks and demonstrates the insulating properties as a dielectric layer for fully spray-coated capacitors. Various characterisation methods are implemented to prove the chemical composition and quality of the FLh-BN inks. The inks are spray-coated onto a glass substrate as a thin dielectric layer, with a bottom and top silver electrode to form a sandwiched capacitor configuration. By investigating the impedance and electrical (current-voltage, I-V) performance, the ϵ_r of the FLh-BN-based dielectric layer is found at 7.9 and the breakdown strength at 14.8 kV/mm. Improving the mass ratio of FLh-BN in the dielectric layer or adding an additional high- ϵ_r material like BaTiO_3 can enhance the ϵ_r value and dielectric breakdown strength of the dielectric layer.

Chapter 6 leverages the known high κ of FLh-BN to produce commercially viable FLh-BN embedded thermal pastes using a biocompatible, scalable, and low-cost process. The process utilises a one-pot mixing step compatible with industrial production. The chapter studies the enhanced κ brought by adding h-BN for the cellulose-based composites and compares the enhancement between the bulk h-BN (Bh-BN) embedded composites and FLh-BN embedded ones. This chapter discusses the composites' rheological characteristics and mechanical properties. Chapter 6 also untap the potential of the FLh-BN-based composites as thermal pastes for commercial applications. They can work as thermal interface materials (TIMs) for heat dissipation from hot spots to heat sinks. These include a hot chip surface and an operating high-power LED surface, achieving a remarkable maximum temperature reduction.

Chapter 7 discusses the synthesis optimisation of $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x , achieving aqueous MXene inks containing a majority of mono-layer and few-layer flakes. The MXenes were characterised via Raman, XPS, AFM, SEM, and XRD to reveal their chemical composition, crystallinity, morphology, and flake sizes. To improve the shelf-life of MXenes, especially the sensitive Ti_2CT_x , keeping the MXene aqueous solutions isolated from light in the fridge (4 °C) and fully exchanging the dissolved O_2 in water by filling N_2 is proposed. Having a

stable MXene suspension in hand and depositing single flakes and thin films for FET devices, the charge transport mechanism of the Ti_2CT_x is found to be compatible with 2D-Mott VRH hopping mechanism. Finally, the chapter explores the application of MXenes, mainly the $\text{Ti}_3\text{C}_2\text{T}_x$ in energy storage devices. The addition of $\text{Ti}_3\text{C}_2\text{T}_x$ into the fabrication process of the electrode materials for supercapacitors enhances the electrochemical performance of the electrode as well as the device, including capacitance, energy density, and power density.

Chapter 2

Production, deposition and characterisation of 2D materials

This chapter aims to figure out the suitable processing techniques for 2D materials and their composites with the best scalability, including production and deposition. Liquid phase exfoliation stands out due to its capability for large processing volumes, operation under ambient conditions, compatibility with versatile liquids and solids, and compatibility with large-area deposition.

To be applicable for energy storage devices and thermal management applications, the materials should exhibit good quality in 2D nature and achieve desired electrical, thermal and electrochemical properties. Therefore, a variety of characterisation techniques for probing the materials quality, including Raman, XPS, microscopy, and XRD have been thoroughly discussed regarding their fundamentals and typical features of 2D materials. A range of characterisation techniques for probing the properties of materials have also been discussed regarding their fundamentals and advantages, including thermogravimetric analysis, electrical conductivity, thermal conductivity analysis, and capacitance analysis. These properties of materials are the key metrics considered for developing energy storage devices and thermal management components.

2.1 2D materials and their corresponding properties

2.1.1 Hexagonal boron nitride (h-BN)

2.1.1.1 Structure of h-BN

Boron nitride (BN) has been widely used as a high-temperature lubricant, release agent, and cosmetic product [6], as shown in Figure 2.1(a). It is a chemical compound that consists of boron and nitrogen at an atomic ratio of 1:1 and exhibits several stable crystal forms, including sp^3 bonded cubic and wurtzite forms and sp^2 bonded hexagonal and rhombohedral forms [7]. Among them, h-BN obtains the most interest, as it has a honeycomb structure analogous to that of graphite [8]. Figure 2.1(b) shows the layered hexagonal structure, with alternating boron and nitride atoms being sp^2 bound by strong covalent bonds in each planar layer, whereas the layers are held together by weak Van der Waals forces. The B-N sp^2 bonding in each layer results in strong in-plane σ bonds, leading to high in-plane κ , chemical stability, and strength, while empty π orbitals make h-BN electrically insulating with a bandgap value of ~ 5.96 eV [9]. The lattice constants between the neighbouring boron (or nitrogen) are $a = 2.50$ Å within each layer and $c = 6.66$ Å between layers [10].

By breaking the Van der Waals force between the layers of bulk h-BN (Bh-BN) crystals using exfoliation via the top-down methods [7], few-layer h-BN nanosheets (BNNSs) with a layer number of 2-10 can be obtained [11]. Monolayer BNNSs are generally synthesised via bottom-up methods [7]. The top-down methods include mechanical exfoliation, chemical exfoliation, electrochemical exfoliation, liquid-phase exfoliation or a combination thereof, and the bottom-up methods include chemical vapour deposition, molecular beam epitaxial, pulsed layer deposition and wet chemical methods. Compared to bulk h-BN crystals, the monolayer and few-layer ones exhibit slightly higher dielectric constants of 6.93 and 3.76 at in-plane and out-of-plane directions, respectively (6.82 and 3.29 for Bh-BN, respectively) [12], better thermal conductivity at $751 \text{ W m}^{-1} \text{ K}^{-1}$ ($390 \text{ W m}^{-1} \text{ K}^{-1}$ for Bh-BN) [13], similar elastic modulus at a range of 0.72-0.95 TPa (0.81 TPa for Bh-BN) [13].

2.1.1.2 Properties of h-BN

h-BN has garnered significant research interest due to its exceptional properties, such as an atomically flat surface free of dangling bonds and charged impurities, superior elastic modulus (0.8-1.0 TPa), excellent mechanical flexibility, and electrical insulation (high breakdown strength up to 0.7-1.2 GV/m, dielectric constant of 3-4) (Figure 2.2) [15–17]. Consequently,

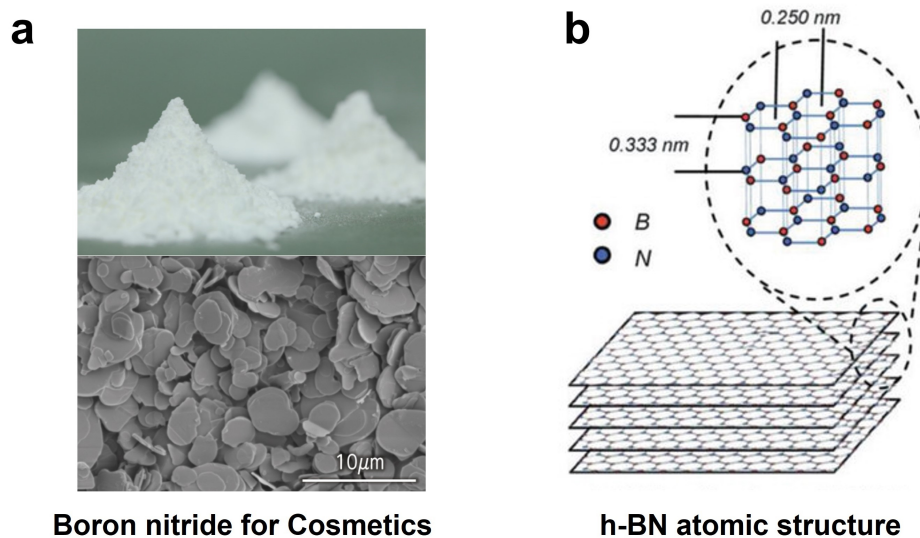


Fig. 2.1 Introduction to boron nitride and the atomic layered structure of h-BN. (a) BN white powders with SEM images showing the particle sizes. (b) The atomic layered structure of h-BN. Image (a) copied from [6], © Tokuyama Corporation; and image (b) adapted with permission [14], © The Royal Society of Chemistry 2012.

it is promising as a gate dielectric [18] and a tunnelling barrier [19], particularly in Van der Waals electronics.

h-BN is also thermally stable at temperatures up to $\sim 1000\text{ }^{\circ}\text{C}$ in air without severe oxidation, and up to $\sim 1400\text{ }^{\circ}\text{C}$ in inert atmospheres without severe decomposition. It is also chemically inert to most acids and bases at room temperature without severe material change, making it highly stable in a wide range of liquid environments, such as a passivation layer [20] for electronics. While h-BN is stable in many chemical environments, the stability is not absolute and can be compromised under extreme conditions. For example, h-BN can undergo hydrolysis particularly at elevated temperatures (above $300\text{ }^{\circ}\text{C}$) and in the presence of moisture [21], which results in the breaking of B-N bonds, producing boric acid (H_3BO_3) and ammonia (NH_3) [21]. Hydrolysis is minimal at room temperature.

h-BN also holds high-speed heat spreading ability due to its superior κ values for both bulk ($390\text{ W m}^{-1}\text{ K}^{-1}$) and mono-layer flakes ($751\text{ W m}^{-1}\text{ K}^{-1}$), which makes it attractive in thermal management applications for electronics [22]. The excellent thermal and chemical stability and low friction coefficient (0.2-0.3) of h-BN also make it promising as a multi-functional coating and lubricant material [23].

Figure 2.2 also shows h-BN: (1) a wide band gap ($\sim 5.9\text{--}6.0\text{ eV}$) with ultraviolet luminescence (peak around 215 nm in the UV range), promising as a detector for photon emission, ultravio-

let and deep ultraviolet (DUV) [24]; (2) a natural hyperbolic material (typically between 6-13 μm wavelengths) for hyperlenses and near-field imaging [25, 26]; (3) a non-linear optical (second-harmonic generation with a non-linear coefficient from 1 to 100 pm/V) and piezoelectric (a piezoelectric coefficient around 0.2 pm/V) material for quantum optoelectronics [27], and nonlinear and stretchable optics [28].

Regarding this work's thermal management and energy storage scope, I will conduct a more detailed literature review of h-BN applications as insulating layers and thermally conductive materials in Chapter 3.

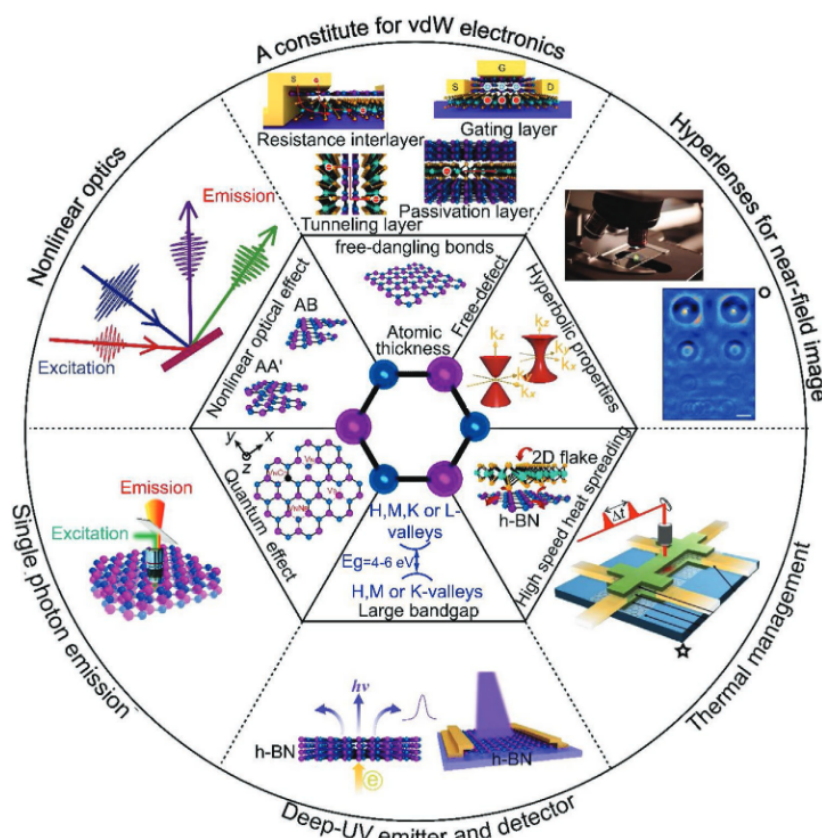


Fig. 2.2 Properties of h-BN and its typical applications. Image adapted with permission [22], © 2020 Wiley-VCH GmbH.

2.1.2 MXenes

MXene is a large family of 2D transition metal carbides, nitrides, and carbonitrides [29]. They have a general chemical formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n=1, 2, 3$ and 4), where M represents early transition metals, X represents carbon and/or nitrogen, and T represents terminated

functional groups (i.e. $-\text{OH}$, $-\text{F}$, and $-\text{O}-$ to $-\text{Cl}$, $-\text{Br}$, $-\text{Te}$, $-\text{NH}$.), as shown in Figure 2.3. With the recent discovery of oxygen substitution in carbide MXenes [30] and formation of oxy-carbides, X can represent oxygen as well (at least in solid-solution MXenes) [29].

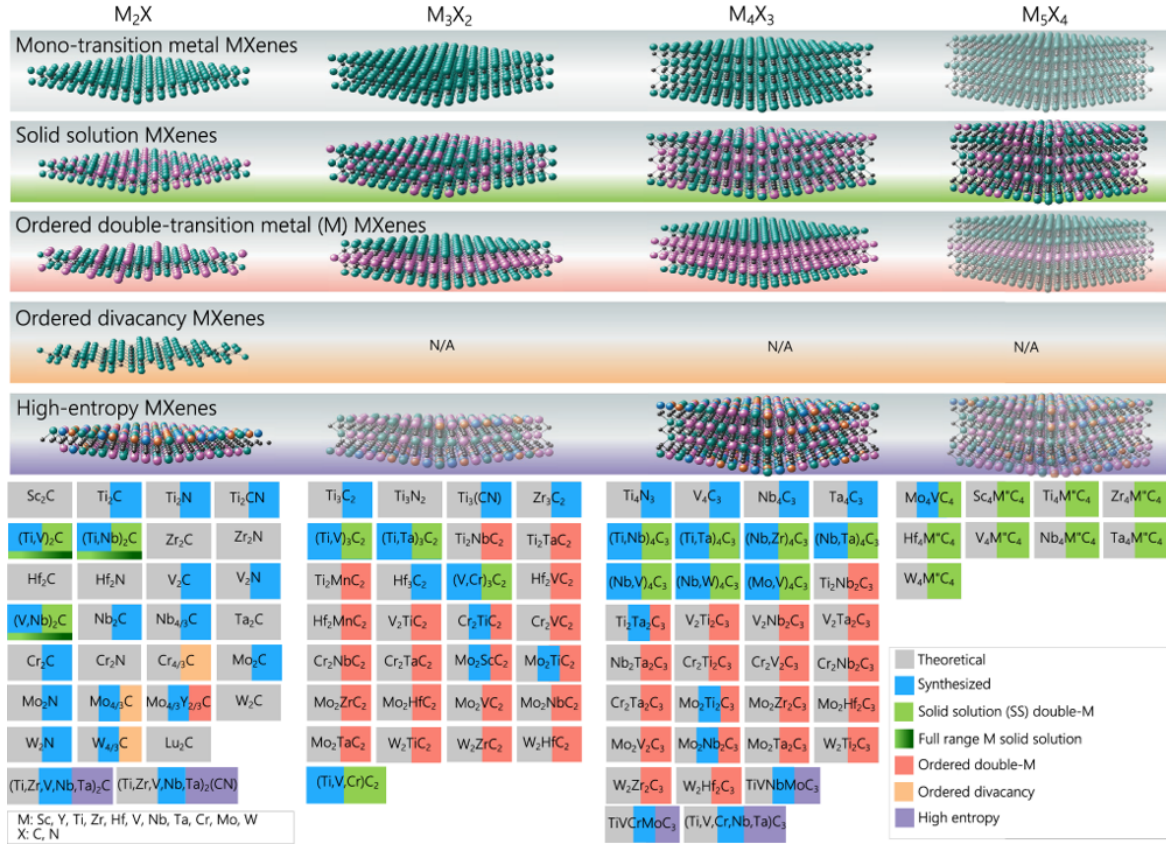


Fig. 2.3 MXene reported so far. Image adapted with permission [29], © 2022, Anasori, B., Gogotsi, Y., under exclusive license to Springer Nature Switzerland AG.

The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was the first one discovered in 2011 [31], by selective removal of the A layer from its precursor, Ti_3AlC_2 MAX (the precursor of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, and A represents the element of group III-VI). The Al was etched using hydrofluoric acid (HF), and the delamination of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was achieved using dimethyl sulphoxide (DMSO) in 2013 [32]. In 2014, a 'One-pot' synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ was proposed using the in-situ HF route by mixing hydrochloric acid (HCl) and lithium fluoride (LiF) [33]. There are also other synthesis methods developed recently to realise fluorine-free products. A detailed overview of the synthesis methods will be discussed in the Section 2.3.

Ti_2CT_x is also one of the most frequently investigated MXenes. It can be synthesised using similar etching and delamination methods from its precursor, Ti_2AlC MAX phase. Through continuous investigation of the MXene family over the past decade, there are over 40+ MX-

enes that can be synthesised in the lab so far (Figure 2.3). They have attracted huge attention in science and technology due to their promising metallic or semi-conducting properties, large surface aspect ratio, high mechanical strength, diverse active surface terminations, and excellent hydrophilicity [34–36].

After decades of research, MXenes, particularly the $\text{Ti}_3\text{C}_2\text{T}_x$, have been extensively explored for their application in supercapacitors [37], catalysts [34], batteries [38], but their low chemical stability, particularly in aqueous colloidal solutions becomes a key barrier to their shelf-life storage and product lifespan [39–41], which will be reviewed in Chapter 4.

2.1.3 Synthesis of 2D materials

The synthesis and processing methods for 2D h-BN nanosheets significantly influence their crystallinity, morphology, and later applications in devices [42]. Various synthesis methods have been developed to fabricate mono-layer and multi-layer h-BN nanosheets, particularly aiming at producing high-quality h-BN nanosheets with large lateral sizes and fewer flake defects via scalable and cost-effective ways [7]. The synthesis methods of 2D materials are usually divided into two categories: bottom-up and top-down methods.

2.1.3.1 Bottom-up methods

The bottom-up methods usually produce 2D materials from their atomic or molecular precursors that are capable of reacting, growing or self-assembling into a 2D structure [43], using molecular beam epitaxial (MBE) [44], chemical vapour deposition (CVD) [45–47], pulsed layer deposition (PLD) [48] and wet chemical methods [49]. A typical bottom-up h-BN growth process consists of a substrate, which is initially annealed and treated, being exposed to precursors containing boron and nitrogen compounds at elevated temperatures and desired pressures. The main factors affecting the quality (number of layers, defects, morphology, orientation) of the grown h-BN film are the synthesis conditions (temperature and pressure), the precursors, and the substrates. For example, Figure 2.4 illustrates the growth mechanism of FLh-BN on Ni(111) [50] via CVD. After the dissociation of borazine, the boron starts to dissolve, and thus, the tri-layer h-BN grows. During the growth process, a thick (~ 200 nm) Ni_{23}B_6 layer is formed on the Ni(111) surface due to the absorbed boron in the Ni substrate and underneath the grown h-BN film. This CVD process can produce high-quality, high-performance wafer-level thin films, but it will introduce defects/pinholes of h-BN nanosheets and require extra efforts to transfer the film for device applications [2].

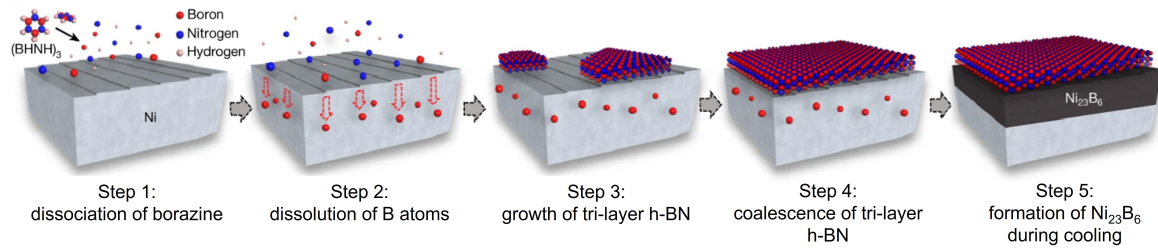


Fig. 2.4 Growth mechanism of FLh-BN on Ni(111). Image adapted with permission [50], © 2022, Springer Nature.

However, these methods require demanding operation conditions involving high temperatures and/or high pressures. In contrast, the top-down methods have the advantage of operating under atmospheric pressure at room temperature (RT). They normally deal with solid or bulk materials, overcoming the inter-layer forces between the layered structure and separating them into individual layers, using mechanical exfoliation [51], chemical exfoliation [52], electrochemical exfoliation [53], liquid-phase exfoliation [54, 55] or a combination thereof.

2.3.1.2 Top-down methods

A. Mechanical exfoliation

Mechanical exfoliation was developed to exfoliate graphite to produce single-layer graphene using mechanical cleavage by Novoselov et al. [56]. After the successful attempt on graphene, Novoselov applied the same method to exfoliate other layered crystals, including h-BN [57]. Pacile et al. [58] reported the first isolation of the h-BN nanosheets on SiO_2 substrates and demonstrated experimentally the crystallinity and continuity of the peeled-off h-BN nanosheets with an ordered hexagonal structure and nanosheet thicknesses ranging from 3.5 nm to 80 nm. However, studies pointed out the difficulty of producing large-size (μm size) and mono-layer (0.33 nm) h-BN nanosheets. A significant contribution to obtaining a larger lateral size ($> 100 \mu\text{m}$) of mono-layer h-BN nanosheets via mechanical cleavage was made by Gorbachev et al. [59], as shown in Figure 2.5(a-b).

Similar to the mechanical cleavage process applying a pulling force to disrupt the Van der Waals interactions between the layers of h-BN, ball milling via shear forces [60] can also be applied to break the inter-layer Van der Waals forces. Figure 2.5(c-d) presents the SEM images and corresponding diagrams showing shear exfoliated h-BN nanosheets by ball milling [60]. The as-produced h-BN nanosheets have a thickness and lateral size of 2-4 nm and $\sim 400 \text{ nm}$, respectively, with a production yield of $\sim 9\%$. Yao et al. [61] introduced an additional 2-hour sonication procedure (low power output of 80 W) after loading the

h-BN powder with a solution of sodium dodecyl sulfate (SDS) and water inside a planetary mill with 200 zirconia balls for 12 hours. The as-prepared h-BN nanosheets exhibited a lateral size ranging from 10 nm to 500 nm and thickness from 1.2 nm to 8 nm, but with a higher production yield of 12% [61]. The production yield and the quality (i.e., size, crystallinity, and defects) of thin h-BN nanosheets are highly dependent on the milling conditions, including the milling speed, the ball size, the ball-to-powder ratio, the choice of the liquid medium [62] and the additional post-processing procedures.

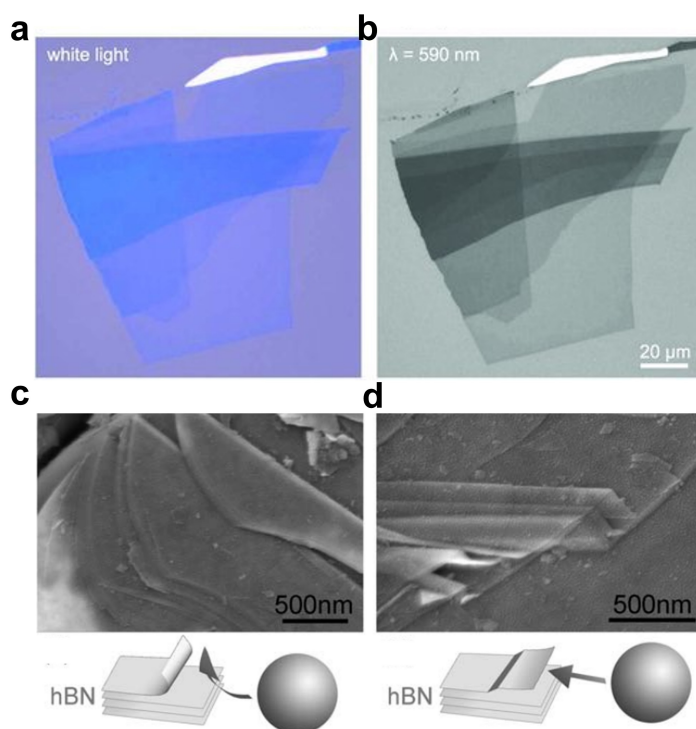


Fig. 2.5 h-BN nanosheets produced via mechanical exfoliation. (a-b) Mechanically cleaved h-BN nanosheets on the SiO₂ substrate; (c-d) SEM images and corresponding diagrams showing exfoliated h-BN nanosheets by ball milling from (c) the edge and (d) the top surface of an h-BN particle. Images (a-b) adapted with permission [59], © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; and images (c-d) adapted with permission [60], © The Royal Society of Chemistry 2011.

B. Chemical exfoliation

Chemical exfoliation uses chemical reactions and/or chemical intercalants to achieve the thinning of bulk crystals down to mono-layer or a few-layer flakes. Chemical reactions can be realised by introducing heteroatoms or functional groups at the material surface to facilitate the cleavage of the layered materials, and chemical intercalants can include acids/bases, inorganic salts, oxidising agents, and reactive functional molecules [63]. One of the most widely applied protocols is the production of graphene oxide (GO) via the Hummers'

methods [63], where graphite is oxidised using strong oxidisers like potassium permanganate (KMnO_4) and sulfuric acid (H_2SO_4). The produced GO can be further reduced thermally, chemically or electrochemically to form conductive reduced GO (rGO). h-BN can also be synthesised similarly but has additional functional groups which might impact the original material properties.

Another widely applied chemical exfoliation technique is the selective etching of A-element from MAX phases to form MXenes [63], using strong acids to enable the chemical reactions and cations/molecules to intercalate and expand the layer distance.

C. Electrochemical exfoliation

Electrochemical exfoliation is another technique used to produce 2D materials, such as graphene or transition metal dichalcogenides (TMDs), by applying an electrical potential to a bulk layered material in an electrolyte solution. The process induces ion intercalation, followed by the splitting of the layers due to electrochemical reactions, resulting in exfoliated nanosheets.

D. Combined methods

The above-mentioned exfoliation methods can be combined to improve the exfoliation yields of 2D materials. For instance, electrochemical and mechanical exfoliation can be combined via electrochemical intercalation with mechanical agitation (e.g., stirring) to enhance exfoliation efficiency. Chemical and mechanical exfoliation uses a chemical treatment to intercalate or weaken the layers, followed by mechanical forces like sonication or shear mixing to fully exfoliate the 2D materials, which is usually classified as a separate category: liquid-phase exfoliation.

E. Liquid-phase exfoliation

Liquid phase exfoliation (LPE) is a process used to separate bulk-layered materials into individual or few-layer nanosheets by dispersing them in a solvent first and then applying mechanical forces, such as ultrasonication and shear forces, or chemical intercalants like surfactants, or a combination of the exfoliation methods [55] to overcome the Van der Waals forces between the layers. Figure 2.6 illustrates a complete LPE process that usually consists of dispersion, exfoliation, and purification (i.e., centrifugation) steps, in which the choice of solvents and stabilisers, the initial concentration of materials, the exfoliation methods, and the centrifugation speed and time play a role in the production yield and the quality of the exfoliated 2D materials.

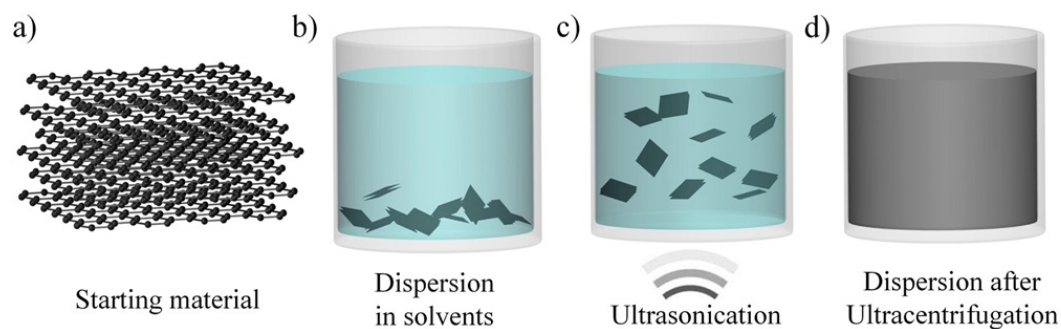


Fig. 2.6 Schematic illustration of the LPE process. (a-b) Dispersion of starting materials in suitable solvents, (c) ultrasonication, and (d) a final dispersion after centrifugation. Image adapted with permission [64], © Copyright 2024 | Optica Publishing Group.

The LPE process has the advantages of resembling the surface tension of the material being exfoliated. The choice of solvents and stabilisers for the LPE of 2D materials can be determined by matching the surface tension, the Hansen solubility parameter [65], or the interfacial entropy [66] of the solvents to those of the aimed 2D materials. Among a wide range of organic and inorganic polar and non-polar solvents that include N, N-dimethylformamide, N-methyl pyrrolidone, isopropanol, ethanol, ionic surfactants, and molten hydroxides including pure water are selected to exfoliate Bh-BN crystals [67–70]. Upon optimising the interaction and surface tension between the chosen solvent and h-BN for a better yield of the final exfoliated h-BN suspensions, IPA was found to be an excellent solvent candidate for the h-BN exfoliation with $\sim 50\%$ (0.06 mg mL^{-1} h-BN nanosheet concentration) yield [71]. Water was also found to be effective in the LPE of h-BN with the assistance of ultra-sonication [72] and microfluidisation [73]. The combined effect of the solvent polarity and ultrasonication power can fully exfoliate h-BN into few-layer nanosheets (0.7–0.9 nm), producing pure aqueous dispersions. However, this process reduces the lateral dimensions of the h-BN flakes due to sonication-assisted hydrolysis, which poses a disadvantage in terms of stability. Introducing an appropriate surfactant, such as sodium carboxymethyl cellulose (CMC), minimises the exfoliation energy and enables a relatively high yield and excellent dispersibility/stability [73, 74].

Scalability discussion: Among all the exfoliation techniques, mechanical exfoliation provides high-quality materials but is not scalable enough for mass production. Chemical exfoliation and electrochemical exfoliation are also restrained within a small scale [63] and encountered the problem of the material being functionalised and defective. In contrast, LPE provides notable advantages, including scalability, versatility, operation under ambient conditions, and better control over material properties with fewer defects, making it a preferred method for large-scale production of 2D materials. First, its compatibility with a wide range

of solvents and crystals makes it suitable for diverse material options. Second, the equipment required for LPE, such as sonicators, centrifuges, and shear mixers, is already industrialised and capable of processing materials at litre scales [75]. By incorporating stabilisers, LPE enables the use of sustainable solvents or even water-based systems, operating at room temperature and atmospheric pressure, which reduces both processing costs and environmental impact. Notably, the technique can achieve a nearly 100% yield for 2D materials under optimised conditions [75]. While challenges remain in optimising yield and quality control at scale, LPE provides a promising pathway for industrialising the production of 2D materials across various applications, including energy storage, thermal management, and electronic devices aimed at supporting CO₂ reduction goals.

2.2 Liquid phase exfoliation of h-BN

Liquid phase exfoliation (LPE) is chosen as the primary method for this work, which requires easy processing, cost-effectiveness, and high-quality materials for energy applications. LPE could produce few-layer defect-free [76] 2D materials and ink-based composites in large quantities [65, 74, 77] with minimal functionalisation. The ability of producing defect-free high quality 2D materials allows LPE to be most suitable for energy applications [78], involving flexible and wearable electronics [79–81], energy storage/harvesting devices [82, 83], biosensors [84], protective coating [23, 85] and catalysis [86, 87].

LPE is based on the principle that conversion of a layered crystal to large quantities of nanosheets in liquids requires two stages: the breaking of bonds to separate the nanosheets from the crystal and stabilisation of the resultant nanosheets against aggregation [88]. To separate the nanosheets from the parent crystal, it is necessary to pump energy into the exfoliation liquid. The commonly used energy can be from shear forces [76], microfluidic [73, 75], and ultrasonic energy [89].

2.2.1 Shear exfoliation

Shear exfoliation applies shear force to the liquids and solids via high-speed rotor/stator [90] or rotating blade mixers [91], as illustrated in Figure 2.7. The materials are firstly suctioned into the centre of the workhead, then centrifuged towards the periphery, driven out of the workhead through perforations by intense hydraulic shear, and finally projected radially at high velocity towards the wall of the mixing container. In this case, the inter-layer attraction forces of 2D materials are overcome, and the separation of layers is achieved.

Applying shear exfoliation to pristine bulk materials, graphite, for example, the resultant dispersion contains few-layer graphene flakes with relatively low defects, in large quantities, with a production rate achieved at 5.3 g h^{-1} [76] and an exfoliation yield $< 3 \%$ (the mass of the obtained few-layer nanosheets compared to the mass of its precursor). The production of graphene can be achieved either under local turbulence (the fluid undergoes irregular fluctuations or mixing, including swirling eddies of various sizes, rapid changes in pressure and velocity, and enhanced mixing of fluid properties like temperature and concentration) [92] or via high-shear laminar flow (the fluid travels smoothly or in regular paths) as long as the shear rates (γ) are above 10^4 s^{-1} [76]. Beyond graphene, wider layered compounds, like h-BN, molybdenum disulfide (MoS_2), tungsten disulfide (WS_2) have been achieved via this shear exfoliation method as well, at a high production rate of 0.95 g h^{-1} , but with a low exfoliation yield $< 1 \%$ [93]. The concentration of the resultant dispersion and the flake size largely depends on the processing parameters, including the type of the work head, the mixing volume, the initial concentration, the shear speed, the shear time, and the surfactant/solvent [76].

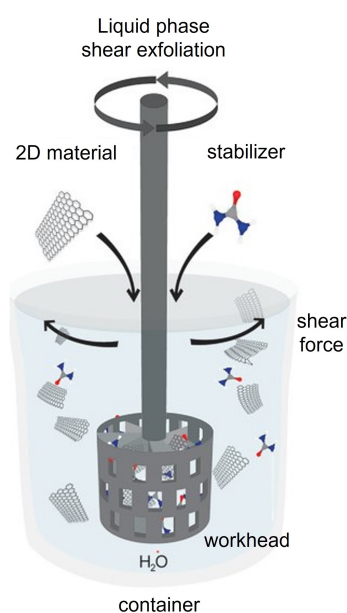


Fig. 2.7 Schematic illustration of the shear exfoliation via a rotor/stator workhead. Image adapted from [90], © Nazmul Karim, Kostya S Novoselov, Daria V. Andreeva, et al. This figure is licensed under the Creative Commons Attribution License.

However, the shear exfoliation is relatively localised in the gap between the rotor and stator [76], which are typically a few micrometres to millimetres. This leads to a nonuniform shear rate distribution within the suspension, which could result in a low exfoliation yield $< 10 \%$ [94]. If designing a larger gap, there should be additional ways (e.g., nanoparticles)

to maintain the shear rate and thus enable shear exfoliation. For example, by introducing microsized nanoparticles that do not exfoliate (i.e. polytetrafluoroethylene (PTFE) particles) as additives during shear exfoliation, the gap between the rotor and stator is dynamically reduced, so that the yield is increased to 30 % [95]. Moreover, shear exfoliation shows limited controllability over the morphology of products in terms of layer number and lateral size [91, 94], which are generally invariant with all process parameters, such as rotor speed, volume, and initial concentration of layered materials. In-situ size and thickness control was demonstrated only by varying the liquid environment (i.e., surfactant concentration in aqueous solution) [91].

2.2.2 Microfluidisation

Compared to shear exfoliation, the exfoliation by the microfluidiser is based on the higher γ from turbulent flow and is applied homogeneously to the whole fluid volume [96].

Figure 2.8 illustrates the microfluidisation process. The bulk crystals and surfactants dispersed in solvents are firstly added into the inlet reservoir, passing through the microfluidiser channel, arriving at the intensifier pump, where a high pressure (up to ~ 207 MPa) [97] is applied to the suspension. Then, the suspension is forced to pass through the microchannel (diameter, $d < 100 \mu\text{m}$) of the interaction chamber, where an intense γ up to $\sim 10^8 \text{ s}^{-1}$ is generated. Within the microchannel, 2D materials undergo collisions with each other and with the channel walls, when shear forces are applied to the 2D materials and delamination into thinner flakes occurs. Afterwards, the processed dispersion is cooled down and collected from the outlet reservoir. The microfluidisation process can be repeated for multiple cycles for scale-up purposes.

Karagiannidis, et al. [75] firstly reported the exfoliation of graphite in aqueous solutions via a microfluidiser, with a high γ of $\sim 10^8 \text{ s}^{-1}$, achieving an ink concentration of 100 g L^{-1} with almost a 100 % exfoliation yield. The resultant average lateral sizes (12 nm thick and over $1 \mu\text{m}$ large) of the graphene flakes are one order of magnitude larger than that produced by shear exfoliation [75]. The method has also been applied to other 2D materials, including h-BN [73, 79, 98], MoS_2 [99]. However, the expense of the microfluidiser in the market is over one order of magnitude higher than that of the shear mixer, and the operation of the microfluidisation requires higher energy consumption.

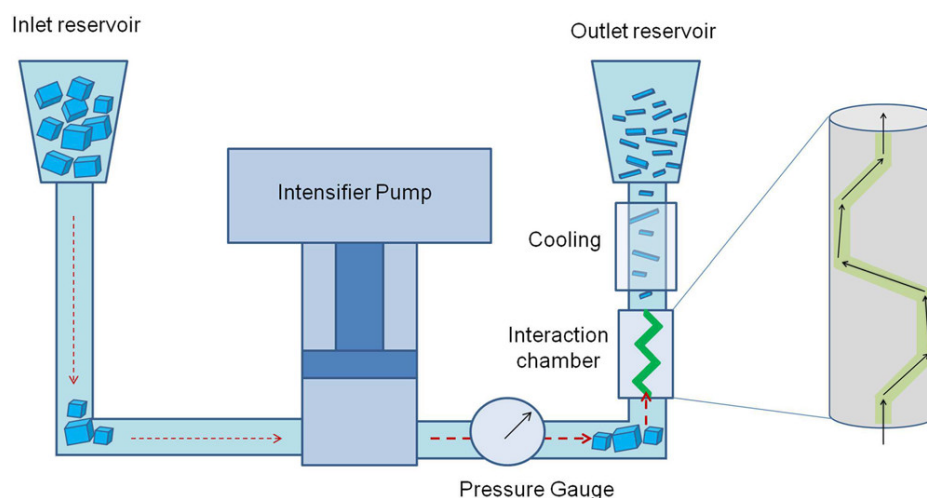


Fig. 2.8 Schematic illustration of the microfluidisation process. Image copied from [75], © 2017 American Chemical Society. This figure is licensed under the Creative Commons Attribution License.

2.2.3 Ultrasonication-assisted exfoliation

Ultrasonication is also a well-studied and applied technique to realise exfoliation. Ultrasonication uses a transducer to generate high-frequency sound waves, which are transmitted into the liquid via a probe (horn), through the transducer, or indirectly via a liquid medium, as shown in Figure 2.9. The ultrasound waves propagate through the liquid, causing alternating cycles of compression (high pressure) and rarefaction (low pressure). These cycles lead to oscillating pressure variations within the liquid [100]. During the rarefaction phase, the pressure drops below the vapour pressure of the liquid, leading to the formation of tiny vapour-filled bubbles, a process known as cavitation. These cavitation bubbles grow during subsequent cycles of compression and rarefaction as they absorb more ultrasonic energy. Once the bubbles reach a certain size, they become unstable and collapse violently during a compression cycle. The implosion of cavitation bubbles generates localised hot spots with extremely high temperatures (up to 5000 K) and pressures (up to 1000 atm) [101]. The collapse of bubbles produces strong shock waves and microjets that can cause physical disruption and erosion of nearby surfaces, which is useful for material breakdown. In such cases, the layered crystals can be broken up into few-layer nanosheets. In the ultrasonication process, the power, amplitude, time, distance of the transducer, and probe surface area determine the amount of energy delivered to the solutions and contribute to the concentration [102] and quality of the resultant materials [100].

There are two types of ultrasonication, probe or bath [103]. Probe ultrasonication immerses the probe into solutions to allow sound wave propagation, while bath ultrasonication places the transducers beneath the solution container with a direct contact to the solution (Figure 2.9(b)) or with an indirect contact via a liquid medium (Figure 2.9(c)) [104]. The bath ultrasonication usually has a low yield [102, 105] as the ultrasonic intensity is low and not uniform [106], which relies on the type and arrangement of the transducers [107]. Compared to bath ultrasonication, probe ultrasonication usually offers more intense ultrasound intensity [108], which could produce the resultant flakes with a higher concentration [105]. However, the larger ultrasonic intensity might have a stronger fragmentation effect, which reduces flake lateral size [109], and it decays exponentially with distance from the probe, which can be fully dissipated within ~ 1 cm [110].

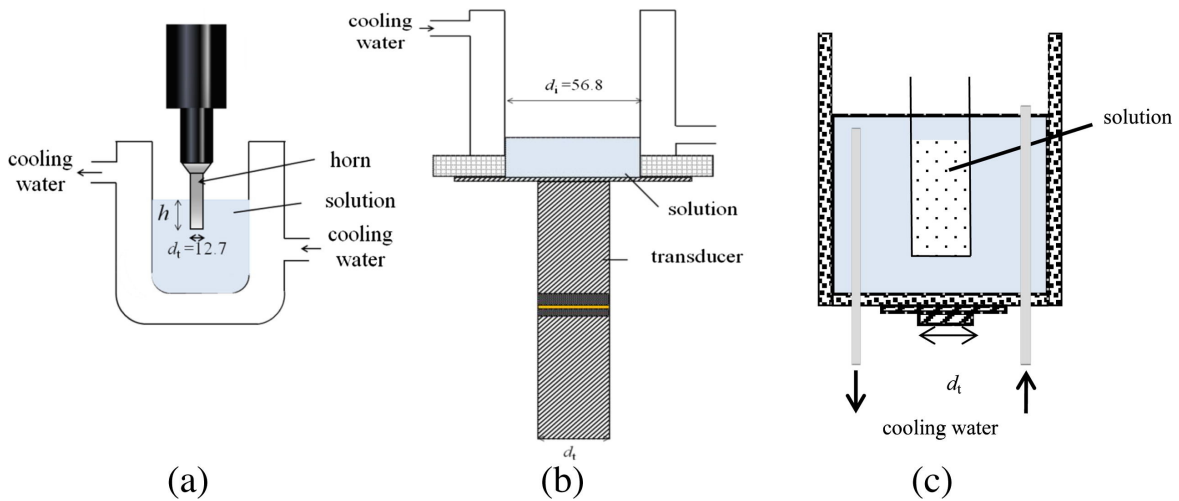


Fig. 2.9 Sonication apparatus with (a) probe type, (b) direct irradiation type, and (c) indirect irradiation type. Images reproduced with permission [104], © 2013 Elsevier B.V.

So far, either ultrasonication techniques are still the most frequently chosen methods to produce LPE 2D materials with few-layer flakes with minimal defects [111, 112]. There are studies reported for partial exfoliation of graphite [113] and single-layer graphene production [114] by sonication. An estimated flake concentration at 0.818 mg mL^{-1} of a graphene dispersion using polyvinyl pyrrolidone (PVP) as the surfactant dispersed in isopropanol (IPA) has been achieved by bath ultrasonication, which is an order of magnitude higher than the other reported values [84]. The obtained graphene flakes have an average thickness of 2.65 nm (layer numbers of 5) and a lateral size of 190 nm. Other 2D materials like h-BN have also been frequently studied under ultrasonication [72, 115, 116]. For example, Yao, et al. [11] obtained a 3.18 mg mL^{-1} few-layer h-BN suspension, showing an average flake thickness

of 6.1 nm and 339 nm in lateral size. In general, ultrasonication produces 2D flakes with minimal lattice defects without prolonged times, allowing lots of different applications [117].

2.2.4 Stabilisation of the exfoliated flakes

Once exfoliated, the production yield and the stabilisation of the 2D flakes are very important [55], as they determine the amount of material produced at one time and the frequency of the synthesis in need over time. This leads us to the net energy cost of exfoliation. During the LPE process of 2D materials, the energetic cost of exfoliation [118, 119] can be minimised via a good match between the targeted crystals and the chosen solvent [117], or addition of suitable surfactants [120, 121].

A good match of the used solvent and the 2D material can maximise the contact area between the liquids and solid, minimise the surface tension of the suspension and reduce the enthalpy energy of mixing [122], thus enabling a negative Gibbs free energy at a given temperature (dispersion occurs without additional energy input). Otherwise, the flakes tend to adhere to each other, which requires more energy to separate them [123]. Surface energies of the solvent and the 2D material [79] or Hansen solubility parameter (HSP) [124, 125] have been studied for the best choice of solvent to obtain a high yield of stabilised suspension of 2D materials. Close surface energies of the solvent and the 2D material can minimise the system enthalpy energy (ΔH_{mix}) via:

$$\Delta H_{\text{mix}} = \frac{2}{t} \times (\sqrt{\gamma_s} - \sqrt{\gamma_{2D}})^2 \times v \quad (2.1)$$

where t and v represents the thickness and volume fraction of 2D materials, γ_s and γ_{2D} represent the surface energies of the solvent and 2D materials, respectively.

In the HSP model, all of the inter-molecular interactions are considered, as shown in the following equation:

$$R^2 = 4(\delta_{D,s} - \delta_{D,2D})^2 + (\delta_{P,s} - \delta_{P,2D})^2 + (\delta_{H,s} - \delta_{H,2D})^2 \quad (2.2)$$

where R represents the HSP distance. The smaller the R value for a given solvent and 2D material combination, the more likely dispersion will occur. $\delta_{D,s}$ and $\delta_{D,2D}$, $\delta_{P,s}$ and $\delta_{P,2D}$, $\delta_{H,s}$ and $\delta_{H,2D}$ is the dispersive (D) inter-molecular forces, polar (P) inter-molecular forces, and hydrogen bonding (H), respectively, between the solvent and the 2D material.

Graphene and h-BN exhibit surface energies of 42 mN/m and 35-37 mN/m, respectively [126]. Organic solvents (e.g. N-Methylpyrrolidone, N,N-Dimethylmethanamide.) are found to be most suitable [65, 127] with close surface tension values at ~ 40 mN/m. However, they are normally toxic with high-boiling points [122], which makes it difficult to remove the solvent after exfoliation. This highly restrains their practical usage. Therefore, sustainable organic solvents with low boiling points (e.g., ethanol and IPA) attract attention and have been studied to exfoliate and stabilise 2D materials. However, they only yield a one-order-of-magnitude lower concentration and poorer dispersion [122, 128, 129], due to a large mismatch of surface energies (ethanol of 19 mN/m and IPA of 21.4 mN/m). Co-solvent systems [122] are proposed in this case to obtain a trade-off between the yield and sustainability, but the temperature-sensitive evaporation issue of the solvents during the LPE process and the stability of the dispersion are still challenging [81].

Among all solvents, water is the most sustainable choice due to its green, biodegradable nature, reduced cost, high solubility and dispersibility for 2D materials. However, water has a high surface tension at ~ 72 mN/m [130]. To reduce the surface tension difference between water and 2D materials, minimising the energetic cost and maximising the yield of LPE, surfactants and stabilisers are then introduced to reduce the surface tension of water by introducing electrostatic repulsion or steric repulsion [131]. The stabilisers used in the LPE of 2D materials are ionic and non-ionic surfactants, as well as polymers. Commonly used ionic surfactants are CMC [73] and sodium deoxycholate (SDC) [132]. An ionic surfactant comprises a non-polar tail and a polar head. The non-polar tail group contacts the basal plane of a 2D flake due to Van der Waals force, and the polar head group protrudes into the liquid. The polar head then undergoes dissociation, resulting in a charge being obtained by the polar head. The charge prevents aggregation of 2D flakes by electrostatic repulsion, allowing a homogeneous and stable dispersion. Similarly, non-ionic surfactants consist of a hydrophilic head and a hydrophobic tail, which prevents aggregation of 2D flakes via steric repulsion. In the case of polymers like PVP [84], polyurethane (PU) [133], the polymer is adsorbed on the surface of the flake at a number of sites with many loops and tails protruding into the solvent, where steric repulsion takes effect [134]. When the flakes approach each other, the polymer chains collide at the same space, and the resulting repulsion force prevents the flake aggregation [135, 134].

The effects of stabiliser on the final yield of 2D materials vary with the choice of stabiliser and their concentration [136]. After the LPE process, stabilisers can be removed via various methods depending on the final need (improving conductivity [84] or dielectric constants [80]), including thermal annealing [137], photonic annealing [84], centrifuge wash [138] and vacuum filtration wash [131].

2.2.5 Centrifugation

Delamination of 2D materials using ultrasonication, shear-mixing, or microfluidisation does not result in 100% exfoliation occurring [139]. The centrifugation process is then applied to sediment out unexfoliated large flakes [140] and/or contaminants [141]. It is also possible to sort out a desired range of flakes with targeted lateral sizes and thicknesses by altering the centrifugation parameters [142], such as centrifuge speed and time. In this case, the physical and mechanical properties of 2D materials can be controlled more precisely.

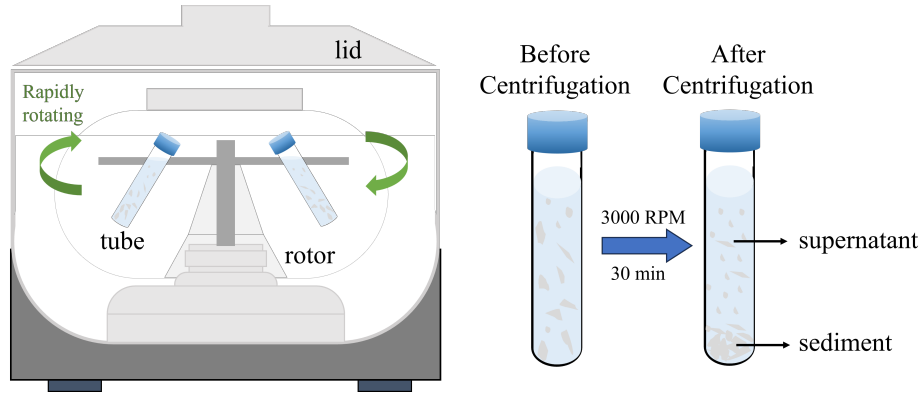


Fig. 2.10 Schematic illustration of the differential centrifugation process.

There are some types of centrifugation, namely differential centrifugation, density gradient centrifugation, rate zonal centrifugation, and isopycnic centrifugation [143], based on the sedimentation rate of a particular flake. The sedimentation rate can be quantified using the sedimentation coefficient defined by Svedberg equation [144] and usually in the order of 10^{-13} s.

In the formulation, purification, and size selection of 2D flakes in suspension, differential centrifugation is the most commonly used method [117, 145–148]. As illustrated in Figure 2.10, the differential centrifugation uses a centrifugal force field generated by a rotor to force the suspension orbit the centre with a certain speed, separating flakes suspended in the liquid into a sediment [149]. During the centrifugation process, three forces exist: the centrifugal force (F_{cen}), the countering buoyant (F_{buo}) and frictional forces (F_{fri}). They are quantitatively determined by the following equations:

$$F_{\text{cen}} = m_{2\text{D}}\omega^2 R_{\text{rad}} \quad (2.3)$$

$$F_{\text{buo}} = -m_0\omega^2 R_{\text{rad}} \quad (2.4)$$

$$F_{\text{fri}} = -f_{\text{coefficient}}v \quad (2.5)$$

where m_{2D} is the mass of the flakes, ω is the angular velocity of the centrifuge rotor, R_{rad} is the radius of the rotation pathway (the distance from the axis of rotation to the bottom of the centrifuge tube), m_0 is the mass of the displaced solvent, $f_{coefficient}$ is the friction coefficient that exists between the solvent and 2D flakes, and v is the sedimentation velocity.

The flakes in suspension will be pushed to the bottom of the tube due to the F_{cen} until it equals to the resisting F_{buo} and F_{fri} , which steers the flake away from the bottom of the tube [139]. The forces are related to the flake size, shape, density, liquid viscosity (η), temperature, rotor type, and centrifugation speed. The speed is usually quantified using revolutions per minute (rpm) and relative centrifugal force (rcf) compared to gravity.

By altering various centrifugation parameters and using different centrifugation types, a range of purposes (i.e. altering the particle size distribution) can be achieved. For instance, Yao, et al. [11] obtained thicker FLh-BN flakes at an average thickness of 6.1 nm with a layer number of approximately 15 after centrifugation at 3000 rpm for half an hour. Fenech-Salerno [84] obtained an average 2.65-nm thick 5-layer graphene after centrifugation at 15,000 rcf for an hour.

2.3 Selective etching and delamination of MXenes

With as-received MAX phases, the synthesis of MXenes can be separated into two steps, selective A-atom layer etching and delamination of the multilayer MXenes (m-MXenes) into single flakes, as shown in Figure 2.11.

2.3.1 Selective A-atom etching

There are three commonly used ways to selectively etch the A element in the MAX phases: HF route, HCl+LiF route, and fluorine-free route [150].

The HF route is the first proposed but most aggressive way to synthesise MXenes from MAX phases. The process generally involves directly immersing the MAX phase in a solution of concentrated HF and leaving the reaction for hours, during which time, the "A" layer from the MAX phase can be selectively etched out, resulting in the formation of MXenes [31, 151]. The resultant dispersion contains m-MXenes which are not readily delaminated into 2D nanosheets [152], as seen in Figure 2.11. For the mostly well-known MXene, $Ti_3C_2T_x$, the *c*-lattice spacing (*c*-LP) of the HF-etched $Ti_3C_2T_x$ is slightly increased to $\sim 19\text{-}20$ Å compared to 18.4 Å of Ti_3AlC_2 , suggesting the formation of surface functional groups [31].

The HF route is straightforward and has been extensively studied. However, using HF is extremely hazardous, posing significant risks during handling, and disposal of HF waste requires careful management due to its toxicity. The resultant MXenes are heavily terminated with fluorine [153], which may limit their application in certain contexts due to altered surface chemistry.

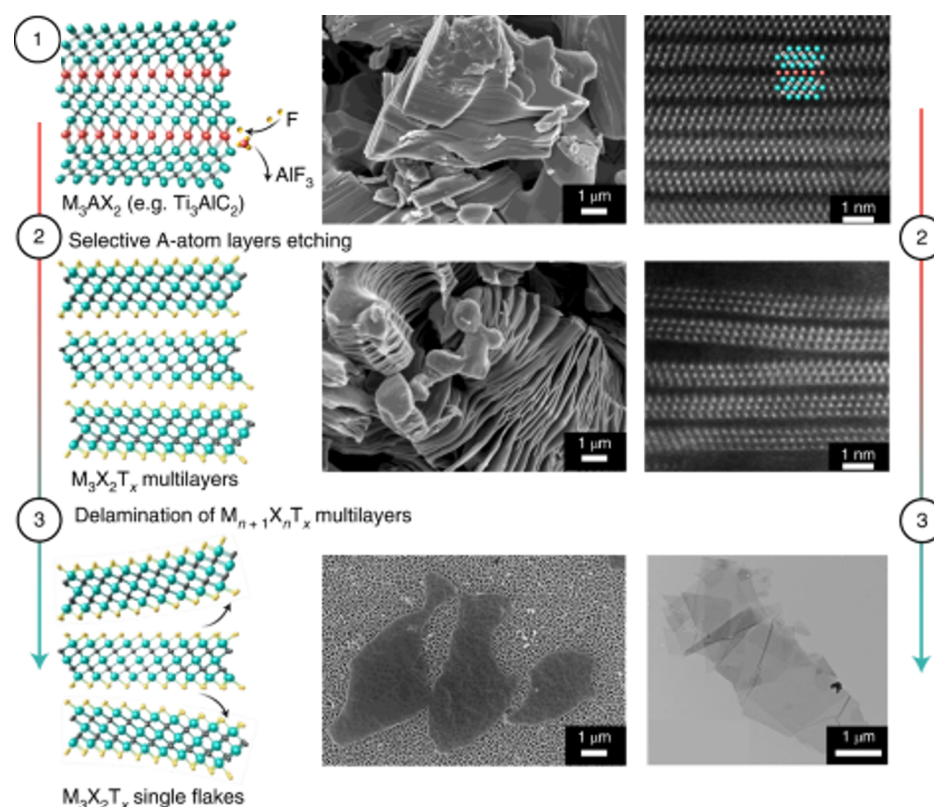


Fig. 2.11 Selective A-atom etching of MAX phases into m-MXenes and delamination of m-MXenes [152]. © 2022 Presidents and Fellows of Harvard College. This figure is licensed under the Creative Commons Attribution License.

Instead of using concentrated HF directly, the acid/fluoride salt etching (e.g., $HCl+LiF$) route is proposed to generate in-situ HF in a more controlled manner by adding LiF into HCl aqueous solution [33]. The MAX phase can be immersed in the solution and left for hours at certain temperatures to allow etching to take place. This route has the additional advantage of introducing cations, Li^+ , which can intercalate the MXene layers and expand the c -LP, and therefore promote delamination spontaneously during the etching process [153]. It is proved by X-ray diffraction (XRD), showing the c -LP of the $HCl+LiF$ etched $Ti_3C_2T_x$ is further increased to $\sim 27-28$ Å [33]. The (002) XRD peak of $Ti_3C_2T_x$ is sharper and more intense compared to that of HF etched one [153], revealing that this route produces better structural order of MXene layers with possible coulombic interaction between MXene flakes, cations

and water molecules. The in-situ HF route is more gentle [153, 154] and produces flakes with fewer defects, compared to the MXenes produced via the HF route which usually have severer structural defects [155, 156]. Lipatov et al. [157] compared the flakes synthesised via the HF route (not conductive) and the ones synthesised by in-situ HF route (conductive) in a transistor structure, revealing that the presence of pin-holes and other structural defects produced in the HF route reduces the stability of MXenes and promotes the oxidation in the ambient environment, and the position of defects can be where the metal oxide grows [158]. Moreover, the less destructive in-situ HF route produces clay-like MXene products with a higher conductivity ($\sim 15,000 \text{ S m}^{-1}$) and larger flake size (several micrometres) [153, 154], compared to 4600 S m^{-1} produced via the HF route. Intercalation by ethanol molecules would enhance the yield, but a reduced conductivity ($\sim 2000 \text{ S cm}^{-1}$) is achieved [159]. Therefore, MXenes in Chapter 7 are synthesised using this favoured route. Other possible acid/fluoride salt mixtures include adding sodium fluoride (NaF) and potassium fluoride (KF) into HCl aqueous solutions [160], also give similar etching behaviour [151]. The choice of salts and acids would affect the surface chemistry of the MXenes, allowing various types of functional groups to terminate.

The fluorine-free routes have been explored to avoid the involvement of unsustainable and harmful fluorine elements during the synthesis, including the electrochemical route [161], alkali route [162], molten salt route [163]. The electrochemical route uses the MAX phase as an electrode in electrolytes like HCl [164], ammonium chloride (NH_4Cl) [161], with a certain applied voltage. Yang [161] found the *c*-LP of the electrochemical synthesised $\text{Ti}_3\text{C}_2\text{T}_x$ is $22.6 \text{ \AA}$ and a high yield over 90% of monolayer and bilayer nanosheets were achieved with a large (over $2 \text{ }\mu\text{m}$) lateral flake size. However, this route creates a risk of the formation of the carbide-derived carbons due to the removal of Ti layers, resulting in impurity in the end product and a low yield of pure MXenes [150]. The alkali route uses bases, like tetramethylammonium hydroxide (TMAOH) [165], potassium hydroxide (KOH) [166] and sodium hydroxide (NaOH) [166] to interact with Ti_3AlC_2 to form the aluminium hydroxide anion ($\text{Al}(\text{OH})_4^-$) surface functionalisation and use cations intercalation to form expanded $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. However, this route requires a high synthesis temperature ($\sim 200 \text{ }^\circ\text{C}$), has a low yield, and the synthesised flakes are prone to be re-stacked with each other. The molten salt route is mostly studied for the synthesis of nitride-based MXenes [150], which is beyond the scope of this work. Overall, the fluorine-free methods are promising yet well understood and require more investigation.

2.3.2 Delamination of multilayer MXenes

Typically, the etched solution requires several cycles of washing to remove any byproducts of the reactions, highly acidic composition, and excessive salts [153]. Afterwards, the delamination is allowed to happen at a pH of $\sim 6-7$. There are several ways to assist the delamination process. Ultrasonication can accelerate and intensify the delamination but introduces defect density and reduces flake lateral size [157]. Organic molecules can be intercalated (e.g., DMSO, urea, and long-chain alkylamines) and later exchanged by water molecules to largely enhance the production yield [32]. However, it is difficult to thoroughly remove the organic molecules, which negatively impact the conductivity of the resultant flakes and films.

Delamination by cations intercalation is the widely applied approach to enhance the final yield by introducing Li^+ , K^+ , Na^+ , Rb^+ , Mg^{2+} , and Ca^{2+} [167], either directly in the etching process or in the delamination process. The introduction of cations gives the MXene films a hygroscopic nature [168]. If the m-MXenes are intercalated with cations, gentle sonication or shear forces are normally assisted, such as mechanical stirring, vortex, and manual hand shaking, to delaminate the m-MXenes into few-layer or single-layer MXenes. This is investigated as the minimally intensive layer delamination (MILD) method [37] to avoid introducing structural defects of the MXene flakes, reducing the lateral size and accelerating oxidation rate.

2.4 Deposition of thin films

This section will go through the thin-film deposition techniques used in the work, including spray coating and spin coating. The deposition mechanism, the requirements, the strengths and weaknesses, and why they are suitable for the job here are discussed. There are also many other thin-film deposition techniques beyond the scope of the thesis, which you can find in reference [55].

In this work, deposition aims to facilitate various material quality characterisation (section 2.5), to fabricate a thin film in layered-structure devices, and to allow single isolated flakes situated on Si/SiO₂ wafer.

2.4.1 Spray coating

Spray coating is a process by which a coating material is applied to a surface using atomisation, droplet deposition, and evaporation, creating a thin and uniform layer. There are different types of spray coating, like air spray systems, ultrasonic spray systems, and electrostatic spray systems. Figure 2.12 [169] illustrates an example of an air-assisted spray coating setup. In this process, the suspension containing the coating material is added into the reservoir, atomised, and pushed out of the nozzle using a pressurised gas onto a substrate. Applying a mask covering the substrate, the pattern of the film can be tailored to specific geometries, and the thickness can be controlled by the times and the amount of spraying. During the process, the atomisation of the liquid happens and results in the production of a spray that contains droplets in the micrometre dimension [170]. Atomisation takes place when the dynamic pressure of an external force exceeds the internal pressure of the droplet. This process can be described by Weber Number (We), a dimensionless number characterising the relative importance of the fluid's inertia compared to its surface tension (γ):

$$We = \frac{\rho v^2 D}{\gamma} \quad (2.6)$$

where, ρ is the density of airflow, v is the velocity, and D is the characteristic length (e.g., the droplet diameter) [171]. A higher We number typically indicates that the fluid is more likely to break into fine droplets. For low-viscosity liquids, atomisation occurs at values greater than the critical $We > 13$ [81]. As droplets are deposited on the substrate, they evaporate and form a thin film. The evaporation rate can be described by D^2 -Law [172].

$$D(t)^2 = D_0^2 - Kt \quad (2.7)$$

where $D(t)$ the droplet diameter at time t , D_0 is the initial droplet diameter, K is the evaporation constant.

Therefore, governed by the above equations via physical parameters, both the liquid atomisation and the drying process affect the uniformity of the resultant film [173]. The film uniformity can be optimised by various factors, such as the nozzle diameter D of the airbrush, the γ and η of the suspension, the K of solvents [174], the nozzle/substrate distance [175], and the temperature of the substrates [176].

Spray coating is a widely-applied deposition technique in graphic art [177] and industrial surface coating [178, 179], allowing cost-effective fast deposition of functional inks on rigid and large-area ($> 1 \text{ m}^2$) substrates [55]. It is also a versatile technique, frequently

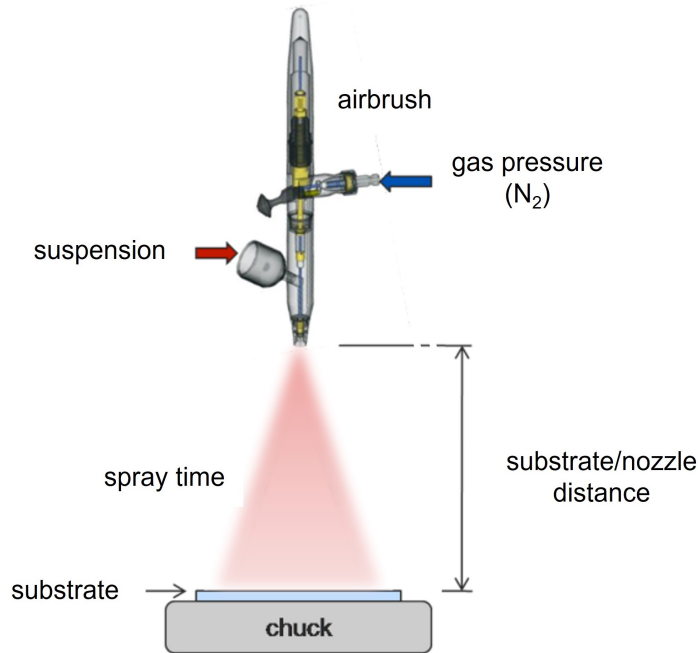


Fig. 2.12 Schematic illustration of the implemented manual airbrush coating system. Image adapted from [169].

used in the deposition of 2D materials, facilitating fast coating of 2D materials to thin films (tens of nanometers to micrometres) in FETs [84], supercapacitors [37], solar cells [180] and layer coatings. Spray coating of r-GO inks on Si/SiO₂ [181] and quartz [182] has been used to demonstrate field effect response with a mobility of $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and transparent conducting films with sheet resistance (R_s) $\sim 2.2 \text{ k}\Omega/\text{sq}$ and transmittance of $\sim 84 \%$, respectively.

Although spray coating is limited to a relatively larger lateral resolution (hundreds of micrometres) compared to that (down to tens of micrometres) of inkjet-printing [55], which is caused by the geometry of mask designs and the possibility of droplets penetration into the gap between the masks and substrates, spray coating produces better uniformity of thin films along lateral directions. Besides, spray coating is preferable in this work for its versatility to a wide range of functional inks, capability of large-area deposition, and controlled uniform film thickness.

2.4.2 Spin coating

Spin coating is another procedure used to deposit uniform thin films onto flat substrates. A machine used for spin coating is called a spin coater or simply a spinner. Figure 2.13

illustrates the whole spin-coating process. A volume of the solvent solution is dispensed onto a substrate which is absorbed into the spin-coater stage via a vacuum pump. The stage will be accelerated to the setting angular velocity (ω , normally ranging from 500 - 6000 rpm) [183], at which the liquid will be spread across the entire substrate surface. At the same time, the solvent evaporates, and the coated material dries into a film structure. The single spin coating process can be repeated to prepare films with different thicknesses using the same material or prepare multilayer structures using various materials. The thickness (t) of the film is influenced by several factors, including the spin speed (ω), solution viscosity (η), and evaporation rate of the solvent. It can be estimated using the following empirical relationship [184]:

$$t \propto \left(\frac{\eta}{\omega^2 \rho} \right)^{0.5} \quad (2.8)$$

The balance between the centrifugal force (ω and density ρ) [185] and the nature of the solvent (η and ρ) [185] controls the flow of the suspension [186] and the thickness of the film [187].

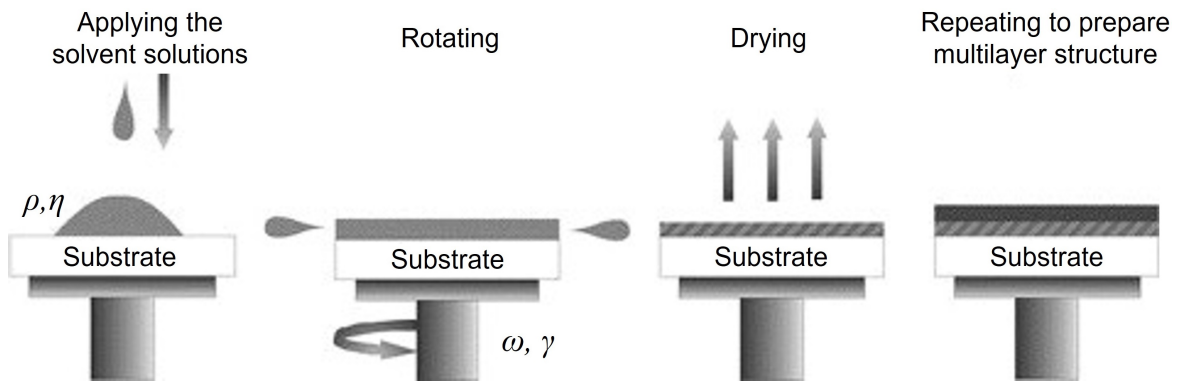


Fig. 2.13 Schematic illustration of the spin coating process. Image adapted with permission [188], © 2019 Elsevier Inc.

Spin coating is a versatile technique to deposit a wide range of materials, including polymers [189], 2D materials [190–192], in non-fullerene solar cells [189], photovoltaic electrodes [193], micro-super-capacitors [194], or field emitters [195]. For example, ref [191] demonstrated that the spin-coated 20-nm thick reduced graphene oxide (rGO) film has a R_s of 2 kΩ/sq with a transmittance above 70% at the λ range of over 400-1100 nm. It can be used as the transparent electrode in polymer-fullerene photovoltaic devices.

The spin coating is chosen for this work because spin coating allows for an ultrathin (< 10 nm) layer of 2D materials fabricated in the form of single flakes if a diluted solution is provided. Moreover, specifically for MXenes, during the spin coating process where the controlled shear forces (centrifugal forces) apply, the m-MXenes flakes can be further delaminated into

thinner flakes, even a mono-layer flake [196]. The mono-layer flake with a micrometre lateral size allows us to deposit metal electrodes on a single flake using electron-beam lithography (EBL) and study the charge transport mechanism of the single flake, which will be discussed in the section 7.3.

2.5 Probing quality of the material

This section will introduce various techniques chosen in this work to characterise the 2D material, such as chemical composition and flake size. Characterisation methods include Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

2.5.1 Molecule identification via Raman spectroscopy

Raman spectroscopy is an analytical technique to observe vibrational, rotational, and low-frequency modes in a material-based system. It is based on inelastic scattering or Raman scattering of monochromatic light from the chemical bonds within a material, which is a non-destructive chemical analysis technique. When a high-intensity laser beam shines on a material, the molecules of the material interact with the photons from the laser, causing the light to scatter [197]. This scattered light can retain the same energy, have lower energy, or have higher energy compared to the incident light, corresponding to Rayleigh scattering, Stokes scattering, and anti-Stokes scattering, respectively [198]. Rayleigh Scattering occurs when the scattered light has the same wavelength (λ) as the incident light. Stokes scattering occurs when the scattered light has lower energy than the incident light, while anti-Stokes scattering occurs when the scattered light has higher energy. Stokes scattering and anti-Stokes scattering are referred to as Raman scattering. The most scattered light is Rayleigh scattering, which does not offer helpful information on materials. However, a tiny fraction (typically 0.0000001%) of the scattered light undergoes Raman scattering, and the energy shift observed in Stokes and anti-Stokes scattering is known as the Raman shift. This shift provides valuable information about the vibrational and rotational modes of the molecules in the material.

Figure 2.14 schematically illustrates the function of a Raman microscope. A monochromatic laser is directed to a microscope after being filtered and reflected. The microscope focuses the laser onto the sample [199, 200], and the interaction of the laser with the sample occurs. The scattered light is then collected by the microscope and directed to the Raman spectrom-

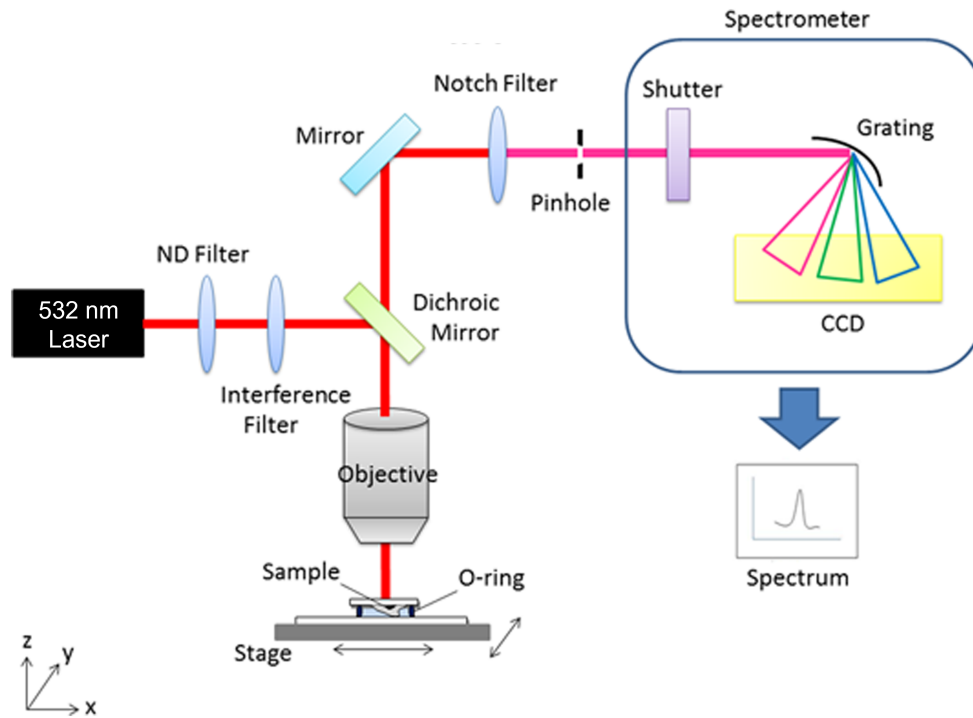


Fig. 2.14 Schematic illustration of a Raman microscope. Image adapted from reference [201]. © 2013 Pei-San Hung, Yi-Chun Kuo, He-Guei Chen, Hui-Hua Kenny Chiang, Oscar Kuang-Sheng Lee. The figure is licensed under the Creative Commons Attribution License.

eter. In the spectrometer, the grating disperses the scattered light onto the long axis of a charge-coupled device (CCD), where the scattered light photons are detected at a specific wavenumber, resulting in a Raman spectrum.

Raman spectroscopy has been frequently used in 2D materials to characterise the material quality [202]. First, Raman spectroscopy is extremely sensitive to the number of layers in 2D materials. For instance, in h-BN, the peak position, shape and intensity vary depending on whether the h-BN is a mono-layer ($1368\text{--}1370\text{ cm}^{-1}$), bilayer ($\sim 1364\text{ cm}^{-1}$), few-layer ($\sim 1365\text{ cm}^{-1}$) or bulk crystals (1366 cm^{-1}) [203]. With an increasing number of layers, the peak is sharper with higher intensities. Second, different 2D materials have unique Raman signatures, making Raman spectroscopy helpful in identifying the composition of a sample. For example, various MXenes have their own characteristic Raman peaks associated with their vibrational modes [204]. $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes have A_{1g} out-of-plane vibrational modes at ~ 200 (flake region) and $600\text{--}800\text{ cm}^{-1}$ (C region), and E_g in-plane vibration modes at $100\text{--}500\text{ cm}^{-1}$ (T_x region) and $500\text{--}700\text{ cm}^{-1}$ (C region) [204].

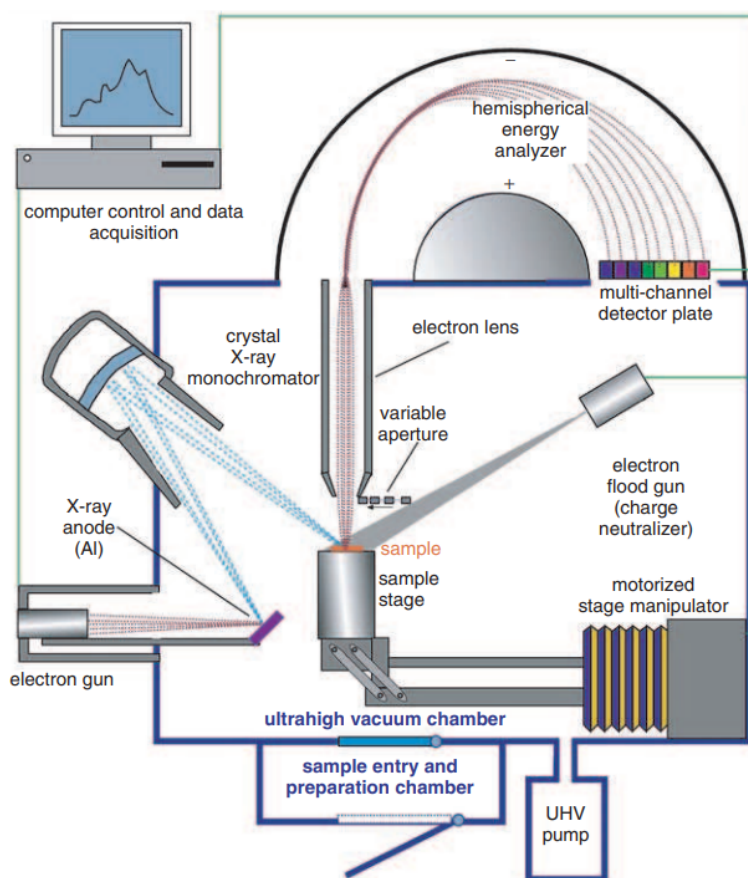


Fig. 2.15 Schematic illustration of an XPS instrument. Image copied with permission [206]. © 2009, John Wiley and Sons.

2.5.2 Chemical compositions via X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analyses the photoelectric effect of a sample surface [205] via X-ray irradiation, revealing the chemical composition (i.e. surface functionality) of materials [206].

Figure 2.15 illustrates the configuration of an XPS instrument. X-rays are generated by bombarding a metallic anode (usually made of aluminium (Al $K\alpha$) or magnesium (Mg $K\alpha$)) with high-energy electrons produced via an electron gun [206]. The generated X-rays contain multiple λ , including both characteristic X-rays and bremsstrahlung (continuum) radiation. The crystal X-ray monochromator selectively transmits only the characteristic X-rays of a specific λ , filtering out the rest [206], ensuring a better resolution. The monochromatic X-rays are directed onto the sample's surface, which is placed on the sample stage under an ultra-high vacuum. The interaction of X-rays with the atoms in the material causes the ejection of core-level electrons. The core electrons absorb the energy of the X-rays and

are ejected from the atoms, which is governed by the photoelectric effect. The emitted photoelectrons have a specific kinetic energy (KE) characteristic of the element from which they are emitted. The ejected photoelectrons are collected by an energy analyser, and they are separated based on their KE within a magnetic field. The separated electrons are then detected by a multi-channel detector, which produces a photoelectron spectrum showing the intensity of the sample ejected electrons over a range of binding energy (BE). The relation between BE and KE is

$$BE = h\nu - KE - \Phi_{\text{spec}} \quad (2.9)$$

where $h\nu$ is the energy of the incident X-rays, Φ_{spec} is the work function of the spectrometre.

However, XPS can only provide chemical composition information at the sample surface ($\sim$ nanometers), because the ejected photoelectrons from the deep sample will undergo an inelastic scattering [207] and therefore have insufficient energy to pass through the energy analyser. Only the ejected photoelectrons from the sample surface have sufficient energy to pass through the energy analyser and can be detected by the multi-channel detector [79].

Within the MXene field, XPS is an attractive technique for investigating surface chemistry [204], distinguishing between different oxidation states of transition metals (e.g., Ti^0 , Ti^{2+} , Ti^{3+} , Ti^{4+}) and identifying functional groups (e.g., $-\text{F}$, $-\text{O}$) via F 1s, O 1s and Cl 2p. The types and amounts of functional groups are crucial for understanding the material's properties, which are often achieved using different synthesis methods and surface modifications, such as oxidation, fluorination, or functionalisation with organic molecules. XPS is such a quantitative tool for monitoring these modifications, allowing researchers to track changes in the functional groups. For example, a peak at 459.0 eV indicates the oxidation of the MXenes in the form of TiO_2 [204]. However, it is hard to trace water and $-\text{OH}$ terminations of MXenes in the ultrahigh vacuum of XPS, and the sample sputtering process, which is often used to clean the surface and improve quality of the spectra, was demonstrated to modify the MXene elemental composition [208].

2.5.3 Lattice spacing via X-ray diffraction

X-ray diffraction (XRD) is an analytical technique used to determine the atomic and molecular structure of a crystal based on the Bragg's equation. By measuring the angles (θ) and intensities of X-rays diffracted by the crystal, it is possible to produce a three-dimensional picture of the electron density within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, disorder, and other information.

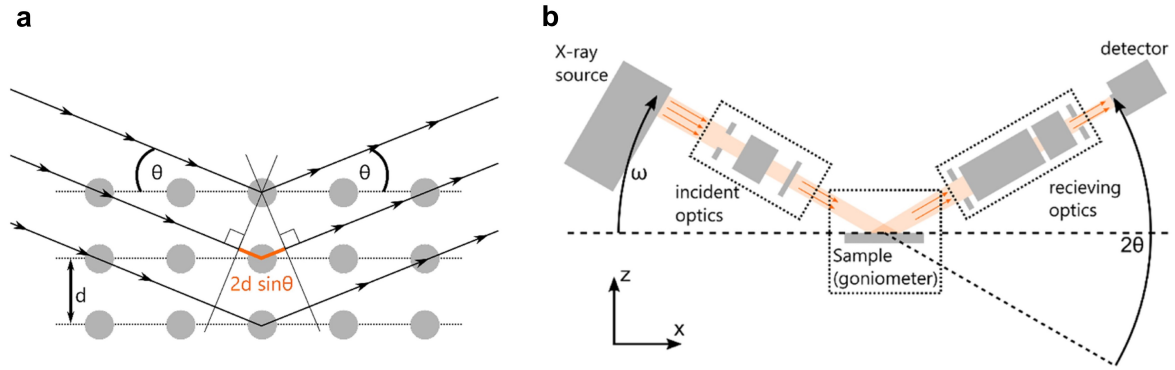


Fig. 2.16 Visualisation of Bragg's Equation (a) and schematic illustration of an XRD instrument (b). Image adapted with permission [209], © 2021, Harrington, G.F., Santiso, J., under exclusive licence to Springer Science Business Media, LLC, part of Springer Nature.

Figure 2.16(a) visualises the Bragg's equation [209]. A crystalline material is scanned with an incident X-ray beam at a certain λ and a θ [210]. The incident X-ray will impinge onto a series of atomic planes with spacing (d) within the material. Due to the crystallinity of the material, the scattered beam angle compared to the horizontal line is equal to θ [209]. The relative phase shifts between the X-ray scattered off the 1st and 2nd plane is given by $2d \sin \theta$ [210]. The constructive interference between the scattered X-rays will take place from certain θ , mathematically shown by the Bragg's equation [209]:

$$n\lambda = 2d \sin \theta \quad (2.10)$$

which relates the angular position of diffracted X-rays to the c -LP and underpins all XRD measurements [209].

Figure 2.16(b) illustrates a configuration of an XRD instrument. X-rays are generated typically by bombarding a metal target (commonly copper, Cu) with high-energy electrons [209]. It is then shaped and focused by incident optics (a series of slits and parallel plates) before impinging onto the sample surface. The scattered X-rays pass through the receiving optics and are collected by the detector. The detector can convert the incoming X-rays to an electrical signal [211], which will be further processed to produce XRD patterns showing the intensity of scattered X-rays as a function of 2θ [211]. The goniometer is able to control the θ between the X-ray source, the detector, and the sample surface [209]. In some diffractometers, the sample is fixed while the X-ray source and the detector rotate in opposite directions (θ - θ goniometer) [209]. Alternatively, the X-ray source is fixed, the sample rotates, and the detector rotates at twice the speed (θ - 2θ goniometer) [209].

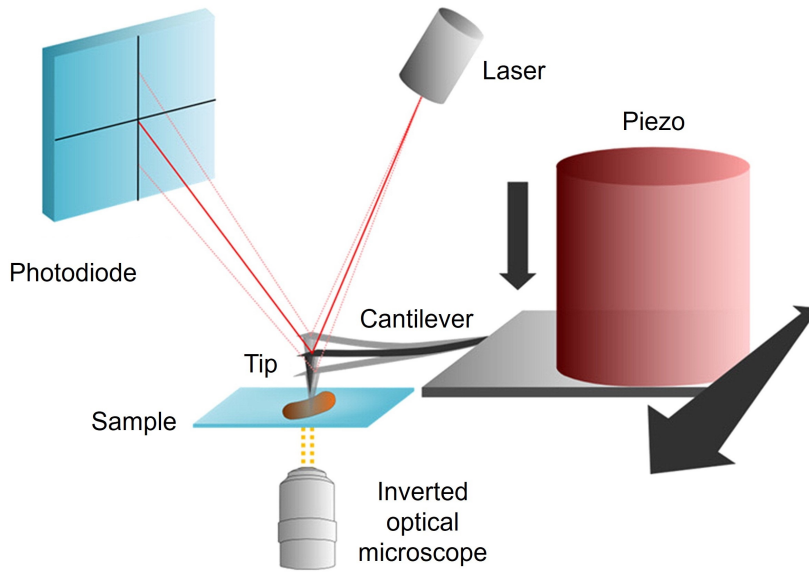


Fig. 2.17 Schematic illustration of the AFM. Image adapted with permission [212]. © 2013 Elsevier B.V.

XRD is one of the easiest ways to confirm that MXenes was produced. The characteristic XRD patterns change when converting the MAX to multilayer MXene and then to delaminated MXenes. For example, the (002) peak of the dried $\text{Ti}_3\text{C}_2\text{T}_x$ multilayer powder is at 9.4° , the peak of the wet multilayer powder shifts to 6.6° , and the peak of the delaminated film is at 8.6° [204]. In this case, the (002) peak position reveals the interlayer spacing of 4 Å and 0.9 Å for the multilayer powder and the film, respectively, telling us the intercalation of ~ 1.4 layers of water and a Li^+ ion, respectively, between the sheets [204]. Besides, XRD provides insights into the degree of crystallinity of MXenes. Sharp and well-defined peaks indicate high crystallinity, while broad peaks can suggest defects, disorder, or small crystallite size.

2.5.4 Flake size via atomic force microscopy

Atomic force microscopy (AFM) can provide precise measurements of the thickness of 2D materials down to the atomic scale and their lateral size information. This is particularly important for confirming the number of layers in 2D materials like h-BN and MXenes, where the difference of properties between monolayer, bilayer, and few-layer samples is critical.

Figure 2.17 illustrates the operation principle of an AFM. The tip is mounted on a micro-fabricated cantilever at one end, and the other end scans the sample surface. The cantilever is connected to a piezo system, which can control the scanning of the tip on the sample

surface in the horizontal and vertical direction (black double arrows in Figure 2.17) [213]. The interaction (repulsive) forces [213, 214] between the sample and the tip-end induces the mechanical deformation (bending) [214] of the tip. When the laser is reflected by the back of the cantilever to the photodiode, the deformation leads to the displacement of the laser beam on the photodiode compared to its original position at no force. The displacement is recorded as the amplitude signal of the cantilever deflection in each scanning line. By assembling multiple scanning lines, a 3D image can be generated with the degree of displacement at each point forming topography images. The scanning mode can be a contact, non-contact, or tapping mode [212, 213, 215]. The contact mode places the probe tip in contact with the sample surface, while the non-contact mode brings the probe tip close to the sample surface [215]. Different from these two modes, the tapping mode operates like the probe is made to oscillate at a certain frequency [215]. Any disturbance to the oscillating amplitude caused by the interaction between the samples and the probe due to the height change of the sample during a scan is recorded to generate the topography image with height information [215]. For example, the thickness of a single-layer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flake deposited on a Si/SiO_2 is determined at 3.0 nm [216] via analysing the oscillating amplitude difference between the probe/substrate interaction and the probe/flake-surface interaction. Later studies show a more precise analysis of the $\text{Ti}_3\text{C}_2\text{T}_x$ flake thickness via the height of the second layer (1.6 nm) contrast to the first layer [216].

AFM can also map the surface morphology of 2D materials, revealing features such as wrinkles, folds, and roughness. If AFM is used in force mode, the mechanical properties of 2D materials, such as Young's modulus and stiffness, can be measured. Another advantage of AFM is that it can operate in air, liquid, or even under vacuum [213] and have a scan at various types of materials without treatment, including polymers [217], biomaterials [218], 2D materials [219].

2.5.5 Flake morphology via scanning electron microscopy

Apart from AFM, scanning electron microscopy (SEM) is another microscopy applied in this work to reveal the high-resolution topography, lateral size, and morphology of 2D materials. Unlike AFM, which relies on repulsive forces, SEM is based on electron scattering of samples.

Figure 2.18 schematically illustrates a scanning electron microscope. Electrons are produced by the electron gun and accelerated by the anode (at a specified accelerating voltage of 1 keV to 30 keV) [221]. The emitted electron beams are then diameter-controlled by the

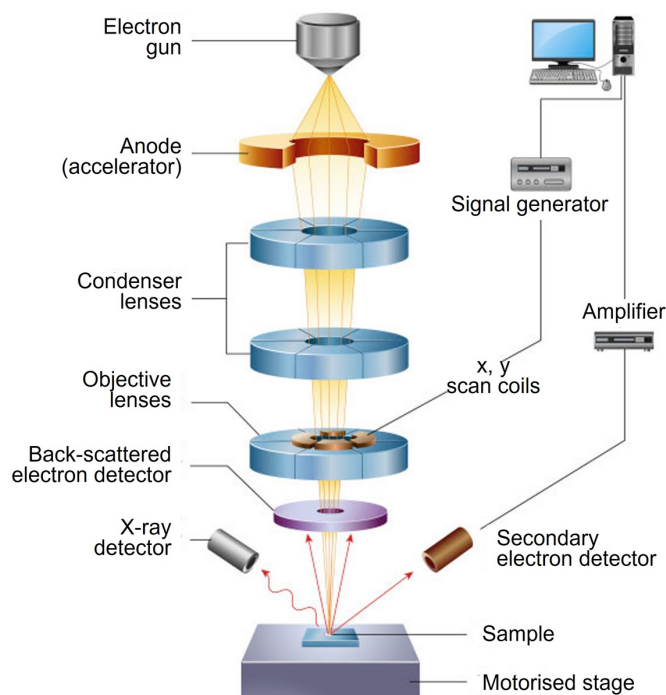


Fig. 2.18 Schematic illustration of a scanning electron microscope. Image adapted from reference [220], © 2024. Nanoscience Instruments.

condenser lenses and apertures and focused by the objective lenses. Above the objective lenses are the scan coils, which control the precise positioning of the sample surface for accurate focusing [221]. The shaped electron beams eventually strike the sample, generating various signals, including secondary electrons, back-scattered electrons, and characteristic X-rays. These signals are then detected by appropriate detectors to reconstruct images based on the topographical or compositional demographic of the sample. Back-scattered electrons (i.e. high energy electrons > 50 eV) [81] are usually applied to reveal the atomic information of the sample, whereas the secondary electrons (i.e. low energy electrons < 50 eV, which are produced more at the edges) [81] is often utilised to image the sample surface and edge. The image quality can be adjusted via emitting current (brightness), accelerating voltage (signal-to-noise ratio), and configuration of lenses (focus).

Regarding insulating materials like h-BN, a thin conducting layer (e.g., a 3-5 nm chromium coating) should be applied to the sample surface to reduce the impact of surface charging, which can damage the sample, produce artefacts, and decrease structural details.

Applying SEM to the characterisation of MXenes, the “accordion” structure indicates the successful A-element etching from the MAX phase [204], as shown in Figure 2.11. Furthermore, SEM images often reveal oxide nanoparticles on the outsides of the layers, indicative

of the aggressive etching process or long-time storage, leading to oxidation occurrence on the surface. By drop-casting delaminated MXene flakes onto conducting substrates, insights into the flake size, large pinholes, and quality of edges can be determined [204].

2.6 Probing properties of the material

This section will describe various techniques chosen in this work to reveal the physical properties (specifically, optical, electrical, thermal and rheological) of the 2D materials and the mechanism of the techniques. The techniques would allow us to obtain the critical properties of h-BN and MXenes and indicate their possible applications.

2.6.1 Optical properties via optical absorption spectroscopy

Optical absorption spectroscopy (OAS) is a technique that measures the absorption of ultraviolet (UV), visible (Vis), and near-infrared (NIR) light by a sample. Nanomaterials interact with light and show their identical optical absorption spectra. OAS is usually the first and the easiest step in characterising 2D material-light interaction [55] via a UV-Vis-NIR spectrophotometre, which can be performed on either suspensions or thin films. In the UV-Vis-NIR region, their distinctive light-absorption peaks can be attributed to the intrinsic electronic transitions and plasmonic effects [196].

Figure 2.19 illustrates the schematic of a UV-Vis-NIR spectrophotometre [222]. The UV-Vis-NIR lights are generated by light sources (such as deuterium (D_2) lamps, tungsten lamps, and Xenon lamps), reflected by a mirror and pass through a filter. All the light sources produce a broad-spectrum white light (polychromatic light). To narrow the polychromatic light down to a selected range of individual λ (monochromatic light), the light passes through a monochromator. The spectrometre can have a single or double optical system. In a single-beam system, the monochromatic light passes through the sample to the detector, before which a baseline or blank sample must be measured. In the double beam type, the monochromatic light is split into two beams via a beam splitter: a reference beam and a sample beam. Two beams enter the chamber through separate optical paths, so the reference/blank and sample can be measured at the same time. The light residue, after passing through the sample and reference, will be absorbed eventually by a detector, which converts the light into an electrical signal. Spectrophotometres normally contain either photomultiplier tube detectors or photodiode detectors. Figure 2.19 shows an example of using photodiodes used to detect light residues from samples and reference. By comparing how much light the

two photodiodes absorb, the attenuation of light intensity through the sample or the light absorption of the sample can be extracted for an individual λ . The process is repeated for different individual monochromatic light across a desired range of λ , enabling an absorption spectrum for a sample [223].

The sample compartment of a UV-Vis-NIR spectrophotometer is typically a black-coloured box with a closing lid. The matt black inside the compartment helps to absorb stray light that may enter the compartment. For absorbance measurement, liquid samples would typically be held in a cuvette with a known, fixed path length. A cuvette is a rectangular liquid holder and is made from glass, quartz, plastic or another material that transmits UV or visible light. Standard cuvettes have a 10 mm path length and are made from quartz to ensure good transmittance of UV wavelength. Solid samples can be held in place for transmittance measurements and can also be measured at various θ of incidence.

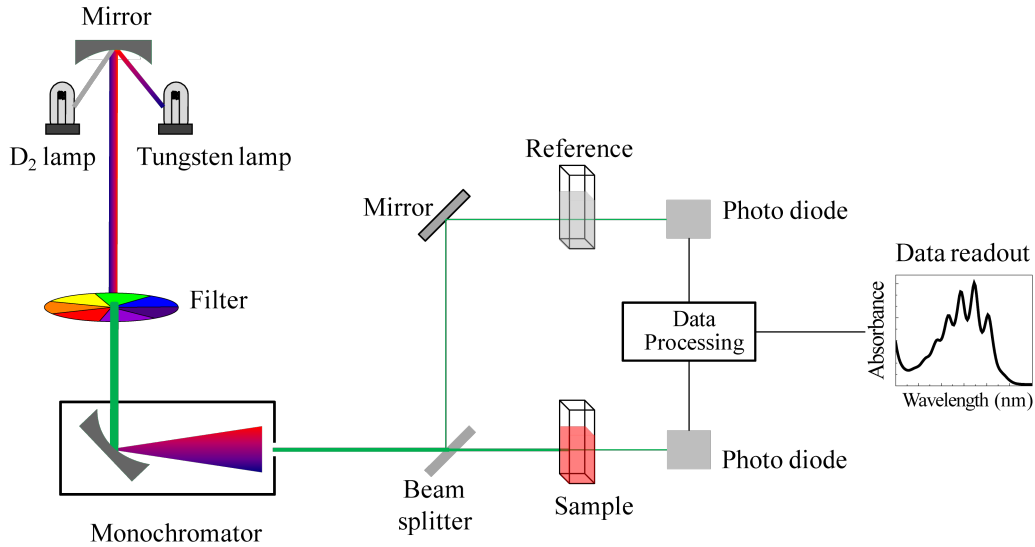


Fig. 2.19 Schematic of UV-Vis-NIR spectrophotometer. Image copied from reference [222].

Beer's Law, also known as the Beer-Lambert Law, is a fundamental principle in spectroscopy that relates the light absorption intensity (A) to the material's quantities, which is governed by:

$$A = cl\alpha \quad (2.11)$$

where c is the concentration (g L^{-1}), l is the beam path length (m) and α is the optical absorption coefficient ($\text{L g}^{-1} \text{m}^{-1}$). The law can be used to quantify the concentration of solutes in a solution (in this case, the concentration of 2D materials dispersed in solvents) if knowing A at a specific λ [224] and α . α can be experimentally determined by extracting the slope value of a linear curve from the measured absorption intensities as a function of

known concentrations [225]. In this work, the $\alpha = 2350 \text{ L g}^{-1} \text{ m}^{-1}$ at 300 nm is utilised for estimating the concentration of few-layer h-BN [226].

Regarding metallic MXenes, the plasmonic peaks are the collective oscillations of free electrons in response to light, indicative of the type and quality of MXenes. For example, The optical absorption spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ has a plasmonic peak around 780 nm, and that of Ti_2CT_x MXene has a plasmonic peak around 550 nm [204].

2.6.2 Electrical properties via four-point sheet resistance measurement

Sheet resistance, R_s is normally used to characterise the electrical resistance of thin films that are uniform in thickness and can be calculated using the equation:

$$R_s = \frac{\rho}{t} \quad (2.12)$$

where ρ is the resistivity and t is the thickness of the thin film.

Four-point probe measuring system is a well-applied technique to measure the R_s of a thin film [227]. Figure 2.20 schematically illustrates how the system works. There are four probes in parallel with a spacing of d (i.e. 1.6 mm), and the height of them is controlled by a lever within the system. When the four probes are brought in ohmic contact with the thin film, the current (I) propagates through the outer probes (1 and 4) and the voltage (V) between the inner probes (2 and 3) is measured. If the thickness of the thin film is smaller than half of the spacing d and the lateral dimension is larger than 40 times of the d [228], the R_s can be simplified to:

$$R_s = \frac{\pi}{\ln 2} \times \frac{V}{I} \quad (2.13)$$

The advantage of the four-point probe system is the separation of the current and voltage electrodes into two pairs, which could eliminate the lead and contact resistance from the measurement [229].

2.6.3 Rheological properties via rheometry

Dynamic viscosity (η) is one of the most important rheological properties of a liquid. Also known simply as viscosity or absolute viscosity, η measures a fluid's resistance to flow or deformation under an applied force. It quantifies the internal friction within the fluid, which arises from the interactions between its molecules as they move past each other. In this work, the rheological characterisation, such as η determination, for h-BN assisted thermal

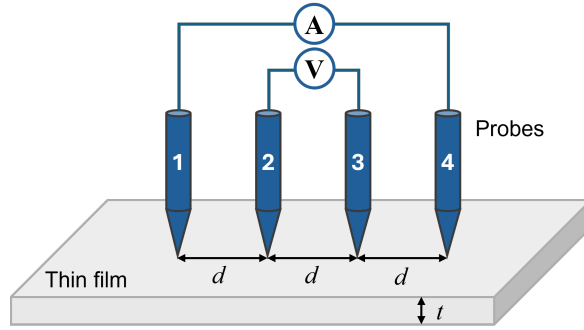


Fig. 2.20 Schematic illustration of a four-point probe measurement system.

composite is essential, as it is one of the key criteria when compared to commercial products to assess the commercial viability.

Figure 2.21 shows how to measure a liquid η . Figure 2.21(a) shows a liquid confined between two stationary ($v_x=0$) parallel plates [230]. The plates have a geometry of area (A) and gap (H) with $H \ll \sqrt{A}$. When a force (F) is applied to the upper plate (Figure 2.21(b)), the upper plate starts to move in the x direction. Assuming the non-slip boundary conditions at both the lower stationary and the upper moving plate, a velocity gradient ($\partial v / \partial y$) occurs in the liquid along H , leading to a shear flow along the y -direction [230]. The shear stress (τ) and the γ can be defined as

$$\tau = \frac{F}{A} \quad (2.14)$$

$$\gamma = \frac{\partial v}{\partial y} \quad (2.15)$$

Therefore, the η of the fluid can be defined as

$$\eta = \frac{\tau}{\gamma} = \frac{F}{A} \times \frac{\partial y}{\partial v} \quad (2.16)$$

The above fundamental theory forms the function of rotating rheometres [231]. Apart from the two parallel plates, other geometries like cone-plate and double-gap (low η fluid) [231] are developed to allow different liquids with a wide range of η values to be measured precisely.

The measured η value of a liquid depends on the working temperature, pressure, and the applied γ . Figure 2.21(c) shows examples of Newtonian, shear-thinning, and shear-thickening liquids. The η of Newtonian liquids is independent of the γ (solid red line). In contrast, the η of shear-thinning liquids (dashed blue line) and shear-thickening liquids (dot-dashed black line) decrease and increase when increasing the γ , respectively.

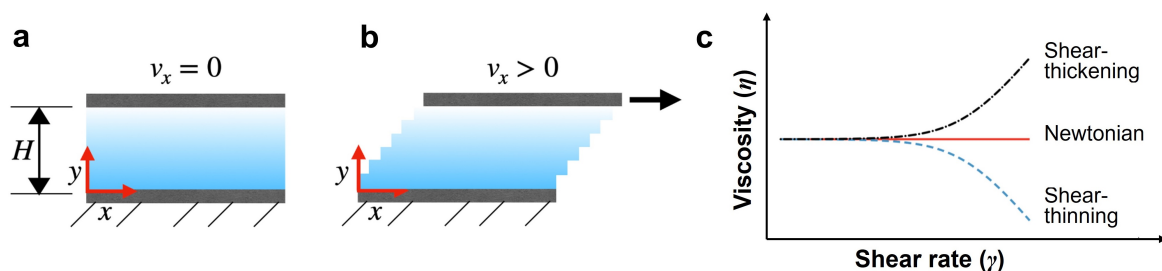


Fig. 2.21 Schematic illustration of measuring the η of a liquid. (a) Liquid between two parallel plates in stationary conditions. (b) A force is applied to the upper plate, leading to a shear flow along the y -direction. (c) Examples of liquids with 3 typical rheological behaviours [230]. The figure is licensed under Creative Common CC BY.

2.6.4 Mechanical properties via tensile measurements

Tensile strength and Young's modulus are the two mechanical properties considered in the work. Tensile strength measures the maximum stress a material can withstand while being stretched or pulled before breaking. It indicates the material's resistance to breaking under tensile forces, and it is crucial for materials used in construction, manufacturing, and structural applications where resistance to breaking under load is important. Tensile strength (σ_t) is marked as the highest point from the strain-stress curve and is calculated using the formula

$$\sigma_t = \frac{F}{A} \quad (2.17)$$

where F is the maximum force applied and A is the original cross-sectional area of the material.

Young's modulus (E), also known as the modulus of elasticity, measures the stiffness of a material by quantifying the relationship between stress (force per unit area) and strain (proportional deformation) in the linear elastic region of the material's stress-strain curve. This property is crucial for designing materials and structures that must deform elastically under load. A higher Young's modulus indicates a stiffer material that deforms less under a given load.

2.6.5 Thermal analysis via TGA/DSC

Thermal analysis is a group of techniques used to study the properties of materials as they change with temperature or their thermal response to a heat input. These techniques could

provide information on the thermal stability, decomposition, specific heat capacity, thermal diffusivity and thermal conductivity of materials.

2.6.5.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is an analytical technique used to measure the change in the mass of a material as a function of temperature under a controlled atmosphere, which is primarily used to study the thermal stability, oxidation, and thermal decomposition of materials [232, 233]. Figure 2.22(a) shows a simple TGA apparatus. The thermobalance is a highly sensitive scale where samples and crucibles are placed during the measurement, and it can measure the sample weight precisely as a function of temperature and time [234]. A sample chamber with radiation shields can create a thermal-adiabatic environment to maximise the sensitivity, accuracy, and precision of weighing [235]. The heat into and out of the material is controlled by the furnace, which is normally a programmable controller and receives the temperature feedback from the inserted thermocouples. A desired gas atmosphere, such as N_2 , Ar/H_2 (argon mixed with 5% hydrogen gas), can be realised by connecting the system to a gas cylinder. A computer is usually equipped to enable timely data acquisition, calculation and analysis of the weight-loss fraction over time/temperature. Before sample measurement, an empty run (only a crucible without any sample) is applied as a baseline correction to remove the thermal oscillations from the ambient environment (i.e., vibration, humidity.).

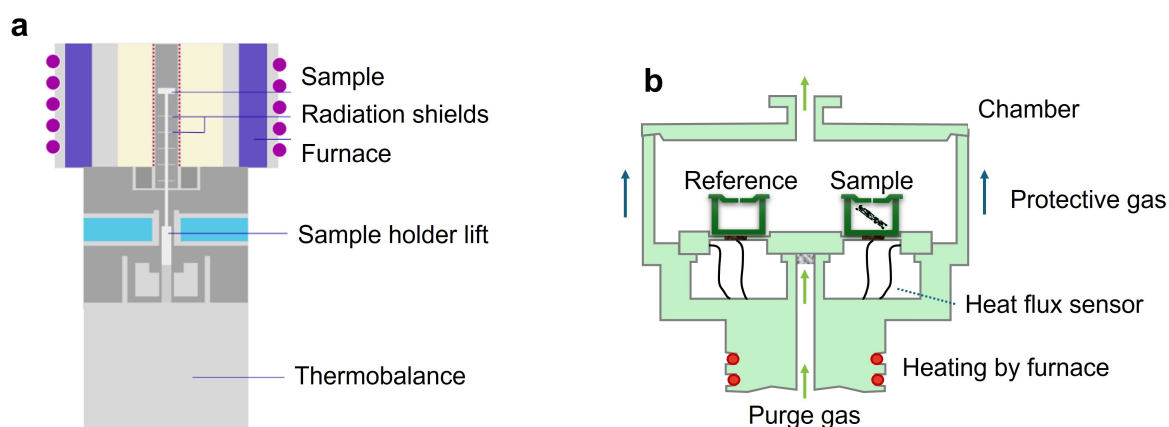


Fig. 2.22 Schematic illustration of (a) TGA and (b) DSC apparatus. Image (a) adapted with permission [236], © 2024 Particle Technology Labs.

TGA is a destructive technique and requires only a small amount ($\sim$ mg) of material. The 1st derivative of thermogravimetric analysis (DTG) is the first derivative of the TGA curve with

respect to temperature. It represents the rate of weight loss as a function of temperature. In the DTG curve, peaks indicate where significant weight loss events occur, and the temperature positions of these peaks provide insight into the thermal stability of the material. A higher temperature peak generally means the material is more thermally stable.

2.6.5.2 Specific heat capacity

Differentiate scanning calorimetry (DSC) is another thermal analysis technique which measures the amount of heat absorbed or released by a sample as it is heated, cooled, or held at a constant temperature under a controlled atmosphere [233, 237]. Figure 2.22(b) illustrates a DSC apparatus. In the chamber, the reference and sample are placed on the stage of the thermobalance and are measured by heat flux sensors. Similar to the TGA apparatus, the sample and reference will be heated by a furnace under a desired gas flow. Obtaining the heat flow information over a range of temperatures via the DSC measurement, information like phase transitions, glass transition, solid-solid transitions, and specific heat capacity can be obtained [236, 237].

In this work, DSC is used to obtain the specific heat capacity (C_p) of the material via the Sapphire standard method [238], following the separate measuring sequence of the empty crucible, sapphire in the crucible and sample in the crucible. The C_p could be obtained via

$$C_{ps} = \frac{\Delta H}{\Delta h} \times \frac{m_r}{m_s} \times C_{pr} \quad (2.18)$$

where C_{ps} and C_{pr} ($J g^{-1} K^{-1}$) is the C_p of the samples and the Sapphire, ΔH and Δh (W) is the difference between the heat flux of the samples or the Sapphire with the heat flux of the baseline, m_r and m_s (kg) refers the mass of the samples and the Sapphire, respectively.

2.6.6 Thermal conductivity via heat transfer measurements

Thermal conductivity, κ , is a material property that measures the ability of a material to conduct heat. It quantifies the rate at which heat is transferred through a material due to a temperature gradient and relates the heat and the temperature gradient via the following Fourier heat transfer law:

$$\rho C_p \frac{\partial T}{\partial \tau} = \frac{\partial}{\partial x} \left(\kappa_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\kappa_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\kappa_z \frac{\partial T}{\partial z} \right) + \Phi \quad (2.19)$$

where ρ and C_p are the density and specific heat capacity of a material, T and τ are the temperature and time of the system, κ_x , κ_y and κ_z are the thermal conductivity values along the x , y and z direction of the material, respectively.

Thermal conductivity is crucial in determining how materials respond to thermal environments and is essential for applications in insulation, electronics, construction, and manufacturing. Methods for κ measurements are mainly divided into the steady-state measurement method (SSM, without considering the dynamic component $\partial T / \partial \tau$) and transient measurement method [239].

2.6.6.1 Steady-state measurement

If the sample is thermally isotropic, the heat transfer is regarded as one dimensional and is measured only when the system reaches the thermal equilibrium, the equation 2.19 can be simplified into $q = -\kappa \frac{\partial T}{\partial x}$. Therefore, the sample is measured by the temperature distribution along a certain length and the κ can be extracted by knowing the input heat flux. This SSM method possesses the advantages of using the simplest equation, direct access to κ and a wide range of measurement temperatures [240]. However, the method can be time-consuming and requires rigorous measurement conditions (adiabatic environment and accurate temperature measurement) and specific sample dimensions [241].

Using a physical properties measurement system (PPMS, Quantum design) with a thermal transport option (TTO, QDS-4084-569, Quantum Design) is a commonly used platform to measure κ via SSM [242]. During the measurement, the TTO puck is covered by the radiation shield (Figure 2.23(a)) to minimise the radiation heat loss. Figure 2.23(b-c) shows the configuration of the TTO puck-mounting station and thermal connections for an idealised sample. The sample is connected to the copper leads using a four-probe configuration [242]. The copper leads are then connected to a heat source, two temperature sensors (hot and cold thermometers) and a coldfoot (heat sink) from the top to the bottom, respectively. A thermally conductive adhesive is applied between the sample and the copper leads, to reduce the thermal contact resistance and to ensure a good measurement accuracy.

The κ of the sample (κ_{sample}) is obtained via [242]:

$$\kappa_{\text{sample}} \frac{\Delta x_{\text{sample}}}{\Delta T_{\text{sample}}} = P_{\text{cond}} = P_{\text{heater}} - P_{\text{rad}} - P_{\text{loss}} \quad (2.20)$$

where the resulting temperature drop (ΔT_{sample}) across a given length (Δx_{sample}) of the sample is recorded after the steady-state temperature distribution is established, P_{cond} is the

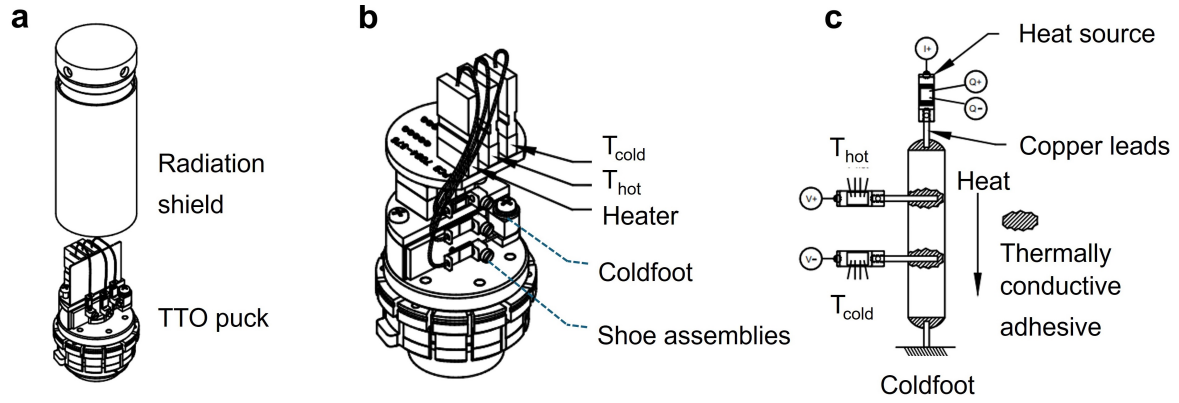


Fig. 2.23 Schematic illustration of (a) the TTO puck with a radiation shield, (b) a detailed TTO puck with illustrating sockets for each shoe assembly, and (c) thermal connections for an idealized sample [242].

conduction heat power through the sample, P_{heater} is the total heater power generated by the heater, P_{rad} is the radiation heat loss, and P_{loss} is the heat loss through the wires, heaters, and sensors.

Radiative loss is estimated via [242]:

$$P_{\text{rad}} = 2\sigma_T S \varepsilon \times T^3 \times (\Delta T_H + \Delta T_C) \quad (2.21)$$

where σ_T is the Stefan Boltzmann constant, S is the surface area of the sample, ε is the infrared emissivity of the sample, T is the average temperature of the puck during the measurement, ΔT_H and ΔT_C are the temperature difference between the hot/cold sensors to the T .

Heat loss can be estimated via [242]:

$$P_{\text{loss}} = d(aT + bT^2 + cT^3) \Delta T_{\text{loss}} \quad (2.22)$$

where a , b , c and d are empirically determined constant, and ΔT_{loss} is the average temperature change of the wires, heaters, and sensors, which in our case was determined by the hot thermometer after the temperature is stabled (change within 0.1%).

2.6.6.2 Transient photothermal deflection technique

The transient methods are generally applied to characterise highly thermally conductive materials [240]. Such method includes laser flash [243], transient plane source [244], and

hot wire [245]. They possess the advantages of fast measurement speed, high accuracy, and low condition requirements [240]. The transient photothermal deflection technique (PDT) is one of the transient thermal methods used to measure the material's thermal diffusivity (D). It uses an optical method to study the thermal behaviour of a material, by detecting small temperature changes near the surface of a material when it is heated by a pump beam. These temperature variations cause changes in the refractive index of a surrounding medium, which in turn deflects a probe beam. The deflection signal is measured by the phase change ($\Delta\phi$) of the probe beam compared to the pump beam and relates the D of the material via the following equation:

$$D = \pi F \left(-\frac{\Delta Y}{\Delta\phi} \right)^2 \quad (2.23)$$

$$l_t = -\frac{\Delta Y}{\Delta\phi} \quad (2.24)$$

where, F is the beam frequency, the l_t is defined as the thermal diffusion length, which could be obtained from the linear part of the phase (ϕ) towards the pump-probe beam distance (Y).

Figure 2.24(a) shows the schematic geometry of the transverse configuration of the PDT [246]. The pump beam, modulated over time, propagates in the $-Z$ direction and arrives at the sample orthogonally. The probe beam (test beam) transits in the X direction at a minimum possible distance from the sample surface. It is orthogonal to the direction of propagation of the pump beam at a certain distance (Y). To focus the pump beam, a cylindrical lens was applied on a strip with a length more significant than the diameter of the sample and with a width of about 0.15 mm. In this case, the heat propagation process has a predominantly one-dimensional character in the $\pm Y$ direction. As a pump beam, a 488 nm Argon (Ar) laser with a power of 50 mW is modulated by a mechanical chopper. Another He-Ne laser as a probe beam focused on the sample surface at a spot size of 0.04 mm.

Figure 2.24(b) presents the PDT measurement results on the GaAs referenced wafer sample at $F=81$ Hz to control the proper functioning of the set-up, obtaining a value of $0.22 \text{ cm}^2 \text{ s}^{-1}$) for the GaAs. The value matches with the known thermal diffusivity of GaAs measured previously [246], which is proof of the correct functioning of the system. Using the same analysis method, the thermal diffusivity measurements of the sample can be performed. To obtain a reliable value, it is necessary to repeat the measurements at various frequencies of the pump laser. Therefore, the l_t as a function of the inverse of the root of the modulation frequency ($\sqrt{1/F}$) is usually plotted based on

$$l_t = \sqrt{\frac{D}{\pi}} \times \sqrt{\frac{1}{F}} \quad (2.25)$$

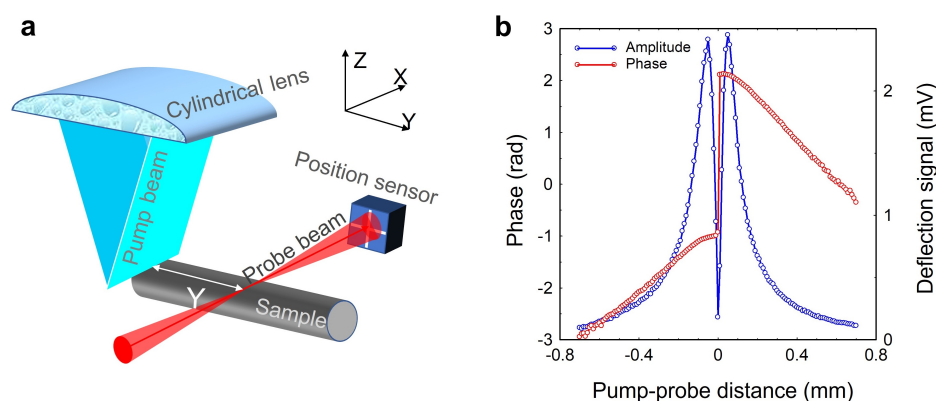


Fig. 2.24 (a) The schematic geometry of the transverse configuration of the PDT and (b) the measurement results of the photothermal deflection at 81 Hz on the GaAs wafer sample used for the control of the good functioning of the set-up.

where D can be obtained from the slope ($\sqrt{D/\pi}$).

2.6.7 Electrochemical properties via CV/GCD

An electrochemical workstation can be utilised to characterise the electrochemical performance of a potential supercapacitor. Figure 2.25 schematically shows the two different types of set-ups, the three-electrode workstation, and the half-flow or full-flow cell workstation [247].

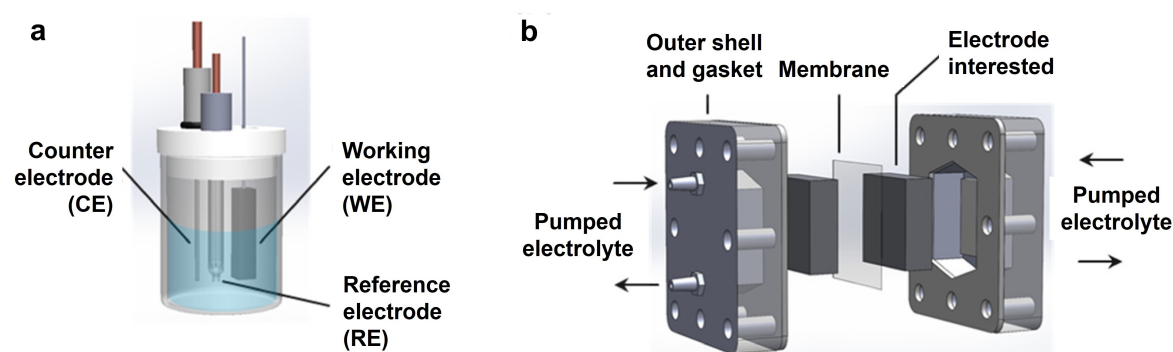


Fig. 2.25 Schematic illustration of the electrochemical characterisation set-ups: (a) a three-electrode configuration. (b) a half- and full-flow cell workstation [247]. The figure is licensed under Creative Common CC BY 4.0.

The three-electrode workstation contains:

- Working electrode (WE): where the compound of interest is reduced or oxidised.

- Counter electrode (CE): this is used to complete an electrical circuit; therefore, the current flow from WE and CE can be measured. Pt electrodes are the most widely applied counter electrode.
- Reference electrode (RE): a stable and non-polarisable electrode. It is used as a reference point against which the potential of other electrodes can be measured. The most common RE is the saturated calomel electrode, Ag/AgCl electrode.
- Electrolyte: the chosen electrolyte can conduct charge, ionic or electronic, depending on the electrode materials used.

The half-flow or full-flow cell is a 2-electrode system, creating a close-to-reality supercapacitor structure. Compared to the 3-electrode workstation, which focuses on the electrochemical potential of the electrode material itself, the 2-electrode configuration demonstrates the material's practical viability as an electrode in a cell.

The workstations allow for evaluating the electrochemical performance via cyclic voltammetry (CV), the galvanostatic charge and discharge process (GCD), and electrochemical impedance spectroscopy (EIS).

2.6.7.1 Cyclic voltammetry

CV measures the current response of an electrochemical system to a linearly swept potential that is cyclically applied to a WE. Based on the CV shape, the electrode materials can be identified to be electron double-layer capacitive EDLC (rectangular), pseudocapacitive (not ideal rectangular), or battery-like (with redox peaks). With the CV curves, it is possible to estimate the specific capacitance (C_s) of the electrode material:

$$C_s = \frac{\int IdV}{mv\Delta V} \quad (2.26)$$

where I is the recorded current density ($A\ g^{-1}$), V is the applied voltage (V), ΔV is the voltage window (V), m is the weight of electrode material (g), and v is the set voltage scan rate ($mV\ s^{-1}$).

The determination of C_s is important, as C_s represents the ability of the material to store charge per unit mass or area of the electrode.

2.6.7.2 Galvanostatic charge and discharge

GCD measurements record the potential variation over time during the charging-discharging process, performed at different current densities (A g^{-1}). With the GCD curves, the C_s of the electrode material is calculated as follows:

$$C_s = \frac{\int I dt}{m \Delta V} = \frac{I \times \Delta t}{m \Delta V} \quad (2.27)$$

where I is the set current density (A g^{-1}), Δt is the whole charging-discharging time (s), m is the weight of electrode material (g), and ΔV is the voltage window (V).

The power density (P , W kg^{-1}) and energy density (E , Wh kg^{-1}) can be estimated:

$$E = C_s (\Delta V)^2 \quad (2.28)$$

$$P = \frac{I \times \Delta V}{m} \quad (2.29)$$

2.6.7.3 Electrochemical impedance spectroscopy

EIS provides the studied supercapacitors with an alternating current ranging from 0.01 Hz to 1 MHz, creating Nyquist and bode plots. By fitting the plots, an equivalent circuit includes series resistance, charge transfer resistance, double-layer capacitance, and Warburg impedance (created by diffusion) can be modelled to simulate the performance of the supercapacitor. The simplest model is an RC circuit, and the impedance amplitude can be given by the equation 2.30 :

$$|Z| = \sqrt{R^2 + \left(\frac{1}{\omega C}\right)^2} \quad (2.30)$$

where R is the series resistance, ω is the angular frequency, and C is the capacitance.

2.7 Conclusion

This chapter aims to figure out the suitable processing techniques for 2D materials and their composites with the best scalability, including production and deposition. Liquid phase exfoliation stands out due to its capability for large processing volumes, operation at ambient

conditions, compatibility with versatile liquids and solids and compatibility with large-area coating deposition. The synthesis of MXenes consists of selective etching using the in-situ HF route (HCl+LiF) and, subsequently, the MILD method. The as-prepared 2D materials can be mixed with other materials to form hybrid composites or layered structures using spray coating.

To be applicable for energy storage devices and thermal management applications, the materials should exhibit good quality in 2D nature and achieve desired electrical, thermal and electrochemical properties. Therefore, a variety of characterisation techniques for probing the materials quality, including Raman, XPS, microscopy, and XRD have been thoroughly discussed regarding their fundamentals and typical features of 2D materials. A range of characterisation techniques for probing the properties of materials have also been discussed regarding their fundamentals and advantages, including thermogravimetric analysis, electrical conductivity, thermal conductivity analysis, and capacitance analysis. These properties of materials are the key metrics considered for developing energy storage devices and thermal management components.

Chapter 3

h-BN based applications in printed electronic devices

This chapter discusses the potential of using h-BN as a dielectric material for printed electronic devices, enabling better device capacitance and reliability. h-BN exhibits comparable dielectric constants (ϵ_r) as SiO_2 and has been fabricated using CVD and MBE as a dielectric thin layer or tunnelling layer for capacitors showing excellent capacitance, breakdown strength (B_v) and tunnelling effects. To enable large-scale production of electronics, printed electronics gain much attention and developing printable dielectric materials is essential. Printed dielectric nanomaterials or printed organic dielectrics often suffer from low $B_v < 1 \text{ MV m}^{-1}$ or low $\epsilon_r < 3$. Production of 2D h-BN using liquid phase exfoliation to form printable h-BN inks shows a promising way to enable a high- ϵ_r dielectric layer for printed electronics. However, LPE-produced h-BN inks typically contain stabilisers, necessitating further investigation into their synergistic effects and optimisation on the ϵ_r and B_v .

This chapter also discusses the potential of using h-BN as a thermal filler for thermal interface materials, which is beneficial for the thermal management of electronic and energy storage devices to achieve the best power and energy efficiency. The current commercialised thermal interface materials show a thermal conductivity (κ) within the range between $1\text{--}4 \text{ W m}^{-1} \text{ K}^{-1}$. Researchers have demonstrated that the κ value can be improved by introducing h-BN as a thermal filler into the matrix, achieving a κ at orders of magnitude higher. However, the materials they produce are usually in the form of films rather than pastes, the latter of which have a wider usage in the industry and exhibit better surface contact and surface wetting due to rheological behaviours. The production methods involved are either not scalable or not

sustainable, involving external fields, vacuum and hazardous solvents. Thus, the commercial viability of those studies is limited despite a good κ of materials achieved.

3.1 Use of h-BN in electronic devices

3.1.1 Electrical insulation of h-BN

h-BN is a promising candidate for dielectric layers in various electronic devices, owning comparable breakdown strength and leakage current densities better than ceramic dielectrics, and enabling ultrathin dielectric layers [248]. Single-layer h-BN flakes have a wide bandgap of ~ 6.47 eV, which is larger than their bulk counterpart (5.95 eV) [249]. The out-of-plane ϵ_r of h-BN is 3.76 and 3.29 for the mono-layer and bulk crystals, respectively, which is comparable to that of SiO₂ (3.8) [250]. Moreover, inorganic h-BN offers better chemical stability against oxygen, moisture, and heat than organic dielectrics [251]. Therefore, it is very promising as 2D material-based electronic devices as dielectric layers.

3.1.2 h-BN based dielectric layer

3.1.2.1 Capacitors

Ahmed, et al. [252] fabricated an h-BN-based metal-insulator-metal (MIM) capacitor. Figure 3.1(a) illustrates the structure of the MIM capacitor, with a bottom electrode of Cr/Au patterned on a p-Si/SiO₂ substrate. They transferred the FLh-BN flakes using polydimethylsiloxane to the deposited Cr/Au electrode. Figure 3.1(b) shares the optical image of the capacitor with the FLh-BN dielectric layer being 32-nm thick. The authors reported that the dielectric layer could endure an electrical field of 7.8 MV cm^{-1} , implying its potential use as a promising dielectric material. Furthermore, the FLh-BN material they exfoliated in their work showed stable dielectric characteristics with temperature changes, revealing its thermal stability in extreme operating conditions.

Jang, et al. [253] also reported a MIM capacitor using h-BN as the dielectric layer, and Figure 3.1(c) shows the schematic diagram. The bottom gold (Au) electrode was fabricated using photolithography on Si/SiO₂ substrates. The h-BN was synthesised via a CVD system, and the films of various thicknesses were transferred onto the bottom Au electrode, followed by another layer of Au electrode on top. The MIM capacitor had a contact area of $5 \mu\text{m} \times 5 \mu\text{m}$, and the obtained ϵ_r of the h-BN layer was at around 3-4. Figure 3.1(d) plots the

breakdown voltage and breakdown strength (B_v) as a function of the h-BN thickness. When the thickness of the transferred h-BN film is < 10 nm, the corresponding breakdown voltage increased linearly as the h-BN thickness increased and the B_v remained at ~ 4 MV cm $^{-1}$. When the thickness of the transferred h-BN film is > 10 nm, the corresponding breakdown voltage increased linearly at a lower slope as the h-BN thickness increased, while the B_v decreased to ~ 2.7 MV cm $^{-1}$ at 20 nm. Compared to thin FLh-BN films (< 10 nm), where Fowler-Nordheim tunnelling provides the dominant carrier transport mechanism, in the thick FLh-BN films (> 10 nm), a trap-assisted Poole-Frenkel emission mechanism constituted the dominant transport mechanism for the leakage current [254].

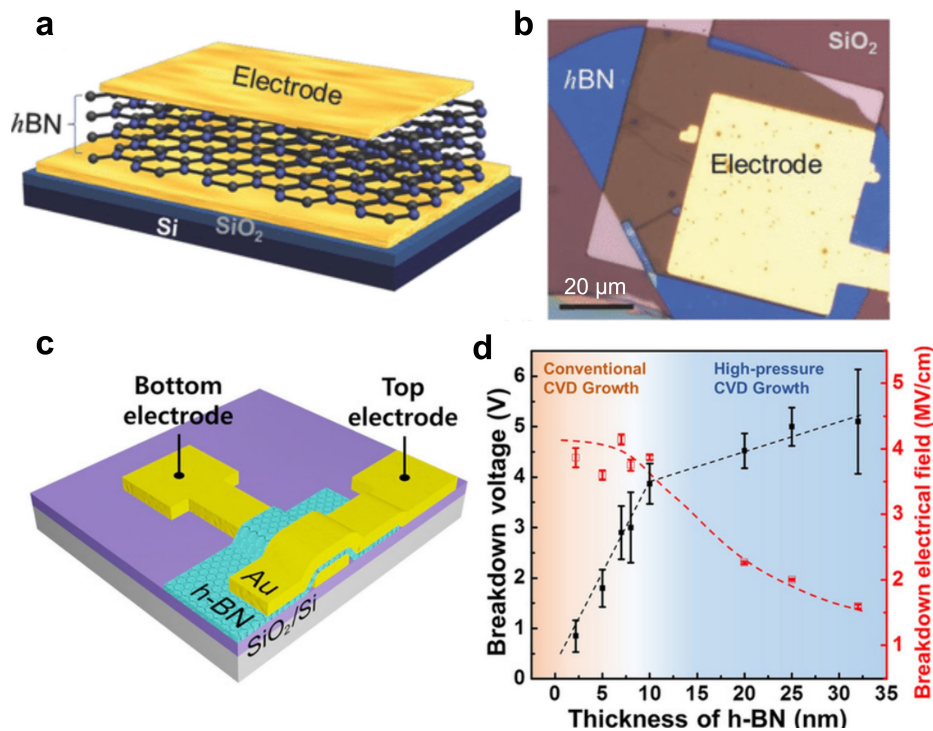


Fig. 3.1 Examples of h-BN used as dielectric layers in capacitors. Schematic (a) and optical image (b) of 32-nm thick h-BN-based MIM capacitor, respectively. (c) A schematic diagram of the h-BN-based MIM capacitors fabricated on a Si/SiO $_2$ substrate, and (d) the breakdown characteristics as a function of the h-BN film thickness [253]. This figure is licensed under the Creative Commons Attribution License. Images (a-b) adapted with permission [252], © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.1.2.2 Transistors

The ultra-flat and dangling bond-free nature of h-BN can improve the performance of gate dielectric layers [248], and the carrier mobility of the channel underlying the gate can be

enhanced because h-BN can effectively screen the effects of phonons and charged impurities [248]. Inserting mono-layer h-BN film between a semiconducting channel and a metal contact can also decrease the contact resistance of the source/drain by modulating the Schottky barrier [248]. Using h-BN in the FET devices as an excellent dielectric layer helps advance the next-generation electronics, including nanowire FETs, and tunneling FETs. [248].

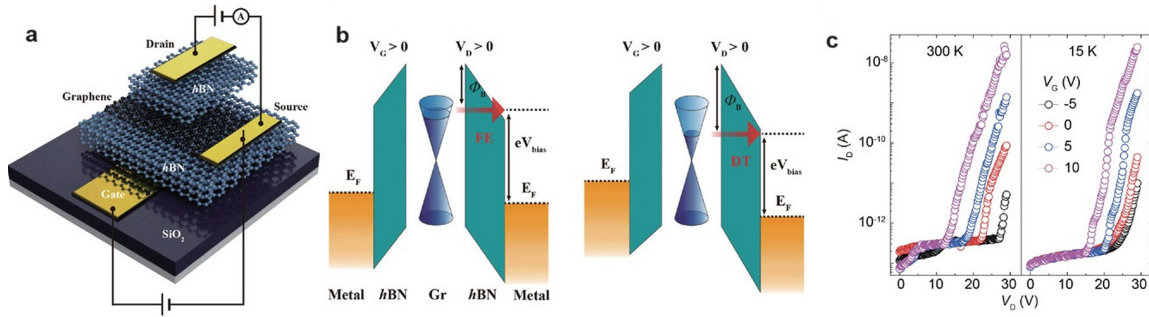


Fig. 3.2 An example of the h-BN dielectric layer used in transistors. (a) Schematic illustration of the semiconductor-less tunnelling FET based on h-BN/graphene/h-BN vertical heterostructure. (b) Schematic energy band diagram and the switching principle of the tunnelling FET device. (c) Output characteristics of the semiconductor-less tunnelling FET at 300 K (left) and 15 K (right). Image adapted with permission [255], © 2022 Wiley-VCH GmbH.

Britnell et al. [256] have demonstrated the first-ever tunnelling FETs using graphene/h-BN stacks, in which a thin tunnelling barrier was created from h-BN or MoS₂ sandwiched between graphene sheets. These FET devices exhibit on-off switching ratios of ~ 50 and $\sim 10,000$, respectively, at RT. More recently, Lee et al. [255] demonstrated a tunnelling graphene-based FET device using h-BN as the gate dielectric and tunnelling layer. Figure 3.2(a) shows the vertical heterostructure of the metal/h-BN/graphene/h-BN/metal, and Figure 3.2(b) schematically illustrates the two underlying tunnelling mechanisms of the device, field emission tunnelling and direct tunnelling through the h-BN layer. Figure 3.2(c) plots the current as a function of the drain voltage, and the device could reach a high current on-off ratio of up to 10^6 . The channel current exhibited similar output characteristics at various gate voltages at both 300 and 15 K, indicating a constant performance without degradation.

3.1.3 Containing h-BN based polymer dielectric layer for printed electronics

Organic dielectrics can offer higher B_v but lower dielectric constant (ϵ_r). For example, the cross-linked polymer blends applied in printed electronics, such as poly(4-vinyl)phenol combined with silane reagents, achieved a ϵ_r of ~ 5.7 and breakdown strengths (B_v) ranging

from 3 to 6 MV cm⁻¹. h-BN can also be embedded into organic polymers as dielectric nanofillers to overcome their low ϵ_r , for printed electronics [257].

Carey et al. [80] demonstrated a printable dielectric ink with FLh-BN flakes and carboxymethyl cellulose (CMC). Figure 3.3(a) shows their MIM capacitor configuration, which used the FLh-BN/CMC as the dielectric layer and used silver as the bottom and top electrodes via fully inkjet printing [80]. They analysed the capacitor capacitance as a function of the dielectric thickness and found a thickness threshold of 1.2 μm , below which short circuit occurs. Regardless the thickness, the dielectric layer exhibited a higher ϵ_r of ~ 7 and a comparable B_v of $\sim 1 \text{ MV m}^{-1}$, which falls in a similar range of polymer printable dielectrics [80]. Grasping this knowledge, they then fabricated a fully inkjet printed FET using graphene-h-BN heterostructures and achieved excellent modulation at different device configurations.

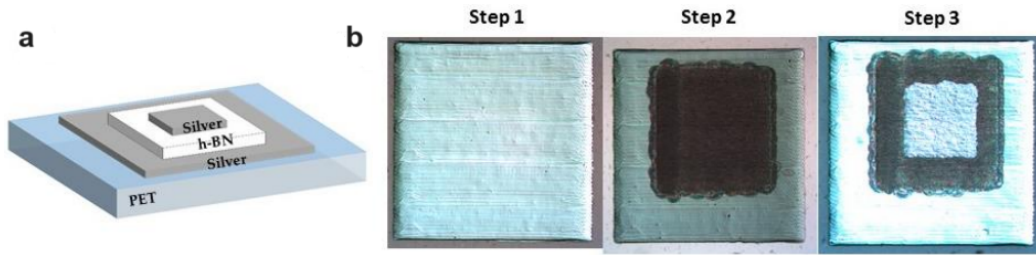


Fig. 3.3 An example of a dielectric layer containing h-BN-based polymer for a printed capacitor. (a) A 3D model of MIM capacitor heterostructure and (b) optical microscopy images of each fabrication step. Image adapted with permission [80], © 2017, Tian Carey et al. The image is licensed under the terms of the Creative Commons CC BY license.

There are other newly published results using an h-BN-based polymer dielectric layer for printed capacitors within my research group. Kim, et al. [73] reported barium titanate (BaTiO_3) nanoparticles as an effective dielectric additive for inkjet-printable FLh-BN inks. The resulting $\text{BaTiO}_3/\text{h-BN}$ thin films reached an $\epsilon_r \sim 16$, higher than that of the FLh-BN dielectric films they tested ($\epsilon_r \sim 10.1$). This result enabled all-inkjet printed flexible capacitors with an areal capacitance of $\sim 10.39 \text{ nF cm}^{-2}$ [73], paving the way to future low-power, printed and flexible electronics. Yao, et al. [11] applied the FLh-BN/CMC material as an insulating layer in spray-coated capacitors and obtained $\epsilon_r \sim$ of 9.7 at the mass loading of 40 wt% FLh-BN.

Summaries of knowledge gaps

To enable large-scale production of electronics, printed electronics gain much attention and developing printable dielectric materials is one of the keys. Thin films of printed nanomaterials often suffer from existing pinholes which results in relatively low breakdown strengths (B_v) of $<1 \text{ MV m}^{-1}$. Organic dielectrics can offer higher B_v but lower dielectric constant (ϵ_r). Production of 2D h-BN using liquid phase exfoliation to form printable h-BN inks shows a promising way to enable a high- ϵ_r dielectric layer for printed electronics, due to its intrinsic excellent ϵ_r . However, the LPE-produced h-BN inks usually contain stabilisers and polymers, so the synergetic effects and optimisation between h-BN and stabilisers on the ϵ_r and B_v of electronics and the optimisation require further investigation.

3.2 Use of h-BN for thermal management of electronics

Beyond the consideration of dielectric properties of high energy capacitors and transistors, κ , as well as stored and discharged energy densities, the thermal stability is comparably important for electronic devices, especially those operated under harsh and extreme conditions [258]. Therefore, the utilisation of highly thermally conductive h-BN in electronic devices is also very promising.

3.2.1 Need for thermal management

According to Moore's Law [259] for the semiconductor industry, the number of electronic devices in an integrated circuit (IC) doubles every other year with a minimal rise in cost, along with the continuous miniaturisation of those devices developed commercially. The ever-increasing device density in ICs [260] leads to a rapid increase in the power density generated in electronic chips, which enables better performance of IC-relying systems, including power systems [261, 262], illuminated signs and displays [263], switches, relays, inverters, and power supplies [260, 264]. However, the higher power density peaks in a single device lead to greater local heat generation during the device's operation. If the heat cannot be dissipated to the environment but accumulates locally, the device's temperature will increase rapidly to over 100°C , which can have detrimental effects on the device's power performance, accelerating their failure rate and reducing their lifetime, even causing thermal runaway (an autonomous and uncontrolled rise in temperature caused by internal short circuits, overcharging, external heating or mechanical collision, leading to rapid heat generation,

potential fires, or explosions) [260]. For these reasons, a more heat-transfer efficient thermal management system with an improved structure design and material selection (e.g., higher κ and higher heat convection rate) shall be crucial to ensure the reliable operation of electronic devices within an optimal operating temperature range [265].

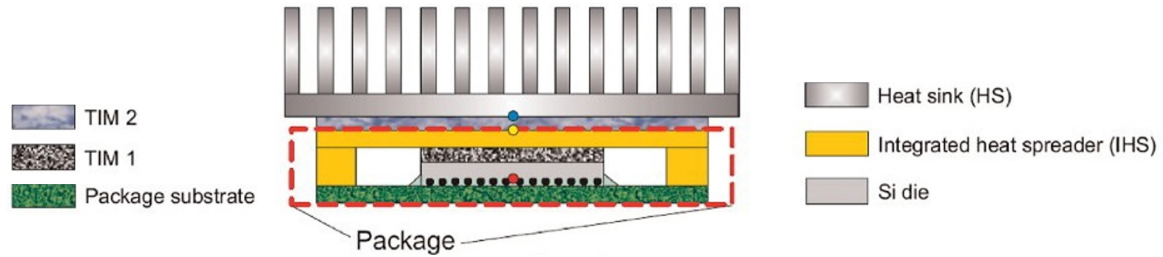


Fig. 3.4 Schematic illustration of a microprocessor package assembly used in a real application scenario of electronics cooling. Images adapted with permission [266], © 2018, SAGE Publications.

Figure 3.4 shows a common thermal management system design for currently Si-based electronics [266], including (1) a thermally conducting component, such as integrated heat spreader (IHS, yellow) or heat pipes [262] to transfer the generated heat from the hot Si die to a cooling component; (2) the cooling component can be a heat sink (HS, shiny grey) or a heat exchanger to dissipate the heat away into the environment or a secondary fluid [267]; (3) the thermal interface materials, TIMs (TIM1 and TIM2) are applied to reduce the thermal contact resistance at the interfacial surface between the Si die and IHS, and between the IHS and the HS [268, 269]. The package substrate (green) can also conduct some heat to the environment depending on the κ values (which are normally very low below $1 \text{ W m}^{-1} \text{ K}^{-1}$).

3.2.2 Development of thermal interface materials

A lot of effort has been put into developing the first two components, but the low κ value ($< 4 \text{ W m}^{-1} \text{ K}^{-1}$) of currently used TIMs always limits the effectiveness of the whole thermal management system. The materials with a high κ used in the system components are essential for a heat-transfer efficient thermal management system. For instance, researchers have been studying for a long time to improve the κ of thermal interface materials (TIMs). For the case of electronics, TIMs are typically designed to be electrically insulating, thermally conducting [270], easy to process on a large scale, and with an excellent κ (in the order or one-order of magnitude higher than a few $\text{W m}^{-1} \text{ K}^{-1}$) and good surface wetting characteristics [271].

Three main categories of TIMs are carbon and metal materials, insulated metal oxides and ceramics, and polymers [258]. Carbon and metal materials are electrically conductive,

which poses a threat to causing short circuits for electronic applications. Metal oxides and ceramics are insulating materials with high κ values up to hundreds of $\text{W m}^{-1} \text{K}^{-1}$. However, they have high density ($\sim 4 \text{ g cm}^{-3}$), require sophisticated processing methods, and are challenging to maintain mechanical flexibility, limiting their use in lightweight or flexible applications. Functional polymers, such as epoxy resins or polyvinyl alcohol (PVA), are ideal for electronic-based TIMs [271–273] due to their excellent insulation and mechanical properties, lightweight, corrosion-resistant and low processing costs. However, they usually exhibit a relatively low κ value of $\sim 0.2 \text{ W m}^{-1} \text{K}^{-1}$ [258, 274], due to that the heat conduction is dominant via phonon transfer from the amorphous arrangement and vibration of molecular chains, compared to metals which rely on faster electron transfer to conduct heat.

To enhance the κ of functional polymers and optimise them as ideal TIMs, their crystalline structure is often refined, or they are embedded with inorganic thermal fillers known for their high κ values. These fillers typically include insulating ceramics or conductive metals [275], as shown in Figure 3.5. Electrically conducting fillers range from metal nanoparticles [258] to graphene and AgNW [276–278], but they potentially pose an additional risk of short-circuits in electronic devices and electrical packaging applications. In this case, ceramic fillers are more appealing due to their electrically insulating but thermally conducting nature. Common thermal ceramic fillers include oxides, such as Al_2O_3 ($20\text{--}30 \text{ W m}^{-1} \text{K}^{-1}$) [279], SiO_2 ($1\text{--}10 \text{ W m}^{-1} \text{K}^{-1}$) [280] and ZnO ($50 \text{ W m}^{-1} \text{K}^{-1}$) [281], carbides such as SiC ($80\text{--}120 \text{ W m}^{-1} \text{K}^{-1}$) [282, 283] and nitrides, such as AlN ($150\text{--}220 \text{ W m}^{-1} \text{K}^{-1}$), BN ($60\text{--}750 \text{ W m}^{-1} \text{K}^{-1}$), and Si_3N_4 ($86\text{--}120 \text{ W m}^{-1} \text{K}^{-1}$) [284, 285]. With the addition of those ceramic fillers, commercial TIMs present a $\kappa \sim 0.8\text{--}4.2 \text{ W m}^{-1} \text{K}^{-1}$ [277, 286]. However, the ever-increasing power density and heat density in miniaturised electronic devices demand more effective heat conduction via TIMs, for instance, with a $\kappa > 10 \text{ W m}^{-1} \text{K}^{-1}$ [287–289].

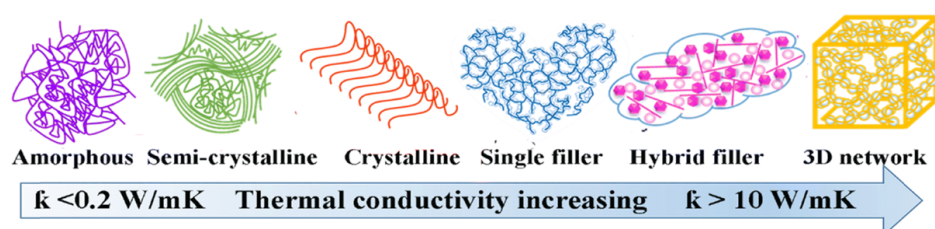


Fig. 3.5 Development of polymer-based thermally conductive composites. Image adapted with permission [258], © The Royal Society of Chemistry 2022.

3.2.3 Thermal conductivity of h-BN

Among the common ceramic thermal fillers, h-BN stands out. The in-plane κ value of h-BN crystals was experimentally measured at $\sim 370 \text{ W m}^{-1} \text{ K}^{-1}$ [8, 290], and the in-plane κ value could further increase with a reduced thickness down to a mono-layer h-BN flake to $\sim 751 \text{ W m}^{-1} \text{ K}^{-1}$ [291]. That is because the adverse impact on the κ from the inter-layer phonon scattering is minimised in a mono-layer h-BN flake [290, 291]. Theoretically, a mono-layer h-BN flake shows a superior intrinsic thermally conducting property, with an in-plane κ calculated to reach $\sim 2000 \text{ W m}^{-1} \text{ K}^{-1}$ [292, 293]. Besides, h-BN shows good anisotropic κ . Anisotropy is the directional dependence of a material's physical properties, meaning that the properties vary based on the direction in which they are measured. In the case of h-BN nanosheets, the κ can be measured in two directions: (1) within the nanosheet plane (in-plane) and (2) perpendicular to the plane (out-of-plane). The out-of-plane κ of h-BN is $\sim 5.2 \text{ W m}^{-1} \text{ K}^{-1}$, which is orders of magnitude lower than its in-plane κ values, making it promising for directional heat transfer in electronics [294].

3.2.4 h-BN based thermally conductive composites

Since h-BN is a promising thermal filler with good thermal conductivity properties, studies have shown that using h-BN for polymer matrix can improve the κ . Take epoxy as a reference. Zhao, et al. [295] demonstrated an h-BN embedded epoxy-based thermally conductive composite as a TIM for electronic packaging. The h-BN/epoxy composite was reported a κ of $\sim 1.09 \text{ W m}^{-1} \text{ K}^{-1}$ at a volume loading of 40 wt.% of h-BN. This is over five times higher than the $\kappa \sim 0.2 \text{ W m}^{-1} \text{ K}^{-1}$ of the pure epoxy, indicating the positive effect brought by the h-BN thermal filler on the κ of the polymer matrix. The idea of using h-BN as a thermal filler for polymer matrix has already been applied to the commercialised TIMs products, with an average reported $\kappa < 3 \text{ W m}^{-1} \text{ K}^{-1}$ [296–298]. However, the achieved κ values are a bit away from what is expected ($> 10 \text{ W m}^{-1} \text{ K}^{-1}$).

Some studies proposed a further improved κ of polymer-based TIMs, using aligned h-BN flakes within composites via different processing techniques. Xu, et al.[299] reported an epoxy-based thermally conductive composite. Figure 3.6(a) depicts the fabrication process of the composite. They used a three-dimensional boron nitride foam (3D-BN) to fill the epoxy, and the composite shows a $\kappa \sim 4.0 \text{ W m}^{-1} \text{ K}^{-1}$ at a 40 vol% loading of 3D-BN. Figure 3.6(b) plots the κ of the 3D-BN/epoxy composites as a function of 3D-BN volume fractions, and the composite exhibits the best $\kappa \sim 6.1 \text{ W m}^{-1} \text{ K}^{-1}$ at a 60 vol% loading of 3D-BN. Figure 3.6(c) compares the κ enhancement of the 3D-BN/epoxy and randomly distributed

BN/epoxy composites, which indicates that the structure of 3D-BN also enables an aligned BN orientation in the composites.

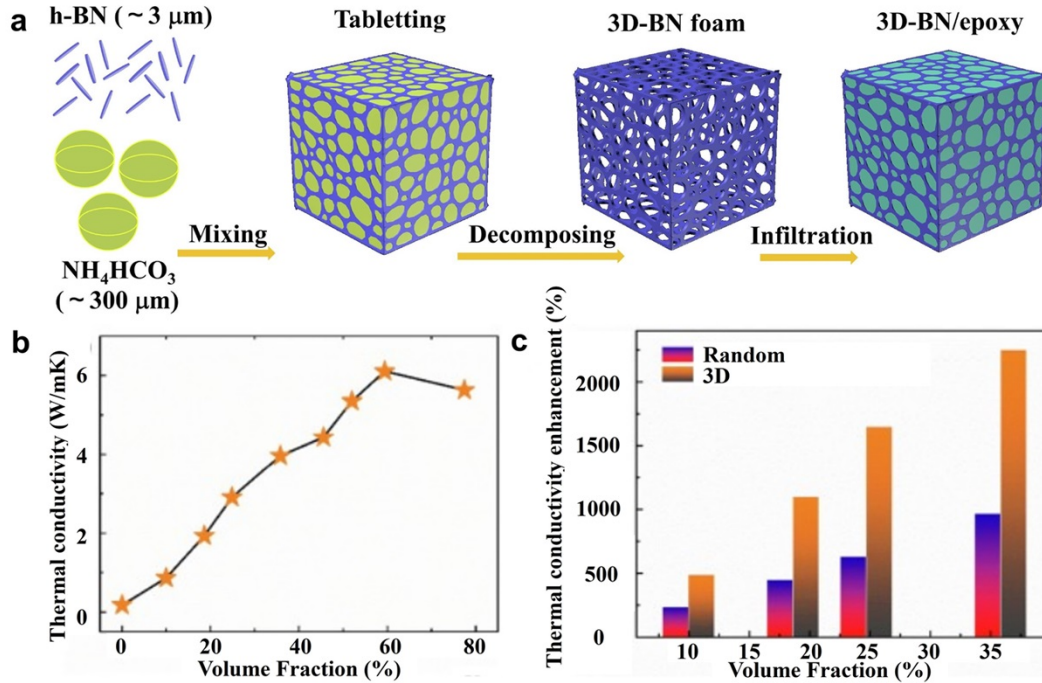


Fig. 3.6 An example of 3D-BN-based epoxy composite with improved κ values. (a) Sketch map depicting the formation process of the 3D-BN/epoxy composites; (b) κ of the 3D-BN/epoxy composites as a function of BN volume fractions; (c) Comparison of κ enhancement of the 3D-BN/epoxy and randomly distributed BN/epoxy composites. Images adapted with permission [299], © 2020 Elsevier B.V.

Similarly, Kim, et al.[300] used an external magnetic field to align the FLh-BN in an epoxy-based composite. The prepared composite achieved a $\kappa \sim 3.445 \text{ W m}^{-1} \text{ K}^{-1}$ at a 30 vol% loading of FLh-BN, and the value almost doubles compared to the κ value ($\kappa \sim 1.765 \text{ W m}^{-1} \text{ K}^{-1}$) of the composite at the same loading but without any FLh-BN alignment. Figure 3.7(a) [301] proposed another novel method to align the FLh-BN flakes in the epoxy-based composite. They demonstrated that bidirectional freeze-drying of the BN nanosheets enables a lamellar structure of a BN nanosheets aerogel, and infiltration of the aligned BN aerogel with epoxy can form a well-aligned BN/epoxy composite. Figure 3.7(b) shows that the composite has an improved in-plane κ value as a function of the BN-nanosheet(BNNS) volume loading, with an excellent in-plane κ of $\sim 6.07 \text{ W m}^{-1} \text{ K}^{-1}$ at only 15 vol% loading of the FLh-BN, while there is no obvious improvement in its out-of-plane κ value. Figure 3.7(c) shows the obtained κ values of the composites at all tested BNNS loadings are higher compared to what has been reported in the literature. Figure 3.7(d) summarises the thermal

anisotropy of the composite at all BNNS loadings, with a value of 12 at 15 vol% loading of the FLh-BN. All obtained anisotropy values are higher than those of the literature.

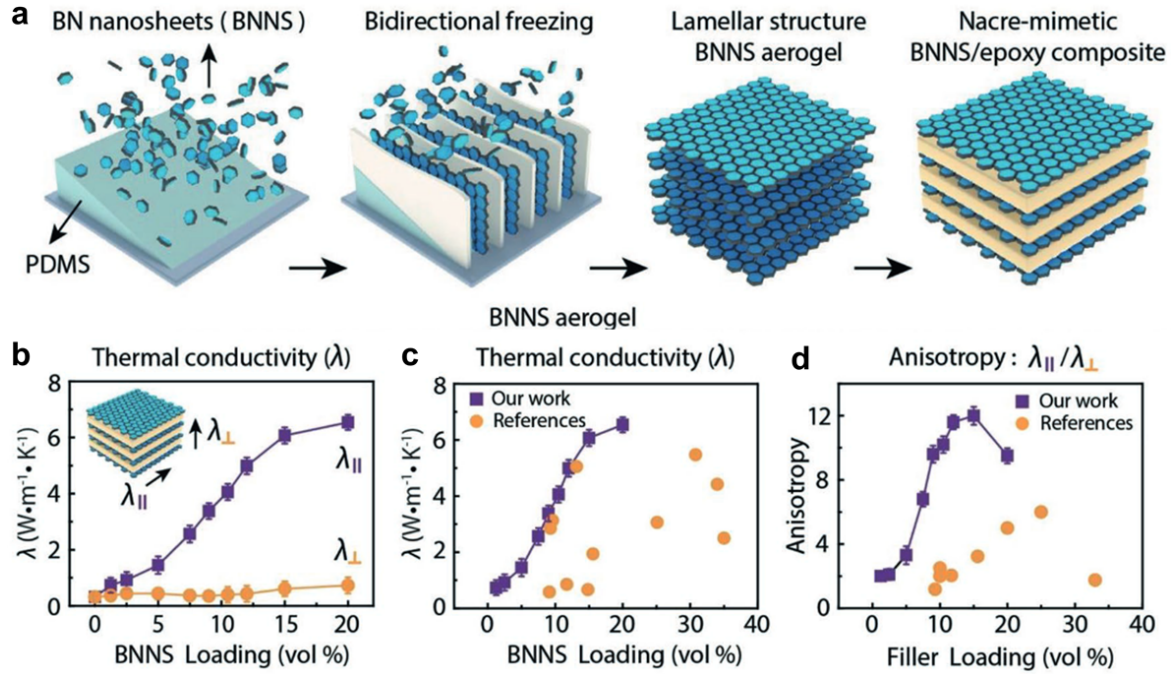


Fig. 3.7 Fabrication and characterisation of the freeze-drying BN nanosheets/epoxy nacre-mimetic composite. (a) Schematic illustration of the fabrication route using a bidirectional freezing technique and epoxy resin infiltration. (b) κ of the composites in the parallel ($\lambda_{||}$) and perpendicular ($\lambda_{\perp}$) directions concerning the lamellar layers. Comparison of the composites with other literature for their κ (c) and anisotropy ($\lambda_{||}/\lambda_{\perp}$) (d). Images adapted with permission [301], © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The choice of polymer matrix also plays a role in the κ values of polymer-based thermally conductive composites. Wang, et al. [302] utilised PVA as the polymer matrix and embedded the PVA with 70 wt.% loading of FLh-BN. The FLh-BN flakes were aligned using vacuum filtration, resulting in the FLh-BN/PVA composite reaching a κ of $\sim 24.6 \text{ W m}^{-1} \text{ K}^{-1}$. Zhang, et al. [303] reported a PE-based thermally conductive composite. Applying a tensile force to stretch and align the BN nanoplatelets, the BN/PE composite reached an extremely high κ value of $\sim 106.2 \text{ W m}^{-1} \text{ K}^{-1}$ at a 15 wt.% loading of the BN.

3.2.5 Thermal performance of h-BN/cellulose composites

Cellulose is attracting more and more interest as a polymer matrix for TIMs. It has been considered one of the most naturally abundant, environmentally friendly, sustainable and

bio-compatible polymers, making it very promising for the next-generation green electronics [304]. Beyond these, cellulose also shows a higher Young's modulus and a lower coefficient of thermal expansion (CTE) than conventional polymers. For example, compared to epoxy with Young's modulus of ~ 3.4 GPa [49] and CTE ~ 45.8 ppm K^{-1} [305, 306], cellulose exhibits Young's modulus of ~ 137.0 GPa and CTE < 10 ppm K^{-1} [307, 308]. In the above-mentioned studies, epoxy was always mixed with h-BN physically at the final stage of the process, while cellulose can directly stabilise h-BN flakes in dispersions at the first stage during the LPE process of h-BN [80], which makes the mixture more uniform [309].

Zeng, et al.[310] mixed BN nanotubes (BNNTs) with cellulose suspensions by stirring adsorption, as illustrated in Figure 3.8(a). The mixed suspension was vacuum-filtrated and self-assembled into a free-standing film. Figure 3.8(b) shows the optical images of the as-prepared free-standing films as a function of BNNT loadings. A pure cellulose film shows a transparent colour, while the BNNT-filled films show a more milky white colour. Figure 3.8(c) plots the change of out-of-plane κ value as a function of BNNT loadings. The in-plane κ value reaches the best of ~ 21.4 W $m^{-1} K^{-1}$ at 25 wt.% loading of BNNTs, while the out-of-plane κ value increases with loadings, reaching ~ 5 W $m^{-1} K^{-1}$ at 40 wt.% loading of BNNTs.

Tian, et al. [311] functionalised the BNNS with glycine to form a BNNS-Gly/cellulose nanofibre (CNF) film (Figure 3.9(a)). The authors proposed a simple and green amino acid-assisted ball milling exfoliation process to reduce the thermal contact resistance between BNNS fillers and cellulose matrix. Figure 3.9(b) shows that the BNNS-Gly filled CNF-based thermal composite achieved a κ of ~ 16.2 W $m^{-1} K^{-1}$ at a 70 wt.% loading of BNNT, which is 1.8-fold of that for BNNS/CNF (9.0 W $m^{-1} K^{-1}$) at the same loading.

Summaries of knowledge gaps

Although current research has achieved a κ of materials/composites orders of magnitude higher, the commercial viability and the technology readiness level are limited. These production processes are not scalable, as they require externally applied magnetic fields or techniques like vacuum filtration or hot pressing/stretching, which are not commercially viable for electronic-grade TIMs. Furthermore, the studies mentioned earlier produced TIMs as films rather than pastes. The pastes can fill in microscopic gaps between surfaces, providing better surface contact and surface wetting. The better surface contact enables a lower thermal contact resistance and improved heat transfer. Among the commercial TIM products in the market, more than 75% belongs to thermal pastes, indicating that TIMs in

the form of paste have greater commercial viability [271]. Therefore, scalable production of thermal interface materials using h-BN to form thermal pastes achieving higher κ than that of commercial products is in great demand.

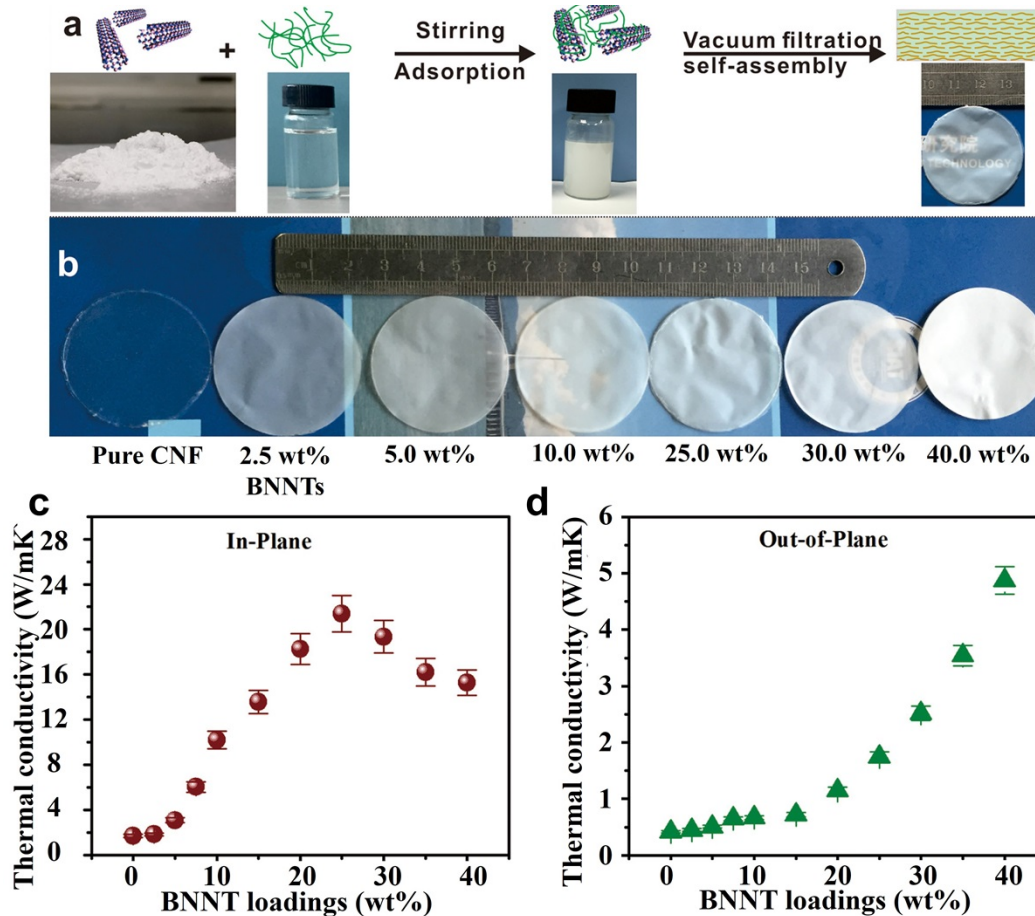


Fig. 3.8 An example of a BN-embedded cellulose-based thermally conductive composite. (a) Preparation and structures of cellulose/BNNT composites, (b) the optical images with different BNNT loadings, and (c) in-plane and (d) out-of-plane κ of the composites with different BNNT loadings. Images adapted with permission [310], © 2017 American Chemical Society.

3.3 Conclusion

This chapter discusses the potential of using h-BN as a dielectric material for printed electronic devices, enabling better device capacitance and reliability. h-BN exhibits comparable dielectric constants (ϵ_r) as SiO_2 and has been fabricated using CVD and MBE as a dielectric thin layer or tunnelling layer for capacitors showing excellent capacitance, breakdown

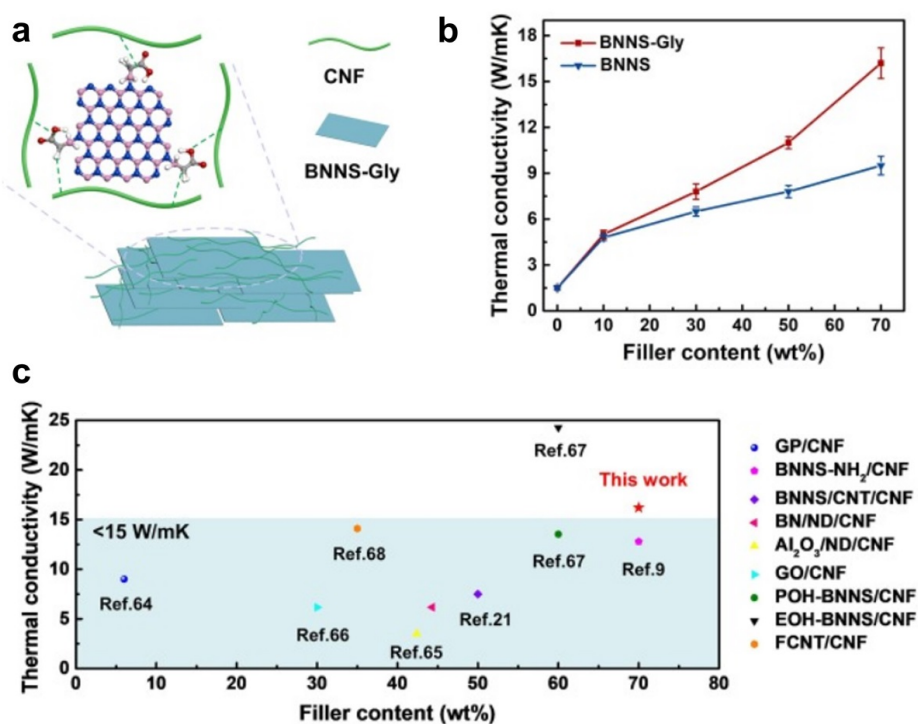


Fig. 3.9 An example of a cellulose-based thermally conductive composite with glycine functionalised BNNS. (a) The schematic diagram showing the BNNS-glycine filled cellulose-based thermal composites, with its (b) in-plane κ values and (c) comparison with the other cellulose-based thermal composite. Images adapted with permission [311], © 2020 Elsevier B.V.

strength (B_v) and tunnelling effects. To enable large-scale production of electronics, printed electronics gain much attention and developing printable dielectric materials is essential. Printed dielectric nanomaterials or printed organic dielectrics often suffer from low $B_v < 1$ MV m⁻¹ or low $\epsilon_r < 3$. Production of 2D h-BN using liquid phase exfoliation to form printable h-BN inks shows a promising way to enable a high- ϵ_r dielectric layer for printed electronics. However, LPE-produced h-BN inks typically contain stabilisers, necessitating further investigation into their synergistic effects and optimisation on the ϵ_r and B_v .

This chapter also discusses the potential of using h-BN as a thermal filler for thermal interface materials, which is beneficial for the thermal management of electronic and energy storage devices to achieve the best power and energy efficiency. The current commercialised thermal interface materials show a thermal conductivity (κ) within the range between 1-4 W m⁻¹ K⁻¹. Researchers have demonstrated that the κ value can be improved by introducing h-BN as a thermal filler into the matrix, achieving a κ at orders of magnitude higher. However, the materials they produce are usually in the form of films rather than pastes, the latter of which have a wider usage in the industry and exhibit better surface contact and surface wetting due to rheological behaviours. The production methods involved are either not scalable or not sustainable, involving external fields, vacuum and hazardous solvents. Thus, the commercial viability of those studies is limited despite a good κ of materials achieved.

Chapter 4

MXenes-based energy storage applications

This chapter explores the potential of MXenes as electrode materials or fillers for energy storage devices. The stability, electrical properties, and electrochemical performance of MXenes as electrodes are critical factors that significantly influence the overall performance of energy storage devices, such as supercapacitors. Therefore, the chapter first discusses the oxidation and stability of MXenes. Isolating MXenes from moisture or oxygen and keeping them under low temperatures can greatly slow down the oxidation process and improve the MXene shelf-storage time. The oxidation prevention, the charge transport mechanism and the electrical properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes are well explored but that of other types of MXenes like Ti_2CT_x requires better understanding. $\text{Ti}_3\text{C}_2\text{T}_x$ shows a metallic behaviour with weak localisation charge transport, which can be a promising electrode candidate for energy storage devices. Researchers have demonstrated that using $\text{Ti}_3\text{C}_2\text{T}_x$ as electrode materials for supercapacitors shows better capacitance compared to currently used carbon materials, due to the pseudocapacitance brought by the high electrical conductivity, fast electron/charge transfer, the large surface area and a large number of active redox sites from Ti and functional groups of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. When formed into thin films or composites, MXenes can be also deposited onto flexible or wearable substrates to enable wearable devices.

4.1 Chemical stability of $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x MXenes

4.1.1 Stability of MXene colloidal solutions and thin films

In this section, the oxidation mechanism of MXenes, the main factors that drive the oxidation and affect the stability of MXene colloidal solutions, and strategies developed so far to improve the stability and long-term storage of MXene colloidal solutions will be reviewed.

4.1.1.1 Oxidation mechanism

Figure 4.1(a) schematically presents the oxidation of MXene from an initial layered structure. After oxidation, the Ti layers diffuse from the middle of the layered structure to the MXene flake surface. The two carbon layers experiences a spacial shrinkage, and the titania (TiO_2) forms over the carbon substrate [312, 313].

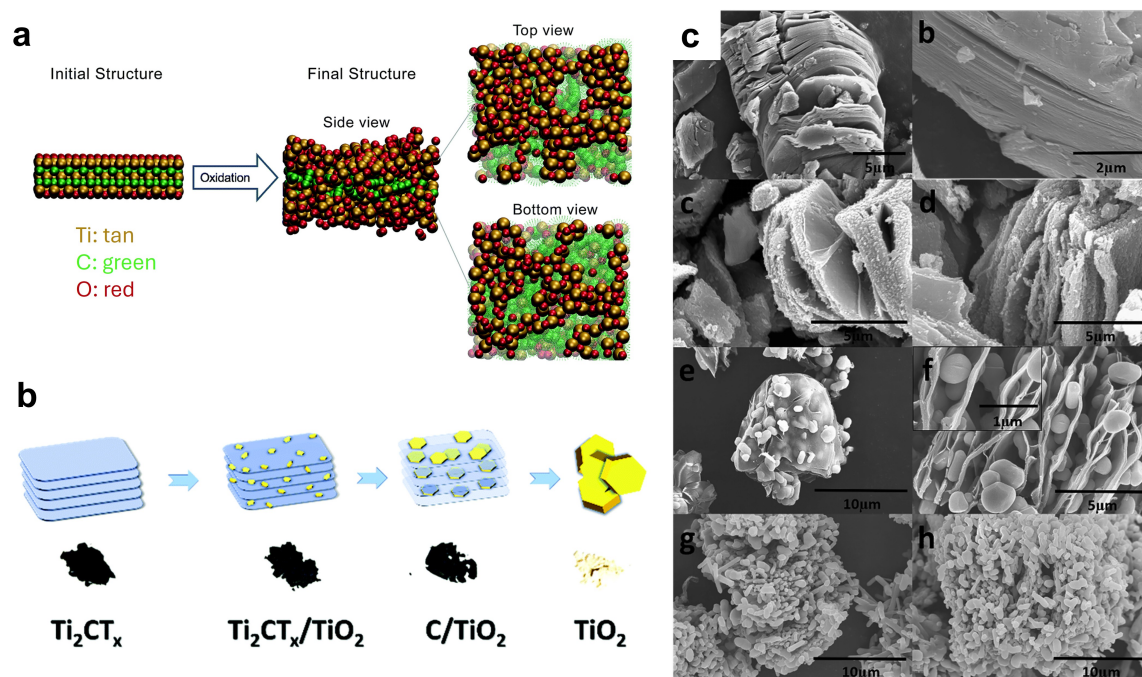


Fig. 4.1 Oxidation mechanism and process. (a) Growth of TiO_2 nanoparticles over the carbon substrate during MXene oxidation. (b) Schematic of the structure evolution and phase transition of Ti_2CT_x over oxidation and representative SEM images (c). Image (a) adapted with permission [312], © The Royal Society of Chemistry 2018; and images (b-c) adapted with permission [314], © The Royal Society of Chemistry 2017.

Figure 4.1(b) presents the step-by-step formation of TiO_2 from Ti_2CT_x . When the temperature is low, the Ti layers react with its oxygen-containing functional groups and the ambient present oxidants (O_2 and moisture) [315] to form the anatase phase of TiO_2 [316], which is regarded as the partial oxidation. As the temperature increases, the partial oxidation is transformed into the complete oxidation [314]. The complete oxidation is the formed anatase TiO_2 phase transformed into the thermally stable rutile TiO_2 phase, creating a carbon/ TiO_2 structure [314] at the end. If exposed to a continuous oxidation environment, the left carbon layer continually oxidises to form carbon oxide (CO) or carbon dioxide (CO_2), and there is only the rutile TiO_2 phase remaining at the end. The whole step-by-step oxidation can be validated by SEM images [314] shown in Figure 4.1(c) from the top to bottom. From the top two SEM images, a fresh multilayer Ti_2CT_x accordin structure is seen, and from the second-row SEM images, the small nanoparticles (anatase TiO_2 phase) are observed at the edge and interlayer space within the structure. Clear carbon substrates with larger particles (rutile TiO_2 phase) are discovered from the third-row SEM images, indicating a complete oxidation. The bottom two SEM images reveal the remaining dense distribution of rutile TiO_2 phase at the end.

The thermodynamics and oxidation kinetics of MXenes have also been studied to fully understand their oxidation behaviour and predict their oxidation rate under different environments. Zhang et al. [317] found the oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ in an aqueous colloidal solution follows an exponential decay behaviour over time, indicating that oxidation occurs rapidly due to the large-area of Ti layers exposed to the air, and the oxidation slows down when part of Ti is somehow encapsulated by TiO_2 . The activation energy of the oxidation reaction is affected by various factors, like temperature and pH, and it can be evaluated based on the Arrhenius equation [318]:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4.1)$$

where k is the oxidation rate, A is the pre-exponential factor, E_a is the activation energy for the oxidation, T is the temperature, and R represents the universal gas constant. Lipatov. et al. [157] expanded the theory by working on a single MXene flake FET. They found that the oxidation initially follows an exponential decay but then follows a linear decrease. Their results indicate that the initially fast oxidation of MXene originates from the flake edge being fully exposed to the air. Once the TiO_2 forms at the edge of the flake, the oxidation rate decreases to a constant value, at which stage, the oxidation proceeds at the MXene/oxide interface [41].

The most common way to detect the oxidation of MXenes is to monitor the colour decay of the MXene aqueous colloidal solution from dark green ($\text{Ti}_3\text{C}_2\text{T}_x$)/red (Ti_2CT_x) to hazy white

(TiO₂) with the naked eye [39, 319–321]. UV-Vis-NIR spectroscopy can be accompanied [322] to quantitatively analyse the colour decay and the degree of oxidation of the MXene aqueous colloidal solution via the normalised absorption intensity. The combined two ways are frequently applied in the studies of MXenes oxidation and stability. Additional ways, such as SEM images (Figure 4.1(c)), Raman peaks, and XPS spectrum, can also be supported from the perspective of the change of material structure and its chemical composition.

Studying the oxidation mechanism and kinetics of MXenes could allow a fundamental comprehension of MXenes, improving their chemical stability and directing their design in different applications.

4.1.1.2 Main factors affecting the oxidation of MXene aqueous colloidal solutions

After knowing the basics of the oxidation mechanism and kinetics, it is imperative to figure out the main factors that drive the oxidation of MXene flakes and, therefore, direct the strategies for stability improvement.

The main factors will be discussed in two categories: internal and external factors. The internal factors relate to the material (e.g., the layered structure, functional groups, flake defects, and flake size). In contrast, the external factors relate to the environment where the MXene flakes are stored (e.g., solvent, atmosphere, temperature and pH).

Internal factors - materials

The stability and oxidation behaviour varies with different types of MXenes, due to the intrinsic chemical composition and related layered structure. Halim et al. [208] discovered that the Ti₃C₂T_x, Ti₂CT_x, Ti₃CNT_x, Nb₂CT_x, and Nb₄C₃T_x displayed various degrees of oxidation. Seredych et al. [155] experimentally etched three multilayer carbide MXenes (Ti₃C₂T_x, Mo₂CT_x, and Nb₂CT_x), and he found that the Ti₃C₂T_x is more thermally stable at 1500 °C under Helium atmosphere, compared to fewer-atomic-layer MXene structures like Mo₂CT_x or Nb₂CT_x. If having the same atomic layer, Ti-based MXenes are less capable of retaining their 2D nature and structure integrity than non-Ti-based MXenes (i.e. Zr₃C₂T_x [323]). Zhou et al. claimed that Zr₃C₂T_x exhibits better structural integrity and remains the 2D nature better than that of Ti₃C₂T_x, which is prone to be transformed into TiC [323]. The authors calculated the BE of the bare 2D Ti₃C₂ and Zr₃C₂ MXenes, together with the bulk TiC and ZrC crystals. Their calculation shows that the BE of the bulk TiC is 8.741 eV, which is larger than that of 8.080 eV of Ti₃C₂ MXene [323]. Thus, the Ti₃C₂ MXene tends

to transform into the more stable TiC configuration under high temperatures. In contrast, 2D Zr_3C_2 presents a slightly higher BE than that of bulk ZrC, and thus, the 2D Zr_3C_2 MXene can easily retain its 2D nature at elevated temperatures [323].

The terminated functional groups of MXenes [39, 41, 316] play a crucial role in the stability of MXene flakes. It has been demonstrated that the as-synthesised MXenes terminated with $-\text{Cl}$ present better stability than MXenes terminated with the $-\text{F}$ and $=\text{O}$ [324, 325]. MXenes terminated with $=\text{O}$ or $-\text{O}$ are more easily oxidised even without the presence of external oxidants [326, 155], because $=\text{O}$ or $-\text{O}$ on the flake surface can act as the reactive forms of O_2 [327].

The stability and oxidation behaviour of MXene flakes is also affected by the structural defects, which originate from the quality of the precursor-MAX phase and the choice of synthesis methods. Mathis et al. [328] reported that adding aluminium in synthesising Ti_3AlC_2 MAX could result in grains with improved stoichiometry and crystallinity. With the modified MAX phase as the precursor, the shelf-life of the as-synthesised $\text{Ti}_3\text{C}_2\text{T}_x$ can be improved up to 10 months [328], which is superior to the stability of the traditional $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous solution (only 1-2 weeks). The MXenes produced via the HF route usually have severe structural defects [155, 156], while the in-situ HF route together with MILD method is more gentle [153, 154], producing flakes with fewer defects. Lipatov et al. [157] compared the flakes synthesised via the HF route (not conductive) and the ones synthesised by in-situ HF route (conductive) in a transistor structure, revealing that the presence of pin-hole and other structural defects reduces the stability of MXenes and promotes the oxidation in the ambient environment, and the position of defects can be where the metal oxide grows [158].

Studies have also shown the dependence of the oxidation rate of MXene flakes on the flake size, with the smaller MXene flakes (mean lateral size of 110 nm) being less stable [317] than larger ones (mean lateral size of 800 nm). This dependence also supports the assumption of flake edge-driven oxidation of MXenes, which is similar to other 2D materials [329]. Therefore, to maximise the lifetime of MXenes colloidal solutions, micron-size large flakes should be prepared [40, 317].

External factors - storage conditions

The stability and oxidation behaviour of the MXene aqueous colloidal solution are strongly affected by its storage conditions, including the exposed atmosphere, the storage temperature, pH, the dissolved O_2 , and the aqueous environment.

Figure 4.2(a) presents the oxidation rate difference of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at three different oxidising environments: dry air, wet air and hydrogen peroxide (H_2O_2) at 1000 K [312]. The structure remains unchanged in the dry air, while in the wet air, some Ti atoms diffuse to the surface of the MXene structure and start to be terminated with $-\text{OH}$. In the H_2O_2 environment, more $-\text{OH}$ groups are formed, which indicates stronger oxidation of the MXene structure compared to that in dry air or wet air.

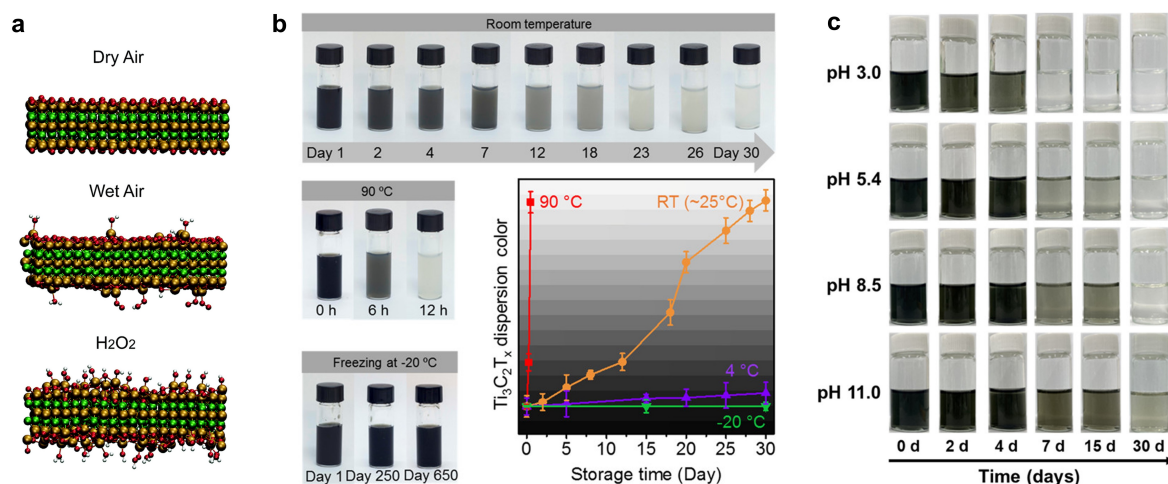


Fig. 4.2 Studies of the effect of the storage conditions on the oxidation rate of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene aqueous solution. (a) The illustrative oxidation rates of the MXene (tan: Ti; green: carbon; red: oxygen) in three different environments: dry air, wet air, and H_2O_2 . (b) Digital photos of the aqueous MXene dispersion stored at RT over 30 days, at 90 °C for 0, 6, and 12 hours, at -20 °C for 250 and 650 days. (c) Digital photos of aqueous MXene suspensions (20 °C) as a function of the oxidation time at different pHs. Image (a) adapted with permission [312], © The Royal Society of Chemistry 2018; image (b) adapted with permission [320], © 2020 American Chemical Society; and image (c) adapted with permission [321], © 2021 American Chemical Society.

The storage temperature affects the oxidation rate based on the Arrhenius equation 4.1.1. Figure 4.2(b) presents the influence of the storage temperature on the oxidation rate of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene aqueous colloidal solution, and the results show that the oxidation rate could then be slowed down by lowering the storage temperature. At 90 °C, the solution fully decays and oxidises in 12 hours, while at RT, the solution fully decays at 30 days [320]. If stored under -20 °C, the solution can be kept with almost no change for years, and the morphology and chemical composition of the MXene flakes are maintained, indicating that freezing prevents the oxidation of MXene flakes and formation of TiO_2 [320]. Doo et al. [321] also investigated the MXene aqueous solution at various temperatures (from 20 °C to 100 °C), showing the accelerated oxidation over an increasing storage temperature. From a different perspective, Habib et al. [330] monitored the change of electrical conductivity

of a bucky paper made from $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous solutions over time to assess the oxidation rate. The electrical conductivity of the bucky paper from a 7-day-old solution is 23% lower compared to that from a frozen solution. They also firstly demonstrated the influence of UV illumination on the oxidation rate of $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous solutions. With no UV illumination on the solution, the electrical conductivity of the prepared paper decreases by over 85 % in 27 days, while with continuous UV illumination on the solution, it took only 24 hours to cause a conductivity loss of > 85 %. This can be attributed to the transformation of UV light to heat, resulting in a temperature increase and radical formation from the oxygen and moisture present in the environment, leading to an increased oxidation kinetics.

Apart from neutral solutions, the pH of the aqueous solution has been investigated, as the pH could affect the formation of reaction intermediates between the $-\text{OH}$ terminal groups and hydron (H^+) or hydroxide ions (OH^-) [321]. Figure 4.2(c) shows the impact of pH on the oxidation rate of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene aqueous solutions. At 20 °C, when the pH increases from 3 to 11, the solution fully decays at Day 7 and Day 30, indicating a slower oxidation rate at basic conditions than that under acidic conditions [321].

Besides the storage temperature, the dissolved O_2 level as well as the presence of the aqueous environment [319] have been regarded as one of the key factors affecting the oxidation behaviour of the MXene aqueous colloidal solutions. Early studies claimed that dissolved O_2 in water plays a significant role in the oxidation of MXene aqueous solutions [317], while more recent investigations have demonstrated that H_2O molecules act as not only a solvent but also an oxidising reagent [319, 330]. Huang et al. [319] found that if water and O_2 were both present, the oxidation rate of MXenes solution was ~ 5 days. If only water (MXene in water saturated with Ar) or O_2 (MXene in IPA saturated with O_2) was present, the oxidation rate for the MXene solutions was ~ 41 days for the former and ~ 2026 days for the latter, although IPA has a higher mole fraction of soluble oxygen (7.82×10^{-4}) [319]. The results suggested that the water plays a more significant role in the oxidation and degradation of MXene solutions compared to the dissolved O_2 . The removal of water by dispersing MXene flakes in other organic solvents validated the above claim and demonstrated how the dispersion media affects the oxidation behaviour of MXenes [331, 330]. Maleski et al. [331] reported that the formation of TiO_2 in the water-based $\text{Ti}_3\text{C}_2\text{T}_x$ solution was much more rapid than MXenes in organic solvents. Habib et al. [330] found the oxidation rate of MXene can be slowed down if stored in a solid form (PVA).

4.1.2 Strategies for improving the stability of MXenes

Identifying the main factors affecting the oxidation of MXenes aqueous colloidal solutions is useful for developing the corresponding prevention measures [40], from both material preparation optimisation and storage conditions regulation.

4.1.2.1 Material preparation optimisation

The synthesis optimisation of both precursor MAX and MXenes can be beneficial to improve crystallinity, minimise the MXene flake defects and thus improve the material chemical stability. The quality, purity and crystallinity of MAX can be improved by varying element density [328] or choosing different types of element sources [332]. It is reported that adding more aluminium [328] or utilising graphite-based carbon [332] in the recipe of Ti_3AlC_2 synthesis could improve its morphology and crystallinity, leading to improved stability of the produced $\text{Ti}_3\text{C}_2\text{T}_x$. In terms of the synthesis of MXenes, gentler etching methods (i.e., the $\text{HCl}+\text{LiF}$ route instead of the HF route) [153] and the MILD method instead of ultrasonication [154] also help to reduce the defect amount and increase the flake size [317], which would lower the oxidation rate of MXene aqueous colloidal solutions.

The functional groups of MXenes can be chemically modified from $-\text{F}$ to $-\text{O}$, with improved surface chemical stability [333]. The modification can be achieved by dispersing $\text{Ti}_3\text{C}_2\text{T}_x$ in an aqueous KOH solution where the $-\text{F}$ can be exchanged by $-\text{OH}$ groups due to the different dissociation energies ($\text{Ti}-\text{F}$ of 569 kJ mol^{-1} and $\text{Ti}-\text{O}$ of $666.5 \text{ kJ mol}^{-1}$) bonds [334]. The resultant $\text{Ti}_3\text{C}_2(\text{OH})_x$ can be calcinated under 450°C in Ar atmosphere and fully transformed into $\text{Ti}_3\text{C}_2\text{O}_x$ through dehydration reaction [334].

4.1.2.2 Regulating storage conditions

Based on the analysis of the main external factors that influence the stability and oxidation rate of MXene aqueous solutions, the storage temperature and the exposure to water/ O_2 are the key. Therefore, it is better to store the MXene solutions at low temperatures (i.e., in the fridge or the freezer) and eliminate either water or the dissolved O_2 .

Figure 4.3(a) shows that the low-temperature stored solution can preserve the solution over 40 days compared to the 4-day shelf-life of a MXene solution stored at RT [317]. If the O_2 is removed by Ar gas [317], the shelf-life of the MXene solution can be preserved for years. That is because the solubility of O_2 in water provides a continuous oxidant for MXene oxidation (Figure 4.3(b)). Without the dissolved O_2 , water also oxidises the MXene flakes in

the Ar-based environment (Figure 4.3(b)). Other inert atmospheres like N_2 and He [155] can protect MXenes being fast oxidised in a similar way to Ar. Compared to the dissolved O_2 , the water also acts as an oxidant and accelerates the local diffusion of Ti^{4+} and O^{2-} ions during the oxidation [335, 336]. Figure 4.3(c) shows the benefit of removing water by IPA on the improvement of the oxidation rate of the MXene solution. The absence of water can also be achieved by dispersing MXene flakes in various organic solvents [331].

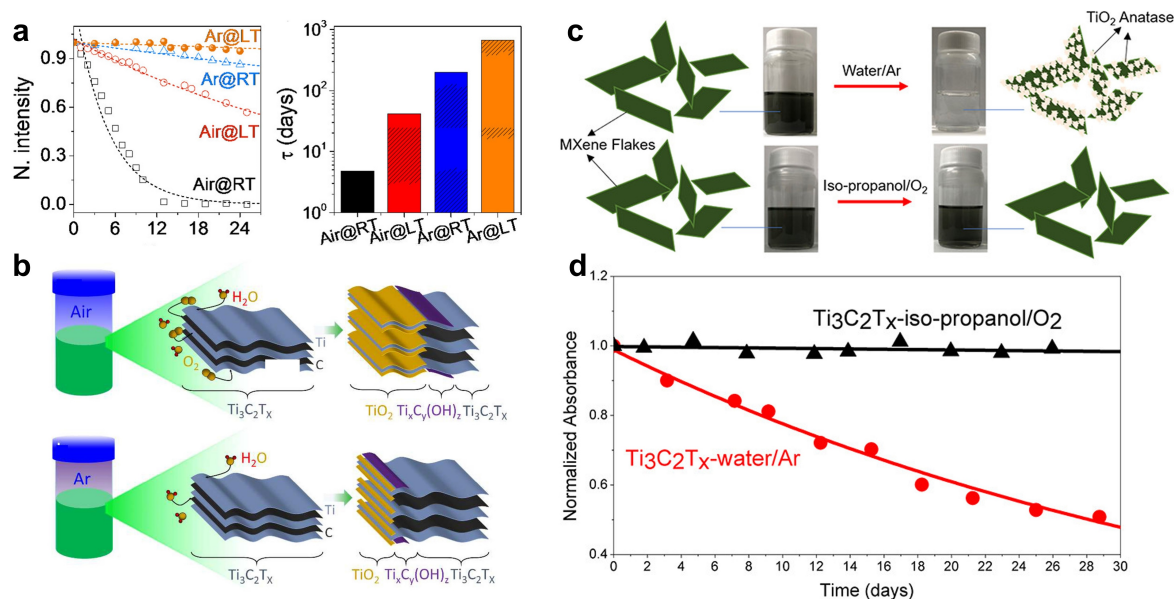


Fig. 4.3 Studies of regulating different storage conditions to decelerate the oxidation rate of MXene aqueous solutions. (a) The absorption intensity and the decay time of the $\text{Ti}_3\text{C}_2(\text{OH})_x$ solutions stored under Air@RT, Air@LT, Ar@RT, and Ar@LT, with (b) illustrative oxidate rates comparison at different gases. (c) Schematic diagram of MXenes oxidation under water/Ar and IPA/ O_2 and (d) their normalised intensity change over time. Image (a-b) adapted with permission [317], © 2017 American Chemical Society; and images (c-d) adapted with permission [319], © 2019 American Chemical Society.

Another method to protect MXene flakes involves forming an anion or layer shield around them [41]. However, this approach is more complex than simply adjusting the storage conditions. It is recommended only if adding anions or layers to the surface of MXene flakes enhances the desired properties for subsequent applications. Otherwise, this process introduces an unnecessary step, requiring complete removal of the added materials to obtain pure MXene flakes.

The aqueous environment with the presence of water or O_2 can be fully removed if MXene flakes are assembled into thin films or 3D structures via vacuum filtration or freeze-drying [317]. The resultant MXene films can be stored under a vacuum or inert atmosphere for long-term preservation. The partial oxidation rate of the MXene films can be further

improved via thermal annealing to remove any water residues trapped between layers under an inert atmosphere such as N_2 . Thermal annealing of MXene flakes and films under inert atmospheres has been demonstrated to be an effective way to reduce and modify the functional groups [337, 338] and promote their intrinsic thermal stability. The annealing process can also potentially be used to heal flake defects without causing harm to the characteristic multi-layer and hexagonal crystal structure of the MXenes [41]. Compared with an un-annealed $Ti_3C_2T_x$ film, Zhao, et al. found that the annealed (at 600 °C under Ar) $Ti_3C_2T_x$ film maintained stable in water for over 10 months [339]. The annealed film actually developed a protective TiO_2 layer on the film surface, which somehow encapsulated the film [339]. They claimed that the TiO_2 layer with compact nanocrystal arrangement prevented the water penetration and deterioration of the internal structure of the MXene film [339].

4.2 Charge transport mechanism of MXenes

Printed electronics using MXene-based inks have the potential to develop large-scale, flexible, and wearable devices. However, the complexity of the ink formulations and the polycrystalline nature of the thin films they produce present significant challenges for understanding the charge transport mechanisms within these devices. Beyond the most frequently studied $Ti_3C_2T_x$, other types of MXenes like Ti_2CT_x and non-titanium MXenes are yet well explored in terms of their intrinsic electronic properties, due to the difficulties in material preparation and nano-device fabrication.

Herein, the charge transport mechanisms of $Ti_3C_2T_x$ based and Ti_2CT_x based devices is reviewed.

4.2.1 Charge transport of $Ti_3C_2T_x$ single-flake based devices

Lipatov et al. [216] first studied the electronic properties of single monolayer $Ti_3C_2T_x$ flakes by designing a field-effect transistor (FET), as shown in Figures 4.4(a-b). Figure 4.4(c-d) plots the drain current as a function of drain-source voltages and gate voltages, respectively. They found that a single $Ti_3C_2T_x$ flake could exhibit a high conductivity (σ) of $4600 \pm 1100 \text{ S cm}^{-1}$ and field-effect electron mobility (μ_{FE}) of $2.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

In 2021, applying the gentler in-situ HF synthesis route using HCl and LiF [340] instead of the aggressive HF route, Lipatov reported the ever-best electronic values for $Ti_3C_2T_x$, with σ up to $11,000 \text{ S cm}^{-1}$ and μ_{FE} of up to $6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [340]. Their work shows that all the

tested $\text{Ti}_3\text{C}_2\text{T}_x$ flakes exhibited very similar breakdown current densities of $\sim 1.2 \times 10^8 \text{ A cm}^{-2}$ [340].

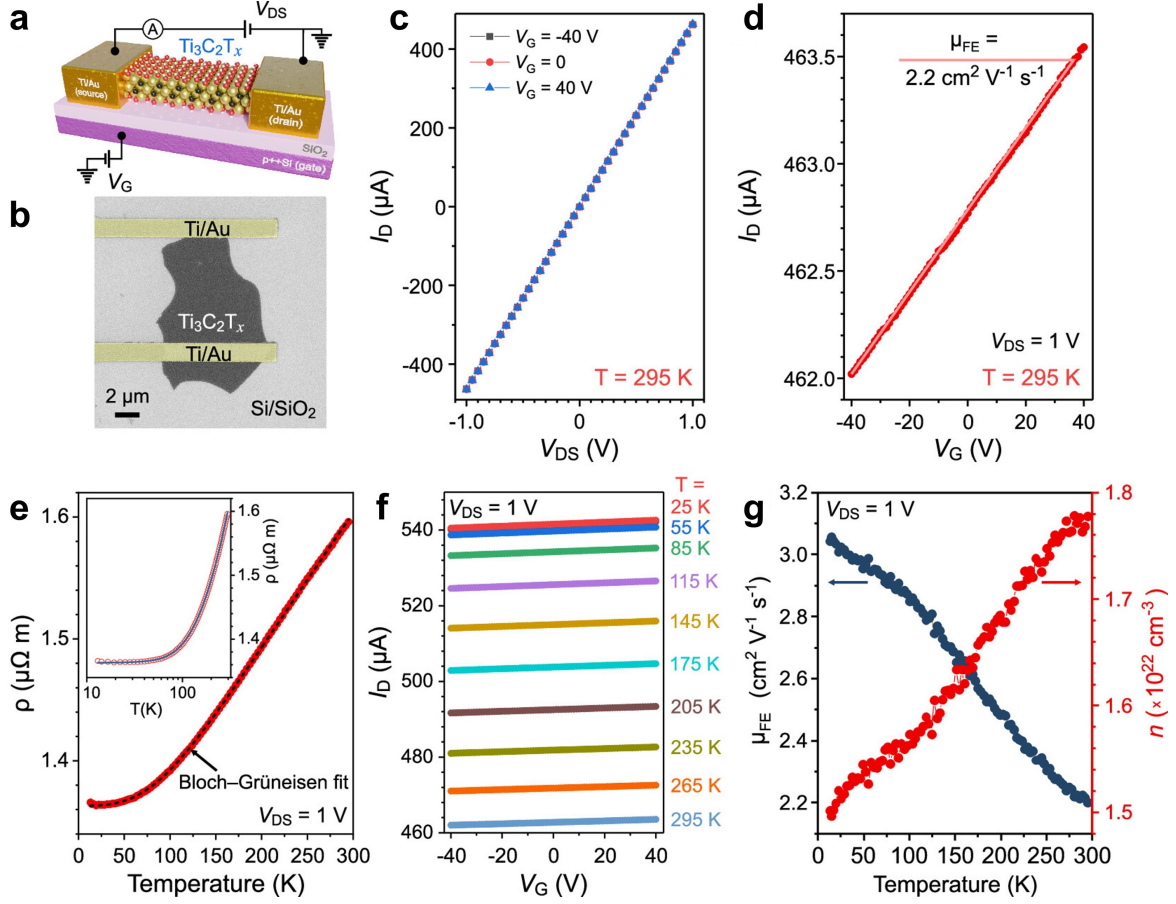


Fig. 4.4 Electronic properties of a FET device based on an individual monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake. (a) Scheme of FET with a $\text{Ti}_3\text{C}_2\text{T}_x$ channel. (b) A false-color SEM image of a $\text{Ti}_3\text{C}_2\text{T}_x$ device. (c) Room-temperature I_D - V_{DS} curves at different gate voltages. (d) Room-temperature transfer characteristic measured at $V_{DS} = 1 \text{ V}$. (e) Temperature-dependent resistance. (f) Transfer characteristics at different temperatures. (g) μ_{FE} and n_0 at different temperatures. Images adapted with permission [341], © 2023 American Chemical Society.

Using the same FET structure for individual monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flakes like what was illustrated in Figure 4.4(a-b), Lipatov et al. [341] recently performed their temperature-dependent resistivity (ρ) measurements and the results are shown in Figure 4.4(e). The ρ increased slowly below 100 K and increased almost linearly as a function of T from 100 K to 300 K. The authors validated the metallic nature of the $\text{Ti}_3\text{C}_2\text{T}_x$ material by fitting the temperature dependence of $\rho(T)$ using the Bloch-Grüneisen model [341]. They also found that at low temperatures below 25 K, the $\rho(T)$ curve exhibited a tail with a semiconductor-like ($d\rho/dT < 0$) behaviour, which can be attributed to the stronger electron scattering effect

from an increased level of disorder because the $\text{Ti}_3\text{C}_2\text{T}_x$ flake had been partially oxidised [341]. Figure 4.4(f) plots the transfer characteristics of the device with slight modulation at all temperatures, and 4.4(g) shows a declining μ_{FE} and a charge carrier concentration (n_0) over an increasing temperature.

4.2.2 Charge transport of $\text{Ti}_3\text{C}_2\text{T}_x$ film-based devices

Halim et al. [342] fabricated a $\text{Ti}_3\text{C}_2\text{T}_x$ -film FET device at a size of $\sim 1 \times 1 \text{ cm}^2$, by selective etching of Al from a sputter-deposited epitaxial Ti_3AlC_2 film. They first reported that the film exhibited a metallic σ down to $\sim 100 \text{ K}$, while below 100 K , the ρ increased with a decreasing temperature [342]. The fabricated film showed a negative magnetoresistance, which they claimed was consistent with a weak localisation charge transport behaviour of many 2D defective solids at low temperatures [342]. Lipatve et al. [216] reported that the ρ of the $\text{Ti}_3\text{C}_2\text{T}_x$ film was one order of magnitude higher than that of individual $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, which indicated a surprisingly good electron transport through the surface terminations between different flakes [216].

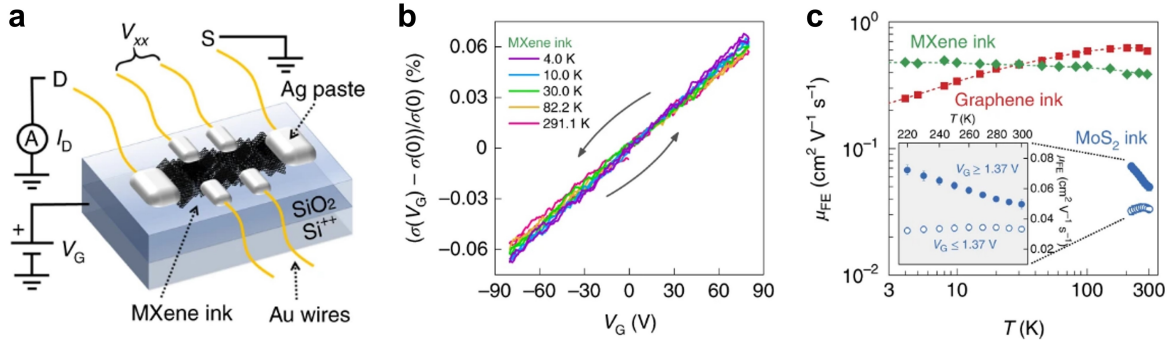


Fig. 4.5 A study on the charge transport mechanism of $\text{Ti}_3\text{C}_2\text{T}_x$ -based devices. (a) Sketch of an inkjet-printed MXene FET; (b) conductivity ratio as a function of gate voltages over an increasing temperature in the MXene-ink FET device; (c) μ_{FE} as a function of temperature in the logarithmic scale for the printed MXene-ink device (green diamonds). Images adapted with permission [329], © 2021, Erik Piatti et al, under exclusive license to Springer Nature Limited.

Beyond the primary studies based on the charge transport of $\text{Ti}_3\text{C}_2\text{T}_x$ film-based devices, Piatti, et al. [329] investigated further, more in detail, the charge transport of a rectangular inkjet-printed $\text{Ti}_3\text{C}_2\text{T}_x$ film from $\text{Ti}_3\text{C}_2\text{T}_x$ colloidal inks. Figure 4.5(a) shows a 30-nm thick $\text{Ti}_3\text{C}_2\text{T}_x$ film printed on a $\text{SiO}_2/\text{Si}^{++}$ substrate. The authors performed a series of studies, including the σ of the film device as a function of T , the σ as a function of a magnetic field (B), and the σ as a function of applied gate voltages (V_G), and accounted those test results for

morphological features of the flakes and printed films. The device σ was 208 S cm^{-1} at 290 K and was nearly independent of T , which indicated a metallic behaviour and was consistent with what was reported for an epitaxial $\text{Ti}_3\text{C}_2\text{T}_x$ film by Halim [342]. Figure 4.5(b) shows the σ of the $\text{Ti}_3\text{C}_2\text{T}_x$ film device increases monotonically with increasing V_G and exhibited no hysteresis, indicating an intrinsic electron conduction behaviour. This was in line with the reported FET behaviour of single-layer $\text{Ti}_3\text{C}_2\text{T}_x$ flakes [216, 343], revealing that the charge transport in printed $\text{Ti}_3\text{C}_2\text{T}_x$ film devices was dominated by the intrinsic intra-flake processes. Figure 4.5(c) shows that when the device is cooled from 290 K to 4 K, the μ_{FE} slightly increases from ~ 0.4 to $\sim 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was typical of disordered metallic systems where the main source of charge-carrier scattering comes from defects.

4.2.3 Charge transport of Ti_2CT_x based devices

Beyond the $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes, another type of Titanium-based MXenes, the Ti_2CT_x has started to obtain the interest. Yet, only a few studies have investigated this material both at film-based and single-flake-based FET devices due to its fast-oxidation nature, uncontrolled termination groups, and smaller sizes, which make it challenging for device fabrication.

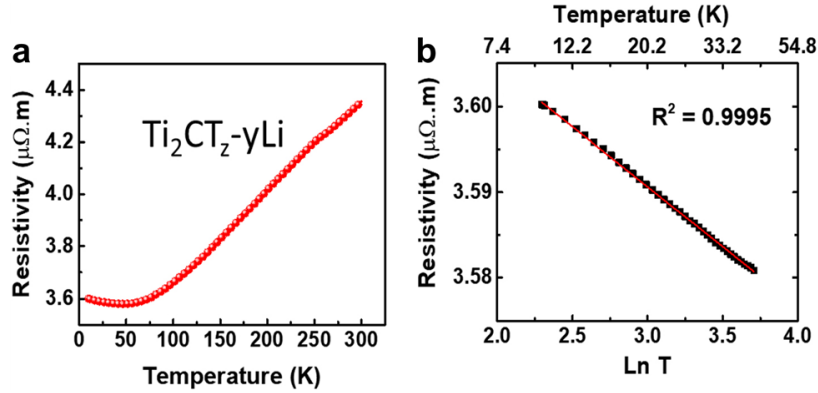


Fig. 4.6 A study on the charge transport mechanism of Ti_2CT_x -based devices. (a) Temperature dependence of resistivity and (b) resistivity versus logarithmic temperature of a $\text{Ti}_2\text{CT}_x\text{-yLi}$ thin film over the 9 K to 35 K temperature range. Images adapted with permission [344], © 2019 IOP Publishing Ltd. This figure is licensed under Creative Commons Attribution 3.0.

Halim, et al. [344] reported the electronic properties of Ti_2CT_x films, as shown in Figure 4.6. The Ti_2CT_x film was etched in a LiF/HCl solution from a physical vapour deposited TiAl_2C epitaxial thin film on a sapphire substrate and was then intercalated with Li^+ to form a $\text{Ti}_2\text{CT}_x\text{-yLi}$ thin film [344]. The film exhibited a typical metallic behaviour with ρ of $\sim 4.4 \mu\Omega\text{m}$ at RT. The authors also performed the spectroscopic ellipsometry measurements

for the Ti_2CT_x film and confirmed the metallic behaviour of the film with weak localisation below 50 K.

However, there is yet any study reported so far for a single Ti_2CT_x flake-based FET device to examine the charge transport mechanism of the material intrinsically and the difference or relation compared to a film-based device. There is yet any report to the best of my knowledge for a Ti_2CT_x film-based or a Ti_2CT_x flake-based FET device to understand the electronic behaviour like magnetoresistance and temperature-dependent sheet conductance (G_s).

4.2.4 Charge transport of other MXenes-based devices

By searching the current literature, only a few studies have been reported so far for the charge transport mechanism for the other promising MXene types, for instance, Nb_2C [344], V_2C . Halim et al. [344] reported that the resistance of the Nb-based films increases with a decreasing temperature, with $414.1 \mu\Omega\text{m}$ at RT. This value is two orders of magnitude more resistant than the Ti-based counterpart. At a lower temperature of 50 K, the resistance of the Nb-based film reaches four orders of magnitude higher. The authors attribute the high resistance of the Nb-based film to a percolation between flakes. They found a scaling natural logarithm of resistance versus $T^{-0.25}$, which was consistent with a 3D VRH mechanism, where hopping within individual flakes was rate-limiting [344]. This implies that the Nb-based flakes are quite defective, and the charge transport is still unclear [344].

4.3 Energy storage applications of MXenes and MXenes-based composites

4.3.1 Introduction to energy storage devices

Background of energy storage

The gradual depletion of fossil fuels and the rise in CO_2 emissions have spurred efforts to explore and develop renewable energy sources such as solar, wind, ocean, and biomass. However, these renewable energy sources cannot be continuously accessible due to their intermittent nature [345]. To harness them effectively, high-energy and/or high-power and long-lasting energy storage devices are developed to store and deliver intermittent energy. The most commonly used electrochemical energy storage devices are batteries, capacitors

and supercapacitors, widely applied in electric vehicles, smart grids, and various portable and wearable electronics [346].

Figure 4.7(a) compares the difference in power densities and energy densities of batteries, capacitors and supercapacitors in a general Ragone plot. Power densities are the rate of energy transfer or conversion per unit mass and indicate how quickly a device can deliver energy, while energy densities measure the amount of energy per unit mass stored in a device and indicate the total amount of energy available. Advanced batteries like lithium-ion batteries normally exhibit a high energy density at an order of 10^2 Wh kg^{-1} because they can store a significant amount of energy through bulk redox reactions in electrodes, shown in the right image in Figure 4.7(b). In contrast to batteries, capacitors usually have higher power densities up to 10^5 W kg^{-1} but lower energy densities down to $10^{-2} \text{ W kg}^{-1}$ (the magenta circle in Figure 4.7(a)). The capacitors store charges at the electrode in the form of an electrostatic field. The choice between batteries and capacitors largely depends on whether the interested applications aim at a high energy or high power output [348].

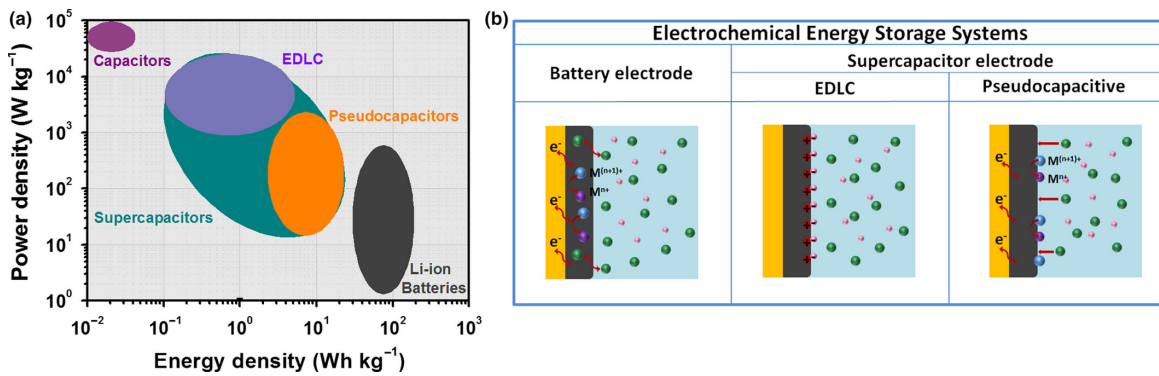


Fig. 4.7 Introduction to energy storage devices and their electrochemical structures. (a) A Ragone plot of different energy storage devices, and (b) a schematic diagram comparing the fundamental charge storage mechanisms of electrode materials in batteries and supercapacitors. Images copied with permission [349], © 2019 Zhengzhou University.

There is a third category of energy storage devices called supercapacitors, which stands out due to a more balanced behaviour of the power and energy density, quicker charging and discharging rates, and extended lifespan [348, 350], compared to batteries and capacitors. As shown in Figure 4.7(a), the supercapacitors occupy the middle and a wide range of power density (10^1 - 10^4 W kg^{-1}) and energy density (0.1 - 10 Wh kg^{-1}) between that of capacitors

and batteries. They can harvest energy in very short periods and subsequently provide a burst of energy whenever needed [350].

Electrochemical storage mechanism of supercapacitors

Figure 4.7(b) shows the two types of supercapacitors: electric double layer capacitor (EDLC) and pseudocapacitors, based on their electrochemical storage mechanism [351–353]. EDLC has an opposite-charge layer at the electrode-electrolyte interfaces forms during the charging process through ion adsorption from the electrolyte by electrostatic attraction. This is a non-Faradaic process. In contrast to EDLC, in the pseudocapacitors, multiple charge transfer processes occur at the electrode-electrolyte interfaces during the charging and discharging process, involving redox reactions, ion intercalations, and electrosorption. This is a Faradaic process.

Performance assessment of supercapacitors

Supercapacitors are generally assessed by their energy and power density, charge/discharge rates, and cycle life, which relates to their energy storage capabilities, energy delivery efficiency, service durability and economics. To achieve optimal performance of supercapacitors, the choice of materials, and the design of the electrode structure and device structure matter. For example, an electrode material is supposed to be designed with (1) a large surface area to allow more charge storage, (2) a high electrical conductivity to allow for the rapid transfer of electrons, (3) a porous structure to facilitate efficient ion transport from the electrolyte to the electrode surface, (3) an electrolyte with high ionic conductivity, and (4) all chosen materials being chemically stable over a wide potential window to ensure numerous cycles without degradation [354].

4.3.2 Charge storage mechanism in MXenes-based supercapacitors

Why MXenes and how?

Electrodes are the key component in supercapacitors. A supercapacitor with good performance requires highly porous electrodes with high specific surface area, high electrical conductivity and good chemical stability [353].

2D materials are particularly interesting as promising electrode materials for supercapacitors owing to their large electrochemically active surfaces [117] and have been explored for

years. For example, activated graphene electrodes have higher volumetric capacitances of $\sim 200\text{--}350\text{ F cm}^{-3}$ compared to that achieved by activated porous carbon electrodes ($\sim 60\text{--}100\text{ F cm}^{-3}$) [355, 356].

MXenes have been proven to be highly promising electrodes for energy storage applications due to their high electrical conductivity and large aspect ratios [357]. Ghidui et al. reported a thick additive-free $\text{Ti}_3\text{C}_2\text{T}_x$ film, achieving a volumetric capacitance of up to 900 F cm^{-3} [33], which exceeds the volumetric capacitance of activated graphene ($\sim 200\text{--}350\text{ F cm}^{-3}$) [355, 356]. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene also exhibits a better gravimetric capacitance of $\sim 320\text{ F g}^{-1}$ than that of the functionalised graphene (close to 200 F g^{-1}) [358]. The substantial volumetric and gravimetric capacitances of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene stem from several reasons: (1) the high conductivity ($11,000\text{ S cm}^{-1}$) [340] facilitating rapid electron transport, (2) the layered structures enabling ionic intercalation and transport, (3) the variable oxidation states of transition metals allowing efficient charge transfer, and (4) $-\text{O}$ terminations offering favourable redox-active sites throughout the charging-discharging process [359].

$\text{Ti}_3\text{C}_2\text{T}_x$ is the most explored MXene type in energy storage devices, so an overview of the charge-storage mechanism of $\text{Ti}_3\text{C}_2\text{T}_x$ -based supercapacitors is given under different factors, and the related electrochemical performance.

Factors affecting MXene-based supercapacitor performance

In general, a supercapacitor usually consists of electrode materials, electrolytes and membranes. The main factors affecting the electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ -based supercapacitors are the choice of electrolytes, the functional groups terminated at the surface of MXene flakes and the design architecture of electrodes.

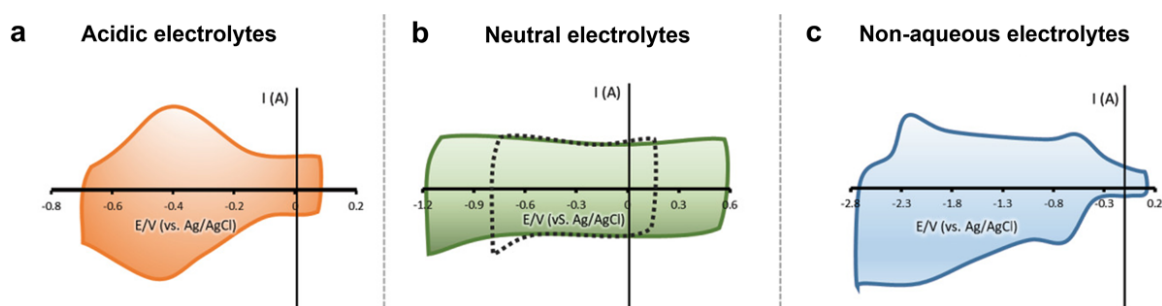


Fig. 4.8 Typical schematic CV plots of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in (a) acidic aqueous electrolytes, (b) neutral aqueous electrolytes and (c) non-aqueous electrolytes. Images adapted with permission [360], © 2023 Doron Aurbach, Daniel Mandler, Netanel Shpigel, et al, Advanced Energy Materials published by Wiley-VCH GmbH.

The choice of the electrolyte affects the electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ as supercapacitor electrodes [360], as shown in Figure 4.8. If using aqueous electrolytes, sulfide acid (H_2SO_4) [361], for example, the H^+ are bonded with the $-\text{O}$ groups at the $\text{Ti}_3\text{C}_2\text{T}_x$ surface (cathode) during the discharging process and the bonds de-associate during the charging process [362]. The bonding and de-bonding cycles are redox reactions, as observed as redox peaks in Figure 4.8(a), which alters the valency states of Ti and thus result in a surface-pseudocapacitive behaviour [362] of the whole device. In contrast to acid electrolytes, an EDLC behaviour is observed in salt-based neutral aqueous electrolytes (i.e., Na_2SO_4 , $(\text{NH}_4^+)_2\text{SO}_4$, and MgSO_4) [359, 363, 364]. The hydrated metal ions (i.e., Na^+ , NH_4^+ , Mg^{2+}) intercalate into the $\text{Ti}_3\text{C}_2\text{T}_x$ interlayers without dehydration [365], which only provides the electrosorption process resulting in the EDLC capacitance, as shown as a square shape in Figure 4.8(b). For aqueous electrolytes, the potential window is rather limited (0.8 V in Figure 4.8(a) and 1.8 V in Figure 4.8(b)), because of the restrained voltage of 2V above which water splitting occurs [353] and irreversible oxidation of MXenes at a positive voltage [366]. The potential window can be extended to over 2 V by adopting non-aqueous electrolytes, such as organic electrolytes [357] or ionic-liquid gel electrolytes [327, 353]. Wang, et al.[367] studied the electrochemical behaviours of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in various organic solvents (1 M LiTFSI salt in propylene carbonate, acetonitrile, and dimethyl sulfoxide), at a wider potential range of -2.4 -0 V. The measured capacities were observed at 110-195 F g^{-1} . Dall'Agnese [358] claimed that their measured capacitance of $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes in acetonitrile (70 F g^{-1}) was lower than that in acidic electrolytes (360 F g^{-1} in 3 M H_2SO_4), which could be attributed to the low conductivity of organic electrolytes [358]. Okubo et al. [368] reported that the solvation energy in non-aqueous electrolytes is much weaker than that for hydration in aqueous electrolytes, and the capacitance of MXene electrodes in nonaqueous electrolytes arises mainly from pseudocapacitance [354].

The functional groups terminated at the surface of MXene flakes serve as active sites for redox reactions [369], which influences the electrochemical performance of MXenes as supercapacitor electrodes. Specifically, the $=\text{O}$ groups demonstrate a higher gravimetric capacitance than other surface terminations such as $-\text{F}$, $-\text{H}$, or $-\text{OH}$ [370]. This is because the $=\text{O}$ groups share more electrons with the M element in the MXene layer, and the conversion between the $=\text{O}$ and $-\text{OH}$ groups provides a large number of active sites for redox reactions [369].

The design architecture of electrodes plays a great role in determining the electrochemical performance of MXene electrodes [369]. Instead of creating a film electrode which most researchers do [33], Huang, et al. [371] developed a 3D open macrostructure for the MXene hydrogel electrode. The 3D open microstructure was fabricated by freeze-drying the

MXene slurry, followed by a carefully designed thawing process in the H_2SO_4 electrolyte. The specially fabricated 3D hydrogel electrode is saturated in the electrolyte and infused with intercalated protons, offering an increased number of surface areas and redox sites for ion storage and facilitating electrolyte diffusion [371]. Xia, et al. [372] produced an electrode with vertically aligned $\text{Ti}_3\text{C}_2\text{T}_x$ through mechanical shearing and self-assembly of a discotic lamellar liquid-crystal phase of $\text{Ti}_3\text{C}_2\text{T}_x$. The authors reported that the electrochemical behaviour of the fabricated electrode decreases the ion transit time and improves the electrochemical kinetics.

4.3.3 Research progress of MXenes-based electrodes for supercapacitors

4.3.3.1 MXenes-based composites as electrodes

The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film electrodes have demonstrated a volumetric capacitance of 1274 F cm^{-3} in $3 \text{ M H}_2\text{SO}_4$ [373], which exceeds those achieved by carbon nanotube (50 F cm^{-3} in solvent-cast poly(vinyl alcohol)/phosphoric acid as solid electrolyte) [374], graphene (376 F cm^{-3} with 6 M KOH as aqueous electrolyte) [355] and rGO (482 F cm^{-3} in $1 \text{ M H}_2\text{SO}_4$) [375]. Other MXenes, such as Ti_2CT_x or V_2CT_x , have also been explored to reveal good capacitance (Ti_2CT_x : 382 F g^{-1} [376] and 452 F cm^{-3} [377]; V_2CT_x : 487 F g^{-1} [378]).

However, $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes have revealed drawbacks such as restacking and easy oxidation (especially in the aqueous environment) [41], inhibiting the development of pure $\text{Ti}_3\text{C}_2\text{T}_x$ as electrode materials. To take the advantage of the high conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ and its high energy-storage characteristics, mixing $\text{Ti}_3\text{C}_2\text{T}_x$ with other electrode materials (such as carbon, metal oxides, conductive polymer) can produce a synergistic improvement of the electrochemical performance for supercapacitor electrodes [354, 369, 379]. Those materials can also act as interlayer spacers to hinder the restacking of $\text{Ti}_3\text{C}_2\text{T}_x$ sheets [354].

MXenes/carbon-based electrodes mix MXenes with carbon-based materials, including active carbon [380], graphene [381], rGO [382], and carbon nanotubes (CNTs) [383]. The carbon-based materials provide high conductive pathways for charge transfer instead of pseudocapitance and can go into the interlayer spacing of MXene sheets suppressing its restacking issues [354, 380]. Li, et al. [380] demonstrated a $\text{Ti}_3\text{C}_2\text{T}_x$ /acid activated carbon (AAC) composite as the supercapacitor electrode. Figure 4.9(a) illustrates the fabrication process of $\text{Ti}_3\text{C}_2\text{T}_x$ /AAC via physical stirring of two solutions at RT for 24 hours [380]. Figure 4.9(b) plots the improved C_s of the fabricated electrode by 48.8 % at 0.5 A g^{-1} ,

compared to a pure $\text{Ti}_3\text{C}_2\text{T}_x$ electrode [380]. The authors claimed that the AAC increased the interlayer spacing of $\text{Ti}_3\text{C}_2\text{T}_x$ sheets and protected $\text{Ti}_3\text{C}_2\text{T}_x$ from aggregation [380]. Li, et al. used the composite and AAC as the anode and cathode at a mass ratio of 2:1, respectively, and Figure 4.9(c) shows that the resulting asymmetric supercapacitor exhibited a C_s of 177 F g^{-1} at 0.5 A g^{-1} (the blue curve). The electrochemical performance of the 2:1 $\text{Ti}_3\text{C}_2\text{T}_x/\text{AAC}$ electrode can maintain its capacitance at 97.4 % after 10,000 cycles. Zhao, et al. [383] demonstrated a sandwich-like $\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$ composite electrode with an improved C_s of 150 F g^{-1} and an improved volumetric capacitance of 390 F cm^{-3} at 2 mV s^{-1} , compared to a pure $\text{Ti}_3\text{C}_2\text{T}_x$ electrode (125 F g^{-1} and 360 F cm^{-3} , respectively). The sandwiched composite electrode also showed a stable volumetric capacitance of $\sim 345 \text{ F cm}^{-3}$ at 5 A g^{-1} with no degradation after 10,000 cycles [383].

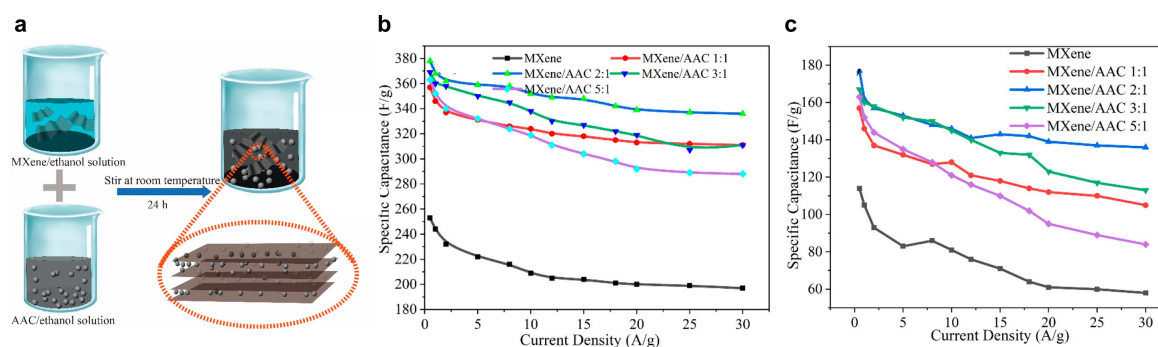


Fig. 4.9 An example of MXene-based composites as electrode materials for supercapacitors. (a) The schematic diagram for preparation of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{AAC}$ composite. (b) C_s of MXene and MXene/AAC composite electrodes at different current densities. (c) The C_s of MXene//AAC and MXene/AAC//AAC asymmetrical capacitances at various current densities. Images adapted with permission [380], © 2020 American Chemical Society.

MXenes/metal-oxide based electrodes mix MXenes with metal-oxides, including MnO_2 [384], ZnO [385], and TiO_2 [386]. Both MXenes and metal oxides exhibit high capacitance [354] as supercapacitor electrodes due to the oxidation-reduction (redox) reactions [354]. The metal oxides can also act as an interlayer spacer to stop the restacking issues of MXenes, and the MXenes with superior conductivity can also act as a conductive substrate for metal oxides to promote electron transfer, resulting in a synergetic effect for electrochemical performance improvement. Wang, et al. [385] reported a sandwich-like $\text{Ti}_3\text{C}_2\text{T}_x/\text{ZnO}$ composite as an electrode material, where ZnO nanoparticles were uniformly distributed on the surface and interlayer of $\text{Ti}_3\text{C}_2\text{T}_x$ sheets and effectively prevented the restacking of $\text{Ti}_3\text{C}_2\text{T}_x$. Their results showed that the composite delivered an improved C_s of 120 F g^{-1} at 2 mV s^{-1} compared to a pure $\text{Ti}_3\text{C}_2\text{T}_x$ electrode (100 F g^{-1}). The sandwich-like $\text{Ti}_3\text{C}_2\text{T}_x/\text{ZnO}$ electrode also exhibited excellent cycling stability with the capacitance retained at 85%

after 10,000 cycles. Cao, et al. [386] reported a $\text{Ti}_3\text{C}_2\text{T}_x/\text{TiO}_2$ composite for supercapacitor electrodes, with a better C_s of 128 F g^{-1} compared to a pure MXene electrode (91 F g^{-1}). The $\text{Ti}_3\text{C}_2\text{T}_x/\text{TiO}_2$ composite was produced by controlling the formation of TiO_2 through monitoring the oxidation degree of $\text{Ti}_3\text{C}_2\text{T}_x$ at RT [386]. The formed TiO_2 nanoparticles could be used to decorate the $\text{Ti}_3\text{C}_2\text{T}_x$ surface and swell the $\text{Ti}_3\text{C}_2\text{T}_x$ layer [386]. The resultant composite had a seven-fold increase in the specific surface area and more Ti active sites [386] compared to $\text{Ti}_3\text{C}_2\text{T}_x$ with no TiO_2 decoration.

MXenes/polymer-based electrodes mix MXenes with conductive polymers like polypyrrole [387], polyaniline [388], and poly(3,4-ethylenedioxythiophene) (PEDOT) [389], which are conductive polymers with intrinsic highly redox-active behaviours [354]. The conductive polymers can provide conductive pathways to facilitate charge transfer, expand the interlayer spacing of MXenes and further boost the mechanical strength and electrochemical capacitance of electrodes. Apart from conductive polymers, electrically neutral polymers like PVA [390] can also be applied to act as an interlayer spacer. Ling, et al. [390] reported a $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVA}$ composite film as supercapacitor electrodes through vacuum-assisted filtration. The resultant $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVA}$ composite electrode offered an improved volumetric capacitance of 528 F cm^{-3} than a $\text{Ti}_3\text{C}_2\text{T}_x$ electrode (367 F cm^{-3}) at 2 mV s^{-1} in an alkaline electrolyte. Adding polymers makes the supercapacitor electrodes promising in flexible and wearable applications [369].

4.3.3.2 Device configuration of MXenes-based supercapacitors

A. 3-electrode or 2-electrode configuration

The electrochemical performance of the lab-produced MXene-based supercapacitors is often tested in conventional three-electrode or two-electrode systems [379]. Figure 4.10 schematically illustrates the configuration difference between the two systems. The two-electrode system (Figure 4.10 (a)) applies one cathode, one anode and an electrolyte, which are sometimes assembled into button cells (with a membrane) to test their practical electrochemical performance as a real device [391]. In contrast, the three-electrode system (Figure 4.10 (b)) has the working electrode (WE), counter electrode (CE) and reference electrode (RE) [392], which is normally used to specifically characterise the electrochemical performance of the active electrode materials [393],

B. Microsupercapacitor configuration

Instead of using two-electrode or three-electrode systems, Figure 4.11 illustrates some newly proposed supercapacitor configurations, including thin-film electrodes with sandwich-type

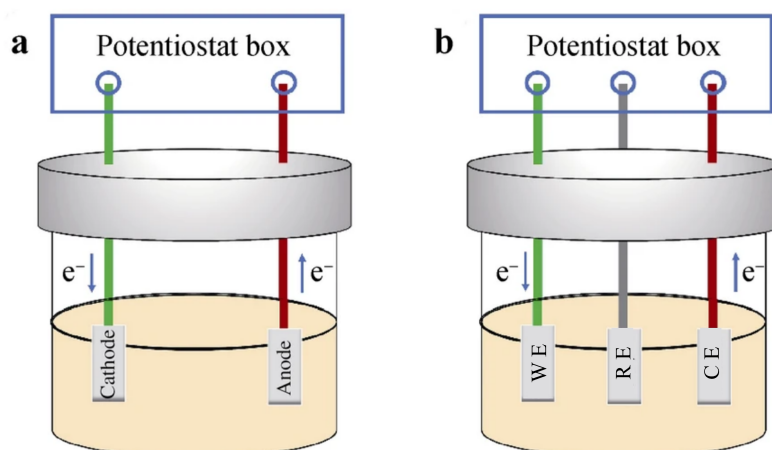


Fig. 4.10 Schematic diagrams of a two-electrode (a) and a three-electrode (b) configuration of electrochemical cells for electrochemical tests. Images copied with permission [394], © 2020, The Nonferrous Metals Society of China and Springer-Verlag GmbH Germany, part of Springer Nature.

structure (thickness $< 10 \mu\text{m}$) (Figure 4.11(a)), fibre-like structure (Figure 4.11(b)), or arrays of planar microelectrodes (interdigital-shaped structure) (Figure 4.11(c)) [354, 395]. The sandwich-type supercapacitors are the most traditional configuration, in which the separator is inserted between the positive and negative electrodes, which are electrolyte-filled and sealed with a shell material. This sandwich-type structure is convenient for scalably producing electrodes with good mechanical properties [354]. It can be assembled with flexible PET films and other packagings, paving the way for flexible supercapacitors [354]. The fibre-like supercapacitors are proposed to tailor the development of compatible energy-storage systems that can be integrated within a textile. The interdigital-shaped structure shows the advantage of requiring no separator due to an insulating gap between the electrodes (Figure 4.11(c)). Those three types of microsupercapacitor configurations have been proposed to meet the demands of device miniaturisation, and the electrodes can often be fabricated via printing, spray coating and laser etching methods [379].

C. Asymmetric and hybrid supercapacitors

In a 2-electrode supercapacitor cell, the configuration can be symmetric, asymmetric and hybrid. A symmetric cell has two similar electrodes concerning the mass, volume and material type, and an asymmetric cell or a hybrid cell has two different electrodes [396]. The asymmetric configuration normally applies electrode materials with similar electrochemical behaviours. In contrast, the hybrid ones normally apply EDLC//pseudocapacitive electrodes or EDLC//battery-type electrodes (Table 4.1), which is a very good approach for having

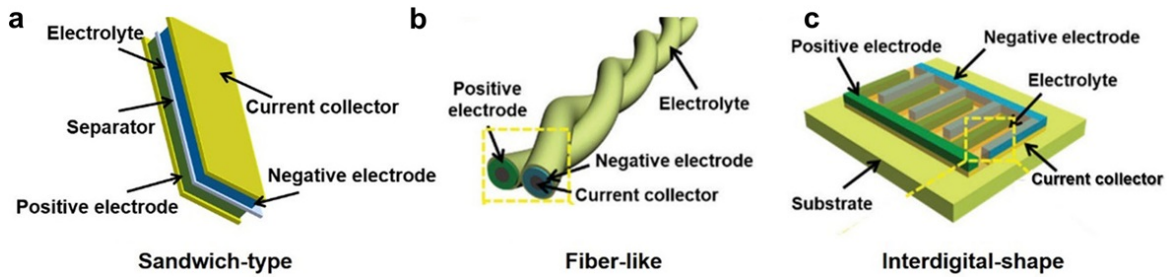


Fig. 4.11 Device configuration of MXene-based supercapacitors: (a) sandwich-type, (b) fiber-like, and (c) interdigital-shape. Images copied with permission [354], © 2019 Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim.

the combined features of high energy storage (faradaic process) and high charging and discharging rates (non-faradaic process) in a single device [397]. Supercapacitors with asymmetric electrodes are also attractive for having an increased operational cell voltage, combining the different voltage windows of the different electrodes, and minimising self-discharging of the cell [396].

Table 4.1 Configuration of asymmetric or hybrid supercapacitor devices

Type	Negative electrode	Positive electrode
Asymmetric supercapacitor	EDLC-1	EDLC-2
	EDLC-2	EDLC-1
	Pseudocapacitive-1	Pseudocapacitive-2
	Pseudocapacitive-2	Pseudocapacitive-1
Hybrid supercapacitor	EDLC	Battery-like
	Battery-like	EDLC
	Pseudocapacitive	Battery-like
	Battery-like	Pseudocapacitive

D. Wearable supercapacitors

Wearable electronics, including wearable supercapacitors, represent a growing field within technology that integrates electronic devices into everyday clothing or accessories, enabling seamless interaction with technology and providing real-time monitoring and data collection. These devices include smartwatches, fitness trackers, smart glasses, smart clothing, and medical sensors, all designed to offer convenience, enhance user experience, and improve health, lifestyle, and productivity [398].

Wearable supercapacitors are typically made using flexible, high-conductivity materials like carbon-based nanomaterials (e.g., graphene, carbon nanotubes), conductive polymers, and

metal oxides, combined with flexible substrates such as textiles or polymers [37]. The main fabrication methods include coating or dipping textiles in solutions containing electrode materials, printing conductive inks directly onto fabrics, and layer-by-layer assembly to create flexible electrode structures [399]. Solid-state or gel electrolytes are used to maintain flexibility and safety. These supercapacitors are assembled in either a sandwich or interdigitated configuration, allowing them to store and deliver energy efficiently while remaining flexible and wearable [395]. For example, Li, et al. [400] demonstrated a cotton-based $\text{Ti}_3\text{C}_2\text{T}_x$ electrode fabricated by dip coating of $\text{Ti}_3\text{C}_2\text{T}_x$ on cotton surfaces. The as-fabricated electrode was tested in a symmetric device configuration in a 1 M H_2SO_4 aqueous electrolyte, and the device achieved an areal capacitance (C_A) of 208 mF cm^{-2} and a maximum energy density of $2 \mu\text{Wh cm}^{-2}$ when tested between 0 and -0.6 V . Wang, et al. [401] reported an N-doped carbon fibre textile dip-coated with the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene to realise a pseudocapacitive supercapacitor electrode. This electrode was tested in an asymmetric supercapacitor with a functionalised carbon fibre textile as the counter electrode and a PVA/ H_2SO_4 gel as the electrolyte [401]. The device achieved a C_A of $\sim 1280 \text{ mF cm}^{-2}$ [401].

Most MXenes-based wearable supercapacitors have been fabricated with a layer of separator or solidified gel electrolyte sandwiched between the textile electrodes. This structure adds asymmetric stress within the layers induced by the movement of the end user, which could impact the electrochemical performance, durability and cycling performance of the devices.

4.4 Conclusions and thesis aims

MXene is a large family of 2D transition metal carbides, nitrides, and carbonitrides. Researchers have demonstrated its promising applications in energy storage devices like batteries and supercapacitors as electrode materials. Due to the large surface area and excellent electrical conductivity, it shows a possibility of enabling high-performance energy storage devices with flexibility and wearability.

However, the current synthesised MXenes can easily oxidise into TiO_2 , while being exposed to moisture and oxygen. Their prone to oxidation can have an adverse influence on the device performance for energy storage as electrode materials, as the electrode oxidation and degradation will impact the charge transfer occurring at the electrode-electrolyte interface, and eventually reduce the capacitance, energy density, power density and thus the lifetime. $\text{Ti}_3\text{C}_2\text{T}_x$ have been extensively studied regarding the oxidation mechanism, the prevention solutions and the intrinsic charge transport, while those of Ti_2CT_x and non-titanium MXenes are yet well explored. The high conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes, the large surface area with

potential redox active sites, and its metallic nature with weak localisation make it attractive as electrode materials, even for flexible and wearable energy storage devices. When depositing MXenes on flexible or wearable substrates, improving the electrochemical performance of the related devices like supercapacitors becomes more complicated due to the wearable configuration and the flexible requirements, which needs more investigation.

To summarise, the work aims to advance the scalable processing of 2D materials, specifically h-BN and MXenes, and their composites and to demonstrate their potential in energy storage devices and thermal management applications, which eventually could support the global CO₂ reduction commitment. Specifically, the main objectives are explored and investigated in the following chapters:

1. To seek scalable and sustainable techniques to produce 2D h-BN, MXenes and their composites.
2. To explore ways of using 2D materials and their composites to enable high-performance energy storage devices with better energy density, power density, device durability, flexibility and wearability.
3. To develop a better thermal management system using 2D materials and their composites with higher thermal conductivities, enabling high-performance energy storage devices operating within the optimal temperature range for the best power rating and energy efficiency.

Through these objectives, the work could demonstrate a foundation for deploying 2D materials in critical applications that can contribute to CO₂ reduction by improving energy efficiency, thermal management, and renewable energy storage.

Chapter 5

Fully spray-coated capacitors using h-BN as a dielectric layer

Printable dielectric inks with desired dielectric properties are in high demand to enable high-performance printed electronic devices [73] with enhanced capacitance and device durability. Printed electronics based on 2D materials have been demonstrated to outperform standard printed electronics for printed ICs [55, 80]. This chapter reports the few-layer h-BN (FLh-BN)-based dielectric inks, which are optimised to achieve a suitable concentration for spray coating and decent flake quality. The FLh-BN-based dielectric inks are produced by ultrasonication-assisted LPE via probe sonication and subsequent centrifugation. Raman, AFM, SEM, and XPS are utilised to examine the chemical composition and flake size of the produced FLh-BN flakes. The lateral size and the thickness of the FLh-BN flakes follow a log-normal distribution, peaking at 352 nm and 6.6 nm, respectively, which aligns well with 2D nature. To examine the dielectric properties of the FLh-BN-based dielectric inks, a metal-insulator-metal (MIM) parallel capacitor is spray-coated, with sprayed silver films as contact electrodes and the FLh-BN-based dielectric film in the middle as an insulating layer. The MIM capacitor exhibits a dielectric constant (ϵ_r) of 7.9. Two ways are explored to further improve the ϵ_r of the dielectric materials, including adjusting the mass ratios of FLh-BN in the dielectric inks and embedding a high- ϵ_r BaTiO₃, achieving a ϵ_r of 17.1 and 16, respectively. The improved ϵ_r values are advantageous to the device capacitance and durability.

5.1 Preparation and characterisation of materials

This section aims to prepare desired FLh-BN-based dielectric inks, which should be suitable for spray-coating to form the dielectric layer in the MIM capacitor. First, the concentration of the FLh-BN ink $c_{\text{FLh-BN}}$ should aim at $\sim 1\text{--}2\text{ mg mL}^{-1}$ and the η of the FLh-BN ink at $\sim 1\text{--}100\text{ mPa s}$, which minimises the time spent for spray coating and prevents the nozzle of the spray gun from being clogged due to the ink being too viscous. Second, the size of the FLh-BN flakes should achieve hundreds of nanometres in lateral sizes and a few nanometres in thickness, respectively, which have been demonstrated to show a good areal capacitance (C_A) of 8.7 nF cm^{-2} [80] as a dielectric layer ($1.2\text{ }\mu\text{m}$) and enable the modulation of graphene-based transistors.

5.1.1 Formulation and characterisation of FLh-BN inks

5.1.1.1 Experimental methods

Formulation of LPE FLh-BN Suspension: The FLh-BN inks are produced via the ultrasonication-assisted LPE. First, bulk h-BN (Bh-BN) powders (Goodfellows B516011, $< 10\text{ }\mu\text{m}$ size) are added to a solvent in which a stabiliser is dispersed in advance. The mixture is then processed by a probe-sonicator/bath-sonicator for several hours. The resulting dispersion is centrifuged (Beckman Allegra 64R, F06050, Fixed-Angle Rotor) at 3000 rpm for 30 minutes to remove any unexfoliated h-BN flake. After the centrifugation, the supernatant (i.e. top 70%) is retained as the final ink for further characterisation. To achieve the desired concentration, the following variables are considered: selection of solvents, selection of stabilisers and their concentrations, selection of sonication types, and selection of the initial Bh-BN input.

OAS: The concentration of the FLh-BN suspension ($c_{\text{FLh-BN}}$) was obtained via the Beer-Lambert Law, which correlates the absorbance $A = \alpha cl$, with the beam path length l (m), the concentration c (g L^{-1}), and the absorption coefficient α ($\text{L g}^{-1}\text{ m}^{-1}$). The FLh-BN suspension was diluted 1:100 with the solvent and optically characterised using a UV-Vis-NIR spectrophotometre (Agilent Cary 60) using a quartz cuvette with a path length of 10 mm are applied. The absorption coefficient of $\alpha = 2350\text{ L g}^{-1}\text{ m}^{-1}$ at 300 nm was utilised [226].

The viscosity η for the prepared suspension was measured using HAAKE MARS 60 with a double coaxial cylinder geometry and the data was fitted using a cross model to determine

the infinite-rate viscosity. All measurements were taken at 25 °C within a shear rate range of 0.01-100 s⁻¹.

The obtained data below were averaged over at least 3 replicates. After the FLh-BN-based inks achieve the desired concentration and η for later spray coating, extensive characterisation methods, including Raman, AFM, SEM, and XPS, are performed to examine the quality of the prepared FLh-BN flakes, including the chemical composition and flake size.

Raman Spectroscopy: Thin films of Bh-BN and FLh-BN were deposited on the Si/SiO₂ substrate, and the Raman spectrum was acquired by a Renishaw in Via micro-Raman spectrometer (WiRe 4.1) using a green 532 nm laser and a $\times 50$ objective, with an incident power of below 1 mW to avoid possible thermal damage.

AFM: The FLh-BN suspension was diluted to 0.01 mg mL⁻¹ and drop-casted onto a pre-cleaned (cleaned with acetone and isopropanol and treated with Ozone) Si/SiO₂ substrate. Measurements were scanned on a 10 μ m $\times$ 10 μ m area of the prepared sample, using an Asylum MFP-3D AFM (Oxford Instruments) with a silicon tip (NuNano Scout 70) in a tapping mode, with a 70 kHz resonance frequency and tip radius curvature of <10 nm. AFM statistical analysis collected on 38 flakes was carried out to reveal the $\langle t \rangle$ distribution and $\langle S \rangle$ distribution of the FLh-BN flakes. The $\langle S \rangle$ was obtained via $\langle S \rangle = xy^{0.5}$, where x and y refer to the length and width of a particular FLh-BN flake. The aspect ratio of an FLh-BN flake was defined as $\langle S \rangle / \langle t \rangle$.

SEM images were acquired using a Zeiss LEO Gemini 1525 FEG-SEM and collected in a secondary electron detection mode using the In Lens and SE2 detectors.

XPS spectrums were acquired using the Thermo Scientific K-Alpha system incorporating a micro-focused Al K α X-ray source. The etching (profiling) was performed using the built-in argon ion sputtering gun, at 500 eV cluster energy and “medium” current setting, with an ~ 0.08 nm s⁻¹ etch rate.

5.1.1.2 Selection of solvents and stabilisers

Selection of solvents: the work takes the ‘Pfizer industrial solvent selection guide’ [402] as a reference to eliminate the issue surrounding scaling of production due to the nature of the solvent and to enable a wider range of applications involving wearable electronics and textiles. Water, acetone, methanol, ethanol, 2-propanol, 1-propanol, 1-butanol, and *t*-butanol are selected separately as green solvent candidates for LPE. Figure 5.1(a) plots the $c_{\text{FLh-BN}}$ dispersed in those solvents, among which water, ethanol, 2-propanol, and 1-propanol are the

four solvents that gave a higher $c_{\text{FLh-BN}}$ of 0.16 mg mL^{-1} , 0.13 mg mL^{-1} , 0.11 mg mL^{-1} and 0.06 mg mL^{-1} , respectively. The left 4 solvents produced a $c_{\text{FLh-BN}}$ below 0.05 mg mL^{-1} . The former 4 solvents are then selected for further studies with the combination of stabilisers, and the latter 4 are discarded to narrow down the choice of solvents.

h-BN is a polar 2D material, so it is expected to interact preferentially with polar solvents [403]. Compared to the non-protic solvent (acetone), the protic solvents (water and alcohols) can be strongly adsorbed on the surfaces and between the h-BN layers, forming “quasi-stable” states through electrostatic interactions that reduce the inter-layer BE and therefore promote the LPE process [403]. Among the studied polar solvents, the best exfoliants might be a sterically less demanding solvent like water [403], or low surface tension dispersing agents like IPA (23.74 mN m^{-1}) and ethanol (22.3 mN m^{-1}) [404].

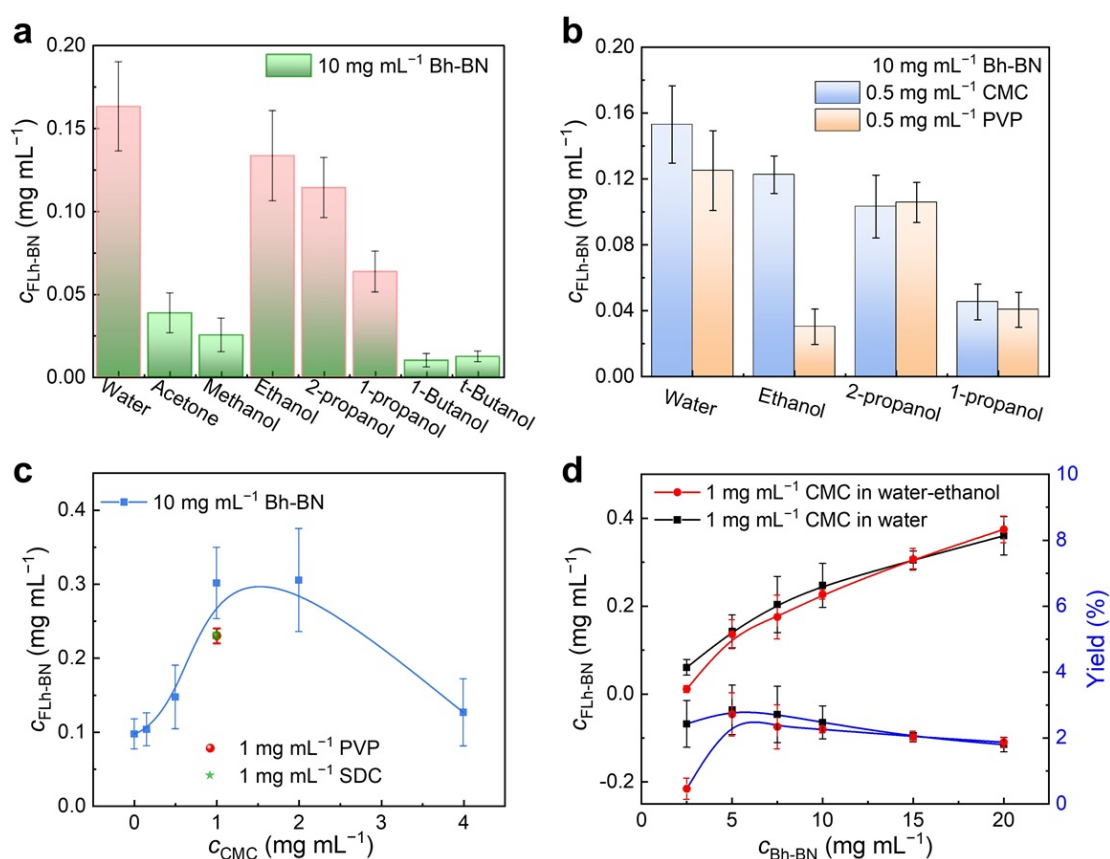


Fig. 5.1 Analysis on the concentration of the FLh-BN ink under different parameters: (a) various green solvents, (b) various combinations of stabilisers dispersed in the chosen solvent, (c) the concentration of the stabiliser-CMC, and (d) the concentration of the Bh-BN input in water and a co-solvent (water:ethanol) system.

Selection of stabilisers: given the best four solvents, to further increase the $c_{\text{FLh-BN}}$ to the aimed values ($1\text{--}2\text{ mg mL}^{-1}$) and increase the dispersion stability and shelf-life, Figure 5.1(b) compares the effect on the $c_{\text{FLh-BN}}$ of the addition of stabilisers, CMC and PVP, in those solvents. CMC and PVP can act as a stabiliser with regions of markedly different polarity, being amphiphilic (they have one hydrophilic side and the other hydrophobic side) [405]. The hydrophobic group contacts the basal plane of FLh-BN flakes due to van der Waals force, and the hydrophilic group protrudes into the solvent. This reduces the surface tension of the liquid by introducing electrostatic repulsion or steric repulsion, achieving a good match of surface tension value between the liquid and 2D material, minimising the energetic cost of exfoliation, and increasing the production yield [135, 134]. The combination of CMC in water and PVP in water gives the best 2 $c_{\text{FLh-BN}}$ values (0.15 mg mL^{-1} and 0.12 mg mL^{-1} , respectively) after centrifugation. However, there is a slight decline in $c_{\text{FLh-BN}}$ after the 0.5 mg mL^{-1} addition of CMC or PVP in water by 0.01 mg mL^{-1} and 0.04 g mL^{-1} , respectively, compared to the equivalent condition of pure water (0.16 mg mL^{-1}). This might be due to the oscillated and unstable bath sonication power.

Figure 5.1(c) also compared the effect on the $c_{\text{FLh-BN}}$ of the 1.0 mg mL^{-1} addition of CMC, PVP, or SDC dispersed in water. The 1.0 mg mL^{-1} CMC in water was the best combination giving $c_{\text{FLh-BN}} \sim 0.3\text{ mg mL}^{-1}$, while the 1.0 mg mL^{-1} PVP or SDC produced the $c_{\text{FLh-BN}} \sim 0.23\text{ mg mL}^{-1}$.

I then studied the influence of the concentration of CMC in water (c_{CMC}) on the $c_{\text{FLh-BN}}$, as shown in Figure 5.1(c). The $c_{\text{FLh-BN}}$ is $\sim 0.10\text{ mg mL}^{-1}$ at $c_{\text{CMC}} = 0.15\text{ mg mL}^{-1}$, while $c_{\text{FLh-BN}}$ increases to $\sim 0.15\text{ mg mL}^{-1}$ at $c_{\text{CMC}} = 0.5\text{ mg mL}^{-1}$. The $c_{\text{FLh-BN}}$ reaches the maximum ($\sim 0.30\text{ mg mL}^{-1}$) at $c_{\text{CMC}} = 1.0\text{ mg mL}^{-1}$. However, further increasing c_{CMC} does not contribute to $c_{\text{FLh-BN}}$ improvement but leads to the ink being too viscous and concentration decline. Therefore, 1 mg mL^{-1} is identified as the optimal c_{CMC} .

Figure 5.1(d) plots the change of $c_{\text{FLh-BN}}$ as a function of the initial input of Bh-BN (precursor), $c_{\text{Bh-BN}}$. Increasing $c_{\text{Bh-BN}}$ from 5 mg mL^{-1} to 20 mg mL^{-1} close-to-linearly increase the $c_{\text{FLh-BN}}$ from 0.14 mg mL^{-1} to 0.35 mg mL^{-1} , respectively. However, the yield (equals to $c_{\text{FLh-BN}}/c_{\text{Bh-BN}}$, which is an indication of material economic effectiveness) peaks at 2.8% at $c_{\text{Bh-BN}} = 5\text{ mg mL}^{-1}$ and decreases slowly to 1.9% at $c_{\text{Bh-BN}} = 20\text{ mg mL}^{-1}$. Therefore, $c_{\text{Bh-BN}} \sim 10\text{ mg mL}^{-1}$ is determined as the optimal parameter to enable a decent $c_{\text{FLh-BN}}$ at 0.21 mg mL^{-1} and a decent yield at 2.3% .

5.1.1.3 Optimise the concentration of the FLh-BN inks

The obtained $c_{\text{FLh-BN}}$ values are still below the desired concentrations ($c_{\text{FLh-BN}} \sim 1\text{--}2 \text{ mg mL}^{-1}$). Inspired by Rafiei, et al. [122], who reported a co-solvent system (a mixture of ethanol and water) to obtain a higher yield of FLh-BN flakes due to the smallest Hansen solubility distance, this work also attempted to add ethanol into the water as a co-solvent as well. The proposed combination of 45:55 water/ethanol (v/v) [122] reduces the surface tension of water (72 N/m) down to 28 N/m [404]. As ethanol has a lower boiling point (78.4 °C) and a faster evaporation rate than water, applying co-solvent using ethanol and water may also be advantageous to accelerate the evaporation rate of solvents during the spray coating process and enable a uniform film formation. Figure 5.1(d) compares the effect on the $c_{\text{FLh-BN}}$ of the combination of 45:55 water/ethanol (v/v) as the co-solvent as reported before [122] with that in the water only. At an initial input of Bh-BN, $c_{\text{Bh-BN}} \sim 15 \text{ mg mL}^{-1}$, both solvent systems produce the final FLh-BN inks at a $c_{\text{FLh-BN}}$ of 0.3 mg mL^{-1} . When $c_{\text{Bh-BN}} < 15 \text{ mg mL}^{-1}$, the solvent of 1 mg mL^{-1} CMC in water produces slightly higher $c_{\text{FLh-BN}}$ by $\sim 0.02\text{--}0.03 \text{ mg mL}^{-1}$, while the co-solvent system of 45:55 water/ethanol (v/v) produces slightly higher $c_{\text{FLh-BN}}$ by 0.01 mg mL^{-1} . Generally speaking, the obtained $c_{\text{FLh-BN}}$ values over a function of $c_{\text{Bh-BN}}$ are very close at $c_{\text{Bh-BN}} > 15 \text{ mg mL}^{-1}$ between the two solvent systems, indicating no significant improvement of $c_{\text{FLh-BN}}$ brought by ethanol.

Optimise the volume ratios of water-ethanol co-solvents: the impact of the ratio of ethanol on the $c_{\text{FLh-BN}}$ is statistically investigated, and the results are shown in Figure 5.2(a). The $c_{\text{FLh-BN}}$ reaches the maximum of 0.23 mg mL^{-1} at 55 vol% ratio of ethanol due to the calculated smallest Hansen Solubility Distance. The $c_{\text{FLh-BN}}$ decreases when either reducing the content of ethanol (i.e. $c_{\text{FLh-BN}} \sim 0.14 \text{ mg mL}^{-1}$ at 20 vol%) or increasing the content of ethanol (i.e. $c_{\text{FLh-BN}} \sim 0.17 \text{ mg mL}^{-1}$ at 90 vol%). This phenomenon can be attributed to the synergistic effects of the reduced liquid surface tension brought by the addition of ethanol [406], the increased c_{CMC} (Figure 5.1(c)) and the impacted ability of FLh-BN dispersed in the solvents.

Utilisation of probe sonication: probe sonication is used to further improve the $c_{\text{FLh-BN}}$, as probe sonication could generate a more dense ultrasonication power than bath sonication. Figure 5.2(b) compares the LPE effects of bath sonication (9-hour on, Branson SFX550, 101-148-062) and probe sonication (3-hour on, Fisherbrand Elmasonic S150 Ultrasonication Unit) on the $c_{\text{FLh-BN}}$. Probe sonication gives a higher $c_{\text{FLh-BN}}$ up to 1.0 mg mL^{-1} , which is over 4 times higher than that produced via bath sonication. That is because the probe ultrasonication usually offers a higher ultrasound intensity [108], which could produce the resultant flakes with a higher concentration [105] as well as a higher yield. Spray coating

an FLh-BN ink with a higher concentration means that the coating process will be more time-effective in achieving a layer with the same thickness. Therefore, the probe sonication technique is preferred here.

Figure 5.2(c) plots the $c_{\text{FLh-BN}}$ as a function of $c_{\text{Bh-BN}}$ using the probe sonication, and a positive correlation is observed. With a higher input of $c_{\text{Bh-BN}}$ up to 50 mg mL^{-1} , the $c_{\text{FLh-BN}}$ is maximised to 3.2 mg mL^{-1} , which exceeds the proposed value of $1\text{--}2 \text{ mg mL}^{-1}$. At an input of $c_{\text{Bh-BN}} = 10 \text{ mg mL}^{-1}$, the obtained $c_{\text{FLh-BN}}$ is 1.0 mg mL^{-1} , which meets the need of $c_{\text{FLh-BN}}$.

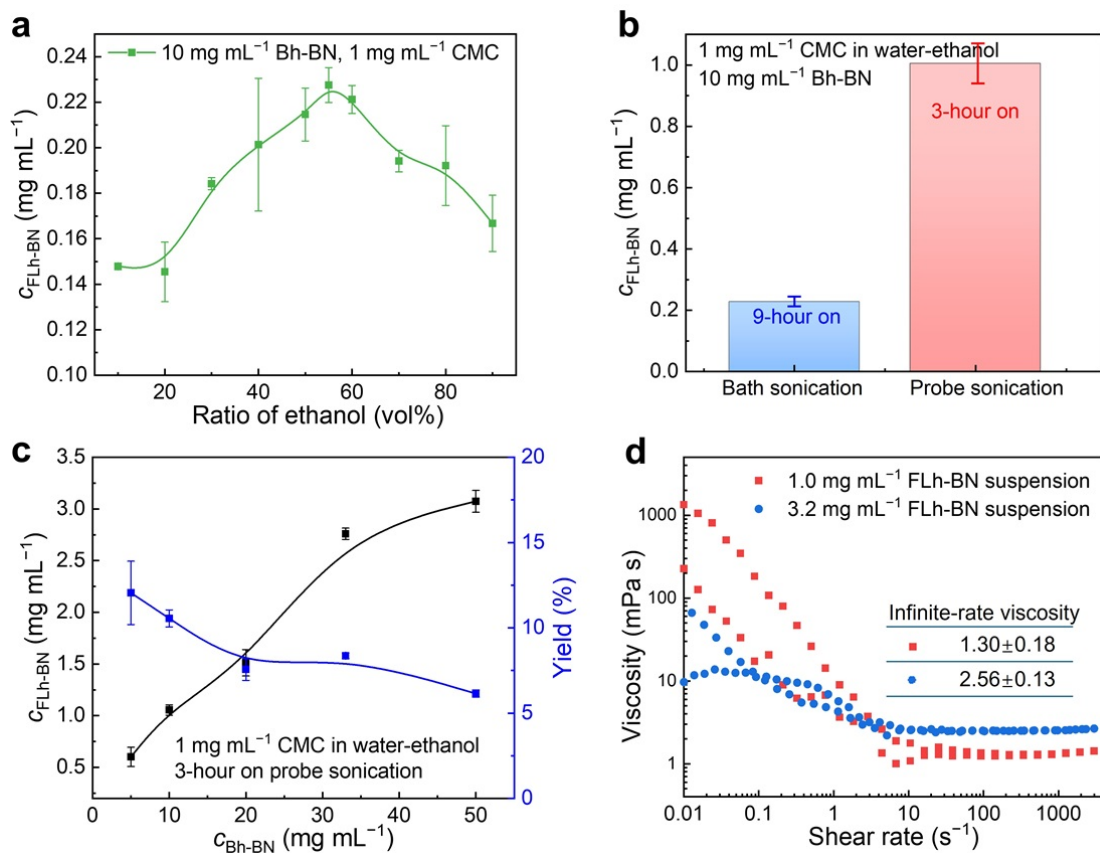


Fig. 5.2 Optimisation on the concentration of the FLh-BN ink suitable for spray coating, including (a) the ratio of ethanol in the co-solvent system, (b) the type of ultrasonication process, (c) the concentration of Bh-BN input, and (d) rheological characterisation of the concentration of an as-prepared FLh-BN ink.

Examine the viscosity (η) of the FLh-BN-based inks: To test the feasibility of spraying those inks produced via probe sonication, their η values are examined with three replicates. Figure 5.2(d) plots the η of the as-prepared FLh-BN inks as a function of shear rate (γ) at $c_{\text{FLh-BN}} \sim 1.0 \pm 0.06 \text{ mg mL}^{-1}$ and $\sim 3.2 \text{ mg mL}^{-1}$, respectively. The infinite-rate η for

each ink is found at 1.30 ± 0.18 mPa s and 2.56 ± 0.13 mPa s, respectively. The η values are within the desirable η range (1-100 mPa s) of spray coating [55]. A high $c_{\text{FLh-BN}}$ value leads to a higher η value of the ink, resulting in a higher chance of the FLh-BN flakes blocking the spray nozzle and reducing the deposition productivity.

5.1.1.3 Characterisation of the FLh-BN-based inks

After the FLh-BN-based inks achieve the desired concentration and η for later spray coating, extensive characterisation methods, including OAS, Raman, AFM, SEM, and XPS, are performed to examine the quality of the prepared FLh-BN flakes, including the chemical composition and flake size.

Figure 5.3(a) shows the optical absorption spectrum of the FLh-BN ink (image in the inset). The spectrum shows a peak located at 205 nm, consistent with previous reports [73, 407], and corresponds to the inter-band transition in the density of states of h-BN, revealing an optical band gap at 6.04 eV. This value is consistent with previous results determining the optical band gap of the FLh-BN flakes from LPE [73, 80]. Using the Beer-Lambert law, the estimated $c_{\text{FLh-BN}} \sim$ is 3.18 mg mL^{-1} [226, 408].

Raman spectroscopy (Figure 5.3(b)) and XPS (Figure 5.3(c-f)) were applied to monitor the quality of the materials. A single resonant Raman peak is observed for both Bh-BN and FLh-BN samples at 1366 cm^{-1} and 1364 cm^{-1} , respectively, corresponding to the E_{2g} phonon vibrational mode. The downshifting of the peak in the case of the FLh-BN indicates the successful exfoliation of the Bh-BN into the FLh-BN flakes [73, 80, 203]. Figures 5.3(c-f) show the XPS spectrum of the B1s, N1s, O1s, and C1s regions of the FLh-BN flakes. The XPS peak centred at 190.5 eV in Figure 5.3(c) is formed due to the B-N bond within the FLh-BN structure [409, 410], and the peak centred at 398.0 eV in Figure 5.3(d) can be assigned to the BE of N-B bond [411], in line with values reported in literature [412] for both peaks. Figures 5.3(e-f) show O1s peak at 532.1 eV and the C1s peak at 284.5 eV, respectively.

The flake thickness ($\langle t \rangle$) and the lateral flake size ($\langle S \rangle$) of the FLh-BN were examined via the AFM statistical analysis (acquired over 38 individual flakes), as shown in Figures 5.4(a,b). The statistic of $\langle t \rangle$ follows a log-normal distribution, peaked at 6.1 nm. Assuming an inter-layer distance of $3.35 \text{ \AA}$ [413, 414] and an approximate 1-nm water layer between the flake and the Si/SiO₂ substrate [415, 416], the FLh-BN flakes consists of an average number of layers, $N \sim 15$. A statistic of $\langle S \rangle = (xy)^{0.5}$ in Figure 5.4(b), where x and y are the length and width of a FLh-BN flake, also follows a log-normal distribution, peaked at 339.0

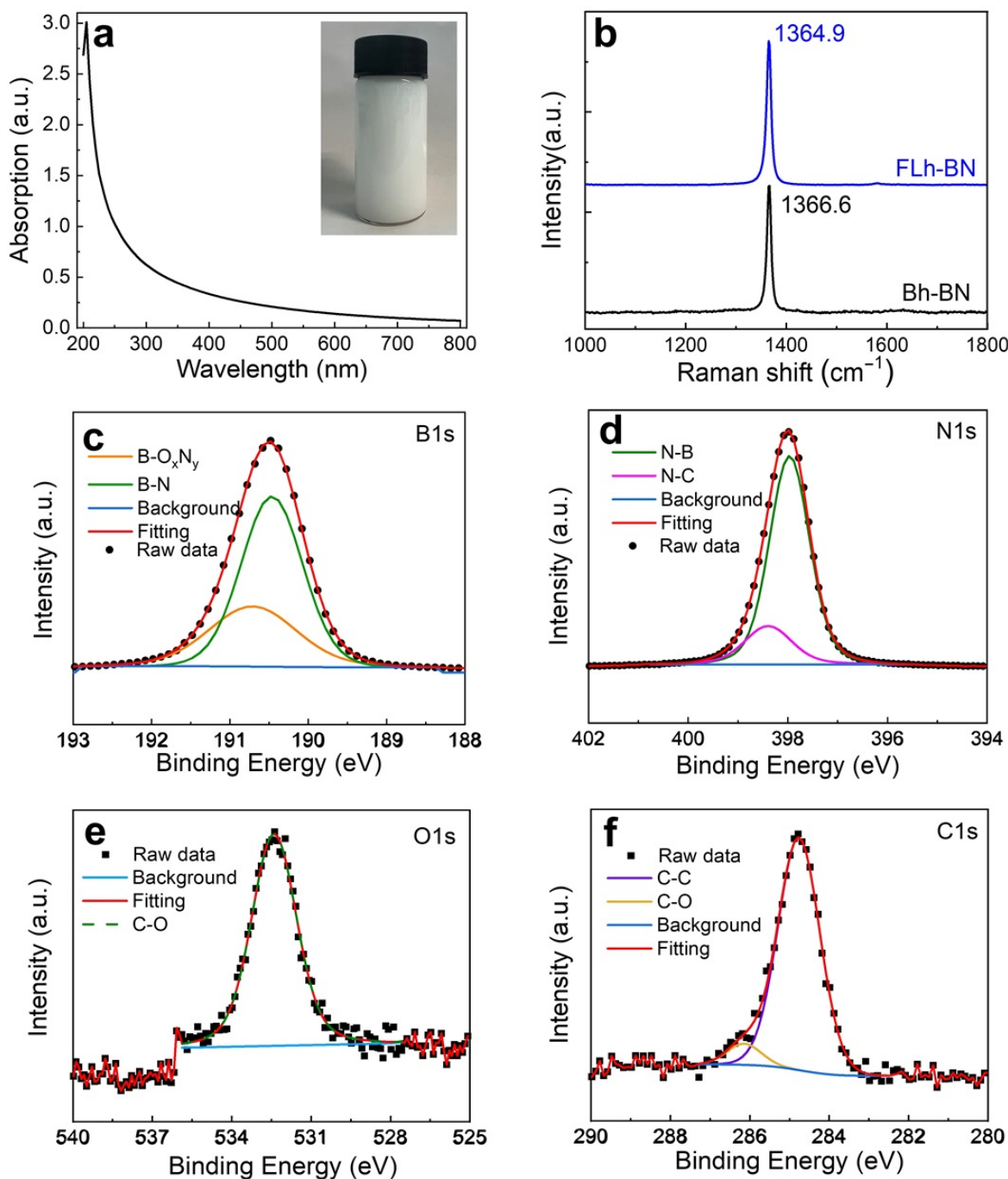


Fig. 5.3 Characterisation of the FLh-BN flakes, including (a) optical absorption spectrum of the FLh-BN ink, with an inset of the undiluted one in the top right corner; (b) Raman spectrum of the Bh-BN and the FLh-BN; High-resolution XPS spectrum of (c) B1s, (d) N1s, (e) O1s and (f) C1s of the FLh-BN. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

nm. The average aspect ratio ($\langle S \rangle / \langle t \rangle$) is calculated at 55.6. Figure 5.4(c) shows the AFM images of a mono-layer FLh-BN flake on a Si/SiO₂ substrate with an $\langle S \rangle \sim 210$ nm, and a $\langle t \rangle \sim 1.5$ nm (height profile in Figure 5.4(d)), indicating a mono-layer h-BN flake plus ~ 1 nm water layer under the flake. This results in a large aspect ratio of 140. Figure 5.4(e) shows the AFM images of a FLh-BN flake on a Si/SiO₂ substrate with an $\langle S \rangle \sim 400$ nm, and a $\langle t \rangle \sim 3.4$ nm (height profile in Figures 5.4(f)), indicating a 7 layer flake plus ~ 1 nm water layer under the flake.

SEM was used to corroborate the statistical analysis of $\langle S \rangle$ of the obtained FLh-BN flakes. Figure 5.4(g) shows a typical SEM image of the FLh-BN flakes deposited on a Si/SiO₂ substrate, and Figure 5.4(i) summarised a statistical analysis over 34 flakes, indicating an average $\langle S \rangle$ at ~ 310 nm and verifying the AFM statistics.

5.1.2 Preparation and characterisation of electrode silver

The silver (Ag) nanoparticle ink is purchased from NovaCentrix (JSAS102A). It comprises 40 wt.% Ag nanoparticles in aqueous solutions [417]. By thermal annealing at 140 °C for 10 minutes, the resistivity of Ag films can achieve $< 3.1 \times 10^{-5} \Omega \text{ cm}$ [417]. The spray-coated Ag films obtained a mean conductivity of $3.75 \times 10^6 \text{ S m}^{-1}$ as electrodes.

5.2 Fabrication of the spray-coated capacitors

The MIM capacitor structure is designed and fabricated to characterise the dielectric properties of the as-prepared FLh-BN-based dielectric inks.

5.2.1 Capacitor configuration

The MIM capacitor structure comprises three different layers fabricated on an optical glass substrate. Figure 5.5(a) schematically illustrates the capacitor configuration used in this work. The capacitor has a sandwiched structure. The first layer was spray-coated with an Ag film with a dimension of $1.0 \text{ mm} \times 10.0 \text{ mm}$, and this was followed by a dielectric layer which has a $2.4 \text{ mm} \times 2.4 \text{ mm}$ dimension. Finally, the top layer was an Ag electrode of $0.6 \text{ mm} \times 10.0 \text{ mm}$ in size. The fabricated capacitor has an actual working area of $1 \text{ mm} \times 0.6 \text{ mm}$ with the dielectric layer thickness being t ($0.5\text{-}3 \mu\text{m}$). The extended length of the electrodes

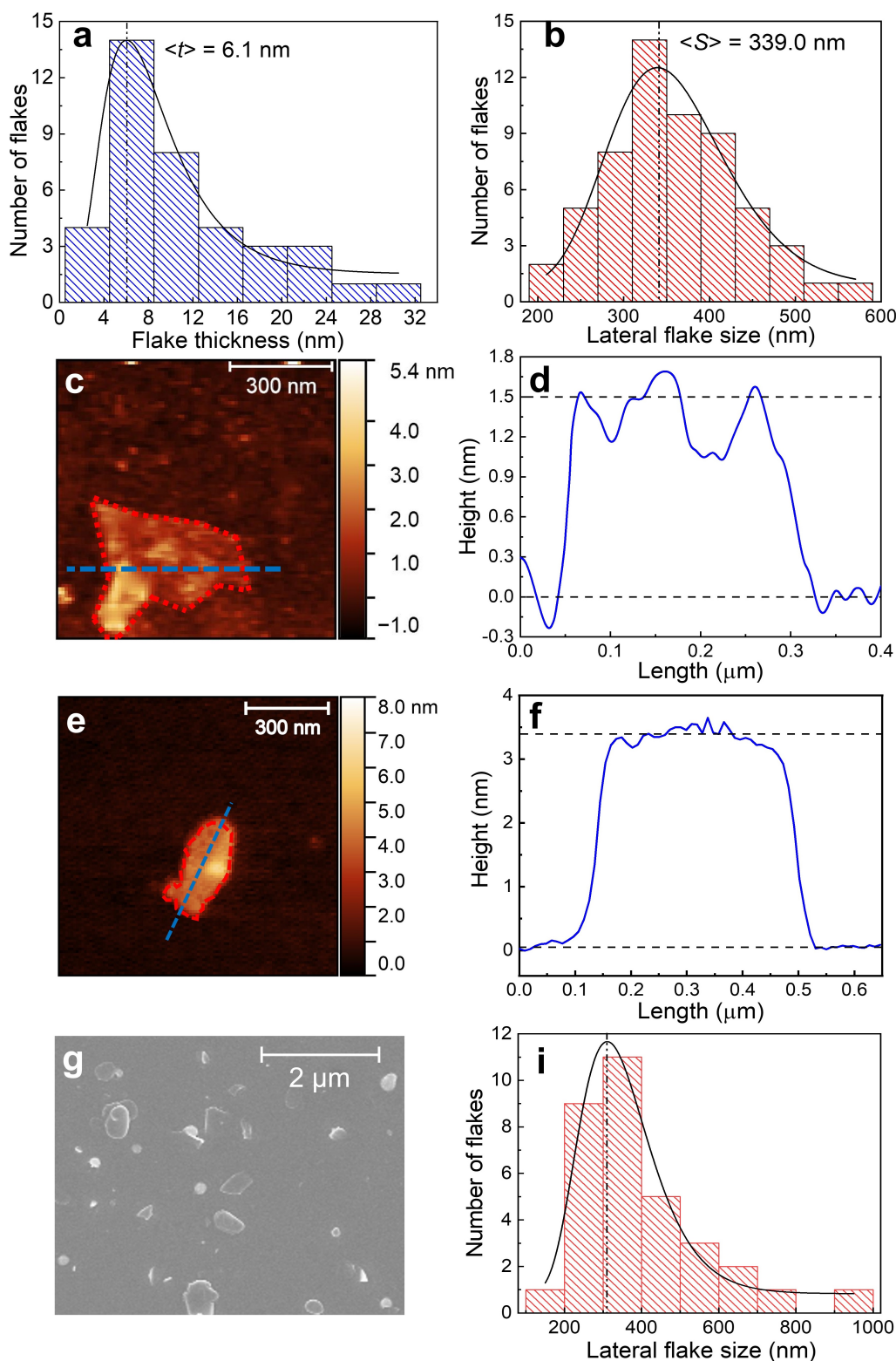


Fig. 5.4 Flake size characterisation of the FLh-BN, including (a) thickness and (b) lateral size distribution by AFM of the FLh-BN flakes; (c) A representative AFM image of a mono-layer h-BN flake; (d) The height profile of the mono-layer h-BN flake in (c); (e) A representative AFM image of a FLh-BN flake; (f) The height profile of the FLh-BN flake in (e); (g) An SEM image of the FLh-BN flakes deposited on a Si/SiO₂ substrate with statistical analysis (h) of flake lateral sizes. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

was designed as the contact ends for electrical measurements, as shown in Figure 5.5(b), to avoid the electrodes being penetrated by the measurement probe, causing capacitor failure.

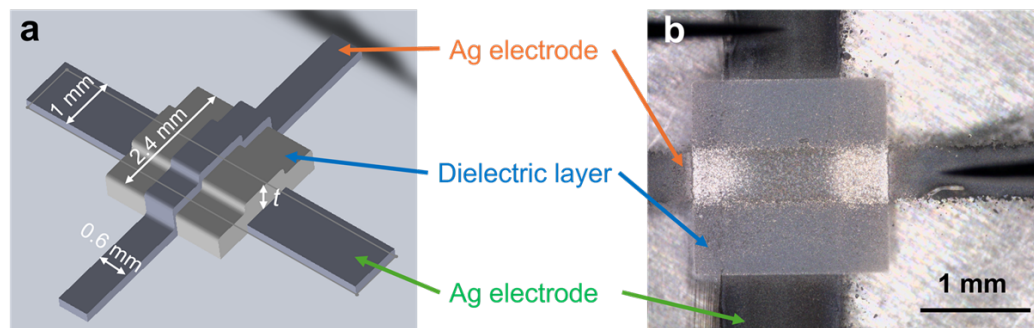


Fig. 5.5 The MIM capacitor fabricated in this work. (a) A 3D model of the capacitor configuration - a MIM sandwiched structure with (b) an optical microscopy image.

The proposed MIM sandwiched structure has the advantage of probing the electrodes without damaging the dielectric layer due to the extended length of the electrodes. The reported structure in literature [73] was designed like a pyramid where the top layer had the smallest size. The pyramid-like structure has a risk of the dielectric layer being penetrated while probing the top electrode layer, resulting in a higher chance of the capacitor being short-circuit and breaking down.

5.2.2 Layer-by-layer spray coating

Substrate treatment: The spray coating method is used to fabricate the capacitor on glass substrates. Figure 5.5(b) shares an optical image showing a spray-coated solid capacitor using FLh-BN as the dielectric layer. The glass substrate was ultrasonicated in 1:1 IPA/Acetone (v/v) for 15 minutes, polished using a fibreless cleaning wipe, followed by a second ultrasonication cleaning step in IPA for another 15 minutes, and a third drying step by compressed N₂ gas. The cleaned glass was UV/Ozone treated to remove any organic and enhance the surface hydrophilicity.

Spray coating protocols: The fabrication of the MIM capacitor was achieved via layer-by-layer spray coating, and the coating process is optimised to enable a uniform film formation, which is discussed in Table A.1 in Appendix A. Table 5.1 summarises the key parameters optimised for spray coating the capacitors. The $c_{\text{FLh-BN}}$ of the used FLh-BN ink was at $\sim 1.0 \text{ mg mL}^{-1}$. The glass substrate was placed on a hot plate with a temperature of 40 °C to accelerate the solvent evaporation rate. The nozzle-substrate distance and angle were kept at 15 cm and 30-45 °, respectively. The flowing N₂ gas was set to 20 psi ($\sim 1.38 \text{ bar}$).

Table 5.1 Optimised parameters for spray coating the capacitors

Parameters	Values	Units
Ink concentration	1.0	mg mL ⁻¹
Temperature	40	°C
Nozzle-substrate distance	15-20	cm
Nozzle-substrate angle	30-45	°
Pressure of N ₂	20	psi

Layer-by-layer coating: The first layer of an Ag film was spray-coated on a glass substrate with a thickness of ~ 200 nm and a resistance $< 5 \Omega$. The second layer was a spray-coated FLh-BN dielectric layer, and the top layer was another spray-coated Ag film. Between the deposition interval of each layer, the material was fully dried in a desiccator for 15 minutes. The volume of the spray-coated FLh-BN ink determines the thickness (t in a range of 0.5-3 μm) of the dielectric layer, which was measured via a profilometer (Dektak@ 150 Surface Profiler). Each type of capacitor using the same dielectric inks was fabricated repeatedly with ≥ 4 different thicknesses, allowing the linear fitting and capacitance extraction of the capacitors with minimal experimental errors.

5.3 Electrical performance of the capacitors

With the as-prepared capacitors, various electrical characterisation methods were conducted to verify their function and work out the dielectric properties (the electrical resistivity (ρ), C_A , ϵ_r and dielectric breakdown strength) of the FLh-BN-based dielectric layer, via the sheet resistance, impedance and I-V tests.

5.3.1 Experimental methodology

The electrical resistivity of the as-prepared capacitor was determined via an LCR meter (TENMA, 72-10465) connected to a probe station (Everbeing). The two electrodes have very low resistivity compared to the dielectric layer, so the contact resistance can be minimised. Therefore, the ρ calculated from the capacitor is assumed to be almost equal to the ρ of the dielectric layer and is calculated as follows:

$$\rho = \frac{1}{\sigma} = R \times \frac{A}{t} \quad (5.1)$$

where σ is the electrical conductivity (S m^{-1}), R is the tested resistance (Ω), t is the thickness of the dielectric layer (m), and A is the capacitor working area (m^2).

The impedance characterisation of the FLh-BN capacitors was performed by BioLogic SP150, from 1-100 kHz with a peak-to-peak voltage of 10 mV. An equivalent series resistor-capacitor (R-C) circuit was used to extract the C_A [418], and the C_A was calculated at 100 kHz. The impedance amplitude is given by the Equation 2.30.

Electrical I-V tests were performed using a Source Measure Unit (AIM-TTi SMU4201) connected to a probe station (Everbeing), where the capacitors were placed on a suspended platform and probed via electrodes (Tungsten) fixed by micropositioners. The I-V tests were conducted by applying step-wise voltages (from 0-40 V at a step of 0.04 V) to the capacitors and recording the response current until a sharp rise of the current was observed.

5.3.2 Minimum thickness of the FLh-BN dielectric layer-Percolation threshold

It is important to know the minimum thickness of the dielectric layer, below which the layer cannot avoid short circuits due to the pin-holes in the network of 2D flakes. Figure 5.6 plots the ρ of the as-fabricated capacitors as a function of the dielectric layer thickness (t). The $\rho \sim 10^8 \Omega \text{ cm}$ is considered as the minimum value to avoid electrostatic charge build-up in an insulating matrix [419], which can be regarded as the minimum value (the red dashed line) of an effective capacitor. When $t \geq 0.9 \mu\text{m}$, the successful rate to fabricate an effective capacitor was 70 % (the unsuccessful capacitors considered were close to the percolation line), while $t < 0.9 \mu\text{m}$, the successful rate was only 50 %. Therefore, $t \sim 1.0 \mu\text{m}$ is considered as the thickness percolation threshold for the FLh-BN working as the dielectric layer.

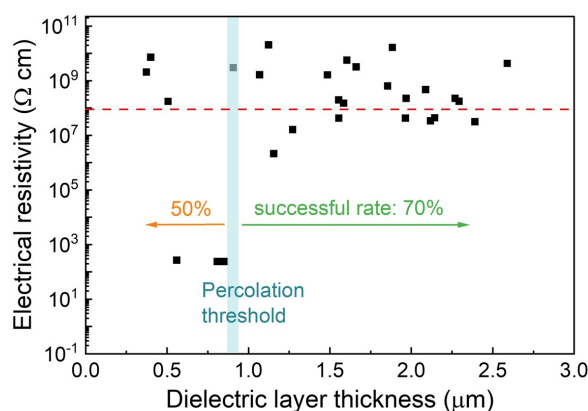


Fig. 5.6 The dielectric resistivity of the FLh-BN layer as a function of the layer thickness t .

5.3.3 Impedance characterisation

Impedance characterisation allows us to figure out the assumed equivalent circuit of the as-prepared MIM capacitors to describe the impedance behaviour and, therefore, to extract the C_A , resistance and ϵ_r .

Two key graphical representations of impedance data, the Bode plot and the Nyquist plot are given. A Bode plot presents the impedance data as a function of frequency using two separate graphs, magnitude plot and phase plot. The magnitude plot draws the magnitude of the impedance ($|Z|$, Ω) as a function of frequency (F , Hz) on a logarithmic scale. The high impedance at low frequencies often indicates capacitive behaviour, while changes at higher frequencies can indicate resistive or parasitic inductive behaviour. A Nyquist plot presents the impedance data in the complex plane, which plots the imaginary part of the impedance (Z_{Im}) as a function of the real part of the impedance (Z_{Re}). Each point on the Nyquist plot represents the impedance at a specific frequency.

Figures 2.30(a,b) show the Bode plot and the Nyquist plot of an as-prepared capacitor using FLh-BN as the dielectric layer. The log value of the impedance reveals a linear decline as a function of the log of frequency, and by fitting the plots, an equivalent series R-C circuit can be extracted ($R = 4.5 \text{ M}\Omega$ and $C = 268 \text{ pF}$). With a decreasing frequency, the magnitude of the impedance increases, due to a great amount of charge stored in the capacitive component, as seen an increasing Z_{Im} of the capacitor response as a function of frequency shown in Figure 5.7(b).

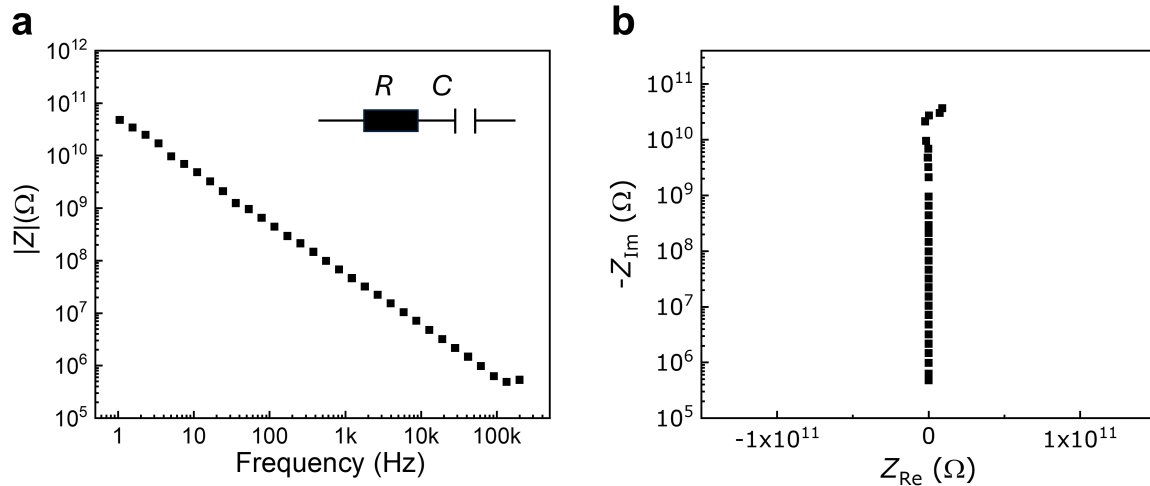


Fig. 5.7 Impedance characterisation of an as-prepared MIM device: (a) the Bode plot and (b) the Nyquist plot.

5.3.4 Analysis of areal capacitance and dielectric constant

Knowing the capacitance value at different frequencies from impedance characterisation, the C_A was calculated by dividing the capacitance (C) at 100 kHz by the actual working area ($A = 1 \text{ mm} \times 0.6 \text{ mm}$). If plotting a curve of C_A versus the inverse of the layer thickness ($1/t$), the ϵ_r (else called the relative permittivity) could be obtained from the slope value based on the following equation:

$$\frac{C}{A} = \epsilon_r \epsilon_0 \frac{1}{t} \quad (5.2)$$

where ϵ_r is the dielectric permittivity of the substance, ϵ_0 is the dielectric permittivity of free space ($8.854 \times 10^{-12} \text{ F m}^{-1}$), t is the thickness of the dielectric layer (μm), and C/A is the areal capacitance C_A ($\mu\text{F m}^{-2}$).

Figure 5.8(a) plots the C_A of the as-prepared capacitors as a function of the inverse of the dielectric layer thickness ($1/t$). The obtained C_A in this work ranges from 30–80 $\mu\text{F m}^{-2}$, which is consistent with the 2.4 to 87 $\mu\text{F m}^{-2}$ range previously reported for a graphene/h-BN/graphene capacitor [418] and an Ag/h-BN/Ag capacitor [80]. When $1/t$ is $\sim 0.37 \mu\text{m}^{-1}$, the C_A is around 32 $\mu\text{F m}^{-2}$, while the $1/t$ is $\sim 0.92 \mu\text{m}^{-1}$, the C_A increases to 74 $\mu\text{F m}^{-2}$. By fitting the data points (the red line), the slope of the curve, namely, $\epsilon_{\text{FLh-BN}}$ is obtained at $\sim 70.04 \pm 8.79 \times 10^{-12} \text{ F m}^{-1}$. Therefore, the ϵ_r is calculated at $\sim 7.9 \pm 1.0$.

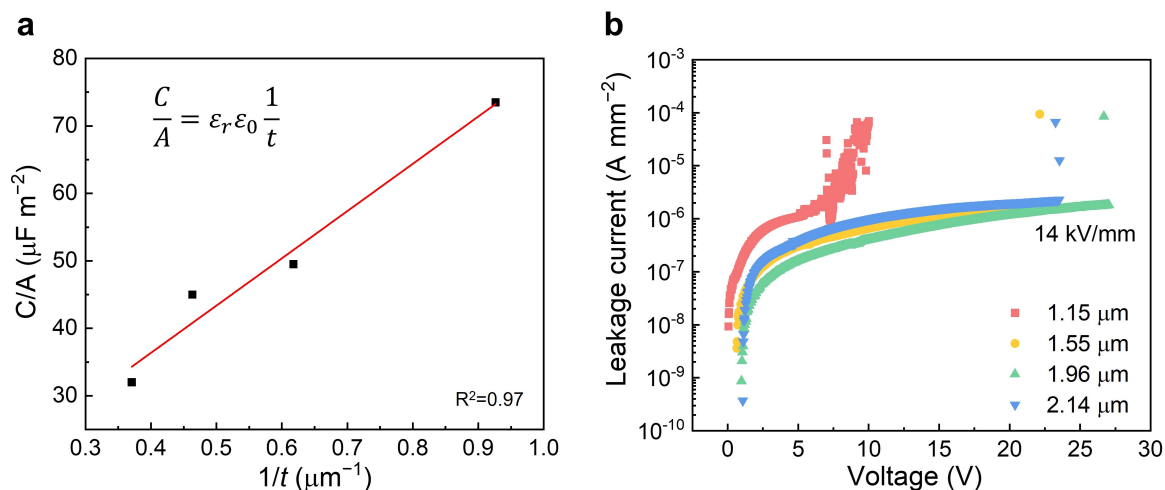


Fig. 5.8 Electrical performance analysis of the as-prepared MIM capacitors. (a) The C_A of the as-prepared capacitors as a function of the inverse of the dielectric layer thickness, and working out the ϵ_r by fitting data points (the red line); (b) Leakage current densities as a function of the applied voltage of the capacitors with various dielectric layer thicknesses.

By searching the literature, single-layer and few-layer h-BN was reported to have an out-of-plane ϵ_r ranging from 3.29 to 3.76, and an in-plane ϵ_r ranging from 6.82 to 6.93 [420]. The

ϵ_r value ~ 7.9 obtained is higher than the literature value, which may be attributed to that (1) the ϵ_r of FLh-BN flakes consists of both the in-plane value and the out-of-plane value due to the random orientation of the FLh-BN flake deposition during the spray coating process; (2) the synergistic effects of water molecules ($\epsilon_r \sim 78.4$) and CMC [421] and FLh-BN flakes on the overall dielectric properties of the layer.

5.3.5 Analysis of leakage current and breakdown strength

Apart from the C_A and ϵ_r , the dielectric breakdown strength is another important index of an insulating material. It indicates the maximum electric field a dielectric (insulating) material can withstand without experiencing failure or breakdown. Figure 5.8(b) plots the leakage current densities at the two silver electrodes and through the dielectric layer of different thicknesses as a function of applied voltages. All the tested capacitors have small leakage current densities below 10^{-6} A mm $^{-2}$. When the t is 1.15 μ m, the breakdown voltage of the capacitor is at ~ 6 V, while when the t reaches 1.96 μ m, a higher breakdown voltage up to 27 V is observed. Taking the capacitor with a ~ 1.55 μ m thick dielectric layer as an example, the breakdown strength is calculated at 14 kV/mm.

By fitting the I-V characteristics, the FLh-BN dielectric layer demonstrates a $\ln(J/V) \propto V$ scaling of conductivity as shown in Figure 5.9, corresponding to the Poole-Frenkel (PF) effect [254]. The PF model describes the conduction of charge carriers (usually electrons or holes) in a dielectric material under an electric field. The electric field lowers the potential barriers around the trap sites within the dielectric film, facilitating the release of trapped electrons into the conduction band, increasing the electrical conductivity. The Poole-Frenkel model can be described [422] as:

$$\ln\left(\frac{I(V)_{\text{PF}}}{V}\right) = \ln(AqN_c\mu) - \frac{q\Phi_T}{k} + \frac{q}{kT} \times \sqrt{\frac{q}{\pi\epsilon_r\epsilon_0}} \times \sqrt{V} \quad (5.3)$$

where N_c , μ , q , V , and Φ_T are the density of states in the conduction band, electronic mobility in the dielectric film, electron charge, electrical field and the trap energy level in the h-BN, respectively.

The results are consistent with what has been reported by Jiang, et al., claiming that in the thick FLh-BN films (> 10 nm), a trap-assisted PF emission mechanism constitutes the dominant transport mechanism for the leakage current [254].

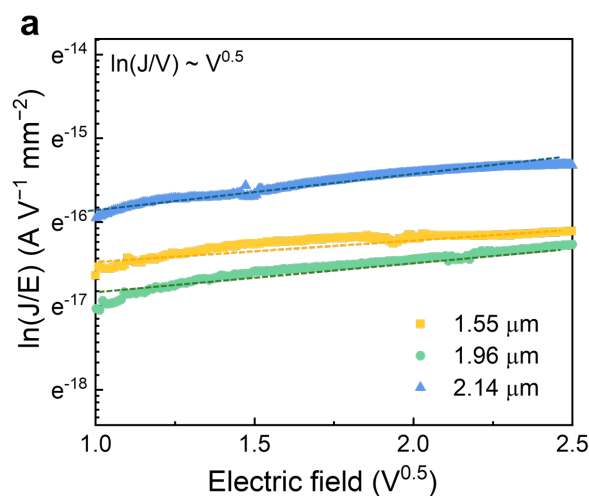


Fig. 5.9 Electrical property analysis, described by the Poole-Frenkel model fitting by plotting J/V versus $V^{0.5}$ (thickness considered).

5.3.6 Methods to improve the electrical performance

This section explored two ways to improve further the dielectric properties (ϵ_r) and breakdown strength values) of the FLh-BN-based dielectric layer in the Ag/FLh-BN/Ag capacitors: to increase the mass ratio of FLh-BN over CMC, and to add high- ϵ_r BaTiO₃ as a dielectric additive to the dielectric layer. The first way is the most straightforward and economical way to figure out the optimal dielectric properties of the inks without adding extra materials and additional processing, while the second way is to invest a small amount of expensive high ϵ_r dielectric material to achieve remarkable enhancement of dielectric properties.

5.3.5.1 Increase the mass ratio of FLh-BN over CMC

The formulation of FLh-BN-based dielectric inks with different mass ratios was achieved by adjusting the mass ratio of FLh-BN and CMC during the LPE process. Three types of dielectric layers with the mass ratio of FLh-BN at 44.5 wt.%, 64.6 wt.% and 84.5 wt.%, respectively, were prepared with replicates of 4, 5 and 8.

Determination of the mass ratios of FLh-BN over CMC in each dielectric layer was realised via TGA characterisation. The tested material was placed in a 70 μ L Pt/Rh crucible, and the TGA was conducted in a temperature range of 80-600 $^{\circ}$ C at a heating rate of 10 K min⁻¹ under a constant N₂ flow at 30.0 mL min⁻¹. Figure 5.10 shows that the FLh-BN (black dots) can maintain its weight up to 500 $^{\circ}$ C with no decomposition [423]. Conversely, the CMC (blue dots) begins to lose weight at around 100 $^{\circ}$ C and undergoes a pronounced

weight reduction ($> 50\%$) by $500\text{ }^{\circ}\text{C}$ due to the decarboxylation and pyrolysis of the cellulose structure [424]. Therefore, tracing the mass loss of CMC in the tested sample enabled us to calculate the relative mass ratio of CMC and h-BN in the dielectric samples (red dots). Take the weight values at $500\text{ }^{\circ}\text{C}$ for both CMC and the tested dielectric samples, the mass loss ratio of CMC ($P_{\text{CMCloss}}\%$) and the mass ratio of FLh-BN ($P_F\%$) in the dielectric sample can be obtained via:

$$P_{\text{CMCloss}}\% = 1 - \frac{m_{\text{CMC},e}}{m_{\text{CMC},i}} \quad (5.4)$$

$$P_F\% = 1 - \frac{1}{m_{\text{sample},i}} \times \frac{m_{\text{sample},i} - m_{\text{sample},e}}{P_{\text{CMCloss}}\%} \quad (5.5)$$

where $m_{\text{sample},i}$ is the initial mass of the dielectric sample before TGA, $m_{\text{sample},e}$ is the final mass of the dielectric sample after TGA, $m_{\text{CMC},i}$ is the initial mass of a pure CMC reference sample before TGA, and $m_{\text{CMC},e}$ is the final mass of a pure CMC reference sample after TGA.

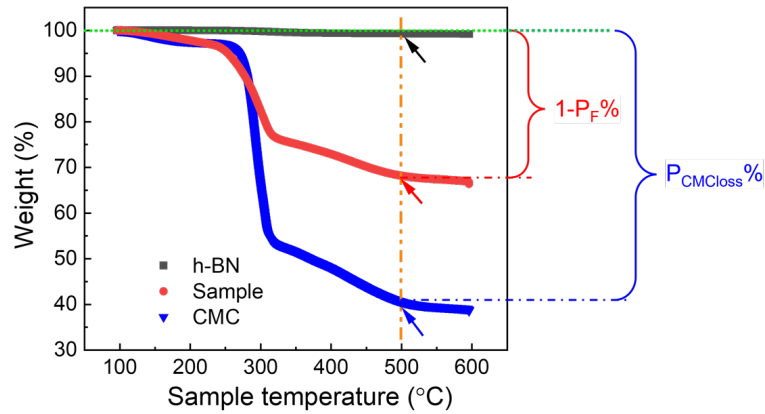


Fig. 5.10 TGA profiles of h-BN, CMC and dielectric materials under N_2 atmosphere.

Figure 5.11(a) plots the C_A of the as-prepared capacitors as a function of the inverse of the dielectric layer thickness. The dielectric layer with 64.6 wt.% of FLh-BN shows C_A ranging from 40 to $90\text{ }\mu\text{F m}^{-2}$, which is higher than that with 44.5 wt.% of FLh-BN. The dielectric layer with 84.5 wt.% of FLh-BN shows the highest C_A , ranging from 90 to $170\text{ }\mu\text{F m}^{-2}$. By doing the linear fitting for each set of data (44.5 wt.%, 64.6 wt.% and 84.5 wt.%), Figure 5.11(b) summarises their corresponding $\epsilon_r \sim 7.9 \pm 1.0$, 13.4 ± 2.4 and 17.1 ± 2.9 , respectively. Increasing the mass ratio of FLh-BN in the dielectric layer over the CMC improves the ϵ_r values of the layer.

Figure 5.11(c) plots the leakage current densities at the two metal electrodes and through the dielectric layers of different thicknesses as a function of applied voltages. The capacitors with the dielectric layer containing 44.5 wt.% and 84.5 wt.% have small leakage current densities below 10^{-6} A mm $^{-2}$, while the one containing 64.6 wt.% shows one order of magnitude higher leakage current densities $\sim 10^{-5}$ A mm $^{-2}$, which may be attributed to the smaller thickness of 0.89 μ m. Considering the thickness values, Figure 5.11(d) summarises the breakdown strength values of the dielectric layer as a function of the mass ratios of FLh-BN. The capacitors with the dielectric layer containing 44.5 wt.%, 64.6 wt.%, and 84.5 wt.% exhibit the breakdown strength values at 14.8 ± 0.8 kV/mm, 29.2 ± 1.5 kV/mm and > 37.4 kV/mm (voltage limit to 40 V), respectively.

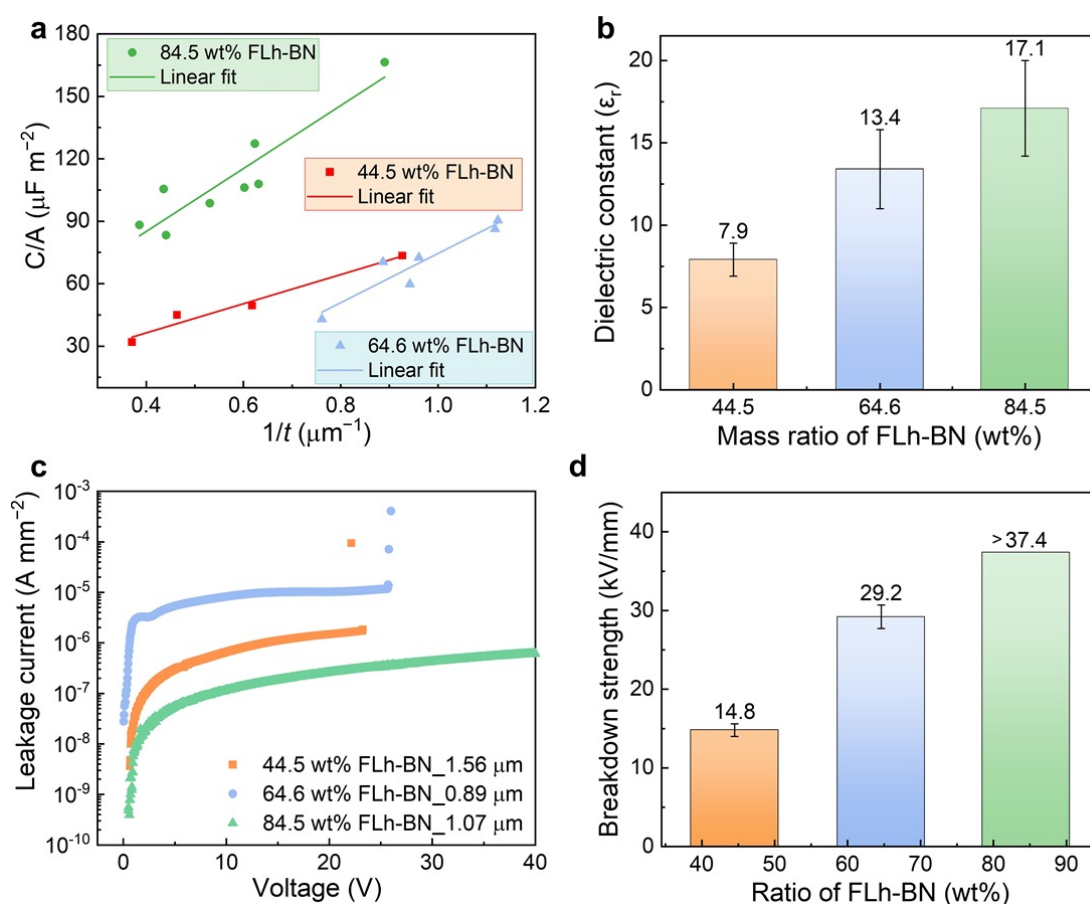


Fig. 5.11 Effect of the mass ratios of FLh-BN on the electrical performance of the as-prepared capacitors: (a) C_A as a function of the inverse thickness of the dielectric layer; (b) ϵ_r values of the dielectric layers; (c) leakage current densities of the capacitors as a function of applied voltages and (d) breakdown strengths of the dielectric layers.

5.3.5.2 Add high- ϵ_r BaTiO₃ as dielectric additives

The formulation of hybrid FLh-BN and BaTiO₃ dielectric ink was achieved by mixing the FLh-BN and BaTiO₃ inks at 9:1 v/v and sonicating the mixture for 5 minutes, allowing a homogeneous ink. The BaTiO₃ ink was formulated the same as the FLh-BN/CMC inks. 10 mg mL⁻¹ of BaTiO₃ nanopowder (cubic crystalline phase) (Sigma Aldrich, no. 467634) was added to the 3 mg mL⁻¹ CMC aqueous solution and sonicated for 9 hours (Fisherbrand FB15069, Max power 800 W). After sonication, the suspension was centrifuged (Thermo Fisher Scientific ultracentrifuge using a TH-641 swinging) at 1000 rpm for 20 min, and the supernatant was carefully collected. The hybrid dielectric ink was printed as a thin film sandwiched by two Ag electrodes, forming a MIM capacitor structure to be electrically characterised. This part was completed by Ryan Macpherson and 4 capacitors were prepared [73].

The MIM capacitors with 10 % BaTiO₃/FLh-BN dielectric layer have a higher C_A than that of the pristine FLh-BN/CMC dielectric layer [73], which represents clear evidence that the 10% BaTiO₃ nanoparticles effectively boost the dielectric performance of the FLh-BN/CMC dielectric layer. As summarised in Figure 5.12(a), the ϵ_r dielectric layer of 7.9 increased to 16.0 after embedding the BaTiO₃ nanoparticles. The achieved enhancement of ϵ_r can be considered by Landauer's effective medium approximation (EMA) with the following equation [425]:

$$x_1 \frac{\rho_1 - \rho_m}{\rho_1 + 2\rho_m} + x_2 \frac{\rho_2 - \rho_m}{\rho_2 + 2\rho_m} = 0 \quad (5.6)$$

where x_1 and x_2 are the volumetric fraction of individual materials, ρ_1 and ρ_2 are the material's properties, and ρ_m is the approximated property of the mixture material [425]. Applying the material 1 and 2 as FLh-BN/CMC and BaTiO₃/CMC, respectively, where $x_1 = 0.9$, $x_2 = 0.1$, $\rho_1 = 7.9$, and $\rho_2 = 430.81$, and using a quadratic formula for ρ_m , the effective solution for the ϵ_r of the mixture is calculated as 13.9, which is slightly smaller than the measured value of 16.0 ± 1.5 . This suggests that there could have been additional synergetic effects occurring once the FLh-BN/BaTiO₃ film is formed. For example, the small gaps between the BaTiO₃ nanoparticles could have been filled by the smaller FLh-BN flakes.

Figure 5.12(b) plots the breakdown voltages of the 10 % BaTiO₃/FLh-BN capacitor compared to the non-additive capacitor. The leakage current densities of the BaTiO₃ embedded capacitor are one order of magnitude lower at 10^{-7} A mm⁻² but remained at the same level of breakdown strength (14.8 kV/mm).

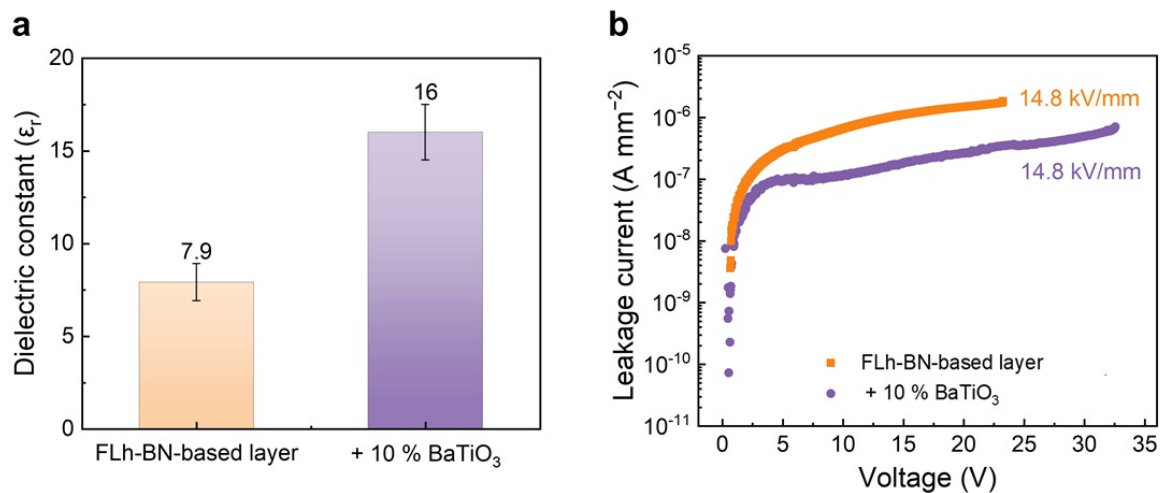


Fig. 5.12 Improvement of the 10 % addition of the high- ϵ_r BaTiO₃ on the electrical performance of the capacitors: (a) ϵ_r enhancement and (b) reduced leakage current densities and improved dielectric strength.

5.4 Conclusion

Printable dielectric inks with desired dielectric properties are in high demand to enable high-performance printed electronics [73]. Printed electronics based on 2D materials have been demonstrated to outperform standard printed electronics for printed ICs [55, 80]. This chapter reports the few-layer h-BN (FLh-BN)-based dielectric inks, which are optimised to achieve a suitable concentration for spray coating and decent flake quality. The FLh-BN-based dielectric inks are produced by ultrasonication-assisted LPE via probe sonication and subsequent centrifugation. Raman, AFM, SEM, and XPS are utilised to examine the chemical composition and flake size of the produced FLh-BN flakes. The lateral size and the thickness of the FLh-BN flakes follow a log-normal distribution, peaking at 352 nm and 6.6 nm, respectively, which aligns well with 2D nature. To examine the dielectric properties of the FLh-BN-based dielectric inks, a metal-insulator-metal (MIM) parallel capacitor is spray-coated, with sprayed silver films as contact electrodes and the FLh-BN-based dielectric film in the middle as an insulating layer. The MIM capacitor exhibits a dielectric constant (ϵ_r) of 7.9. Two ways are explored to further improve the ϵ_r of the dielectric materials, including adjusting the mass ratios of FLh-BN in the dielectric inks and embedding a high- ϵ_r BaTiO₃, achieving a ϵ_r of 17.1 and 16, respectively.

Chapter 6

Efficient heat dissipation using h-BN based composites for thermal management

While advanced dielectric materials can enhance the performance and durability of electronic and energy storage devices, ensuring safe operation with maximized power and energy efficiency is equally important. Power and energy efficiency improve when devices operate within optimal temperature ranges [258]. Excessive temperatures and non-uniform temperature distribution negatively affect device performance. Therefore, effective thermal management, supported by materials with advanced thermal conductivity, is crucial for maintaining stable device temperatures and ensuring reliable operation.

Commercial thermally conductive dielectric materials typically exhibit κ ranging from 0.8 to 4.2 W m⁻¹ K⁻¹. h-BN is reported as a highly thermally conductive 2D material, which can be incorporated as thermal fillers to impart high κ to polymer-based composites. A cellulose-based composite embedded with FLh-BN flakes, achieving a ~ 21.7 W m⁻¹ K⁻¹, prepared using a cost-effective and scalable procedure, is demonstrated. This value is > 5 times higher than the κ observed in composites embedded with Bh-BN ($\kappa \sim 4.5$ W m⁻¹ K⁻¹), indicating the benefits of the superior κ of FLh-BN on the κ of h-BN polymer composites. When applied as a paste for TIMs, the FLh-BN composite can reduce the maximum temperature ($T_{\max}$) by 24.5 °C of a heating pad at a power density (h) of 2.48 W cm⁻² compared to Bh-BN composites at the same h-BN loading. The results provide an effective approach to improve the κ of cellulose-based thermal pastes for TIMs and demonstrate their viability for heat dissipation in ICs and high-power electronic devices.

6.1 Preparation of h-BN based composites

6.1.1 Choice of cellulose as polymer matrix

Cellulose is attracting more and more interest as a polymer matrix for TIMs. It has been considered one of the most naturally abundant, environmentally friendly, sustainable and bio-compatible polymer, which therefore makes it very promising for the next-generation green electronics [304]. Beyond these, cellulose also shows a higher Young's modulus and a lower coefficient of thermal expansion (CTE) than conventional polymers. For example, compared to epoxy with Young's modulus of ~ 3.4 GPa [49] and CTE ~ 45.8 ppm K^{-1} [305, 306], cellulose exhibits Young's modulus of ~ 137.0 GPa and CTE < 10 ppm K^{-1} [307, 308]. In the mentioned studies in Chapter 4, epoxy was always mixed with h-BN physically at the final stage of the process, while cellulose can directly stabilise h-BN flakes in dispersions at the first stage during the LPE process of h-BN [80], which makes the mixture more homogeneous [309].

6.1.2 Fabrication methods of composites

In this work, two types of h-BN, namely Bh-BN and FLh-BN have been prepared. Accordingly, two types of related composites, using Bh-BN or FLh-BN as thermal fillers in a CMC polymer matrix - a Bh-BN embedded composite (Bh-BN/CMC) and an FLh-BN embedded composite (FLh-BN/CMC) have been fabricated and compared. The composites were fabricated in the form of pastes or dry rods/films to be suitable for various characterisation and κ measurements. The work would like to demonstrate (1) the effect of Bh-BN as thermal fillers on the κ of the CMC-based composites; (2) the effect of exfoliation of Bh-BN into FLh-BN flakes on the κ of the CMC-based composites.

Figure 6.1(a) demonstrates the fabrication process of the Bh-BN/CMC composite. First, the initial Bh-BN and CMC powders are weighed using the microbalance to determine the relative mass ratio. Second, the weighed Bh-BN and CMC powders are decanted into a glass bottle and mixed using vortex for 5 minutes to enable a homogenous mixture (Stage 1). Then, the powder mixture is compressed using the hydraulic press at 15 tons for 30 minutes to produce a compact pellet (Stage 2). Afterwards, the pellet is dissolved in DI water in a vial to form a viscous paste (Stage 3). The paste is finally shaped into a rod at a diameter of 13 mm to create a symmetrical structure (Stage 4) for PPMS measurements [242]. Figure 6.1(b) demonstrates the fabrication process of the FLh-BN/CMC composite. The FLh-BN

suspension is produced via the LPE process (Stage 1-2), as described in Section 5.1. At the next stage, the FLh-BN suspension is mixed with a 3 mg mL^{-1} CMC aqueous solution, and the mixed solution is stirred on a hot plate using a magnetic bar for 1 hour to form a viscous paste. Finally, the paste is shaped into a dry, freestanding thin film with a thickness of $\sim 7.5 \text{ }\mu\text{m}$ suitable for the PPMS measurements [242].

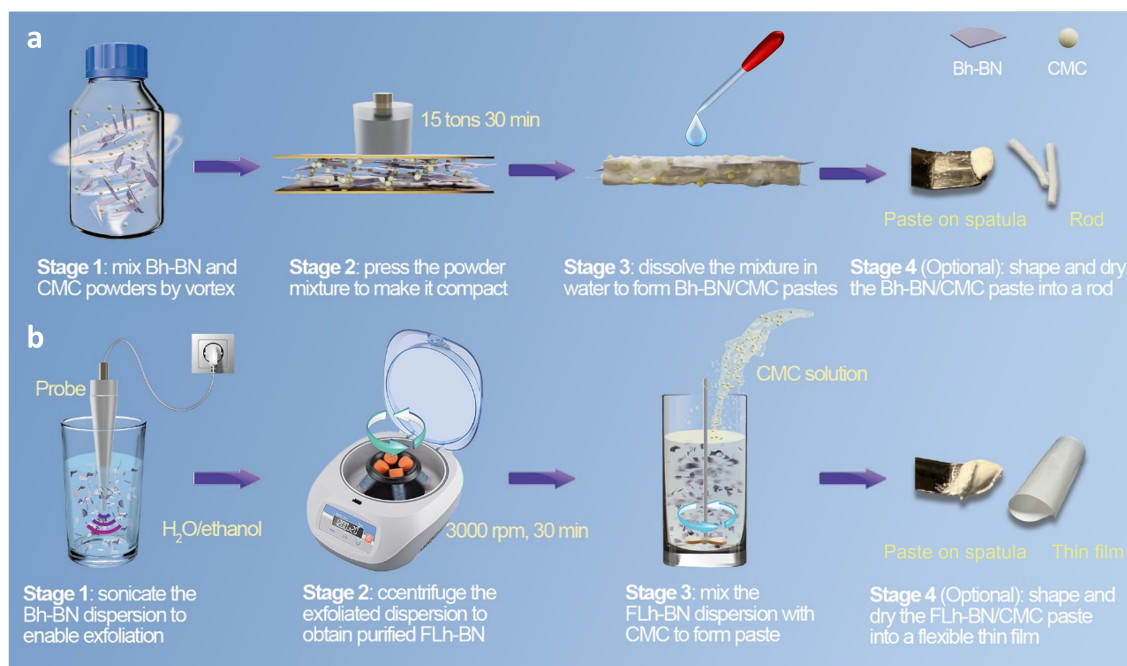


Fig. 6.1 Schematic illustration of the sample preparation process of (a) Bh-BN/CMC, and (b) FLh-BN/CMC, at RT. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

6.1.3 Characterisation methods of composites

TGA and DSC were performed using a Netzsch 449 F5 under an Ar/H_2 atmosphere with a flow rate of 50 mL min^{-1} , starting from room temperature up to $500 \text{ }^\circ\text{C}$ at a heating rate of 5 K min^{-1} . Samples were placed in a $70 \text{ }\mu\text{L}$ Platinum (PtRh 80:20%) crucible (Mettler Toledo, ME-51119654) and another empty platinum crucible was used as the reference. Baseline correction was applied to remove any impact from the ambient environment (i.e. vibration and humidity). To measure the C_p , the Standard Sapphire Method [238] was applied using Equation 2.18 and the sapphire used in this work has a geometry of 5.2 mm in diameter and 0.25 mm in thickness, which has a similar heat mass with the samples for the best accuracy. 3 replicates for each sample were performed to minimise the experimental errors.

Thermal diffusivity D was determined using the PDT method. The PDT used a 488 nm Ar laser with a power of 50 mW as a pump beam and a He-Ne laser focused close to the surface of the sample at a 0.04 mm spot size as a probe beam. The measurements were performed at 6 pump frequency (F) values as a function of the pump-probe distance (Y). The thermal diffusion length (l_t) was obtained from the linear part of the phase toward Y . With plotting l_t as a function of $F^{-0.5}$ and obtaining the slope values, the D value of the sample was obtained by applying the equation 2.23. The PDT setup was corrected and validated by measuring the D of GaAs at $0.22 \text{ cm}^2 \text{ s}^{-1}$ at the frequency of 81 Hz.

The densities ρ of the composite was calculated by $\rho = m/V$, where the mass (m) was weighed using a micro-balance (KERN ABT IOO-5NM) and the volume (V) was determined by multiplying the cross-sectional area and the thickness of the sample. 3 replicates for each sample were performed to minimise the experimental errors.

The porosities of the composite were determined by analysing the gap region in the SEM images. SEM was performed by May Ching L using a ZEISS with an Xbeam 540. The inter-flake gap region was enhanced contrast and analysed using ImageJ to obtain a percentage value.

The thermal conductivity κ determined via the SSM method using Equation 2.19 was performed at a PPMS (DynaCool System, Quantum Design) with a TTO (DynaCool CAN-based D670, Quantum Design). Samples were mounted on a TTO puck, using a four-probe lead configuration. The leads connected the sample to a heater, a hot temperature sensor, a cold temperature sensor, and a coldfoot, respectively. A conductive adhesive (silver conductive paint SCP03B, Electrolube) was applied to reduce the thermal contact resistance between the leads and the sample. The puck was covered by an isothermal radiation shield to reduce the radiation loss. The measurements were operated under an ultrahigh vacuum from 275 to 325 K. 3 replicates for each sample were performed to minimise the experimental errors.

6.2 Thermal properties of h-BN based composites

6.2.1 Thermal stability

Take the Bh-BN/CMC composites as an example. The TGA analysis was conducted to reveal their thermal stability at varying compositions [426]. Figure 6.2(a) plots the corresponding TGA curves as a function of temperature up to 500 °C, showing the difference of composites'

mass loss. The pure Bh-BN sample (black dotted curve) maintains its weight up to 500 °C, consistent with previously published studies [423], indicating no decomposition of the material. Conversely, the pure CMC sample (red dotted curve) begins to lose weight at around 80 °C, decreasing by about 10 % by 207 °C, which can be attributed to the presence of moisture content in the sample [424]. A more pronounced weight reduction to approximately 58 % at 500 °C is due to the decarboxylation and pyrolysis of the cellulose structure [424].

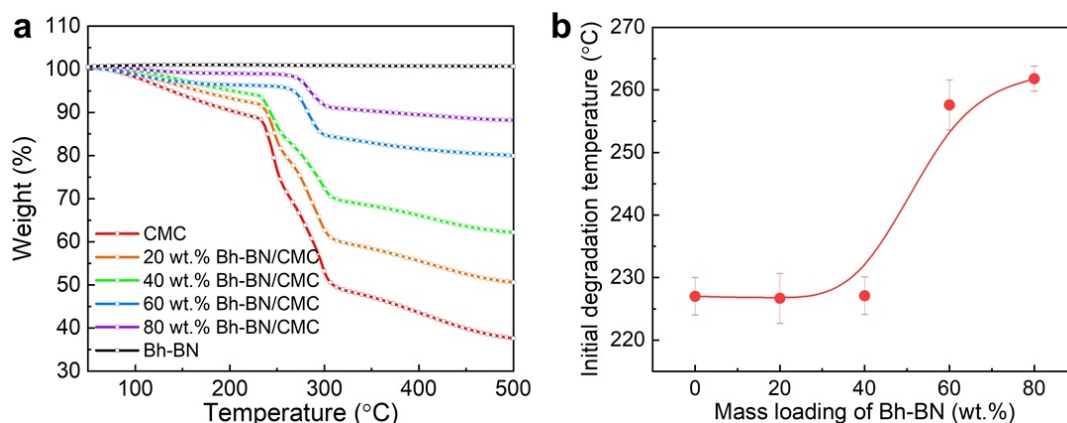


Fig. 6.2 TGA of CMC, Bh-BN, and their composites at different compositions. (a) The weight loss of CMC, 20 wt.%, 40 wt.%, 60 wt.%, 80 wt.% Bh-BN/CMC and Bh-BN as a function of temperature; (b) The initial decomposition temperature of Bh-BN/CMC as a function of the Bh-BN mass loading. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

Using the first derivative analysis of TGA, the initial thermal degradation temperatures of the Bh-BN/CMC composites could be extracted. Figure 6.2(b) summarises the degradation temperature difference as a function of various mass loadings of Bh-BN. The inclusion of Bh-BN as a thermal filler raises the degradation temperature for the composite materials from 227 °C for the pure CMC to approximately 256 °C for the composite with a 60 wt.% loading of Bh-BN, indicating the enhanced thermal stability [426] and improved heat dissipation at typical operational temperatures (50–120 °C) in power electronics [427].

6.2.2 Thermal diffusivity

The thermal diffusivity (D) measurement and analysis of the Bh-BN/CMC composites were determined using the PDT method, as described in Section 2.6.6. Figure 6.3(a) plots the modulus (blue curve) and phase (red curve) of the deflection signal relative to the pump-probe distance (Y) at a pump laser frequency (F) of 16 Hz for the 60 wt.% Bh-BN/CMC

composite. To obtain a reliable value, it is necessary to repeat the PDT measurements at multiple frequencies of the pump laser. Figure 6.3(b) plots the thermal diffusion length (l_t) as a function of the inverse of the root of the modulation frequency ($F^{-0.5}$), for the Bh-BN/CMC composite embedded with a mass loading of Bh-BN at 80 wt.%. By fitting the data points and correlating the slope of the curve to the Equation 2.25, the D value of the composite could be extracted at a $D \sim 0.093 \text{ cm}^2 \text{ s}^{-1}$.

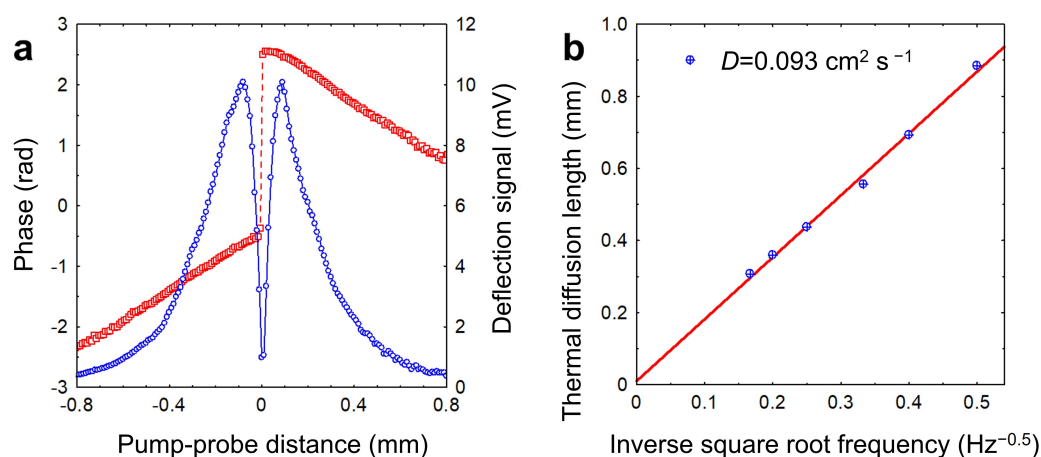


Fig. 6.3 PDT characterisation of the as-prepared Bh-BN/CMC composites. (a) The modulus (blue curve) and phase (red curve) of the deflection signal at the pump laser frequency $F=16$ Hz as a function of the pump-probe distance (Y) for the 60 wt.% Bh-BN/CMC composite; and (b) the thermal diffusion length as a function of the inverse of the root of the modulation frequency for the 80 wt.% Bh-BN/CMC composite. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

Repeating the same method for each Bh-BN/CMC composite, Figure 6.4(a) summarises their D values as a function of the mass loading of Bh-BN, from 0 wt.% to 90 wt.%. For the pure CMC (0 wt.% Bh-BN) sample, the D value was found at $\sim 0.012 \text{ cm}^2 \text{ s}^{-1}$, and the D doubles at 20 wt.% mass loading of Bh-BN. The D keeps increasing to $0.053 \text{ cm}^2 \text{ s}^{-1}$ at 60 wt.% mass loading of Bh-BN after which the increment becomes more rapid. At 90 wt.% mass loading of Bh-BN, the D reaches $\sim 0.12 \text{ cm}^2 \text{ s}^{-1}$, being 10 times to that of the pure CMC sample. The experimental data points were fitted with a quadratic polynomial fitting with the equation shown in the plots, with the best $R^2 \sim 0.995$. The D is a measure of the heat transfer rate inside a material when the material is heated. The results of Figure 6.4(a) indicate that with more addition of Bh-BN, the composites transfer the heat faster and the ratio of the heat accumulated inside the material to increase the entropy and temperature becomes lower.

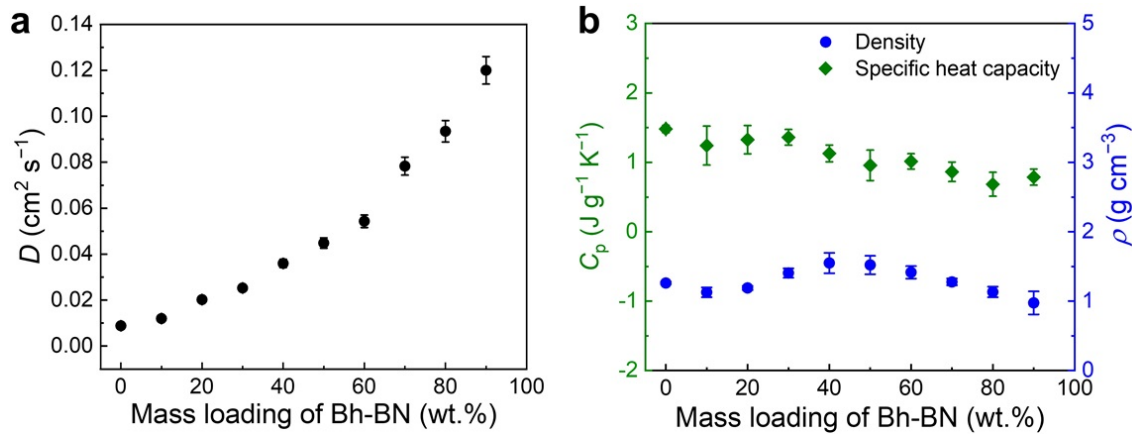


Fig. 6.4 Thermal properties of the as-prepared Bh-BN/CMC composites as a function of the mass loading of Bh-BN. (a) The D results and (b) the C_p (green diamond scatters) and the ρ (blue circle scatters) as a function of the mass loading of Bh-BN. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

6.2.3 Specific heat capacity

Figure 6.4(b) plots the C_p values of Bh-BN/CMC composites (green diamonds) as a function of the mass loading of Bh-BN, from 0 wt.% to 90 wt.%. The C_p has an average value of $\sim 1.2 \text{ J g}^{-1} \text{ K}^{-1}$ with some variation over the function of the Bh-BN mass loading. The C_p varies from $\sim 1.25 \text{ J g}^{-1} \text{ K}^{-1}$ at 10 wt.% Bh-BN mass loading to $\rho \sim 1.15 \text{ g cm}^{-3}$ at 40 wt.% Bh-BN mass loading. When the mass loading of Bh-BN further increases, the C_p shows a generally slight decline to $\sim 0.8 \text{ J g}^{-1} \text{ K}^{-1}$ at 80 wt.% Bh-BN mass loading.

6.2.4 Density and porosity

Figure 6.4(b) shows the determined ρ values of Bh-BN/CMC composites (blue dots), as a function of the mass loading of Bh-BN, from 0 wt.% to 90 wt.%. The ρ has an average value of $\sim 1.28 \text{ g cm}^{-3}$ with some variation over the function of the Bh-BN mass loading. It oscillates from $\rho \sim 1.27 \text{ g cm}^{-3}$ at 10 wt.% Bh-BN mass loading to the highest $\rho \sim 1.55 \text{ g cm}^{-3}$ for the composite with 40 wt.% Bh-BN mass loading, above which the ρ decreases slowly to $\sim 0.98 \text{ g cm}^{-3}$ for the composite with 90 wt.% Bh-BN mass loading. The decreasing trend of the ρ can be attributed to the increasing porosity of the composites when the mass loading of Bh-BN increases.

Figure 6.5 shows the SEM images of the Bh-BN/CMC composites at 40 wt.%, 60 wt.%, and 80 wt.% mass loadings of Bh-BN, respectively. Applying the ImageJ by setting a contrast

between brightness and darkness, I separated the material region with the air-gap region as highlighted in red in Figure 6.5(d-e). Calculating the percentage of the air-gap region (red area in total), the gap region occupies 5.3 % for the 40 wt.% Bh-BN/CMC composite, while there is a larger gap percentage at 11.8 % for the 60 wt.% Bh-BN/CMC composite. For the 80 wt.% Bh-BN/CMC composite, the gap region occupies the largest ratio at 16.3%. The increasing percentage of the air gap results in an increased porosity and can explain the slight decrease of the ρ of the Bh-BN/CMC above 40 wt.% loading of Bh-BN.

Here I would like to acknowledge the support of May Ching Lai from the University of Cambridge to do the SEM characterisation using a ZEISS with an X-beam 540.

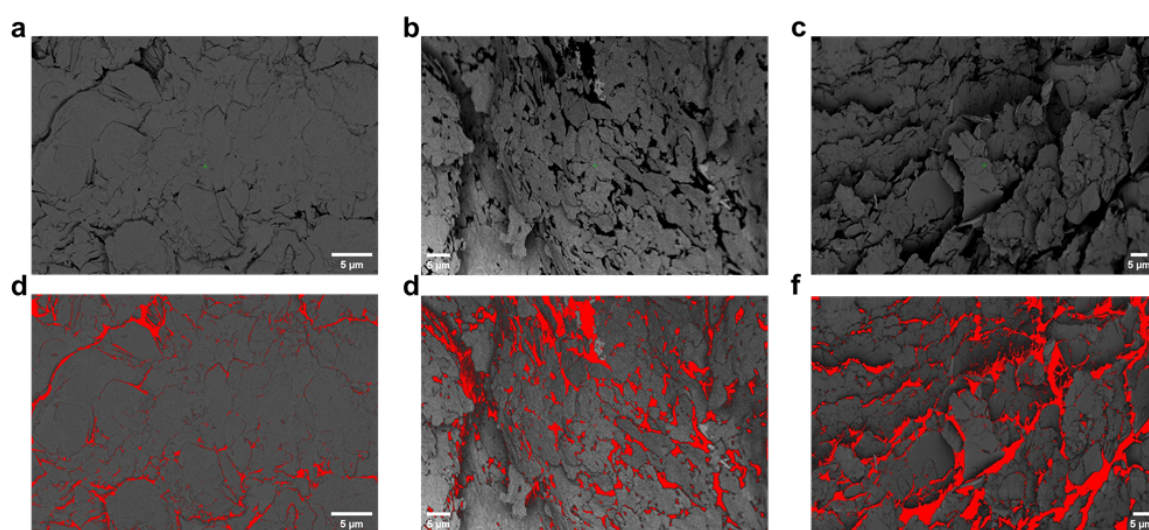


Fig. 6.5 SEM images showing the inter-flake gaps in the Bh-BN/CMC composites at a mass loading of Bh-BN at (a) 40 wt.%, (b) 60 wt.%, and (c) 80 wt.%. The gap area (darker regions in the SEM image, highlighted in red in the bottom panels) was identified by ImageJ to be (d) 5.3% for 40 wt.%, (e) 11.8% for 60 wt.%, and (f) 16.3% for 80 wt.%. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

6.2.5 Thermal conductivity

6.2.5.1 The effect of h-BN mass loadings

The κ values of Bh-BN/CMC and FLh-BN/CMC were determined through two distinct techniques: the SSM and the transient PDT, as described in Section 2.6.6 and Section 2.6.6. The SSM measurements were carried out using a PPMS (Quantum Design) equipped with a TTO. In the SSM approach, a known steady-state heat flux (q) was applied to the sample,

and the resulting temperature differences (ΔT) across a specific length (Δx) of the sample were measured once thermal equilibrium was achieved. These measurements allowed us to calculate the κ values via

$$\kappa_{\text{SSM}} = -\frac{q\Delta x}{\Delta T} \quad (6.1)$$

This technique is often employed to determine the κ of TIMs [428]. The PDT [429] obtains the D values of the sample by directing a laser onto the sample's surface to measure the l_t as a function of the laser frequency, as described in Section 2.6.6. Applying the equation, $\kappa_{\text{PDT}} = D \times \rho \times C_p$, the κ of the composites can be calculated.

Take the Bh-BN/CMC composites with various compositions as an example. Figure 6.6(a) shows the κ_{SSM} (black squares) and κ_{PDT} (red circles) values for the Bh-BN/CMC composites, as a function of the mass loading of Bh-BN from 0 wt.% to 90 wt.%. The pure CMC sample which has 0 wt.% mass loading of Bh-BN has a $\kappa_{\text{SSM}} \sim 1.4 \text{ W m}^{-1} \text{ K}^{-1}$ at RT. The κ_{PDT} instead gives a slightly higher value of $\sim 1.68 \text{ W m}^{-1} \text{ K}^{-1}$. Both values are higher than what has been published before, $\kappa = 0.65 \text{ W m}^{-1} \text{ K}^{-1}$ [430]. The difference can be attributed to that the CMC powders were wet with water to form a robust sample during the sample preparation (Figure 6.1(a)), and the water molecules work as a contact filler in the sample to reduce the air gap between the CMC polymer chains, resulting in a lower thermal contact resistance [431].

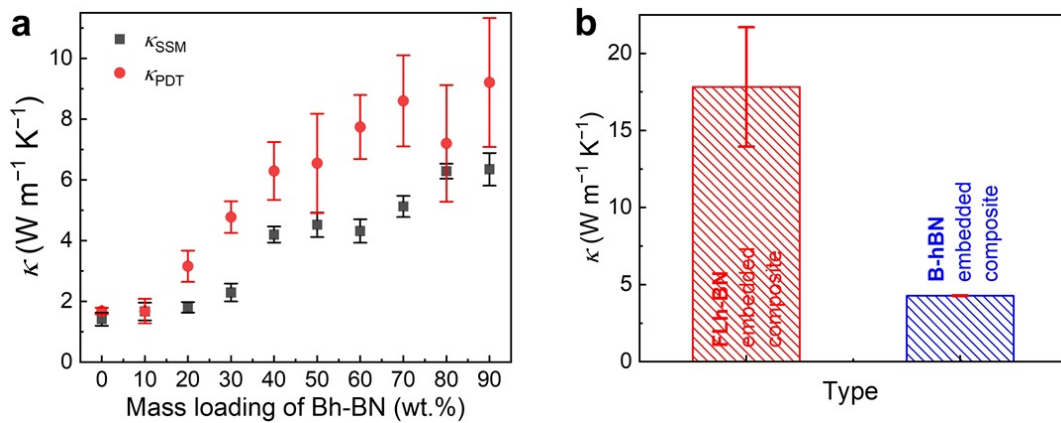


Fig. 6.6 The κ values for the Bh-BN/CMC composites as a function of the Bh-BN mass loading. (a) The κ values of the Bh-BN/CMC composites using the SSM and PDT methods; and (b) the κ comparison of the 60 wt.% Bh-BN/CMC and the 60 wt.% FLh-BN/CMC composites. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

The 10 wt.% Bh-BN/CMC composite exhibited a κ_{SSM} of $1.65 \text{ W m}^{-1} \text{ K}^{-1}$ and a κ_{PDT} of $1.7 \text{ W m}^{-1} \text{ K}^{-1}$, respectively at RT. Above the mass loading of Bh-BN at 10 wt.%, both

κ_{SSM} and κ_{PDT} were seen an increase as a function of the mass loading of Bh-BN. The κ of the 20 wt.% Bh-BN/CMC composite increases to κ_{SSM} of $\sim 1.81 \text{ W m}^{-1} \text{ K}^{-1}$ and κ_{PDT} of $\sim 3.15 \text{ W m}^{-1} \text{ K}^{-1}$ by 29.3 % and 87.5 %, respectively, compared to that of the 10 wt.% Bh-BN/CMC composite. There observed a rapid increase of both κ_{SSM} and κ_{PDT} in the range of 20 wt.% - 40 wt.% Bh-BN mass loading. At the 40 wt.% Bh-BN mass loading of Bh-BN, the κ_{SSM} reaches $\sim 4.2 \text{ W m}^{-1} \text{ K}^{-1}$ with an enhancement of 132 %, and the κ_{PDT} reaches $\sim 6.3 \text{ W m}^{-1} \text{ K}^{-1}$ with an enhancement of 100 %. The rapid increase can be explained by the previously proposed percolation threshold theory [432]. When the Bh-BN loading is above 20 wt.% (the percolation threshold value in this work), the Bh-BN material develops a continuous thermal conducting path on its own [432], resulting in more effective phonon transmission channels compared to the ones that CMC forms. This leads to a faster heat transfer within the composite due to the higher κ value of Bh-BN, which at the same time suppresses the phonon scattering at the Bh-BN/CMC interface [433].

The 50 wt.% Bh-BN/CMC composite exhibited a κ_{SSM} of $\sim 4.4 \text{ W m}^{-1} \text{ K}^{-1}$ and a κ_{PDT} of $\sim 6.54 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, above which loading the increasing rates of both κ_{SSM} and κ_{PDT} slow down. This can be attributed to the larger porosity observed in the composites with higher Bh-BN mass loadings, where more air gaps exist, leading to a higher thermal contact resistance and poorer thermal conductive paths. Figure 6.6(a) shows that the 90 wt.% Bh-BN/CMC composite had a κ_{SSM} of $\sim 6.4 \text{ W m}^{-1} \text{ K}^{-1}$, and a κ_{PDT} of $\sim 9.21 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, with the latter being almost an order of magnitude higher than that measured for CMC.

There were certain differences between the obtained κ_{SSM} and κ_{PDT} values, and the differences in the ranges of 30 wt.% - 40 wt.% and 60 wt.% - 70 wt.% of the Bh-BN mass loading are the most significant. This can be attributed to the inaccurate emissivity estimation of the sample when performing the SSM measurement at RT [242], at which the proportion of the radiative heat losses compared to the total input heat power are larger than the conditions at lower temperatures ($< 300 \text{ K}$). It is suggested that an estimation error of κ_{SSM} can be $\sim \pm 1 \text{ W m}^{-1} \text{ K}^{-1}$ at RT. Besides this, an additional κ might be lost due to the non-ignorable thermal contact resistance between the copper leads and the sample in the 4-probe configuration. The thermal contact resistance mainly comes from the attached silver epoxy ($\sim 2.0 \text{ W m}^{-1} \text{ K}^{-1}$) on those contact electrodes, with $\sim 40 \text{ K W}^{-1}$ per unit area.

6.2.5.2 The effect of exfoliated h-BN

Based on the above discussion, the 60 wt.% is identified as the optimal Bh-BN mass loading for the composite to reach a decent κ . Increasing the mass loading of Bh-BN at higher ratios (i.e. 80 wt.%) could increase the κ value as shown in Figure 6.6(a), but at the expense of the mechanical strength of the polymer matrix [434], which will be discussed in the following section. Therefore, it is usually not recommended to apply a high mass loading of h-BN as thermal fillers [435].

The optimum mass loading value was kept to compare the performance difference of Bh-BN and FLh-BN as thermal fillers in the CMC polymer matrix. Figure 6.6(b) shows the measured κ_{SSM} values of 60 wt.% Bh-BN/CMC composite and of the 60 wt.% FLh-BN/CMC composite. The 60 wt.% FLh-BN/CMC composite has as a mean κ_{SSM} of $\sim 17.8 \text{ W m}^{-1} \text{ K}^{-1}$, with a maximum measured κ_{SSM} value of $\sim 21.7 \text{ W m}^{-1} \text{ K}^{-1}$, which is almost five times larger than the measured κ_{SSM} value ($\sim 4.5 \text{ W m}^{-1} \text{ K}^{-1}$) of the 60 wt.% Bh-BN/CMC composite. This fascinating comparison indicates the positive impact on the κ of the composites embedded with the FLh-BN flakes compared to that with the Bh-BN flakes, which is also in line with the higher κ value observed for the FLh-BN flakes compared to that of Bh-BN [290].

6.3 Mechanical properties of the composites

6.3.1 The tensile test method

The tensile tests for both the FLh-BN/CMC and Bh-BN/CMC composites were conducted using a specially designed apparatus operating in an enclosed container (Waysafe GP540), including a Retro-Fit variable speed controller (2100-REE10, Solotec) and a modular force tensile stage (Linkam MFS system). The composites were affixed to a standard paper strip (a designed test free-length of 15 mm) via an epoxy (Araldite Rapid) at the two ends and allowed to be cured at RT for at least one week. For each composite, a single pull-out test was carried out by a 20 N force beam at a force resolution of 0.1 mN, and 5 repeats were performed. During each tensile test, the force beam was fixed on the modular force tensile stage and operated at $16.67 \mu\text{m s}^{-1}$. By recording the force (N) change within the composite as a function of the composite extension (mm), the tensile stress (MPa) (equal to the force per cross-sectional area) as a function of the strain (% , equal to the extended ratio of the composite length) could be obtained.

6.3.2 Tensile strength and Young's modulus of the composites

Figure 6.7(a) plots the tensile stress as a function of the strain for the Bh-BN/CMC composites averaged over 5 replicates, at 0 wt.%, 20 wt.%, 40 wt.%, and 60 wt.% mass loadings of Bh-BN, respectively. There observed a larger stress up-limit, a corresponding larger strain within the composite, and a larger slope when the mass loading of Bh-BN increases from 0 wt.% to 40 wt.%. However, the stress limit decreases at 60 wt.% compared to that of 40 wt.% but is still higher than that of 0 wt.%. To quantitatively compare the difference, Figure 6.7(b) summarises the maximum tensile strength values (orange bars) and the Young's modulus values (green bars) for the Bh-BN/CMC composites. Young's modulus was calculated based on the slope of the linear part of the strain-stress curve.

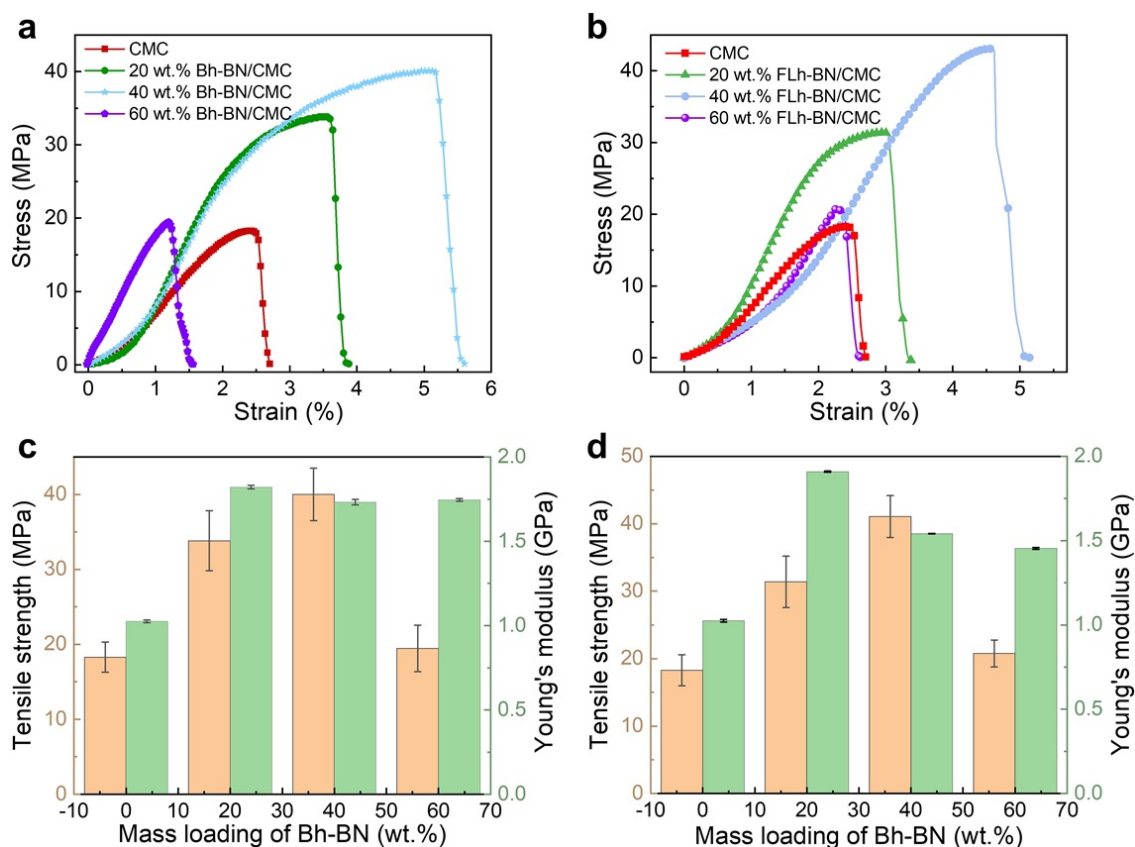


Fig. 6.7 Mechanical performance of the Bh-BN/CMC and FLh-BN/CMC composites. Strain-stress curves of (a) the Bh-BN/CMC composites and (b) the FLh-BN/CMC composites; summaries of tensile strength and Young's modulus of (c) the Bh-BN/CMC composites and (d) the FLh-BN/CMC composites.

The pure CMC sample with 0 wt.% mass loading of Bh-BN has a tensile strength of 18.3 MPa. When the mass loading of Bh-BN increases to 20 wt.% and 40 wt.%, the tensile

strength increases to 33.9 MPa by 85.2% and 40.0 MPa by 119%, respectively. This great increment can be attributed to the improved interfacial adhesion between the Bh-BN filler and the CMC polymer matrix. Instead, the tensile strength of the 60 wt.% Bh-BN/CMC composite decreases to 19.44 MPa but is still 6.3 % higher than that of the CMC sample. The decline can be attributed to the interruption of the CMC polymer cross-linking in the presence of the excess Bh-BN fillers [436]. Note that the 80 wt.% Bh-BN/CMC composite failed the tensile test without producing any valuable data, proving that further increasing the mass loading of Bh-BN within the composite would be at the expense of the mechanical strength of the polymer matrix and consistent with the previous findings [434, 435]. For Young's modulus, it is found that the inclusion of Bh-BN generally increases Young's modulus of the Bh-BN/CMC composite to ~ 1.8 GPa from ~ 1.0 GPa for the pure CMC.

Figure 6.7(c) plots the tensile stress as a function of the strain for the FLh-BN/CMC composites and Figure 6.7(d) summarises the tensile strength values (orange bars) and the related Young's modulus values (green bars) for the FLh-BN/CMC composites. The pure CMC sample with 0 wt.% mass loading of Bh-BN has a tensile strength of 18.3 MPa. When the mass loading of FLh-BN increases to 20 wt.% and 40 wt.%, the tensile strength increases to 32.2 MPa by 75.9% and 43.5 MPa by 137.7%, respectively. This great increment can be also attributed to the improved interfacial adhesion between the FLh-BN filler and the CMC polymer matrix. Instead, the tensile strength of the 60 wt.% FLh-BN/CMC composite decreases to 20.77 MPa but is still 13.6 % higher than that of the CMC sample. For Young's modulus, it is also found that the inclusion of 20 wt.% FLh-BN increases the Young's modulus of the FLh-BN/CMC composite to ~ 1.9 GPa from ~ 1.0 GPa for the pure CMC. Further increasing the mass loading of FLh-BN to 40 wt.% and 60 wt.%, their Young's modulus values decline to ~ 1.55 GPa and 1.45 GPa, respectively, which are still ~ 50 % higher than that of the pure CMC.

6.4 Rheological behaviour of the composites

As described in the literature review in Section 3.2, the vast majority of the results published on the κ of h-BN/polymer composites are obtained from the composites in the form of films or fibres. On the contrary, more than 75% of commercial TIMs for heat dissipation in electronics on the market are mainly in the form of thermal pastes rather than in the form of films or fibres. Thermal pastes can fill in any microscopic gaps between the two surfaces, providing better surface contact and heat transfer than films do.

Therefore, here demonstrate the compatibility of our composites with commercial thermally conducting pastes by implementing rheological characterisation.

6.4.1 The rheological test methods

The rheological properties are the characteristics of a material that describe its flow and deformation behaviour under applied forces [437], including τ and γ , η , thixotropy, viscoelasticity, yield stress [438].

The rheological characterisation for the 60 wt.% FLh-BN/CMC and 60 wt.% Bh-BN/CMC composites in the form of thermal pastes were performed with 3 repeats each, using the HAAKE MARS 60 rheometer with a P35-geometry parallel plate. 1 mL paste was attached to a lower plate and covered with an upper plate. For the η determination, which is one of the criteria for the commercial thermal pastes, a range of γ from 0.01 s^{-1} to 2.0 s^{-1} (0-10 rpm) were applied [439–441].

6.4.2 Viscosity of the composite as thermal pastes

Figures 6.8 (a,b) plot the hysteresis loops (γ and τ) of the 60 wt.% FLh-BN/CMC (blue dots) and 60 wt.% Bh-BN/CMC (red dots) pastes, respectively. The 60 wt.% Bh-BN/CMC pastes experienced two orders of magnitude lower stress at the backward loop compared to the stress at the forward loop. This thixotropic behaviour indicates the composite exhibits a reduced η when subjected to τ (like stirring or shaking) and returns to its original η over time once the stress is removed. This makes the composite easier to process and spread, which is promising as an industrial thermal paste. On the contrary, the 60 wt.% FLh-BN/CMC thermal paste shows no obvious hysteresis loop [442].

Figure 6.8(c) plots the η as a function of γ . The 60 wt.% FLh-BN/CMC and 60 wt.% Bh-BN/CMC pastes have a η of $273,584 \pm 3,256 \text{ mPa s}$ and a η of $674,806 \pm 4,599 \text{ mPa s}$, respectively, at 0.017 s^{-1} (1 rpm), which both fall within the η range (10^4 - 10^6 mPa s) of commercial thermal pastes [439–441]. Both pastes exhibit a shear-thinning property, a property of non-Newtonian fluids where the η of the fluid decreases with an increasing γ .

Figure 6.8(d) points the yield stress of the 60 wt.% FLh-BN/CMC (21.2 Pa) and 60 wt.% Bh-BN/CMC (7.4 Pa) pastes, respectively. The values were obtained at the maximum η , which reveals that the pastes behave in a completely elastic manner [442] below the yield stress, whereas it is prone to flow above the yield stress, which is crucial for TIM product delivery and usage. The low yield stress values of the as-prepared pastes for manufacturers

to reduce the force required to initiate pumping through a pipeline or to fill a container with the product and for end-customers to make it easier to dispense the paste from a syringe.

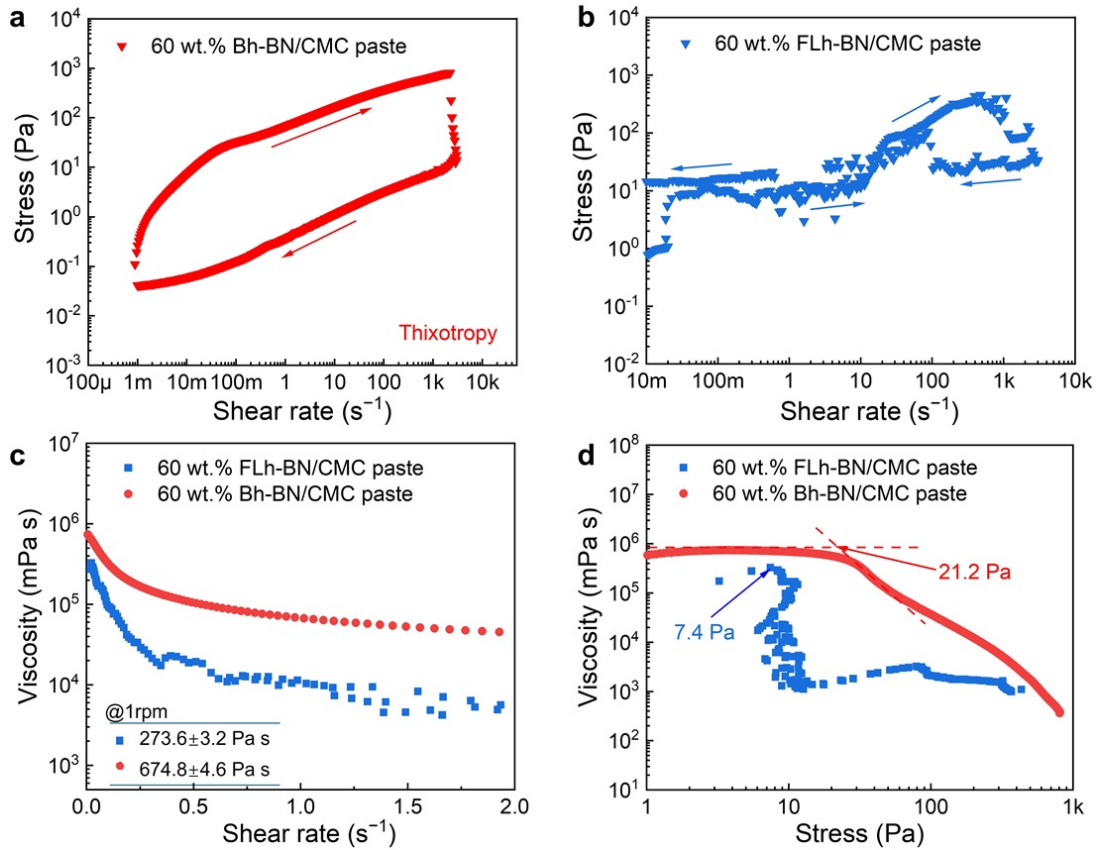


Fig. 6.8 Rheological properties of the composites in the form of thermal pastes, including the thixotropic hysteresis loops (γ and τ) of (a) the 60 wt.% FLh-BN/CMC and (b) the 60 wt.% Bh-BN/CMC pastes, (c) the flow curves: the η profile as a function of γ ; (d) the yield stress obtained at the maximum η .

6.5 Case studies of practical thermal performance of the composites

6.5.1 Enhanced heat dissipation as thermal pastes for integrated-circuits (ICs) chips

6.5.1.1 Custom-built temperature measurement protocol

To study the practical heat dissipation effect of the Bh-BN/CMC and FLh-BN/CMC pastes as TIMs for IC chips, here established a simplified thermal management setup with a real-time temperature monitoring function. The setup was also applied to study the enhanced heat dissipation of the FLh-BN/CMC paste over the Bh-BN/CMC one at different heat power densities (h) and at various convection rates.

Figure 6.9 illustrates the configuration of the thermal management setup, which is composed of a heat generation component, a heat conduction component, a cooling component, and a real-time temperature monitoring component. The heat generation component is a resistance heater ($1.6 \text{ cm} \times 2.1 \text{ cm}$, Vishay Resistor, LTO150F4R700JTE3, thermal resistance of 1.5 K W^{-1}) which can be powered by a DC digital power supply (RS-PRO RS3005D). The heat conduction component in this work is the as-prepared Bh-BN/CMC or FLh-BN/CMC pastes. The cooling component includes a heat sink (Aluminium, thermal resistance of 0.5 K W^{-1} , $60 \times 60 \times 47 \text{ mm}$) coupled with a power-adjustable fan (Thermoelectric devices, TDEX3132/100/FMF12G). The real-time temperature monitoring component involves several K-type thermocouples plugged into a temperature data logger (TASI, TA612C), with a temperature range of $\pm 200 \text{ }^{\circ}\text{C}$ (resolution of $0.1 \text{ }^{\circ}\text{C}$) at a temperature accuracy $< 0.5 \text{ }^{\circ}\text{C}$.

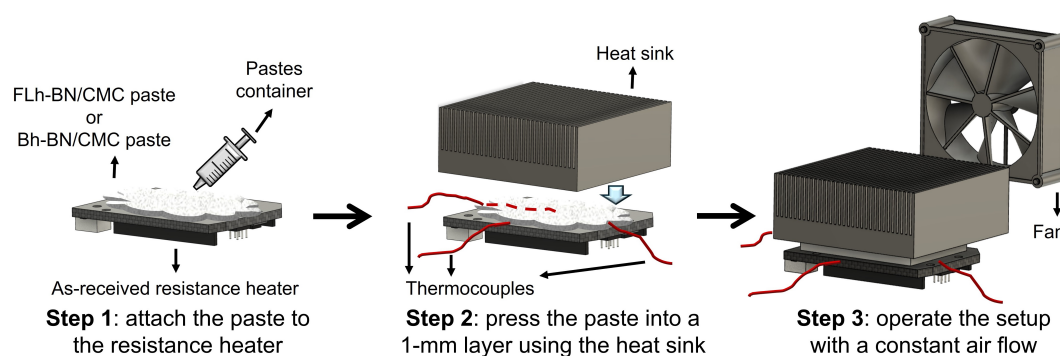


Fig. 6.9 Configuration of the custom-built temperature monitoring setup. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

Figure 6.9 also shows the step-by-step establishment of the whole setup. First, the FLh-BN/CMC or the Bh-BN/CMC paste contained in a syringe is uniformly blade-coated onto one side of the resistance heater. The other side of the resistance heater is encapsulated using a thermal-insulating material (Silicon mat) to simulate the adiabatic environment of a real IC chip. Second, the thermocouples are affixed at both sides of the heater to monitor its real-time temperature evolution and the temperature uniformity ($\Delta T = T_{\max} - T_{\min}$) across the whole surface area of the resistance heater during the measurement. The thickness of the paste is determined at 1 mm, which is larger than the usual bond-line thickness ($\sim \mu\text{m}$) of TIMs in electronics because the insertion of thermocouples enlarges the gap between the resistance heater and the heat sink. Finally, the fan is applied at the side of the heat sink to ensure a constant and sufficient heat dissipation amount. To start the measurement, the heat is generated by forcing a current through the heater, and the amount of heat is determined by multiplying the current and the responded voltage. The fan is adjusted to control the surrounding air velocity at 3.6 m s^{-1} . When the system reaches thermal equilibrium, the maximum temperature of the resistance heater ($T_{\max}$) and the temperature difference (ΔT) are recorded and compared.

Applying the custom-built temperature measurement setup, I was able to statistically investigate and compare the practical heat dissipation effect of the Bh-BN/CMC and FLh-BN/CMC pastes as TIMs for ICs chips, as well as the enhanced heat dissipation of the FLh-BN/CMC paste over the Bh-BN/CMC one at different required heat inputs and at various convection rates, which have been discussed in details below.

6.5.1.2 Mass loadings of Bh-BN

Figure 6.10(a) shows the $T_{\max}$ as a function of the mass loadings of Bh-BN in the Bh-BN/CMC pastes, at a heat power density (h) of 1.24 W cm^{-2} . To compare, the initial $T_{\max,i}$ when there was no paste applied as the TIM between the resistance heater and the heat sink was tested. The initial $T_{\max,i}$ significantly reached $\sim 123.4^\circ\text{C}$, due to the poor κ of air ($0.03 \text{ W m}^{-1} \text{ K}^{-1}$). When applying the pure CMC (0 wt.% Bh-BN) paste as the TIM, the $T_{\max}$ greatly declined to $\sim 55.4^\circ\text{C}$ by over 55 %, which indicated that the significance of using TIMs in the thermal management system to reduce the interfacial thermal contact resistance. Increasing the Bh-BN mass loading to 40 wt.%, 60 wt.% and 80 wt.%, a further drop of $T_{\max}$ was obtained to $\sim 43.1^\circ\text{C}$, $\sim 39.9^\circ\text{C}$ and $\sim 33.4^\circ\text{C}$, respectively. The close-to-linear decline of the $T_{\max}$ of the resistance heater as a function of an increasing mass loading of Bh-BN demonstrated the enhanced heat transfer (heat conduction) and reduced thermal contact resistance, brought by the addition of Bh-BN in the pastes, which can be mainly

attributed to the obtained higher κ value at a higher mass loading of Bh-BN as shown in Figure 6.6(a).

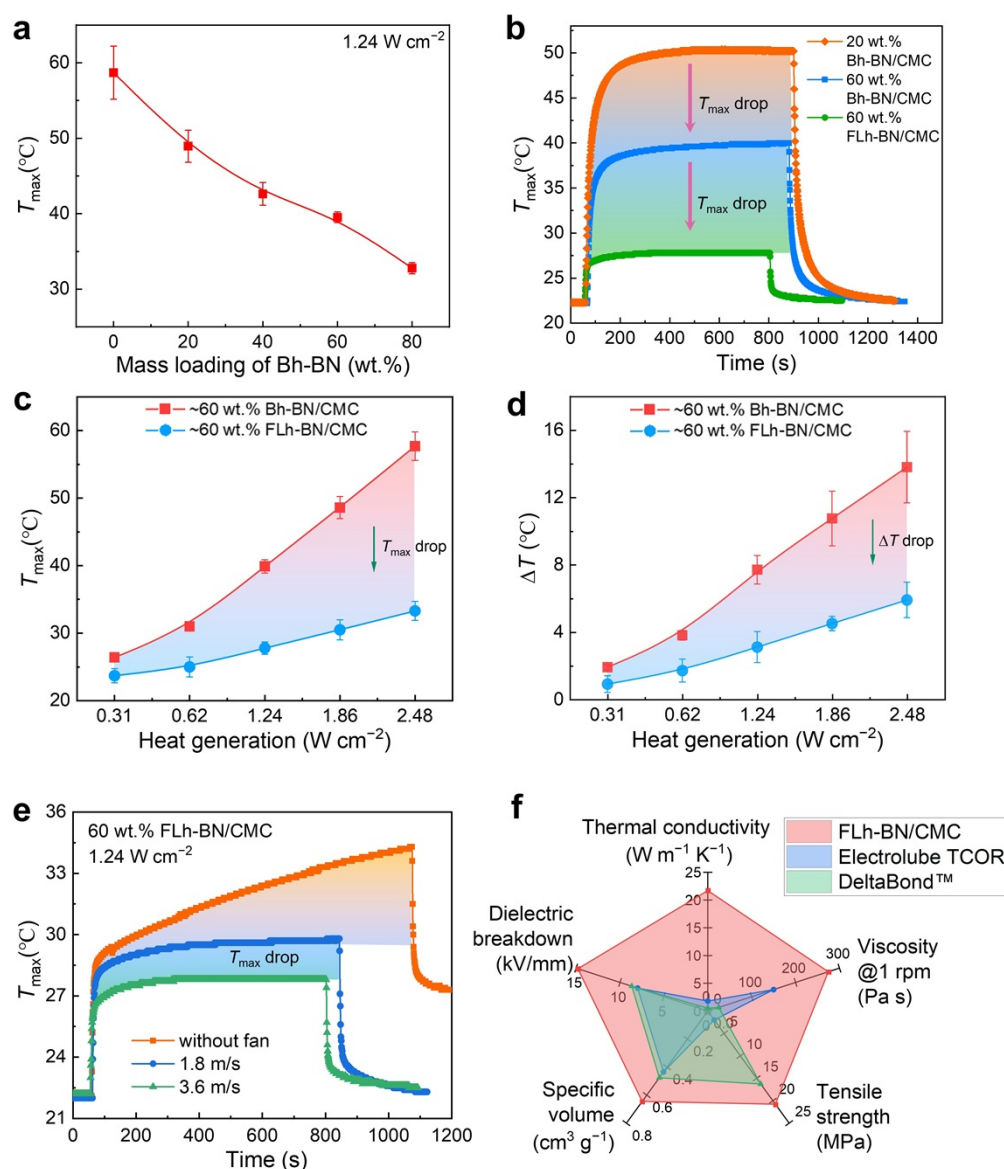


Fig. 6.10 Enhanced heat dissipation as thermal pastes for the ICs chips. (a) The $T_{\max}$ performance of the Bh-BN/CMC at different mass loadings, (b) real-time temperature evolution of the heater using different thermal pastes at 1.24 W cm^{-2} , (c) $T_{\max}$ and (d) ΔT of the 60 wt.% FLh-BN/CMC compared with that of the 60 wt.% Bh-BN/CMC, at different heat power densities; (e) $T_{\max}$ of the 60 wt.% FLh-BN/CMC at different convection rates, and (f) the radar plot comparing key parameters of our composite compared to the commercial thermal pastes [443, 444]. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

6.5.1.3 Effect of FLh-BN over Bh-BN

Figure 6.10(b) records and compares the real-time temperature evolution of the resistance heater using the 20 wt.% Bh-BN/CMC paste, the 60 wt.% Bh-BN/CMC paste, and the 60 wt.% FLh-BN/CMC pasts at 1.24 W cm^{-2} , respectively. For the 20 wt.% Bh-BN/CMC paste, the T_{max} of the resistance heater reached $\sim 50^\circ\text{C}$, as summarised in Figure 6.10(a). Increasing the mass loading of Bh-BN to 60 wt.%, a significant drop of T_{max} was observed by 10.1°C by 20 %. If keeping the mass loading of the thermal filler constant but replacing the Bh-BN with the exfoliated FLh-BN, a significant drop of T_{max} was further seen to 27.8°C by 12.1°C . With this interesting finding, a more detailed comparison of the thermal performance of using the Bh-BN/CMC paste and the FLh-BN/CMC was conducted below.

6.5.1.4 Performance evaluation of FLh-BN/CMC at different heat power densities

Figures 6.10 (c,d) summarise the comparison of the T_{max} and ΔT of the resistance heater coated with the 60 wt.% Bh-BN/CMC paste (red squares) and the 60 wt.% FLh-BN/CMC (blue circles) paste, as a function of heat power densities (h). At a low h like 0.31 W cm^{-2} and 0.62 W cm^{-2} , the T_{max} values of both types of pastes were maintained below 35°C , and the corresponding ΔT values were both kept below 5°C . At $h = 1.24 \text{ W cm}^{-2}$, if applying the Bh-BN/CMC paste, the T_{max} of the resistance heater increased to $\sim 39.9^\circ\text{C}$ with a corresponding ΔT rising to $\sim 8.3^\circ\text{C}$, while applying the FLh-BN/CMC paste, the T_{max} was still maintained well at $\sim 27.8^\circ\text{C}$ with a corresponding ΔT of only $\sim 3.1^\circ\text{C}$, respectively. This noticeable reduction in both the T_{max} by 12.1°C and ΔT by 5.2°C of the resistance heater from the 60 wt.% FLh-BN/CMC paste indicates the better heat conduction capability due to the higher κ observed in Figure 6.6(b), compared to that of the 60 wt.% Bh-BN/CMC.

The reduction of T_{max} and ΔT is more significant at higher h values. At $h = 1.86 \text{ W cm}^{-2}$ and $h = 2.48 \text{ W cm}^{-2}$, if applying the Bh-BN/CMC paste, the T_{max} of the resistance heater increased to $\sim 57.7^\circ\text{C}$ with a corresponding ΔT rising to $\sim 15.1^\circ\text{C}$, while applying the FLh-BN/CMC paste, the T_{max} was maintained well at $\sim 33.2^\circ\text{C}$ with a corresponding ΔT of only $\sim 5.9^\circ\text{C}$, respectively. The large drop of T_{max} at $\sim 42.5\%$ and of ΔT at $\sim 60.9\%$ brought by the 60 wt.% FLh-BN/CMC paste compared to the 60 wt.% Bh-BN/CMC paste is a direct demonstration of the 5 times higher κ value of the 60 wt.% FLh-BN/CMC composite than that of the 60 wt.% Bh-BN/CMC composite.

6.5.1.5 Performance evaluation of FLh-BN/CMC at different convection rates

By demonstrating the excellent heat dissipation performance of using the FLh-BN/CMC paste as a TIM for IC chips, Figure 6.10(e) further shows the performance at different convection rates. In the setup, the convection rate could be modulated by controlling the power of the adjustable fan, therefore leading to a controllable velocity of the surrounding air. Based on the heat convection mechanism of fluid [445], a higher air velocity means a higher convection rate, which could result in a larger amount of heat dissipated into the ambient environment.

At the previous setting for the air velocity at 3.6 m s^{-1} (green dots), the T_{max} of the resistance heater was kept at 27.8°C , while at an air velocity of 1.8 m s^{-1} (blue dots), the T_{max} only increased slightly by 1.9°C to 29.7°C , well maintained below 30°C . A lower air velocity favours the reduction of the power and energy consumption of the whole thermal management system, which is more sustainable and more environmentally friendly. The usage of the 60 wt.% FLh-BN/CMC paste in this work demonstrated the possibility of an energy-saving route.

If the fan was not used to accelerate the natural air velocity, the whole system could not reach thermal equilibrium at 20 minutes, as the continuously increasing T_{max} (orange dots) shown in Figure 6.10(e), indicating the importance of the cooling system. Only by combining all the essential parts, including the heat conduction and heat dissipation (cooling) components, can a desired thermal management performance be achieved.

6.5.1.6 Commercial viability

The commercial viability of the 60 wt.% FLh-BN/CMC composite as a promising thermal paste has been compared to some products that have already been on sale in the market [443, 444], by considering 5 key parameters (κ , η , tensile strength, dielectric breakdown strength, and the specific volume) using a radar plot.

As shown in Figure 6.10(f), the Electrolue TCOR thermal paste [443] exhibits a κ of $18 \text{ W m}^{-1} \text{ K}^{-1}$, a η of 150 Pa s , a tensile strength of 2 MPa , a specific volume of $0.435 \text{ cm}^3 \text{ g}^{-1}$, a breakdown strength of 8 kV/mm , and the DeltaBond thermal paste [444] gives a κ of $0.5 \text{ W m}^{-1} \text{ K}^{-1}$, a η of 25 Pa s , a tensile strength of 16.27 MPa , a specific volume of $0.476 \text{ cm}^3 \text{ g}^{-1}$, a breakdown strength of 8.88 kV/mm . The 60 wt.% FLh-BN/CMC paste shows an extraordinary performance at all 5 aspects, with a higher κ of $21.7 \text{ W m}^{-1} \text{ K}^{-1}$ (better heat conduction ability and lower thermal contact resistance), a higher η of 273.6 Pa s (easier to

be processed and controlled during the manufacture), a stronger tensile strength of 20.77 MPa (a higher mechanical strength), a larger specific volume ($1/\rho$) of $\sim 0.64 \text{ cm}^3 \text{ g}^{-1}$ (a lower density and a more compact component for lightweight applications), and a stronger breakdown strength of 14.6 kV/mm (better electrically insulating property), indicating its promising commercial viability.

6.5.2 Enhanced heat dissipation as thermal pastes for high-power light-emitting (LED) chips

6.5.2.1 Coating of the thermally conductive layer on the LED chip

Figure 6.11(a) demonstrates the process of attaching the FLh-BN/CMC paste or the Bh-BN/CMC paste to a high-power LED chip (ams OSRAM, GW CSSRM3), with an illustration (left) and an optical image (right). The LED chip was electrically soldered on an LED prototyping board (Part No.-282, Polymer Optics) and the paste was uniformly blade-coated onto the board.

During the measurement, the board was connected to a DC power supply (RS PRO RS3005D) using electrical wires and biased with a voltage of 3.2 V and a current of 1.4 A to enable the maximum light-emitting power. The real-time temperature data of the operating high-power LED chip was recorded using an infrared thermal imaging camera (UNI-T UTi120S, range of -15°C to $+550^\circ\text{C}$, at an accuracy of maximum between $\pm 2^\circ\text{C}$ and $\pm 2\%$, with imaging pixels of 256×192). The measurements were repeated 3 times for each type of coating (Figure A.7 in Appendix A).

6.5.2.2 Enhanced heat dissipation results

Figure 6.11(b) plots the evolution of the maximum temperature across the whole LED prototyping board as a function of time, without paste (red dots), with the 60 wt.% Bh-BN/CMC paste (green dots), and with the 60 wt.% FLh-BN/CMC paste (blue dots), and Figure 6.11(c) shows the corresponding infrared images under the 3 cases, at 2 s, 5 s, 60 s and 120 s, respectively. During the LED light-emitting, the maximum temperature reached 95.4°C after an operation time of 120 s, as revealed in the top-right image in Figure 6.11(c). When the 60 wt.% Bh-BN/CMC paste was coated onto the board, the maximum temperature was reduced to 84.9°C by 10.5°C at 120 s, as revealed in the middle-right image in Figure 6.11(c). When the 60 wt.% FLh-BN/CMC paste was coated onto the board, the maximum

temperature was further reduced to 74.2 °C by 21.2 °C at 120 s, as revealed in the bottom-right image in Figure 6.11(c). The ~ 21.2 °C reduction is clear evidence of the enhanced heat dissipation performance of the FLh-BN/CMC composite as a thermal paste for high-power LED chips.

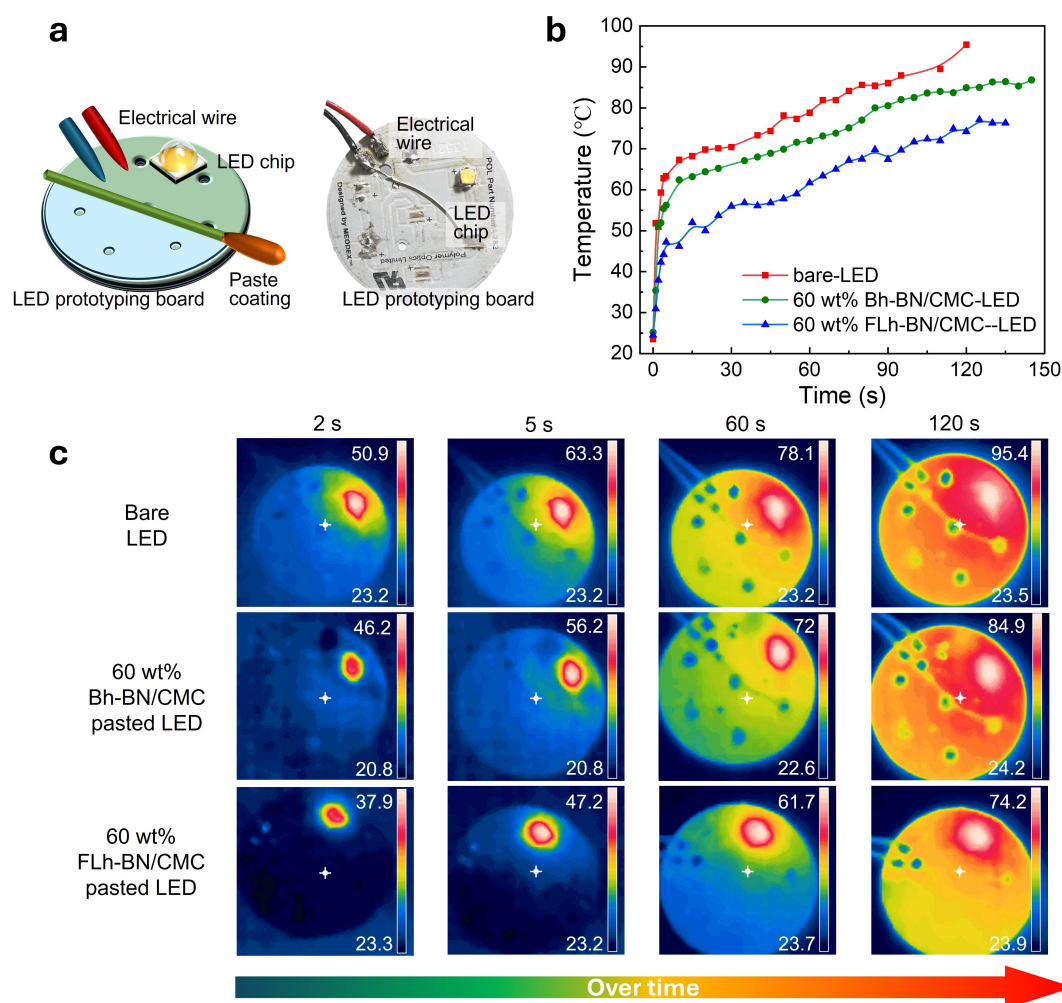


Fig. 6.11 Use of the as-prepared pastes for heat dissipation enhancement of a high-power LED chip: (a) schematic illustration of a soldered LED chip attached with a paste, with a real test image; (b) the recorded LED core temperature evolution over time without (red) or with (green: Bh-BN/CMC; blue: FLh-BN/CMC) the pastes, (g) infrared thermal images of the temperature evolution of the soldered LED chip over time. Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

6.5.3 Enhanced heat dissipation of thermally coating textiles

Another promising application in the thermal management pertains to heat dissipation in textile-based industries, such as personal wear [446]. Heat stress has an adverse impact on personal health and reduces work productivity, but the heat transfer of current textile materials is poor [446]. Therefore, it is crucial to develop and promote advanced textile technologies for regulating personal thermal comfort [447]. In the field of advanced textiles with passively regulating heat conduction properties, there are generally two categories: conductive cooling textiles with an enhanced κ and conductive warming textiles with a reduced κ [448]. The high κ of the h-BN-based composites obtained in this work is promising for the conductive cooling textiles.

One way to introduce a conductive cooling effect to textiles is to apply thermally conductive materials as layered coatings on the fibre surface [449]. For example, Abbas et al. [449] applied a resin coating containing multi-walled CNTs onto the surface of cotton fabrics. They reported an improved κ of the fabric by 150 % if coated with 50 % of multi-walled CNTs, and the coated fabric demonstrated a 3.9 °C lower equilibrium surface temperature than the uncoated fabric if being contact with a 50 °C surface [449].

Additionally, thermally conductive materials can be embedded within the fibre structures of textiles to offer improved heat conduction, which is considered a more durable alternative for the human body conductive cooling [448]. For example, Wu et al. [450] fabricated a cellulose-BNNT textile with an excellent axial κ of 2.9 W m⁻¹ K⁻¹, which demonstrated much better static and dynamic personal cooling effects than commercial cotton textiles because the textile emits much higher heat radiation if being contact with the body skin.

6.5.3.1 Enhanced cooling effect by an FLh-BN-based composite coated textile

As shown in Figure 6.12(a), a piece of non-woven cotton (0.035 W m⁻¹ K⁻¹) textile was coated using the FLh-BN/CMC pastes to form a thermally conductive film. The FLh-BN/CMC coated textile and an uncoated piece of textile (used as a control sample) were placed above a heater and their equilibrium (average) temperatures were recorded using the infrared thermal imager. The measurements were repeated 3 times (Figure A.8 in Appendix A).

Figures 6.12(b-e) show the infrared images of the FLh-BN coated (left) and uncoated textiles (right) at the nominal heater temperatures of 44, 55, 66, and 76 °C, respectively. In contact with the hot surface at all tested temperatures, the FLh-BN coated textile demonstrates a lower

equilibrium temperature by ~ 3.2 °C, 4.4 °C, 7.9 °C, and 12.8 °C, respectively, compared to the uncoated piece. The large reduction of the equilibrium surface temperature of the coated textiles indicates better heat conduction due to the surface coating of the thermally conductive FLh-BN/CMC composite.

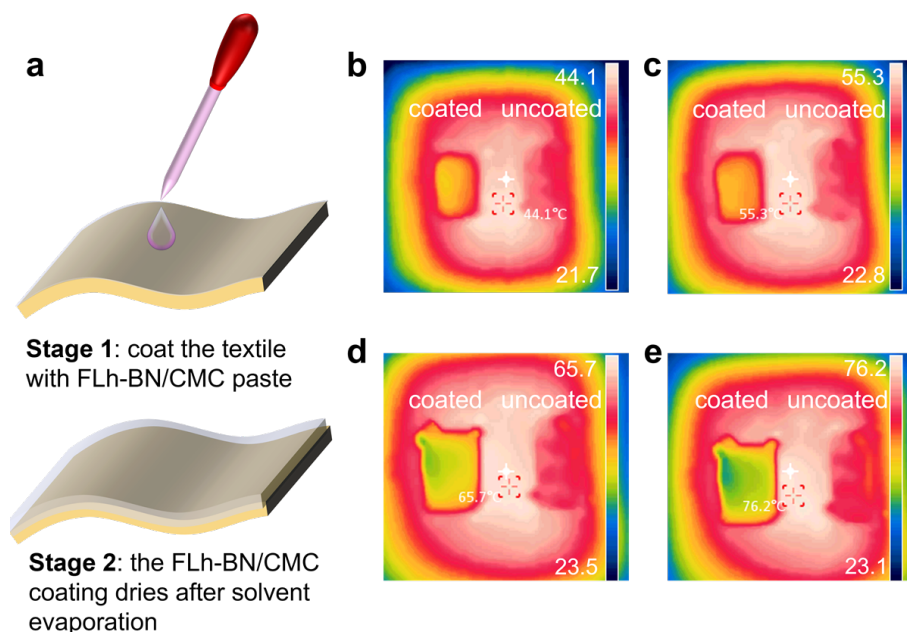


Fig. 6.12 Use of the FLh-BN/CMC pastes as thermal coatings for thermally conductive cooling textiles. (a) Schematic illustration of paste coating on a textile; (b-e) the equilibrium temperature comparison between a coated textile (left) and an uncoated textile (right) above the same heater at different temperatures (b-44 °C; c-55 °C; d-66 °C; e-76 °C). Image adapted with permission [11]. © 2024 Yao, et al. Advanced Functional Materials published by Wiley-VCH GmbH. The image is under the terms of the Creative Commons CC BY license.

6.5.3.2 Enhanced κ by an FLh-BN embedded polymer fibre

Figure 6.13 shows a thermally conductive fibre made by extrusion of the FLh-BN/CMC pastes. The extrusion process was done by Sihui Liu. The FLh-BN/CMC paste was transferred into a syringe and injected into a rotated glacial acid coagulation bath. The paste was squeezed at 2 mg h^{-1} . The fibre was then collected from the coagulation bath and dried. 3 replicates for each sample were performed to minimise the experimental errors. The FLh-BN/CMC fibre exhibited a mean diameter of $81.7 \text{ }\mu\text{m}$ and achieved a κ of $12.5 \pm 2.7 \text{ W m}^{-1} \text{ K}^{-1}$. This value is 10 times higher than that of an equivalent CMC fibre ($1.4 \pm 0.2 \text{ W m}^{-1} \text{ K}^{-1}$).

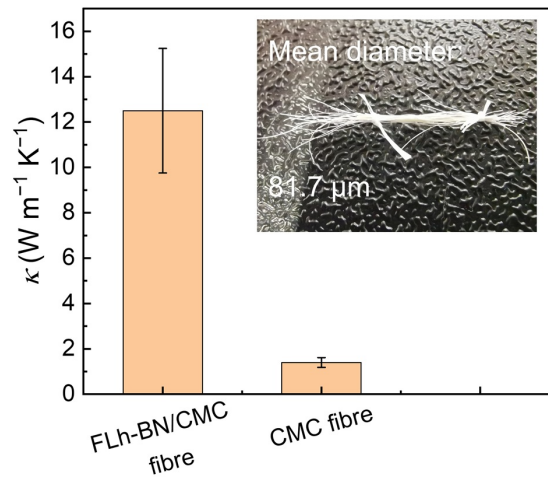


Fig. 6.13 The κ enhancement of the FLh-BN/CMC in the form of a fibre.

6.6 Conclusion

Commercial thermally conductive dielectric materials in electronic packaging typically exhibit κ ranging from 0.8 to 4.2 $\text{W m}^{-1} \text{K}^{-1}$. h-BN flakes are promising thermally conductive materials for the thermal management of next-generation electronics. A cellulose-based composite embedded with FLh-BN flakes was prepared using a cost-effective and scalable procedure, achieving a $\kappa \sim 21.7 \text{ W m}^{-1} \text{K}^{-1}$. This value is > 5 times higher than the κ observed in composites embedded with Bh-BN ($\kappa \sim 4.5 \text{ W m}^{-1} \text{K}^{-1}$), indicating the benefits of the superior κ of FLh-BN on the κ of h-BN polymer composites. When applied as a paste for TIMs, the FLh-BN composite can reduce the maximum temperature (T_{max}) by 24.5 °C of a heating pad at a power density (h) of 2.48 W cm^{-2} compared to Bh-BN composites at the same h-BN loading. The results provide an effective approach to improve the κ of cellulose-based thermal pastes for TIMs and demonstrate their viability for heat dissipation in ICs and high-power electronic devices. The key novelties are summarised as follows"

(1) The vast majority of the results published on the κ of h-BN/polymer composites are obtained from samples in the form of films or fibres. On the contrary, more than 75% of commercial TIMs for heat dissipation in electronics (by far the largest market of thermally conducting composites) are mainly in the form of thermal pastes rather than in the form of films or fibres. Thermal pastes can fill in any microscopic gaps between the two surfaces, providing better surface contact and heat transfer than films do. In this work, a novel FLh-BN/polymer composite was fabricated in the form of thermal pastes with high κ and commercial viability compared to thermally conducting films reported in the literature.

(2) The compatibility of our composite with commercial thermally conducting pastes is demonstrated by designing a composite with rheological characteristics compatible with market requirements for TIMs.

(3) The proposed method for the production of the FLh-BN thermally conducting paste is simple and scalable with commercial relevance, involving only a one-pot mixing. Conversely, thermally-conducting films reported in the literature are not scalable. The composites reporting the highest κ yet require externally applied magnetic fields or techniques such as vacuum filtration or hot pressing/stretching, which are inappropriate and costly for commercial mass production.

Chapter 7

Stability and electrochemical analysis of MXenes for energy storage applications

The previous chapters focused on enhancing the durability and efficiency of energy storage devices by utilizing h-BN as dielectric and thermal interface materials. To further improve device performance, including capacitance, power, and energy densities, the electrochemical performance of the electrodes is a crucial factor. Therefore, this chapter investigates MXenes, another 2D material which can be highly conductive, as potential electrode candidates for energy storage devices.

This chapter discusses the key oxidation factors of Ti_2CT_x aqueous solutions, including the presence of water and oxygen, the light illumination, and the storage temperatures. Keeping the solutions isolated from light at 4 °C and exchanging the dissolved O_2 in water by filling N_2 can extend the shelf-life of the Ti_2CT_x aqueous solution from 3 days to over 2 months. The charge transport mechanism of the Ti_2CT_x is studied to better understand its electronic properties, and is found to be compatible with the 2D-Mott VRH hopping mechanism. Compared to Ti_2CT_x , $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits metallic behaviour with high electrical conductivity. The addition of $\text{Ti}_3\text{C}_2\text{T}_x$ into the carbon-based electrode materials for textile-based supercapacitors has been investigated. These supercapacitors are electrochemically stable between ± 2.6 V and demonstrate a maximum areal capacitance of 148.7 mF cm^{-2} , an energy density of $0.921 \text{ mWh cm}^{-2}$, and a power density of 1.01 mW cm^{-2} . The addition of MXenes improves the areal capacitance by 120% compared to carbon electrodes and a cycling performance over 2000 cycles without severe capacitance loss, enabling high-performance textile-based energy storage devices.

7.1 Synthesis and characterisation of MXenes

7.1.1 Synthesis of mono-layer and few-layer MXene solutions

The $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x MXenes are separately synthesised from MAX phase (Ti_3AlC_2 and Ti_2AlC) powders (Carbon-Ukraine Ltd.) using the in-situ HF route through the addition of LiF into HCl, which is a simplified and safe synthesis method improving MXene performance in energy storage applications [33, 153]. As reported in [37], HCl (12 M) is added into DI water in a vented polyethene (HDPE) container, followed by adding the LiF powder into the solution. The mixture is stirred for 5 minutes using a magnetic PTFE bar to dissolve the salt fully. The MAX powder is then carefully added to the solution for over 10 minutes to avoid initial overheating by aggressive exothermal reactions. The container is then immersed in a silicon oil bath to allow a selective Aluminium etching. The exact amount of used chemicals in the recipe can be found in Table 7.1.

Table 7.1 Synthesis recipes of $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x

Name of MXenes	Synthesis parameters					
	H_2O (mL)	HCl (mL)	LiF (mg)	MAX (mg)	Temperature (°C)	Time (hours)
$\text{Ti}_3\text{C}_2\text{T}_x$	6.0	14.0	1.5	1.0 (Ti_3AlC_2)	45	24
Ti_2CT_x	4.8	11.2	1.0	0.9 (Ti_2AlC)	25	15

After the etching process, the mixture is washed for 3-4 cycles via centrifugation (GT2R centrifuge, Fisher, TX-400 rotor) until the pH of the supernatant reaches approximately 6. In each washing cycle, the solution is added with DI water and centrifuged at 800-3000 rcf for 5 minutes. The supernatant is discarded, and the sediment is redispersed in DI water for the next washing cycle. After the final washing cycle, the collected sediment is "clay"-like multilayer MXenes (m-MXenes).

The m-MXenes can be fully redispersed in DI water and be manually shaken (MILD method [157]) to allow delamination of m-MXenes flakes. The suspension is centrifuged at 800 rcf for 10 minutes, and the supernatant is collected as the delaminated MXenes (d-MXenes) solution.

7.1.2 Characterisation of the MXenes flakes

XRD patterns were acquired by a Bruker diffractometer (D8 advance, AXS system), scanning within a 2θ range from 5° to 70° at a step scan of 0.02° , with a fixed slit size of 0.6 mm. The XRD samples were deposited as thin films on pre-cleaned. Other characterisation methods, including OAS, Raman, XPS, AFM and SEM, have been described in the sub-subsection 5.1.1.

7.1.2.1 Optical characterisation

Figure 7.1 shows the optical absorption spectrum of (a) $\text{Ti}_3\text{C}_2\text{T}_x$ and (b) Ti_2CT_x acquired in the UV-Vis-NIR region. For $\text{Ti}_3\text{C}_2\text{T}_x$, there are two peaks centred at ~ 270 and ~ 325 nm, respectively, which originate from the smaller flakes (lateral size of $\sim 0.3 \mu\text{m}$) and larger flakes (lateral size of $\sim 0.8 \mu\text{m}$) [317, 451], respectively. The broad peaks at ~ 770 nm are due to the plasmonic effects of $\text{Ti}_3\text{C}_2\text{T}_x$ [452], which gives its aqueous solution the green colour [204] and suggests the high quality and conductive nature [329, 453]. In contrast, the Ti_2CT_x has a plasmonic peak at ~ 520 nm, which gives its aqueous solution the vine colour [204].

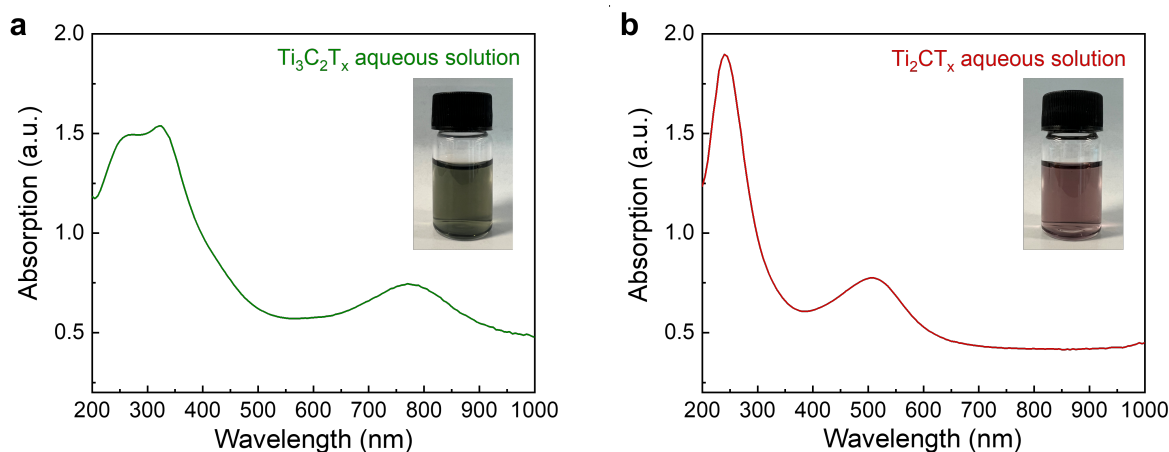


Fig. 7.1 OAS analysis of $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x aqueous solutions. UV-Vis-NIR spectrum of (a) $\text{Ti}_3\text{C}_2\text{T}_x$ and (b) Ti_2CT_x aqueous solutions, with upper-right inset images showing the real solutions.

7.1.2.2 Flake size characterisation by SEM and AFM

Figure 7.2 shows the SEM images of m-MXenes (a, b) and d-MXenes (c, d), illustrating the difference of layer numbers visibly between m-MXenes and d-MXenes. The SEM images

were acquired using a Zeiss LEO Gemini 1525 FEG-SEM and collected in a secondary electron detection mode using the In Lens and SE2 detectors. Figures 7.2(a,b) show that the m-MXenes are observed as the flakes stacked together from a side view after Al was etched away from the MAX phases. Figures 7.2(c,d) show the single-layer d-MXenes flakes, which are fully delaminated from the m-MXenes. The outside layer of the Ti_2CT_x single layer is formed with TiO_2 nanoparticles (higher brightness in Figure 7.2(d)). The single d-MXenes flakes are further characterised by the flake thickness and lateral size by AFM.

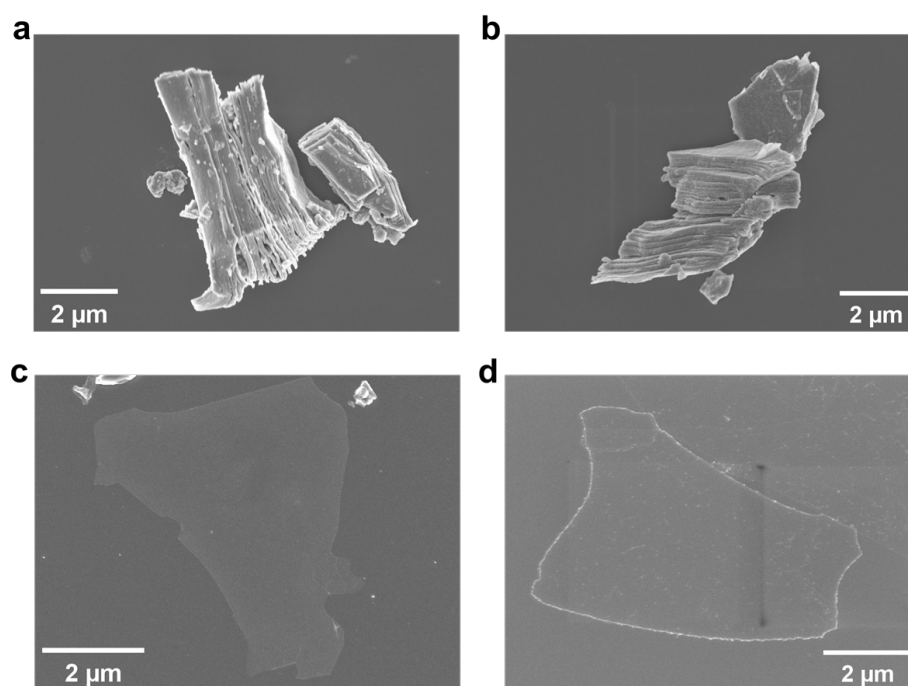


Fig. 7.2 SEM images of m-MXenes (a) $\text{Ti}_3\text{C}_2\text{T}_x$ and (b) Ti_2CT_x ; SEM images of d-MXenes, a single flake of (c) $\text{Ti}_3\text{C}_2\text{T}_x$ and (d) Ti_2CT_x .

Figure 7.3 shows the AFM statistics used to estimate the thickness ($\langle t \rangle$) and lateral size ($\langle S \rangle$) distribution of the MXene flakes. The AFM sample was prepared by drop-casting a diluted ink (0.01 mg mL^{-1}) onto a pre-cleaned Si/SiO_2 substrate. AFM analysis was collected separately from 89 $\text{Ti}_3\text{C}_2\text{T}_x$ flakes and 38 Ti_2CT_x flakes, using the Keysight 5500 SPM AFM (Keysight Technologies). Measurements were scanned on a $20 \mu\text{m} \times 20 \mu\text{m}$ area at a scanning rate of 0.40 Hz using a point probe (Silicon-SPM-Sensor, PPP-NCLR-50, Nano-sensors) operating in a tapping mode.

Figure 7.3(a) shows that the statistics of $\langle t \rangle$ and $\langle S \rangle$ for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene both follow a log-normal distribution peaked at 2.61 nm and $2.81 \mu\text{m}$, respectively. From density functional theory (DFT) calculations with transmission electron microscopy (TEM) studies, the thickness of a monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake is 0.98 nm [454]. Experimentally, Lipatov et

al. identified a $\text{Ti}_3\text{C}_2\text{T}_x$ flake relative to Si/SiO_2 substrates with a thickness of 2.7 nm as a monolayer flake. They also observed the height of the folded region of the same flake relative to the rest of the flake is around 1.5 nm, which corresponds to a monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake [157, 455]. The larger height (2.7 nm) of the flake relative to the Si/SiO_2 substrate can be attributed to the water molecules trapped under the monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake and a great amount of terminated functional groups attached to the surface of the flake [37]. The AFM statistics indicate the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$ solution consists of $\sim 70\%$ monolayer and bilayer flakes. Figures 7.3(b, c) present a high-resolution AFM image for a monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake with a $\langle t \rangle$ of 2.43 nm and a $\langle S \rangle$ of 2.5 μm .

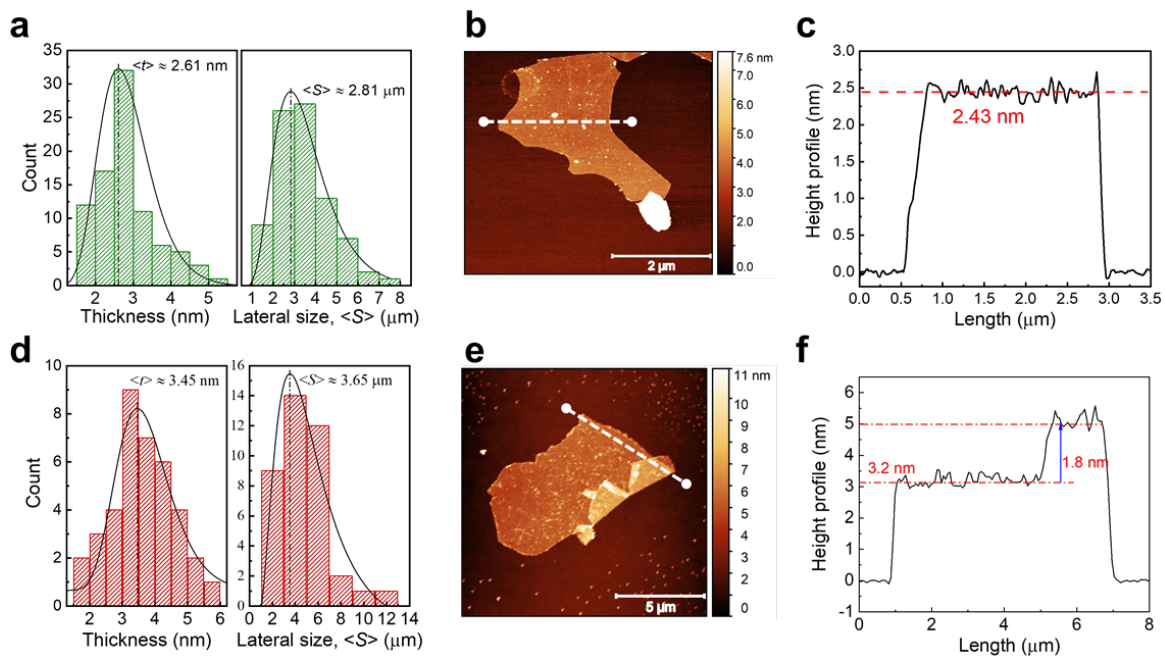


Fig. 7.3 Flake size analysis of MXenes via AFM. (a) AFM statistics on the thickness and lateral size over 89 $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, (b) a typical monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake and (c) its height profile over the lateral length; (d) AFM statistics on the thickness and lateral size over 38 Ti_2CT_x flakes, (e) a typical monolayer Ti_2CT_x flake and (f) its height profile over the lateral length.

Figure 7.3(d) shows that the statistics of $\langle t \rangle$ and $\langle S \rangle$ for Ti_2CT_x MXene also both follow a log-normal distribution peaked at 3.45 nm and 3.65 μm , respectively. Figures 7.3(e, f) present a high-resolution AFM image for a folded Ti_2CT_x flake with a $\langle t \rangle$ of 3.2 nm and a $\langle S \rangle$ of 6.6 μm . The thickness of the folded part relative to the flake is 1.8 nm, which indicates it is mono-layer. The additional thickness of 1.4 nm can be attributed to the water molecules trapped between the flake and the substrate.

7.1.2.3 Structural quality by Raman spectrums

Raman spectroscopy is used to monitor the structural quality of MXenes. Figure 7.4(a) shows the Raman spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (green plot) compared to its MAX precursor Ti_3AlC_2 (black plot). $\text{Ti}_3\text{C}_2\text{T}_x$ shows two broad resonant regions, denoted as the T_x region between ~ 223 and $\sim 480 \text{ cm}^{-1}$ and the C region between ~ 503 and $\sim 750 \text{ cm}^{-1}$ [329]. The convoluted peaks in the T_x region originate from the in-plane E_g vibrations of functional surface groups, while the convoluted peaks in the C region are caused by both in-plane E_g vibrations and A_{1g} out-of-plane vibrations of the carbon atoms. An additional peak appears at $\sim 205 \text{ cm}^{-1}$ and is caused by an A_{1g} out-of-plane vibrational mode that originates from the Ti atoms and functional $-\text{OH}$, $-\text{O}$ and $-\text{F}$ surface groups [456].

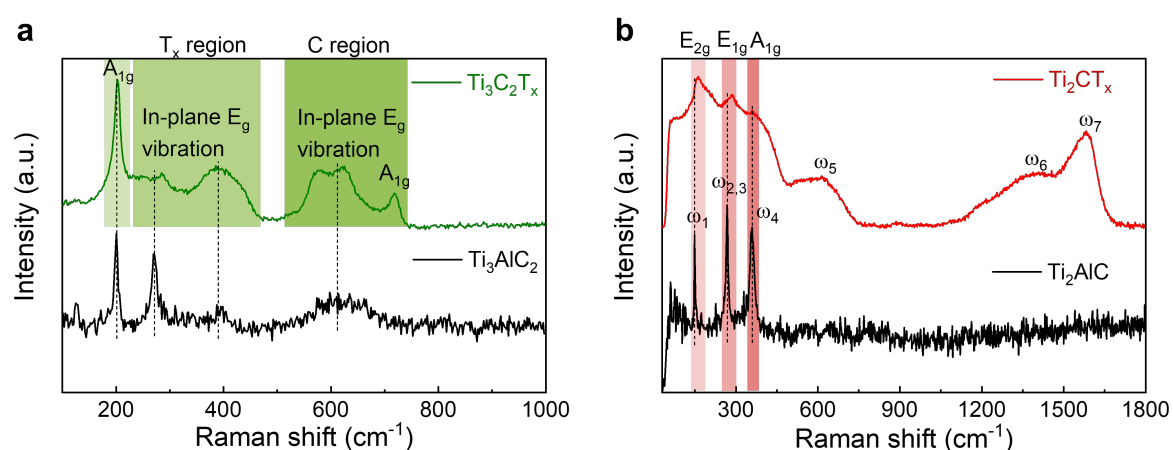


Fig. 7.4 Raman spectrum of (a) $\text{Ti}_3\text{C}_2\text{T}_x$ (green curve) and Ti_3AlC_2 (black curve); (b) Ti_2CT_x (red curve) and Ti_2AlC (black curve).

Figure 7.4(b) shows the Raman spectra of Ti_2CT_x (red curve) and Ti_2AlC (black curve). The peaks observed for Ti_2AlC (ω_1 , $\omega_{2,3}$ and ω_4) correlate to the Raman active modes of E_{2g} , E_{1g} , and A_{1g} , respectively [457], which originate from the shear and longitudinal vibrations of the Ti and the Al atoms [458]. The slightly weak broad peak (ω_5) at $\sim 616 \text{ cm}^{-1}$ may be attributed to non-stoichiometric TiC_x [458]. The peaks of Ti_2CT_x are upshifted and broadened, which indicates the successful etching of the Al atom from Ti_2AlC phase (as validated from XRD patterns in the section below) and the termination of functional groups [459]. The two peaks (ω_6 and ω_7) observed at 1340 cm^{-1} and 1576 cm^{-1} originate from the D and G bands of amorphous carbon, respectively, which indicates the existence of free carbon in the disordered Ti_2CT_x after the etching and exfoliation process [460].

7.1.2.4 The degree of etching and delamination by XRD patterns

XRD is used to indicate the degree of etching and delamination. Figure 7.5(a) shows XRD patterns of the delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ (light green curve), multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ (dark green curve), and the Ti_3AlC_2 (black curve). The disappearance of the non-basal plane peaks of Ti_3AlC_2 (39°) in the XRD peaks of $\text{Ti}_3\text{C}_2\text{T}_x$ indicates the successful removal of Al. All observed peaks of $\text{Ti}_3\text{C}_2\text{T}_x$ are attributed to the basal-plane diffraction [31]. The first (002) peak of the multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ down-shifts to $2\theta = 7.7^\circ$ compared to that of Ti_3AlC_2 at $2\theta = 10^\circ$ [31]. The first (002) peak is also less ordered, indicating that the interlayer spacing of $\text{Ti}_3\text{C}_2\text{T}_x$ becomes larger after Ti_3AlC_2 is etched [461]. The further downshift and of the first (002) peak of the delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ compared to that of multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ revealed that the restacked structure of MXene nanosheets has more $-\text{OH}$ groups to form a higher hydration state [461]. The (002) characteristic peak of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ is also less ordered, indicating that the interlayer spacing becomes larger after the MILD exfoliation [153].

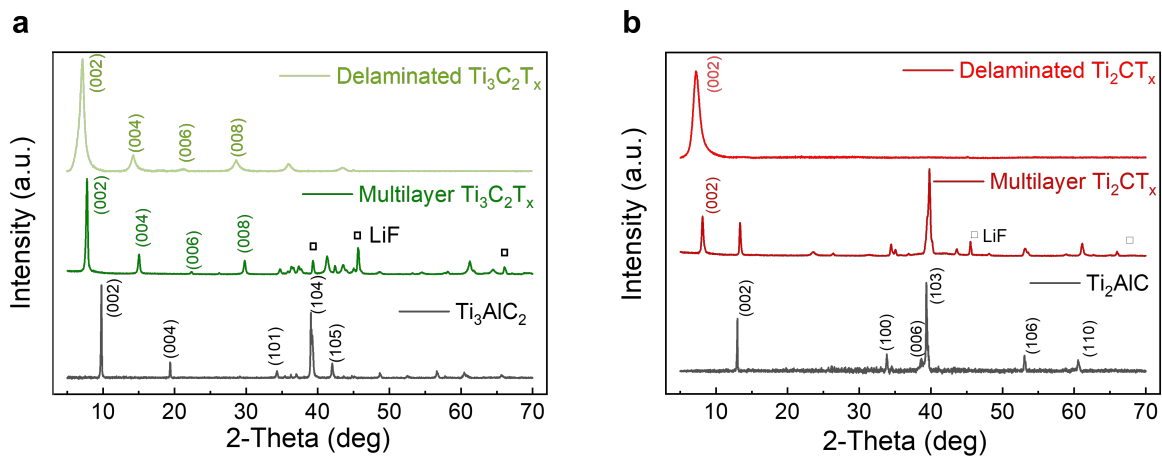


Fig. 7.5 XRD patterns of (a) delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ (light green curve), multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ (dark green curve) and Ti_3AlC_2 (black curve); (b) delaminated Ti_2CT_x (light red curve), multilayer Ti_2CT_x (dark red curve) and Ti_2AlC (black curve).

Figure 7.5(b) presents the XRD patterns of delaminated Ti_2CT_x (light red curve), multilayer Ti_2CT_x (dark red curve) and Ti_2AlC (black curve). Most peaks of Ti_2AlC lost intensity, and the (002) peak of the multilayer Ti_2CT_x is shifted to a lower angle at $2\theta = 8.1^\circ$ ($10.7 \text{ \AA}$), compared to that of Ti_2AlC ($2\theta = 13^\circ$), which indicates the successful etching of the Al atom [462]. The further downshift of the characteristic (002) peak to $2\theta = 7.2^\circ$ ($12.4 \text{ \AA}$) indicates the delamination of the m-MXenes into single-layer flakes [153]. The remaining peaks of Ti_2AlC phase, such as the peak at 13° in the multilayer, suggest the MAX phase was only partially etched.

7.1.2.5 Stoichiometry characterisation by XPS spectrum

XPS is used here to assess their stoichiometry. Figure 7.6 shows the XPS spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, including the high-resolution spectrum of (a) Ti 2p and (b) C 1s. The Ti 2p region comprises three doublet peaks. The Ti(II) and Ti(III) peaks are attributed to the formation of termination groups like $-\text{O}$, $-\text{OH}$, and $\text{OH}-\text{H}_2\text{O}$ [456]. The asymmetric Ti-C (Ti2p3, ~ 454.7 eV; Ti2p1, ~ 460.0 eV) peaks are shifted to a larger BE compared with its precursor Ti_3AlC_2 phase (Ti-C 2p3, ~ 454.6 eV) [463]. This is attributed to the Al atom in the MAX phase powder being replaced by more electronegative termination. The C 1s region consists of two non-doublet peaks. The graphitic C-C formation (~ 284.3 eV) occurs due to the selective dissolution of Ti during etching, and the sharp peak at ~ 281.8 eV belongs to the Ti-C bond which indicates the high quality of the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$. For Ti_2CT_x , the Ti-O (Ti 2p3, ~ 458.0 eV; Ti 2p1, ~ 464.4 eV) originates from the oxidation of the Ti_2CT_x at the edges forming Ti-O or Ti-OH terminations and TiO_2 aggregates [458, 464].

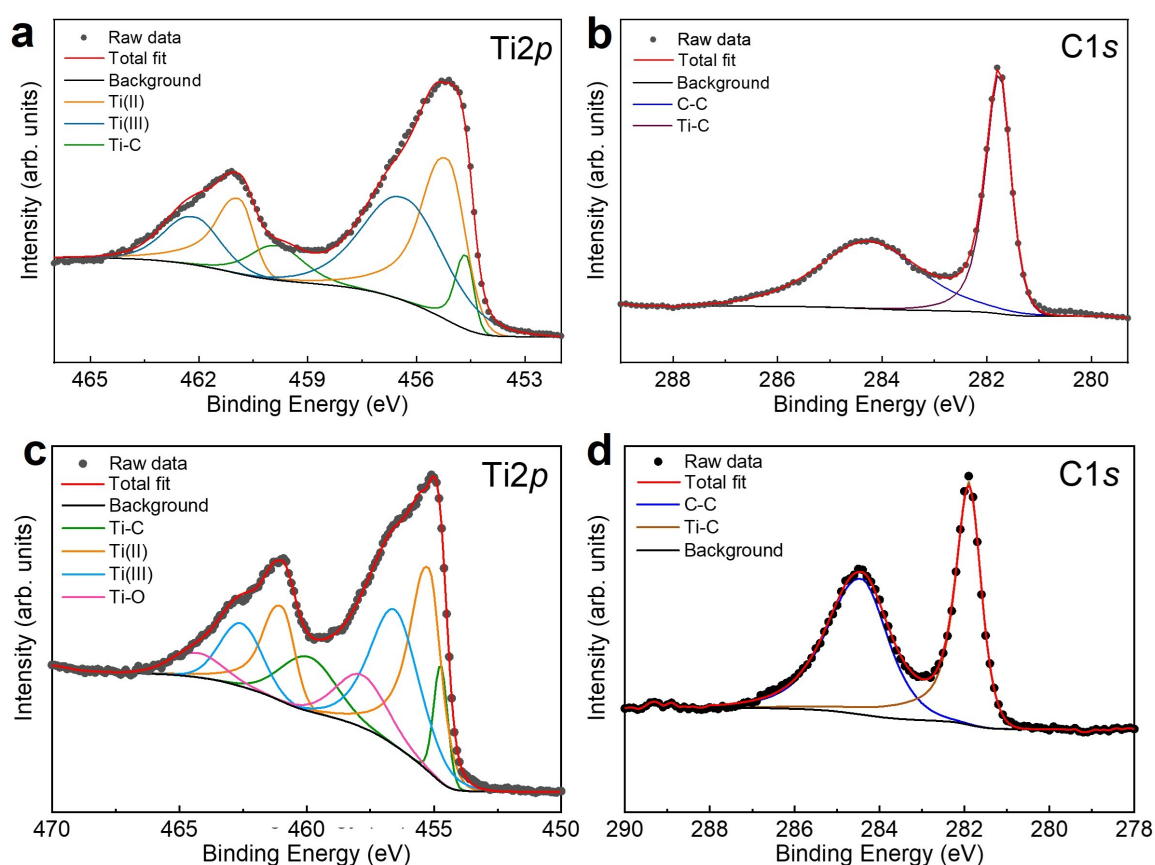


Fig. 7.6 XPS spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, including the high-resolution spectrum of (a) Ti 2p, (b) C 1s, and XPS spectra of Ti_2CT_x of (c) Ti 2p and (d) C 1s.

7.1.3 Conductivity analysis of the MXene film

The as-prepared MXene suspensions' capability for spray-coating transparent and conductive patterns is assessed. The sheet resistance (R_s) and optical transmittance ($T\%$) of the spray-coated films are measured on a transparent substrate. The transparent substrate was UV/Ozone-treated borosilicate glass, featuring a surface roughness < 15 nm with an optical transmittance of approximately 99% (Pyrex 7740-Polished Prime grade). The $T\%$ within a flat UV region is considered and compared (550 nm and 700 nm for the $\text{Ti}_3\text{C}_2\text{T}_x$ film and the Ti_2CT_x film, respectively) to avoid the effect from plasmonic influence.

Figure 7.7 plots the relation between $T\%$ and R_s of the $\text{Ti}_3\text{C}_2\text{T}_x$ film (a) and the Ti_2CT_x film (b). For the $\text{Ti}_3\text{C}_2\text{T}_x$ film, when the film $T\%$ is 85 %, the corresponding R_s is 10 k Ω/sq , and when the film becomes thicker and more conductive to $R_s \sim 1$ k Ω/sq , the $T\%$ declines slowly to 80 %. When the film reaches ~ 100 Ω/sq , similar to that of bulk MXene materials (unexfoliated), the $T\%$ decreases to ~ 50 %. A thick film with almost no $T\%$ could reach R_s a few Ω/sq . The Ti_2CT_x film shows a similar trend of the correlation between the film $T\%$ and the film R_s as that of the $\text{Ti}_3\text{C}_2\text{T}_x$ film but exhibits a higher R_s at the same $T\%$ value.

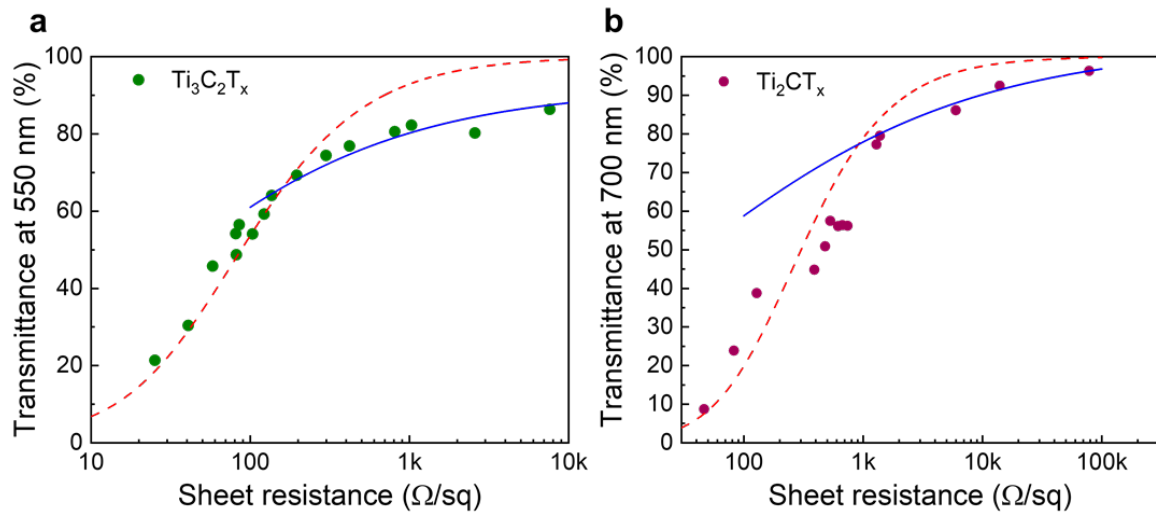


Fig. 7.7 Transmittance analysis verse sheet resistance of the MXene film, (a) $\text{Ti}_3\text{C}_2\text{T}_x$ and (b) Ti_2CT_x , with the dashed lines showing the bulk region fitting and the solid lines representing the percolation region fitting of the conductivity.

The film $T\%$ represents the film thickness to some extent. Below some critical thickness, the nanostructured film stops behaving like bulk, and the conductivity decreases with a decreasing thickness [465]. This phenomenon has been described for networks of nanotubes, nanowires, and graphene sheets [74, 465]. Such behaviour can be attributed to a deviation from bulk-like behaviour for thin films, which is electrical percolation [465]. Percolation

is the onset of conductivity across a previously insulating region once conducting links have been added at a density exceeding some critical value, the percolation threshold. As more links are added, new conducting paths are formed and the conductivity increases. The bulk-like and the percolation for the conductivity behaviour can be described as follows [465], respectively:

$$T = \left(1 + \frac{Z_0 G_0}{2R_s \sigma_{\text{bulk}}}\right)^{-2} \quad (7.1)$$

$$T = \left(1 + \frac{1}{\Pi} \left(\frac{Z_0}{R_s}\right)^{\frac{1}{n+1}}\right)^{-2} \quad (7.2)$$

where $Z_0 = 377 \, \Omega$ is the free-space impedance, $G_0 \sim 6 \times 10^{-5} \, \Omega^{-1}$ is the universal optical conductance, Π is the percolative figure of merit [74, 465], and n is the percolation exponent.

The plots are fitted with the dashed lines representing the bulk regime using Equation 7.1 and the solid lines representing the percolative regime using Equation 7.2. The experimental $T\%$ deviates from the dashed lines (bulk-like conductivity behaviour) for $T > 70\%$ and $T > 80\%$ for the $\text{Ti}_3\text{C}_2\text{T}_x$ film and the Ti_2CT_x film, respectively, above which is a percolative conductivity behaviour.

Factors affecting percolative behaviour

Given the equation 7.2, Π is a dimensionless number where large values of Π give low R_s coupled with high $T\%$. This means the critical thickness for the percolation threshold is small at large values of Π . Π can vary with the amount, size and shape of the material [196, 465]. For example, De, et al. demonstrated that the shape and lateral size reduction of a conducting nanostructure AgNWs could result in a higher percolative Π . Alternatively, thin metal platelets could also produce good-quality films with a high percolative Π [465] compared to conducting flakes (graphene and silver nanoparticles). Apart from Π , the percolation exponent ε also affects the percolative behaviour. ε is related to the dimension of the film system and is expected to increase with particle size and decrease with the concentration of conductive particles per unit area [466, 467]. A high ε gives low R_s coupled with high $T\%$. Therefore, the MXene flakes with a high aspect ratio (larger flake lateral size) could reduce the percolation threshold [196], meaning fewer flakes are needed to form a continuous conductive network. Elongated or large flakes can span greater distances and connect more easily to neighbouring flakes, facilitating the formation of a conductive pathway.

Factors affecting mechanical properties

Lipatov, et al. reported that the $\text{Ti}_3\text{C}_2\text{T}_x$ monolayers exhibited a high Young's modulus of 0.33 ± 0.03 TP [468]. The large size of individual flakes is expected to translate into improved electrical and mechanical properties of MXene films [196]. Larger, more elongated

flakes (high aspect ratio) provide better reinforcement because they offer more surface area for interaction and better stress distribution. Shekhirev, et al. claimed that the $\text{Ti}_3\text{C}_2\text{T}_x$ bilayers show higher elasticity values ($326 \pm 29 \text{ N/m}$) than the $\text{Ti}_3\text{C}_2\text{T}_x$ mono-layer ($655 \pm 19 \text{ N/m}$). If forming MXene films, the mechanical properties are also affected by the film thickness (amount of materials) and flake size. For example, Luo, et al. found that when the film thickness increases from 2.3 to 17 μm , the tensile strength and elastic modulus drop from 61 to 36 MPa and from 17 to 8 GPa, respectively, which can be attributed to more structural defects presented in the through-the-thickness direction as the film thickness is increased [469]. Luo, et al. also found the $\text{Ti}_3\text{C}_2\text{T}_x$ film consisting of smaller flake sizes via moderate ultrasonication pretreatment improved the compactness of the film, enabling the film exhibiting a linear stress-strain relationship without plastic-like deformation and the resulting tensile strength is enhanced to 85 MPa by 24 MPa for the 5 μm thick $\text{Ti}_3\text{C}_2\text{T}_x$ film.

7.2 Improved storage conditions of MXenes solutions

Because the as-obtained MXenes are always in a thermodynamically metastable state [40], they tend to react with trace oxygen or oxygen-containing groups to form metal oxides or degrade, leading to a sharply declined activity and impaired performance. This largely restrains their practical applications. Therefore, it is essential to investigate the stability (i.e. oxidation rate) of the MXene aqueous solution, and propose strategies to enhance the stability.

In this section, the observed oxidation phenomenon of the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x aqueous solutions, the main factors that promote the oxidation rate and accordingly the best storage conditions will be discussed.

7.2.1 Stability and oxidation phenomenon of MXenes by OAS

The optical absorption intensity in the UV-Vis-NIR region of the as-synthesised MXene suspensions was utilised in this work to examine the oxidation behaviour, which is regarded as the most straightforward evaluation method [39]. Figure 7.8 shows the UV-Vis-NIR absorption intensity decay over time of the as-prepared MXene ($\text{Ti}_3\text{C}_2\text{T}_x$ (a) and Ti_2CT_x (b)) aqueous solutions. The fresh $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous solution contains both the smaller flakes ($\langle S \rangle \sim 0.3 \mu\text{m}$) and larger flakes ($\langle S \rangle \sim 0.8 \mu\text{m}$) with the peaks at ~ 270 and $\sim 325 \text{ nm}$, respectively [317]. As time goes by, the relative intensity of these two peaks changes, and the plasmonic peak red-shifts and decays. From day 26, the peak at $\sim 325 \text{ nm}$ almost disappears.

From day 34, the peak at ~ 270 nm is broadened, and the plasmonic peak weakens, indicating the large portion of TiO_2 generation [470]. That is because the surface terminations on the flakes change initially, resulting in the change in the electronic structure and charge density of MXenes and shifts in the plasmonic resonance frequency. When the flakes begin to oxidise into TiO_2 , the intensity of the flake peaks at lower wavelengths weakens, and the plasmonic resonance decreases and disappears.

Compared to the oxidation rate of $\text{Ti}_3\text{C}_2\text{T}_x$ being a month, the oxidation rate of Ti_2CT_x is faster within 3 days. The fresh Ti_2CT_x aqueous solution has a narrow peak at ~ 230 nm and a wide plasmonic peak at ~ 520 nm. On day 2, the two peaks start to decay and get broadened, which fully decays on day 3. Compared to $\text{Ti}_3\text{C}_2\text{T}_x$ (the single layer of which has five-atom thickness), Ti_2CT_x (the single layer of which has three-atom thickness) produces CH_4 faster so that it is more susceptible to oxidation and is more unstable [319].

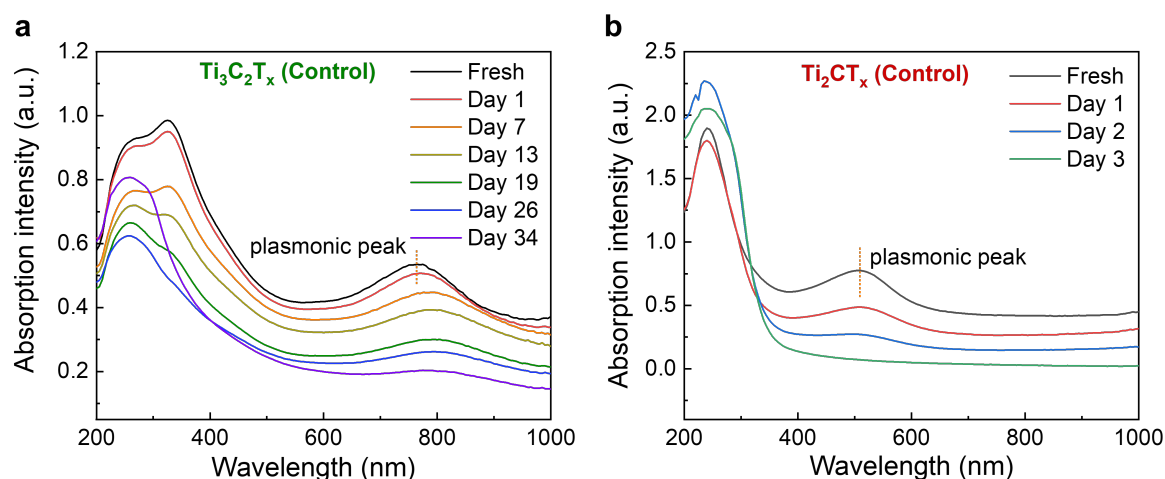


Fig. 7.8 UV-Vis-NIR absorption intensity decay over time of the MXene aqueous solutions stored at RT at ambient environment: (a) $\text{Ti}_3\text{C}_2\text{T}_x$ and (b) Ti_2CT_x .

AFM and SEM imaging are utilised to further characterise the oxidation phenomenon of the MXene flakes. Take Ti_2CT_x as an example. Figure 7.9 shows an AFM image and SEM images of a fresh Ti_2CT_x flake and oxidised flakes, with Raman tracing TiO_2 . A fresh flake (flake 1 in Figure 7.9(a) and Figure 7.9(c)) has a clear edge, whereas the oxidised flake has a rough edge with TiO_2 particles [314] (flakes 2-4 in Figure 7.9(a) and Figure 7.9(d)). The height profiles in Figure 7.9(b) compare the height difference between the fresh flake 1 and the oxidised flakes 2 and 4. Along the whole scanning lateral length, the height information within the flat region in the middle relative to the substrate (adjusted to ~ 0 nm) can be regarded as the flake thickness. Flake 1 (pink line) exhibits a thickness of 1.65 nm with a smooth step height at the edge relative to the substrate. However, Flake 2 (also 4, green

and blue lines) exhibits a thickness of 4.6 nm but with an additional 1 nm at the flake edges, indicating the flake edge is thicker and rough, which can be attributed to the formation of TiO_2 particles at the flake edge. Figure 7.9(c) confirms the existence of TiO_2 , with the observed peaks at 260 and 618 cm^{-1} , the Raman peaks of the rutile phase of TiO_2 [314]. Since the Raman traces are not obvious, I am contacting my collaborators to confirm the oxidation of a single Ti_2CT_x flake via TEM and ARPES characterisation.

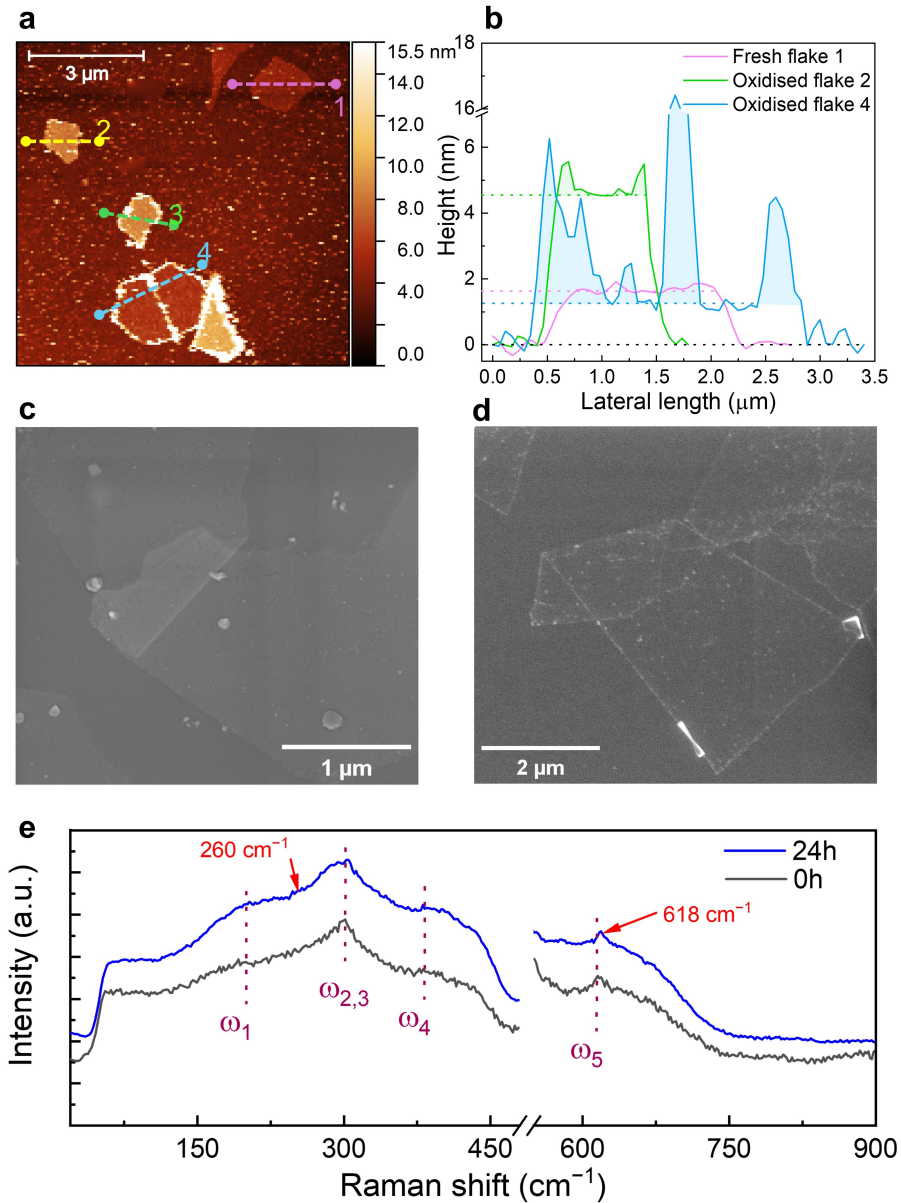


Fig. 7.9 Trace the oxidation of Ti_2CT_x flakes. An AFM image of fresh flakes and edge oxidised flakes (a) with their height profiles (b); SEM images of (c) a fresh Ti_2CT_x flake and (d) oxidised flakes, and (e) Raman spectrum of an oxidised Ti_2CT_x flake.

Overall, Figure 7.8 records the fast oxidation rate of $\text{Ti}_3\text{C}_2\text{T}_x$ (a) and Ti_2CT_x (b) aqueous solutions. The shelf-life of both MXenes is less than a month, which is way shorter compared to graphene suspensions [84], which can last for years. The fast oxidation rate of both MXenes is disadvantageous for the storage of MXenes suspensions and restricts their use in various applications [41]. Therefore, the following section takes Ti_2CT_x aqueous solutions, which are less studied compared to the $\text{Ti}_3\text{C}_2\text{T}_x$ solutions, as an example to analyse the main storage factors that drive the oxidation in the lab and propose related methods to prevent fast oxidation.

The exposure to light, the storage temperature, the dissolved O_2 and the chosen solvent are considered and analysed statistically, listed in Table 7.2. The light exposure is controlled by whether or not the solution is covered by an aluminium foil sheet, and the storage temperature is controlled by whether the solution is placed in the fridge (4°C) or on the bench (RT). The dissolved O_2 is controlled by whether the solution is open to air or sealed and exchanged with N_2 . For each comparison, 3 replicates were obtained to confirm the oxidation trend.

Table 7.2 Main factors controlled in the studies of oxidation of MXenes

Sample label	Controlled factors			
	Solvent /	Dissolved oxygen level /	Temperature ($^\circ\text{C}$)	Light exposure (hours/day)
Control	H_2O	saturated	20	12
L0	H_2O	saturated	20	0
L0-T4	H_2O	saturated	4	0
L0-T4- N_2	H_2O	~ 0 (N_2)	4	0
L0-T4-IPA	IPA	saturated	4	0
L0-T4-ethanol	Ethanol	saturated	4	0

Figure 7.10(a) schematically illustrates the setup of decreasing the dissolved O_2 level in the Ti_2CT_x MXene aqueous solution. The Ti_2CT_x MXene solution is stored in a sealed container to prevent gas exchange between the inner part of the container and the atmosphere. A long needle penetrates the sealing rubber into the solution, and the other side is connected to the compressed N_2 gas. Through the needle, the continuous N_2 bubbling in the solution pushes the O_2 out of the container through the short needle. The N_2 bubbling lasts for at least 6 minutes to ensure a complete gas exchange. Figure 7.10(b) shows a similar setup of how to extract the MXene solution from a sealed container. A syringe is connected to a long needle, which penetrates the sealing rubber into the solution and collects the solution by pulling, while the decreasing pressure in the container brought by the decline of liquid volume is compensated by pure N_2 from a balloon through a short needle.

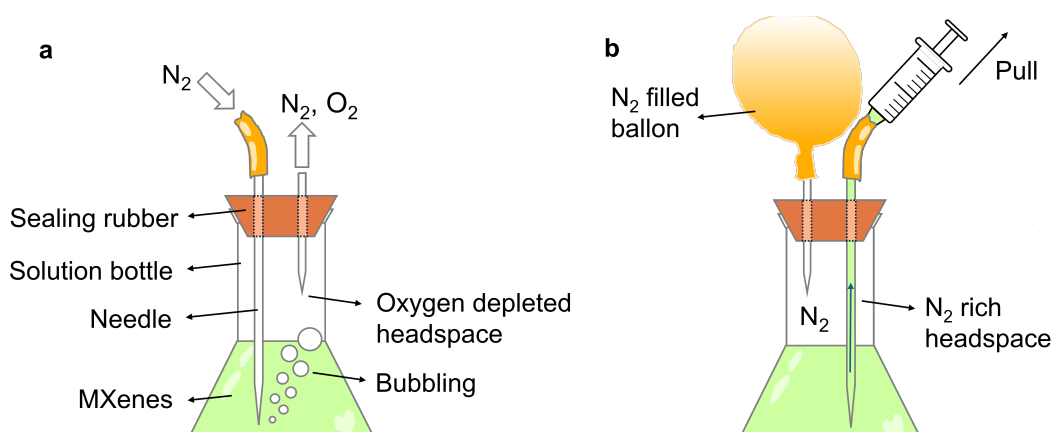


Fig. 7.10 Decrease the oxidation rate of Ti_2CT_x aqueous solutions by exchanging O_2 to N_2 via a custom-built setup. (a) Schematic illustration of the setup, using compressed N_2 flow to exchange the dissolved O_2 , and (b) the way to extract the N_2 filled sealed solution.

7.2.2 Storage temperature and light exposure

Figure 7.11(a,b) presents the UV-Vis-NIR absorption intensity decay of the L0 MXene solution (a) and of the L0-T4 MXene solution (b) over time. Compared to the control solution (Figure 7.8(b)), the isolation of the MXene solution from daylight slows down the oxidation rate of the solution to 4 days, but the impact is weak. If the solution is stored in the fridge (4°C) while being isolated from the light, the MXene solution can last longer and fully decays at day 7. The results are consistent with what has been found in the literature (lowering the storage temperature could improve the shelf-life of $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous colloidal solution [317]). However, compared to the shelf-life (over a month [317]) of $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous colloidal solution stored at 4°C , the shelf-life Ti_2CT_x aqueous colloidal solution stored at 4°C is still short within a week. More prevention steps are required to be explored.

7.2.3 The dissolved oxygen

Figure 7.11(c) presents UV-Vis-NIR absorption intensity decay over time of the oxygen-free Ti_2CT_x aqueous solution (L0-T4- N_2). The dissolved O_2 was fully removed by filling continuous N_2 flow for 6 minutes. There observed the dramatically decreased oxidation rate of the Ti_2CT_x aqueous solution. Both the absorption intensity, shape, and position of the plasmonic peak maintain almost no change after 72 days. It was validated by the Raman spectrum comparison (Figure 7.11(d)) of the film made from the fresh solution and the solution at Day 72, showing the same peak and peak position of ω_1 , $\omega_{2,3}$, ω_4 and ω_5 .

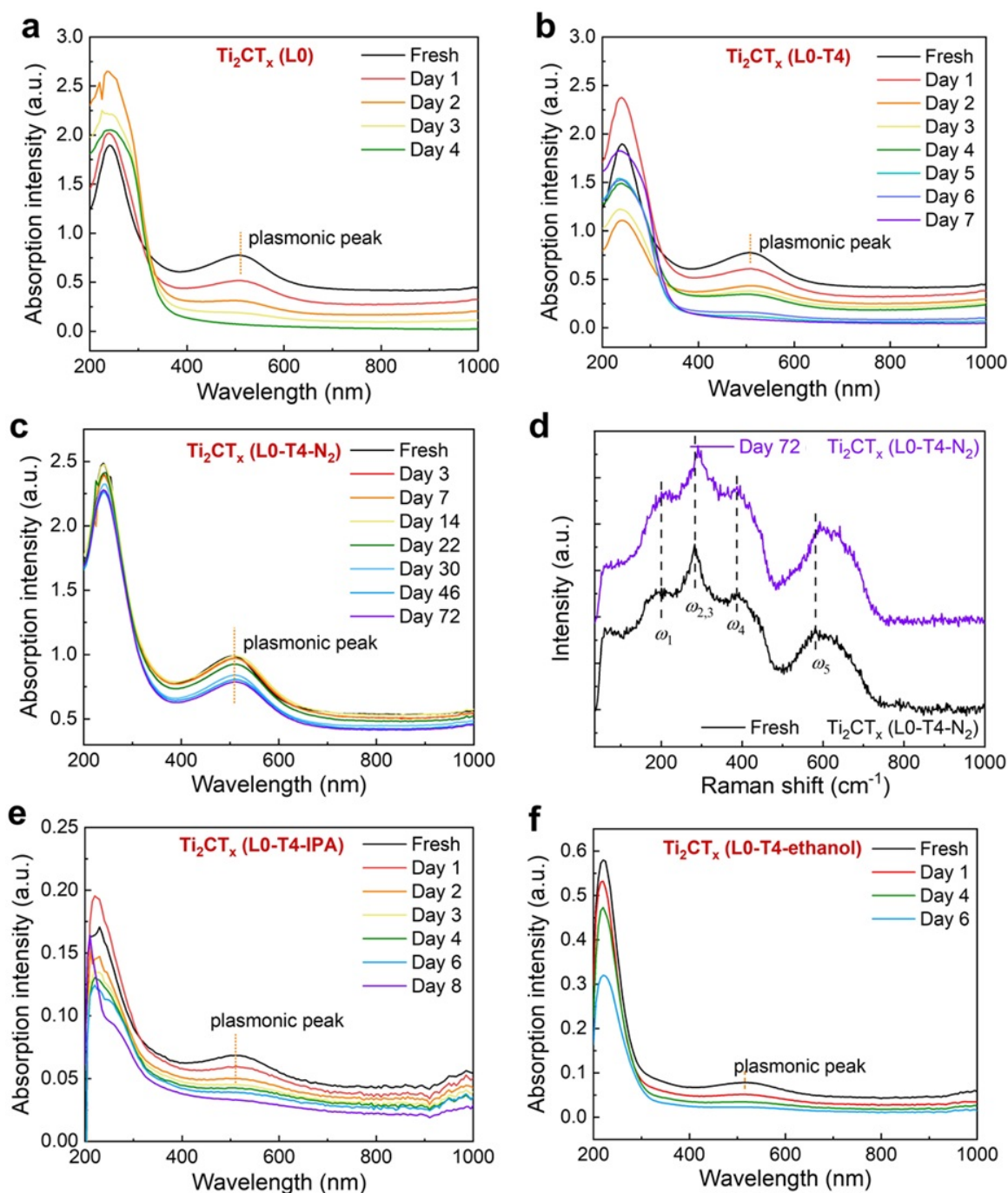


Fig. 7.11 UV-Vis-NIR absorption intensity decay over time of the Ti_2CT_x aqueous solutions stored at different conditions with no light illumination: (a) at RT (L0), (b) at 4 °C (L0-T4), (c) 4 °C with N_2 filled (sample L0-T4- N_2), (d) the Raman spectrum comparison of the film made from the L0-T4- N_2 solution at Day 72 compared to that from a fresh solution, (e) in IPA (L0-T4-IPA) and (f) in ethanol (L0-T4-ethanol).

7.2.4 The stored solvent (presence of water)

Figure 7.11(e,f) presents the UV-Vis-NIR absorption intensity decay over time of (e) the Ti_2CT_x solution in IPA (L0-T4-IPA) and (f) the Ti_2CT_x solution in ethanol (L0-T4-ethanol). Both solutions decayed within a week. The results are inconsistent with literature [319], which can be attributed to the water residue in the solution, which slowly degrades the Ti_2CT_x flake. Besides, compared to Ti_2CT_x aqueous solutions, the intensity of the IPA-based and the ethanol-based Ti_2CT_x solution is weaker, indicating a lower concentration and a lower yield, which is not favoured for supercapacitor fabrication using spray coating deposition (section 7.4.2).

7.2.5 Best storage conditions

Therefore, considering both the concentration/yield of the Ti_2CT_x solution as well as the shelf-life (flake stability), it is recommended to keep the solution isolated from light in the fridge (4 °C) and fully remove the dissolved O_2 by filling N_2 .

7.3 Charge transport mechanism of MXenes

As reviewed in Section 4.2, the charge transport mechanism of $\text{Ti}_3\text{C}_2\text{T}_x$ in both single flake and film (inter flake) has been studied extensively, while that of other types of MXenes, such as Ti_2CT_x and non-Titanium based MXenes is still unclear. This section then investigates the charge transport mechanism of Ti_2CT_x in device configurations of single-flake and film-based field-effect transistors (FETs). The study is ongoing with my collaborators.

7.3.1 Fabrication of field-effect transistors

Figure 7.12(a) illustrates the configuration of a single Ti_2CT_x flake device with an optical microscopy image (Figure 7.12(b)). The Ti_2CT_x single flakes were deposited on a p-doped Si/SiO₂ substrate via spin coating a 50 μL of the Ti_2CT_x aqueous solution at 2000 rpm for 30 seconds. The deposited substrates were spin-coated with a Poly(methyl methacrylate) (PMMA) layer at 5000 rpm for 60 seconds and baked at 180 °C for 15 minutes. The Ti/Au (5/35 nm) contact electrodes were deposited by Dr. Luca Anzi from Politecnico di Milano using e-beam lithography, to form the source and drain electrodes for the FET.

Figure 7.12(c) illustrates the configuration of a Ti_2CT_x film device with an optical microscopy image (Figure 7.12(d)). The Ti_2CT_x films were deposited on a p-doped Si/SiO_2 substrate via spray coating a 500 μL of the Ti_2CT_x aqueous solution using the developed protocol (Table 5.1). The substrates were drop-cast with small ($\sim 100\ \mu\text{m}$) droplets of electrically conductive silver paste (RS Components) by Dr. Erik Piatti from Politecnico di Torino. Each type of FET has replicates ≥ 4 .

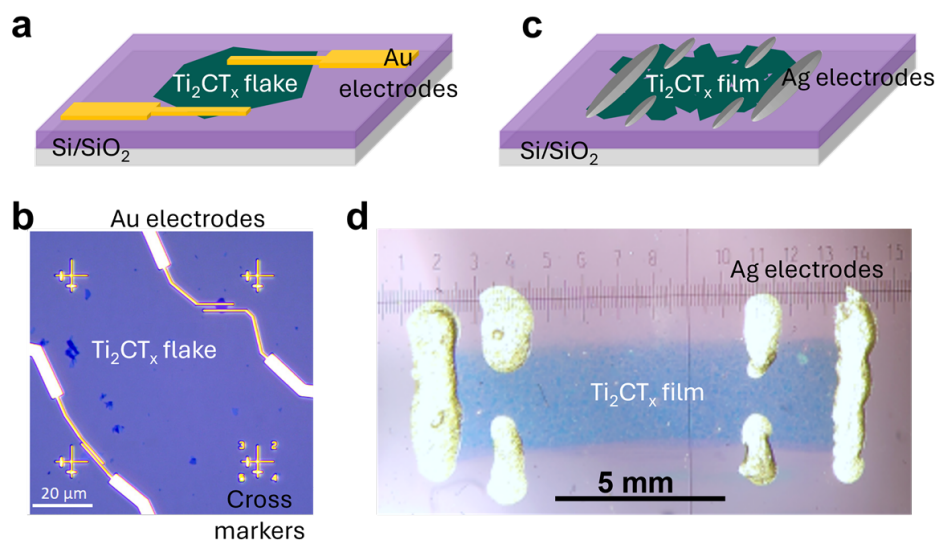


Fig. 7.12 Device configuration of a single Ti_2CT_x flake device by (a) schematic illustration (a single Ti_2CT_x flake (dark cyan) deposited on a Si/SiO_2 substrate (purple), with Au electrodes (yellow) deposited on top), (b) an optical microscopy image (single Ti_2CT_x flakes (dark blue) deposited on a Si/SiO_2 substrate (purple), with Au electrodes (shiny yellow) deposited on top); and a Ti_2CT_x film device by (c) schematic illustration (a Ti_2CT_x film (dark cyan) deposited on a Si/SiO_2 substrate (purple), with Ag electrodes (grey) deposited on top), and (d) an optical microscopy image (a Ti_2CT_x film (light blue) deposited on a Si/SiO_2 substrate (purple), with Ag electrodes (shiny grey) deposited on top).

Temperature-dependent charge transport measurements were performed in the high-vacuum chamber of a Cryomech pulse-tube cryocooler with a base temperature of 2.8 K. Magnetic-field-dependent measurements were performed in a helium atmosphere in the variable-temperature insert of an Oxford Instruments ^4He cryostat equipped with a 9 T superconducting magnet.

7.3.2 Charge transport investigation

Temperature-dependence conductance and magnetoresistance analysis were performed by Dr. Erik Piatti from Politecnico di Torino, to examine the charge transport mechanism of the

Ti₂CT_x devices. The electrical conductivity in any hopping regime follows a temperature dependence of the type [329]:

$$\sigma(T) = \sigma_0 \times \exp[-(\frac{T_0}{T})^p] \quad (7.3)$$

where T_0 is the characteristic temperature, σ_0 is the conductivity for $T \rightarrow \infty$ and p is an exponent that depends on the specific type of hopping mechanism. For the variable-range hopping (VRH) mechanisms, $p < 1$. VRH is a conduction mechanism in disordered materials, such as amorphous semiconductors [329] and granular electronic systems [471], where the charge carriers move through the material by "hopping" between localised states. This process is thermally activated and is distinct from standard conduction mechanisms, such as band conduction, which occurs in crystalline solids. The Mott VRH mechanism exhibits $p = 1/(1 + d)$, with d the dimensionality of the system [329].

Figure 7.13(a) presents an excellent scaling of sheet conductance (G_s) as an exponential of $T^{-1/3}$ for both the film device and single-flake device, which is compatible with 2D Mott VRH hopping type. This is further confirmed by determining the reduced activation energy as $W(T) = \partial(\ln \sigma)/\partial(\ln T)$. Figure 7.13(b) shows a negative linear fit of $\ln W$ versus $\ln T$, confirming the 2D VRH mechanism.

The 2D-Mott VRH mechanism is further confirmed by performing magnetoresistance measurements. The standard magnetoresistance expression for hopping transport [472] is:

$$MR = -C_{\text{sat}} \frac{B}{B_{\text{sat}}} + t^2 \frac{B^2}{B_c^2} \quad (7.4)$$

where B_{sat} and B_c are the characteristic values of B related to localisation length (ξ_{loc}); C_{sat} is the positive saturation constant, and $t^2 = 0.0893$ is a numerical coupling constant [472]. Figures 7.13(c,d) show a negative linear correlation of the magnetoresistance change ratio, $MR = [R_s(B) - R_s(0)]/R_s(0)$ with a quadratic high-field ($B(T)$) upturn for both the single-flake and film FET devices, consistent with 2D-Mott VRH.

The same charge transport behaviour within the Ti₂CT_x single flake and film devices indicates that hopping transport is intrinsic to the material and changes little from the single flake to the film, which is different from the charge transport of Ti₃C₂T_x (intrinsic metallic behaviours with weak localisation hopping mechanism [329]). Therefore, it is hypothesised that the charge transport mechanism of Ti₂CT_x devices is dominated by hopping between non-oxidised patches within each flake. Our collaborators in Italy are currently assessing this

hypothesis via transmission electron microscopy analysis and angle-resolved photoemission spectroscopy characterisation.

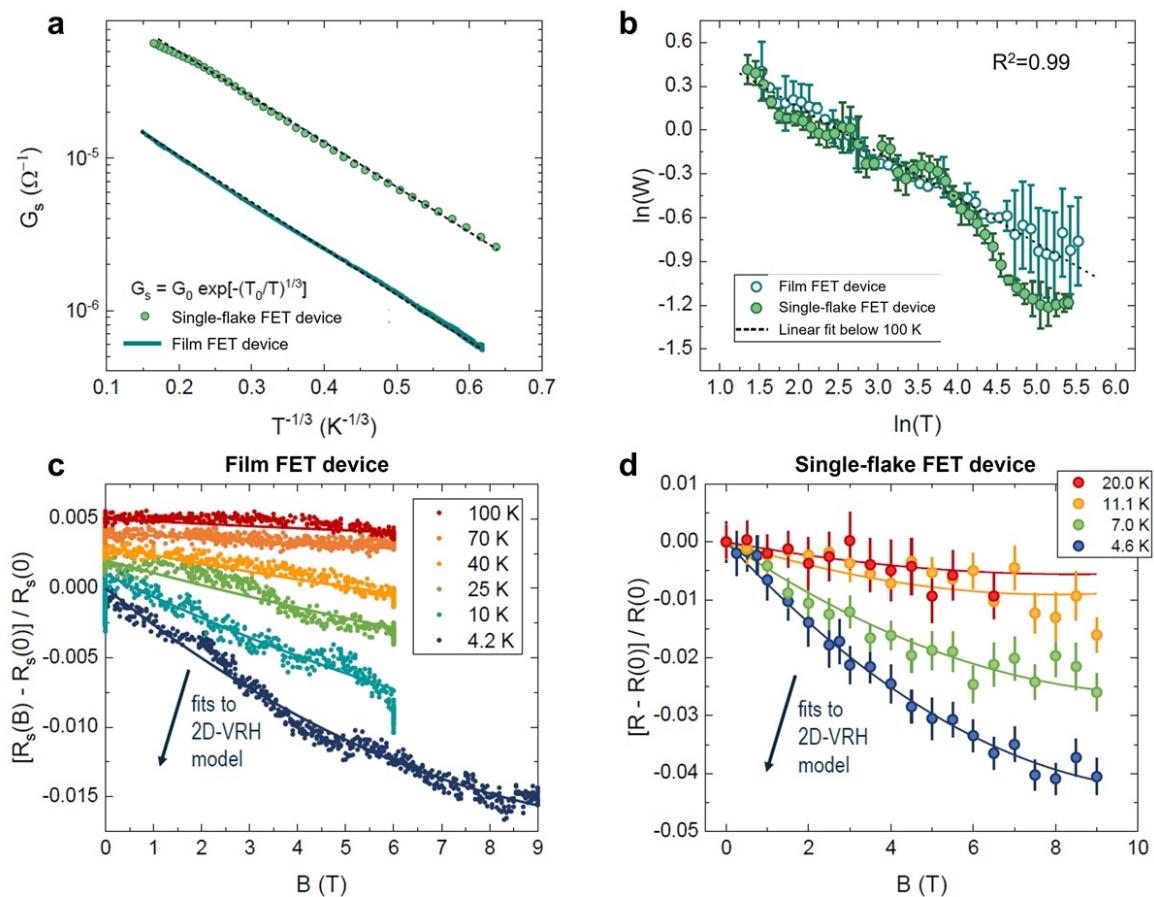


Fig. 7.13 Temperature-dependence conductance (a, b) and magnetoresistance (c, d) analysis of the Ti_2CT_x devices.

7.4 $\text{Ti}_3\text{C}_2\text{T}_x$ -based electrodes for textile energy storage devices

This is collaborative work with Dr. Sheng Yong and Prof. Stephen Beeby at the University of Southampton. They contributed to the device preparation and the electrochemical characterisation, and I contributed to the electrode preparation and characterisation.

7.4.1 Introduction to textile-based supercapacitors

Textile-based energy storage devices are becoming increasingly important for advancing future wearable electronics and electronic textiles (e-textiles) [473]. Among various energy storage options, supercapacitors stand out due to their simple structure and high power density, making them a promising candidate for powering a wide range of applications [474], including personal electronics [475], health-monitoring sensors [476], and implanted devices [477]. Integrating supercapacitors into textiles is particularly appealing for wearable electronics and e-textiles [478], as it requires preserving essential fabric properties such as mechanical flexibility, drape, lightweight, and washability. The key challenges in designing textile supercapacitors lie in developing efficient textile- or fibre-based functional electrodes with high porosity and conductivity and incorporating these electrodes into a device structure that includes a separator and current collectors [479].

7.4.1.1 Motivation of using activated carbon

Activated carbon (AC) has been extensively explored as a promising material for textile supercapacitor electrodes [480]. Its porous structure offers a large surface area, facilitating the formation of a double-layer structure at the interface between the electrode material and the electrolyte, resulting in high double-layer capacitance. In previous studies [481], AC-based supercapacitors were successfully fabricated on a single layer of polyester-cotton textile using spray-coated AC electrodes, a co-polymer membrane, and an organic electrolyte. These flexible capacitors achieved a capacitance of 38.2 mF cm^{-2} [482]. Compared to other porous supercapacitor electrode materials like CNTs [483], graphene [484], and rGO [485], AC is a more cost-effective option, although it naturally has lower electrical conductivity. However, this limitation can be mitigated by incorporating a small percentage of conductive additives, such as carbon black [486], silver [487], carbon nanotube [488], carbon onions [489], graphene [490] and rGO [491]. These hybrid composites of functional additives and AC offer an attractive solution for improving the performance of supercapacitor electrodes while keeping costs low.

7.4.1.2 Motivation of using MXenes

In recent years, numerous studies have shown that combining highly conductive MXenes with carbon-based materials to create hybrid electrodes can significantly enhance electrochemical

performance while keeping costs low. The research progress and promising advantages of using MXenes as electrode materials have been reviewed in Section 4.3.3.

In this work, a novel textile supercapacitor made from solution-processed $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes and AC within a single layer of polyester-cotton textile was introduced, which includes an integrated polymer separator and is tested with an organic electrolyte. The fabrication process is scalable and compatible with existing textile industry practices. The textile was integrated with a co-polymer membrane to form the separator, and the electrodes were fabricated on both sides of the textile using a controlled spray coating process, followed by an additional layer of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films. The electrode materials were prepared in a composite using commercially available AC, polymer binder ethylene-vinyl acetate (EVA), and $\text{Ti}_3\text{C}_2\text{T}_x$ (blending). Comparative tests with plain carbon-based textile electrodes showed that incorporating MXenes into the textile electrode increased the C_A of the supercapacitor by 220 %, demonstrating a scalable approach for achieving high-performance energy storage devices in textiles. This study is the first to demonstrate that by adding just 10 wt.% multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (m- $\text{Ti}_3\text{C}_2\text{T}_x$ or m-MXenes) to the AC electrode or by spray coating delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (d- $\text{Ti}_3\text{C}_2\text{T}_x$ or d-MXenes) while maintaining a high proportion of AC, the supercapacitor electrodes exhibit a better capacitance and remain cost-effective.

7.4.2 Preparation and characterisation of $\text{Ti}_3\text{C}_2\text{T}_x/\text{AC}$ electrodes

7.4.2.1 Electrode preparation

In this work, AC and/or $\text{Ti}_3\text{C}_2\text{T}_x$ were used as electrode materials. AC (Yp-80F) was purchased from Kuraray Chemical. $\text{Ti}_3\text{C}_2\text{T}_x$ was synthesised using the selective etching and MILD methods, which have been described in Section 7.1.

To study the benefits of $\text{Ti}_3\text{C}_2\text{T}_x$ as an electrode additive for the textile supercapacitor, four types of hybrid electrodes were fabricated, as listed in Table 7.3. The A and C electrode slurry was prepared via dissolving AC and EVA (polymer binders) in trichlorobenzene (TCB) (5-minute ultrasonication in the glove box) at the weight ratio of 85:15 [492]. The B and D electrode slurry was prepared by dispersing AC, m- $\text{Ti}_3\text{C}_2\text{T}_x$ and EVA in TCB at the weight ratio of 75:10:15 (5-minute ultrasonication in the glove box). EVA acting as a polymer binder could make a mechanically robust electrode coating on the textile. The C and D electrodes were spray-coated with an additional thin layer (~ 20 nm) of d- $\text{Ti}_3\text{C}_2\text{T}_x$ on the both sides of the electrodes.

Table 7.3 Types of the electrodes for supercapacitors

Amount of electrode materials	Types of the electrodes/supercapacitors			
	A	B	C	D
AC	0.85	0.75	0.85	0.75
m- $\text{Ti}_3\text{C}_2\text{T}_x$	0	0.1	0	0.1
EVA	0.15	0.15	0.15	0.15
spray coating of a d- $\text{Ti}_3\text{C}_2\text{T}_x$ layer	/	/	~ 25 nm	~ 25 nm

7.4.2.2 Electrode characterisation

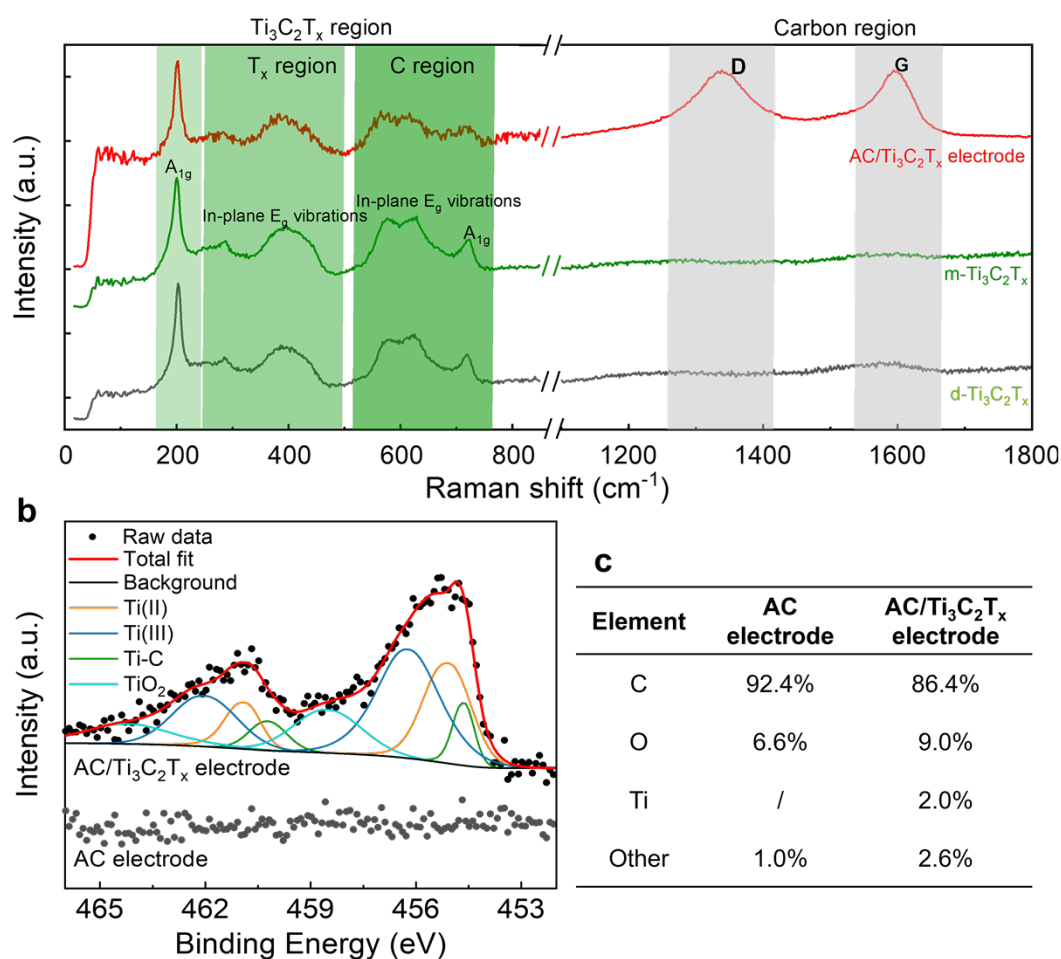


Fig. 7.14 Electrode characterisation of the AC electrode and the AC/ $\text{Ti}_3\text{C}_2\text{T}_x$ electrode via (a) Raman spectrum, (b) high-resolution XPS spectrum of Ti2p and (c) element analysis based on the XPS survey. Image adapted with permission [37]. © 2023 Wiley-VCH GmbH.

Raman spectroscopy and XPS were conducted to demonstrate the presence and quality of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes in the fabricated electrodes. Figure 7.14(a) shows that the Raman peaks at $\sim 1334\text{ cm}^{-1}$ and $\sim 1595\text{ cm}^{-1}$ comes from the D and G peaks of AC, which is the main electrode material utilised in the supercapacitors. The peaks occurred at lower Raman shifts originate from the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, which indicates the presence of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in the MXene-infused AC electrodes. Figures 7.14(b-c) show the presence of the Ti 2p region of $\text{Ti}_3\text{C}_2\text{T}_x$ in the XPS spectrum of the MXene-infused AC electrodes, compared to the absence of Ti 2p region of MXene in the XPS spectrum of the AC-only electrode (as compared to Figure 7.6).

7.4.3 Fabrication of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{AC}$ textile-based supercapacitor

7.4.3.1 Use of materials

Textile: The polyester cotton textile was obtained from Klopman. The textile was plain woven with a polyester (diameter of $12\text{ }\mu\text{m}$) and a cotton (diameter of $15\text{ }\mu\text{m}$) with 16.5 ends per inch (or 9.05 picks per inch). The textile has an areal weight of 27.1 mg cm^{-2} and a thickness of $250\text{ }\mu\text{m}$.

Membrane: The membrane material was prepared from a co-polymer solution containing PMMA ($M_w = 120,000\text{ g mol}^{-1}$), EVA (vinyl acetate 25 wt.%), ethanol and isoamyl acetate.

Electrolyte: 1 M tetraethylammonium tetrafluoroborate (TEABF_4) in DMSO was used as an organic electrolyte.

Current collector: A spring-loaded grade 303 stainless steel was used as the current collector.

7.4.3.2 Fabrication process of the electrodes

Figure 7.15 shows the detailed fabrication process of the textile supercapacitors. At the first stage, the surface of the polyester cotton textile was shaved to reduce its pilosity. Then, the co-polymer solution (containing PMMA, EVA, ethanol and isoamyl acetate) was screen-printed on the top of the textile followed by phase inversion, and it was cured in a vacuum oven at $23\text{ }^\circ\text{C}$. The resultant thickness of the membrane layer is $\sim 100\text{ }\mu\text{m}$. At the third stage, the prepared electrode slurry (AC or AC/m- $\text{Ti}_3\text{C}_2\text{T}_x$) was spray coated on both sides of the textile, and on each side, the loading of electrode material was 4.85 mg cm^{-2} . At the final stage for C and D electrodes, an additional thin ($\sim 20\text{ nm}$) layer of d- $\text{Ti}_3\text{C}_2\text{T}_x$

was spray coated onto both sides. All the prepared supercapacitors (containing the textile membrane and electrodes) were then dried (at 120 °C for 20 minutes) under Ar atmosphere before being cut into a circular shape with a diameter of 1 cm (area of 0.785 cm²). They were then immersed in the organic electrolyte (1 M TEABF₄ in DMSO) under vacuum at ~ 25 mbar for 20 minutes. The fabricated supercapacitors were eventually compressed using a spring-loaded current collector (grade 303 stainless steel).

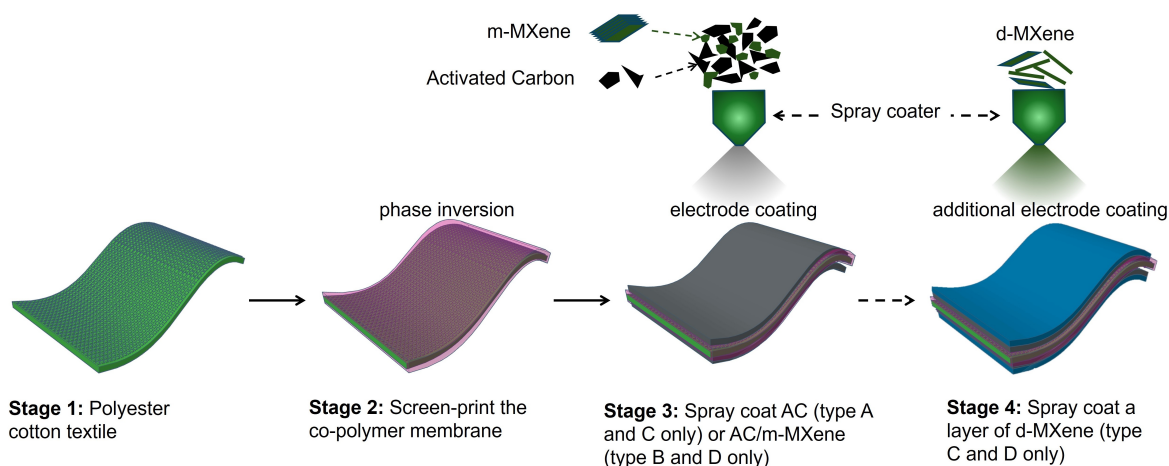


Fig. 7.15 Steps highlighting the fabrication process of the textile supercapacitors. Image adapted with permission [37]. © 2023 Wiley-VCH GmbH.

In Figure B.4 in Appendix B, the contact angle measurements (θ_c) of water and DMSO was performed to demonstrate the wettability of the supercapacitors. The A (Figure B.4(a)) and B (Figure B.4(b)) supercapacitors show a hydrophobic behaviour with a θ_c of water at 110.1 ° and 112.37 °, respectively, while the C (Figure B.4(c)) and D (Figure B.4(d)) supercapacitors show a hydrophilic behaviour with a θ_c of water at 56.7 ° and 64.6 °, respectively. This shows the presence of a hydrophilic layer of d- $\text{Ti}_3\text{C}_2\text{T}_x$ on the surface of electrodes. Figure B.4(e-h) in Appendix B demonstrates the absorption of DMSO by the textile supercapacitors as a function of time between 0.03 s and 0.70 s from the time the testing drop impacts with the textile supercapacitors. Note that DMSO is absorbed by the textile supercapacitor in less than 0.7 seconds, indicating a fast and complete absorption of the electrolyte into the porous electrode.

7.4.3.3 Textile supercapacitor assembly and electrochemical methods

All textile supercapacitors were vacuum-impregnated with an organic electrolyte 1 M TEABF₄ in DMSO. The textile supercapacitors were cut into a circular shape with a diameter of 1 cm (area of 0.785 cm²) and immersed in the organic electrolyte under vacuum at ~25

mbar for 20 minutes. The testing of textile supercapacitors was performed in a Swagelok PFA tube fitting, where the supercapacitors were compressed with a spring-loaded grade 303 stainless steel current collector.

The weight of the textile supercapacitors was measured using a Voyager Pro balance, a TEM image was taken with FEI Tecnai T12 Transmission Electron Microscope, and SEM images and EDX results were taken on a Phenom Prox with an accelerating voltage of 10 kV.

The electrochemical performance of the textile supercapacitor was obtained through an Autolab pgstat101 (Metrohm Autolab, The Netherlands). Electrochemical impedance spectroscopy measurements were performed between 0.01 and 10 MHz with a peak-to-peak voltage of 10 mV. Cyclic voltammetry (CV) results were collected at scan rates of 50 mV s⁻¹ and voltages varying between ± 1.8 V unless stated in the texts. Galvanostatic cycling (GC) tests were obtained at a cycling current of 1 mA cm⁻² and between 0 and 1.8 V unless stated in the texts.

7.4.4 Electrochemical performance of the Ti₃C₂T_x/AC textile-based supercapacitor

The textile supercapacitors were tested using two electrodes in a Swagelok PFA tube fitting. The testing methods include CV, GCD, and EIS. The energy and power density results are shown in Ragone plots, and all the following results were averaged over five repeats. This section has been experimentally conducted by my collaborator, Dr. Sheng Yong, at the University of Southampton. The promising results have been published in *Advanced Materials Technology* [37], where we both co-first-authored.

7.4.4.1 GCD and CV tests

GCD and CV performances are the basic electrochemical characterisation to demonstrate the supercapacitors' capacitance. Figure 7.16(a) shows the GC plots of supercapacitor A, B, C, and D between 0.0 and 1.8 V at a constant cycling current of 1 mA cm⁻², demonstrating linear and symmetrical charge and discharge profiles. The supercapacitor A (bare AC electrode) has an C_A of ~ 30.6 mF cm⁻², and supercapacitor B shows an C_A of ~ 75.5 mF cm⁻² with m-Ti₃C₂T_x additive in the electrode, which is ~ 2.5 times higher than that of supercapacitor A. Supercapacitor C has a similar improvement compared to supercapacitor A, achieving a $C_A \sim 63.1$ mF cm⁻² with the additional thin layer of d-Ti₃C₂T_x. Supercapacitor D was fabricated with additive m-Ti₃C₂T_x in the AC electrode and additional thin layer coating of

d-Ti₃C₂T_x, and the GC results demonstrated the highest $C_A \sim 84.2 \text{ mF cm}^{-2}$, indicating that the combination of Ti₃C₂T_x both within and on the surface of the AC electrode improves the C_A of the textile supercapacitor.

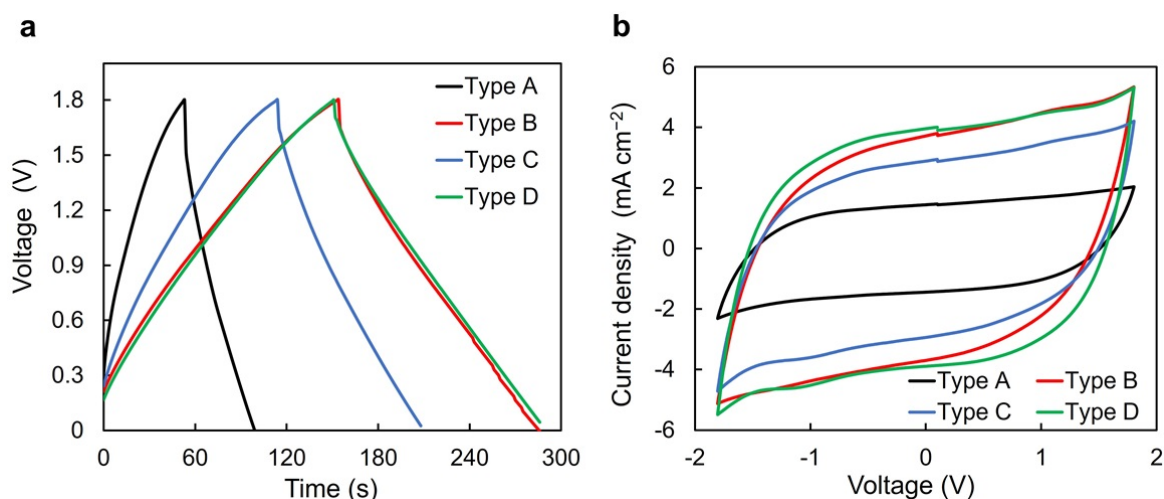


Fig. 7.16 Electrochemical performance of the as-prepared supercapacitors A (black), B (red), C (blue) and D (green): (a) GC plots tested at a constant cycling current of 1 mA cm^{-2} , (b) CV plots tested at a scan rate of 50 mV s^{-1} . Image adapted with permission [37]. © 2023 Wiley-VCH GmbH.

Figure 7.16(b) shows the CV plots of supercapacitor A, B, C, and D between $\pm 1.8 \text{ V}$. There is no presence of redox peak in the four plots, indicating that the supercapacitors fabricated in this work operated in an electrostatic electrical double-layer way. Compared to the CV curve of supercapacitor A, the addition of m-Ti₃C₂T_x and/or d-Ti₃C₂T_x in the supercapacitor B, C and D all enhance the electrical networks of the AC electrode. It is worth noting that the d-Ti₃C₂T_x layers in supercapacitors C and D act as a current collector rather than an energy storage layer.

When comparing the GC and CV plots of supercapacitor B and D, the GC curve of supercapacitor D almost saturates and overlaps with that of supercapacitor B. In contrast, the CV curve of supercapacitor D exhibits a more rectangular shape.

7.4.4.2 Electrochemical impedance spectroscopy (EIS)

To understand the role of m-MXene and/or d-MXene played in the supercapacitor electrodes, EIS characterisation was conducted to determine the change in the Ohmic series and charge transfer resistance within the supercapacitor.

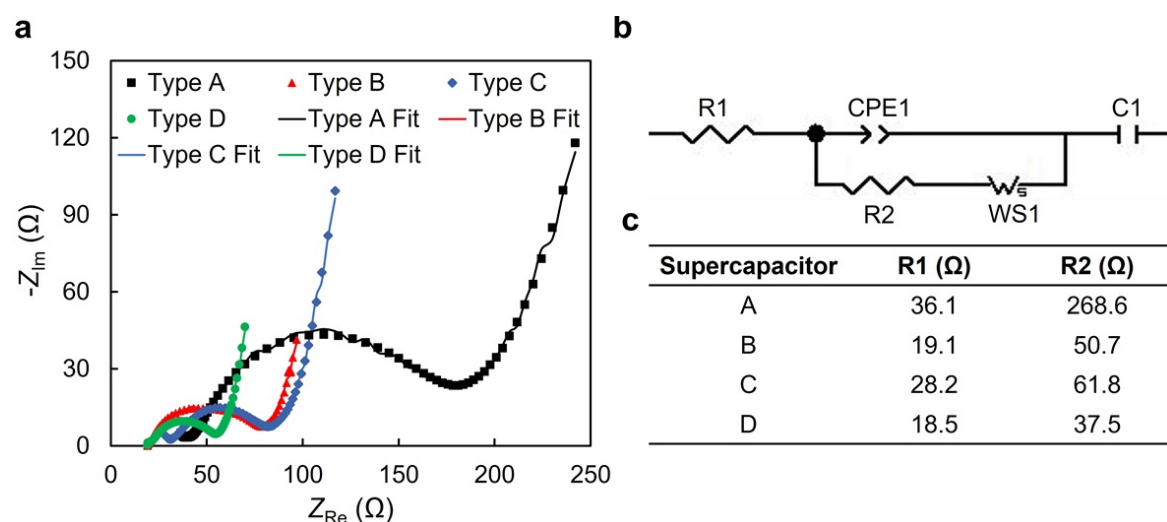


Fig. 7.17 Impedance characterisation of supercapacitors using different electrode materials. EIS results of (a) supercapacitor A (black), B (red), C (blue), and D (green) between 0.01 and 10 MHz with a peak-to-peak voltage of 10 mV, (b) its equivalent circuits, with $R1$ and $R2$ representing the Ohmic series resistance and charge transfer resistance, and (c) the $R1/R2$ fitting result. Image adapted with permission [37]. © 2023 Wiley-VCH GmbH.

Figure 7.17(a) shows the EIS test results of all the supercapacitors, with an equivalent circuit to fit the EIS data shown in Figure 7.17(b). $R1$ and $R2$ represent the ohmic series resistance and charge transfer resistance, respectively [493]. Figure 7.17(c) summarises the fitting result of $R1$ and $R2$ values of supercapacitor A, B, C and D. The supercapacitor A had the resistance values of 36.1Ω ($R1$) and 268.6Ω ($R2$). With the addition of $m\text{-Ti}_3\text{C}_2\text{T}_x$ in the AC electrode, supercapacitor B demonstrated the resistance values of $R1 \sim 19.1 \Omega$ and $R2 \sim 50.7 \Omega$, and with the additional thin layer coating of $d\text{-Ti}_3\text{C}_2\text{T}_x$ on the surface of the AC electrode, supercapacitor C showed the resistance values of $R1 \sim 28.2 \Omega$ and $R2 \sim 61.8 \Omega$. It indicates that $\text{Ti}_3\text{C}_2\text{T}_x$ reduced both $R1$ and $R2$ values, while the $m\text{-Ti}_3\text{C}_2\text{T}_x$ had a more significant effect of resistance decline. With the combination of $m\text{-Ti}_3\text{C}_2\text{T}_x$ and $d\text{-Ti}_3\text{C}_2\text{T}_x$, supercapacitor D was reported with the lowest resistance values, with $R1 \sim 18.51 \Omega$ and $R2 \sim 37.5 \Omega$. The decline in the resistance of the supercapacitors could contribute to lowering the electrical energy losses and increasing the energy storage performance at higher current densities.

7.4.4.3 Areal capacitance and energy/power density of supercapacitors

A Ragone plot is a graphical representation used to compare the performance of energy storage devices, such as batteries, supercapacitors, and fuel cells. It plots specific energy

(energy density) against specific power (power density) on a log-log scale, allowing for a clear comparison of different types of energy storage technologies.

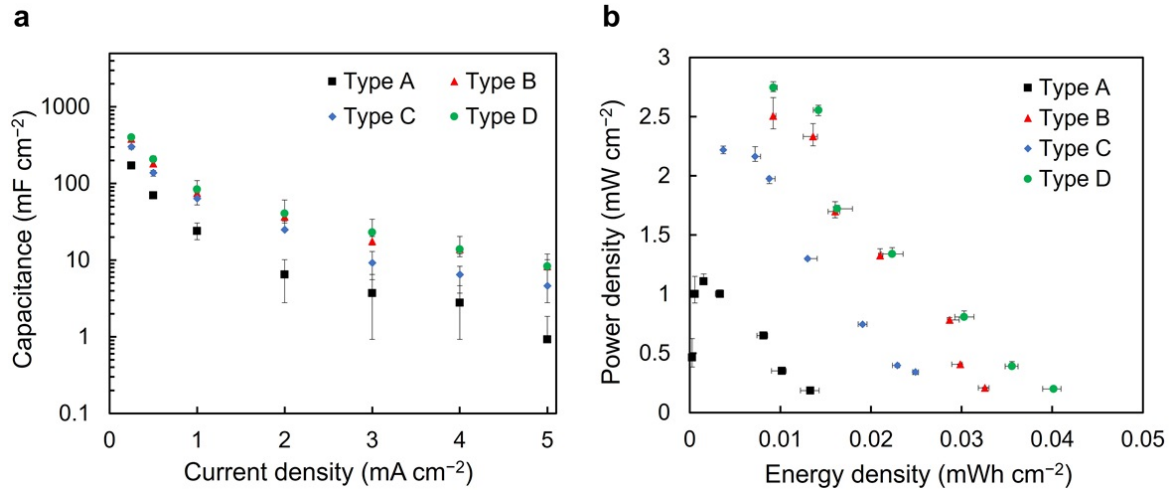


Fig. 7.18 Performance comparison of supercapacitors using different electrode materials. (a) The capacitance of supercapacitor A (black), B (red), C (blue), and D (green) at different current densities, (b) the Ragone plot of supercapacitor A (black), B (red), C (blue) and D (green) tested at 0.25, 0.5, 1, 2, 3, 4 and 5 mA cm^{-2} . Image adapted with permission [37]. © 2023 Wiley-VCH GmbH.

Figure 7.18(a) shows the C_A of supercapacitors A, B, C, and D as a function of applied current densities. Supercapacitor D achieved the highest $C_A \sim 400 \text{ mF cm}^{-2}$ at 0.25 mA cm^{-2} , which is 132%, 5%, and 32% higher than that achieved by supercapacitor A ($\sim 172.2 \text{ mF cm}^{-2}$), B ($\sim 380.6 \text{ mF cm}^{-2}$), and C ($\sim 301.8 \text{ mF cm}^{-2}$), respectively. At the current density of 5 mA cm^{-2} , the C_A of supercapacitor D ($\sim 8.3 \text{ mF cm}^{-2}$) is found to be 8 times higher than that of supercapacitor A ($\sim 0.92 \text{ mF cm}^{-2}$) and 80 % higher than that of C ($\sim 4.62 \text{ mF cm}^{-2}$), while supercapacitor B achieved the same C_A value ($\sim 8.33 \text{ mF cm}^{-2}$) as D. The result suggests that at such high cycling current density, the thin layer coating of d- $\text{Ti}_3\text{C}_2\text{T}_x$ on the electrode surface makes no contribution to the C_A , indicating that the AC/m- $\text{Ti}_3\text{C}_2\text{T}_x$ electrode has already provided sufficiently high inherent conductivity and the current flow is pre-dominantly within the electrode. Without the m- $\text{Ti}_3\text{C}_2\text{T}_x$ in the electrode, the benefit of the additional thin layer of d- $\text{Ti}_3\text{C}_2\text{T}_x$ can be observed by the 5 times increment in C_A of supercapacitor C compared to that of A.

Figure 7.18(b) shows the Ragone plots of supercapacitor A, B, C and D at 0.25, 0.5, 1, 2, 3, 4 and 5 mA cm^{-2} . Supercapacitor D, which has the AC/m- $\text{Ti}_3\text{C}_2\text{T}_x$ electrode with a thin layer of d- $\text{Ti}_3\text{C}_2\text{T}_x$ on the surface demonstrated the best energy storage performance regarding energy and power densities. As the current density varies from 0.25 to 5 mA cm^{-2} , the

energy density of supercapacitor D declined from 0.04 to 0.009 mWh cm⁻² while its power density increased from 0.2 to 2.74 mW cm⁻², respectively. Supercapacitor A failed to follow a standard power and energy density correlation at 4 and 5 mA cm⁻², at the discharge rate of which the electrical energy was lost faster than for the other three types of supercapacitors due to the high R1 and R2.

7.4.4.4 Cycling performance

Cycling performance is a critical parameter in evaluating the performance and longevity of supercapacitors. It is the ability of a supercapacitor to maintain its energy storage capacity and overall performance over a large number of charge-discharge cycles. Figure 7.19 shows the loss in C_A (normalised capacitance, C_e/C_0) as a function of cycle times of the four supercapacitors in an ambient environment. C_0 represents the initial areal capacitance obtained from the first cycle, and C_e represents the C_A obtained from a certain cycle. Overall, all supercapacitors do not suffer from a great loss in their C_A , while capacitance loss is more common in secondary batteries due to redox reactions, such as metal dendrites issues.

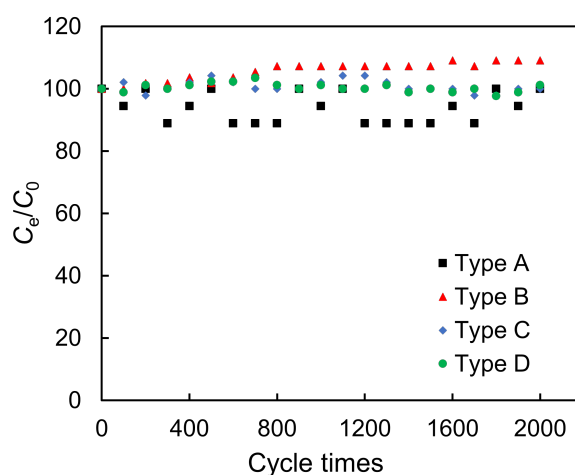


Fig. 7.19 Cycling performance of supercapacitors using different electrode materials. Capacitance change of supercapacitor A (black), B (red), C (blue) and D (green) over 2000 cycles (~ 55 hours). Image adapted with permission [37]. © 2023 Wiley-VCH GmbH.

Supercapacitor A exhibited a C_e/C_0 fluctuation of $\sim 11\%$ over 2000 cycles due to the poor wettability of the AC electrode and the coverage variation of the electrolyte during the charge and discharge process. With the help of the m-Ti₃C₂T_x and/or d-Ti₃C₂T_x, the wettability of the electrodes improved (Figure B.4), so the C_e/C_0 fluctuation of the supercapacitor B, C, and D is greatly reduced. The C_e of supercapacitor B increased by $\sim 9\%$ over 2000 cycles, which indicates the coverage of the electrolyte improved during cycling. Such changes in

normalised capacitance are not observed in the C_e performance of supercapacitors C and D. It can be attributed to the initial full coverage of the electrolyte across the whole electrode, which brought by the better wettability of the electrode due to the thin layer coating of d- $\text{Ti}_3\text{C}_2\text{T}_x$.

7.5 Conclusion

This chapter discusses the key oxidation factors of Ti_2CT_x aqueous solutions, including the presence of water and oxygen, the light illumination, and the storage temperatures. Keeping the solutions isolated from light in the fridge (4 °C) and fully exchanging the dissolved O_2 in water by filling N_2 can extend the shelf-life of the Ti_2CT_x aqueous solution from 3 days to over 2 months. The charge transport mechanism of the Ti_2CT_x is studied to better understand its electronic properties, and is found to be compatible with the 2D-Mott VRH hopping mechanism. Compared to Ti_2CT_x , $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits metallic behaviour with high electrical conductivity. The addition of $\text{Ti}_3\text{C}_2\text{T}_x$ into the carbon-based electrode materials for textile-based supercapacitors has been investigated. With an organic electrolyte, 1 M tetraethylammonium tetrafluoroborate in dimethyl sulfoxide, these supercapacitors are electrochemically stable between ± 2.6 V and demonstrate a maximum areal capacitance of 148.7 mF cm^{-2} , an energy density of $0.921 \text{ mWh cm}^{-2}$, and a power density of 1.01 mW cm^{-2} . The addition of MXenes improves the areal capacitance by 120% compared to carbon electrodes and a cycling performance over 2000 cycles without severe capacitance loss, enabling high-performance textile-based energy storage devices.

Chapter 8

Conclusions and future outlook

8.1 Conclusions

Energy transition from fossil fuels to renewable energy sources using energy storage devices is a continuing trend and contributes to global CO₂ reduction. However, existing energy storage technologies suffer from insufficient energy/power densities, energy loss and thermal issues during operation. 2D materials, with their exceptional electrical, thermal, and electrochemical properties, offer promising solutions as dielectric, electrode, and thermal interface materials to enhance energy and power densities and optimise energy efficiency. The work aims to advance the scalable processing of 2D materials, specifically h-BN and MXenes, and their composites and to demonstrate their potential in energy storage devices and thermal management applications, which eventually could support the global CO₂ reduction commitment.

h-BN is a wide bandgap semiconducting layered material. Within each layer, alternating boron and nitrogen atoms are held together by sp² covalent bonds arranged on a honeycomb lattice, similar to graphene. h-BN possesses superior properties, including high in-plane thermal conductivity (κ), chemical stability, strong mechanical strength, and electrical insulation with a bandgap value of ~ 5.96 eV. Our work in Chapter 5 unleashes the production of few-layer h-BN (FLh-BN) flakes and their composites using ultrasonication-assisted liquid phase exfoliation. The h-BN-based composites work as insulating layers in fully spray-coated capacitors, achieving excellent insulating properties (dielectric constant, ϵ_r of 7.9 and dielectric breakdown strength up to 14 kV/mm). Chapter 6 explores the effects of the h-BN on the κ of the cellulose-based composites and compares the enhancement between bulk h-BN (Bh-BN) embedded cellulose composites and the FLh-BN embedded ones. The

FLh-BN/cellulose composite could reach a κ of up to $\sim 21.7 \text{ W m}^{-1} \text{ K}^{-1}$, which is five times higher than that of Bh-BN embedded cellulose composites. The commercial viability of the FLh-BN-based cellulose composites is demonstrated in several ways. First, the composites are developed using a biocompatible, scalable, and low-cost process, which utilises a one-pot mixing step compatible with industrial production. This is advantageous to the non-scalable techniques reported in the literature (requires externally applied magnetic fields, vacuum filtration or hot pressing/stretching). Second, the composites are produced in the form of pastes with reported rheological characteristics (dynamic viscosity, $\eta \sim 273.6 \text{ Pa s}$ at 1 rpm). The obtained viscosity is within the viscosity range of commercial thermally conducting pastes. Third, Chapter 6 also untaps the potential of the FLh-BN-based composites as thermal pastes for commercial applications. They can work as thermal interface materials (TIMs) for heat dissipation from hot spots to heat sinks, including a hot chip surface and an operating high-power LED chip surface, achieving a reduction of 24.5°C and 9°C , respectively, compared to that of the Bh-BN composites.

MXenes (2D transition metal carbides, nitrides, and carbonitrides) are a versatile and rapidly growing family of 2D materials with a wide range of applications in energy storage, electronics, water purification, and more. Their unique properties, including high conductivity, hydrophilicity, and mechanical strength, make them promising candidates for advanced technological applications. In Chapter 7, $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x MXenes were successfully synthesised using an in-site $\text{HCl}+\text{LiF}$ selective etching route and delaminated into mono-layer and few-layer flakes with minimally intensive layer delamination (MILD). However, the fast oxidation of MXenes restrains their practical usage. The main factors of MXene storage conditions that drive the oxidation of MXenes were then studied, including the storage temperature, the storage solvent, the dissolved gas and the light illumination. To improve the chemical stability and shelf-life storage of MXenes aqueous solutions, especially the Ti_2CT_x (3 days without treatment), isolation from light, a low storage temperature down to 4°C (e.g., kept in the fridge) and an inert gas environment (Nitrogen gas, N_2) should be combined to ensure 2-month storage of MXenes aqueous solutions. The charge transport mechanism of the Ti_2CT_x was found to be compatible with the 2D-Mott VRH hopping mechanism. Finally, the chapter took the $\text{Ti}_3\text{C}_2\text{T}_x$ as an example to demonstrate the application of MXenes in energy storage devices. The 10 wt.% addition of $\text{Ti}_3\text{C}_2\text{T}_x$ into the fabrication process of the electrode materials for supercapacitors would enhance the electrochemical performance of the electrode as well as the device, including capacitance ($\sim 220\%$ enhancement), energy density, and power density.

Through these investigations, the work demonstrates a foundation for deploying 2D materials in critical applications that can contribute to CO_2 reduction by improving device reliability,

energy efficiency and renewable energy storage capabilities. It provides several key avenues for future research and development in energy storage devices. First, the techniques developed in this work involving liquid phase exfoliation and large-area coating/mixing are versatile and compatible with a wide range of materials. Second, the work explores 2D materials as potential candidates for energy storage devices from the perspective of materials. Future work could also explore the combination of these materials with other 2D materials or composites to create hybrid systems that address multiple challenges at the same time. Third, the applications of these materials could be extended beyond energy storage to areas such as coatings and sensing, further expanding their potential for diverse technological advancements making the best use of their superior properties.

8.2 Future work

8.2.1 h-BN based thermal pastes

8.2.1.1 Understanding of ultrathin dielectric layer for electronics

The thickness threshold achieved for the FLh-BN/CMC dielectric films in Chapter 5 is around 1 μm , a limitation for advanced applications of ultrathin films (nanometers) in microelectronics and nanodevices [494, 495]. Future work should explore other techniques like liquid-liquid assembly or Langmuir-Blodgett assembly to create nanoscale thin and dense films (down to tens of nanometers) from discrete 2D flakes by LPE [496]. The assembly of 2D flakes occurs at the interface where two immiscible liquids meet, and 2D materials are deposited. The nanoparticles or molecules can spontaneously organize into ordered structures and self-assemble into continuous films driven by van der Waals forces, electrostatic interactions, and capillary forces. By varying the concentration of the particles, the types of liquids, and the conditions such as temperature or pH, the assembly process can be controlled to produce different structures, ranging from monolayers to more complex 3D architectures. A monolayer of graphene nanosheets was obtained beforehand via self-assembly at the liquid-liquid interface [497]. This close-packed monolayer structure shows a high electrical conductivity of more than 1000 S cm^{-1} [497]. Similarly, an ultrathin h-BN-based dielectric layer is possible, and the effect of polymers on the self-assembly should be explored, which, as far as the author knows, is yet to be well understood.

8.2.1.2 Comprehensive understanding of the rheological properties

A comprehensive investigation of the rheological properties of the FLh-BN/CMC and Bh-BN/CMC thermal pastes is necessary. This includes strain relaxation, hysteresis behaviour, and temperature-dependent rheological behaviour, which can be performed via a rheometer [230]. Understanding these properties can unlock new applications in protective coatings and lubricants, where the behaviour of composites under varying mechanical stresses and temperatures is critical for performance. Mastering their rheological properties could guide the optimisation of the formulation and fabrication of composites for various purposes.

8.2.1.3 Challenges of measuring the κ of monolayer and FLh-BN flakes

One of the difficulties in measuring the κ of the FLh-BN/CMC composites in this work is the robustness of the composites embedded with high mass loadings (i.e. 80 wt.%) of FLh-BN. That was caused by the mismatch of the composite stiffness and the applied external force occurring during the sample mounting process. Therefore, it motivates the author to explore the mechanical properties beyond the tensile strength discussed in this dissertation, such as toughness, flexural strength, impact strength, hardness, and other mechanical characteristics. Alternatively, exploring the κ of the composites with high FLh-BN load via different techniques. For example, if the sample can be fabricated into thin films, the thermal conductivity measurement via Linsesis LFA equipment might be possible. The Linsesis LFA instrument requires a thin film of the aimed material deposited on a SiN_x membrane and applies the 3ω technique to obtain its thermal conduct behaviour in the in-plane direction [498]. There are also other techniques, such as laser flash, that can be combined to cross-check the accuracy of the measurement.

Another big challenge found in the work of the dissertation is the correct estimation or measurement of the emissivity of the composites during the heat transfer measurement [499]. The recommended value of 20% at RT is suggested by the system manual, but it is worthwhile to investigate it more in detail to obtain a more accurate estimation.

8.2.1.4 Applications in thermal comfort wears

Exploring the use of FLh-BN in passive cooling for textiles [447] offers an intriguing avenue for advanced thermal comfort in wearable technology. Investigating the integration of FLh-BN with textiles through thermal coating or fibre configuration could lead to the development of advanced materials that provide better thermal regulation for human bodies. Apart from heat conduction via textiles, thermal radiation through garments, heat dissipation through sweat evaporation and heat convection through environmental fluids should also be considered [448]. Hence, it is worth investigating the emissivity of the fabricated composites again.

8.2.2 MXene-based energy storage applications

8.2.2.1 Surface functionalisation

The chemical structure of MXenes can be investigated and tailored to form various functional groups (T_x), enabling different flake properties, such as using different etching and delamination agents and post-annealing in different gases [500]. Modifying the surface chemistry may also help enhance the chemical stability and prevent fast oxidation, such as ion-shielding and layer-shielding [41]. Functionalisation of MXenes to be linked with other 2D materials like MoS_2 is also proposed to be applicable for energy storage applications [501].

8.2.2.2 Charge transport mechanism of Ti_2CT_x and other types of MXenes

The charge transport behaviour within the Ti_2CT_x single flake and film devices both follow the 2D-Mott VRH hopping mechanism, indicating that hopping transport is intrinsic to the material and changes little from the single flake to the film. It is hypothesised that the charge transport mechanism of Ti_2CT_x devices is dominated by hopping between non-oxidised patches within each flake. However, this should be further confirmed and investigated. Our collaborators in Italy are currently assessing this hypothesis via transmission electron microscopy analysis and angle-resolved photoemission spectroscopy characterisation.

Regarding other types of MXenes, there are very few studies reported so far for the charge transport mechanism, for instance, Nb_2C and V_2C . The majority of publications still focus on synthesis optimisation and material characterisation. The obtained monolayer and few-layer flakes are hundreds of nanometers small, which restrains their utilisation in the single-flake FET fabrication. However, it is possible to discover precursor MAX phases with larger particle sizes and explore the electrochemical delamination of MXenes to produce a high-yield MXene suspension with larger lateral flake sizes.

8.2.2.3 Optimisation for industrial mass production

To achieve a higher technology readiness level, the synthesis of MXenes needs further optimisation for industrial-scale mass production. The currently popular synthesis methods involve selective etching and electrochemical etching [152]. These methods are limited to lab-scale and the use of corrosive acid during the synthesis process. Efforts should focus on developing a greener synthesis route [502], streamlining the synthesis process, reducing synthesis costs, and improving the yield to meet the demands of industrial applications.

8.2.2.4 Exploration of new types of MXenes

MXene is a large family of 2D transition metal carbides, nitrides, and carbonitrides. There are many more types of MXenes to be explored experimentally, as shown in Section 2.3. The

electronic properties of MXenes apart from $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x remain underexplored due to the challenges in material preparation and nano-device fabrication. Future research should aim to overcome these challenges by developing new synthesis methods and fabrication techniques. Understanding the intrinsic electronic properties of new types of MXenes could open up new avenues for their application in electronic and energy storage devices [38].

References

- [1] Kostya S Novoselov, Andre K Geim, Sergei V Morozov, De-eng Jiang, Yanshui Zhang, Sergey V Dubonos, Irina V Grigorieva, and Alexandr A Firsov. Electric field effect in atomically thin carbon films. *science*, 306(5696):666–669, 2004.
- [2] Ningqiang Shi, Ling Li, Peng Gao, Xiangqian Jiang, Jiandong Hao, Chuncheng Ban, Ruigeng Zhang, and Zhenxing Liu. Synthesis of two-dimensional hexagonal boron nitride and mid-infrared nanophotonics. *ACS Applied Electronic Materials*, 5(1):34–65, 2022.
- [3] Sergio Pinilla, João Coelho, Ke Li, Ji Liu, and Valeria Nicolosi. Two-dimensional material inks. *Nature Reviews Materials*, 7(9):717–735, 2022.
- [4] The environmental impact of battery production for electric vehicles. [online; accessed 06-November-2024].
- [5] Verified Market Research. Global thermal paste market size by type (silicon free, silicon based), by application (water coolers, air based heat sinks), by geographic scope and forecast, 2024. [Online; accessed 21-March-2024].
- [6] Tokuyama Corporation. Boron nitride for cosmetics, 2024. [Online; accessed 15-July-2024].
- [7] Andrew E Naclerio and Piran R Kidambi. A review of scalable hexagonal boron nitride (h-bn) synthesis for present and future applications. *Advanced Materials*, 35(6):2207374, 2023.
- [8] EK Sichel, RE Miller, MS Abrahams, and CJ Buiocchi. Heat capacity and thermal conductivity of hexagonal pyrolytic boron nitride. *Physical review B*, 13(10):4607, 1976.
- [9] GR Bhimanapati, NR Glavin, and Joshua Alexander Robinson. 2d boron nitride: synthesis and applications. In *Semiconductors and semimetals*, volume 95, pages 101–147. Elsevier, 2016.
- [10] Ki Kang Kim, Soo Min Kim, and Young Hee Lee. A new horizon for hexagonal boron nitride film. *Journal of the Korean physical society*, 64:1605–1616, 2014.
- [11] Chengning Yao, Grigore Leahu, Martin Holicky, Sihui Liu, Benji Fenech-Salerno, May Ching Lai, Maria Cristina Larciprete, Caterina Ducati, Giorgio Divitini,

- Roberto Li Voti, et al. Thermally conductive hexagonal boron nitride/polymer composites for efficient heat transport. *Advanced Functional Materials*, page 2405235, 2024.
- [12] Akash Laturia, Maarten L Van de Put, and William G Vandenberghe. Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. *npj 2D Materials and Applications*, 2(1):6, 2018.
- [13] Qunhong Weng, Xuebin Wang, Xi Wang, Yoshio Bando, and Dmitri Golberg. Functionalized hexagonal boron nitride nanomaterials: emerging properties and applications. *Chemical Society Reviews*, 45(14):3989–4012, 2016.
- [14] Yi Lin and John W Connell. Advances in 2d boron nitride nanostructures: nanosheets, nanoribbons, nanomeshes, and hybrids with graphene. *Nanoscale*, 4(22):6908–6939, 2012.
- [15] Kailiang Zhang, Yulin Feng, Fang Wang, Zhengchun Yang, and John Wang. Two dimensional hexagonal boron nitride (2d-hbn): synthesis, properties and applications. *Journal of Materials Chemistry C*, 5(46):11992–12022, 2017.
- [16] Lu Hua Li, Jiri Cervenka, Kenji Watanabe, Takashi Taniguchi, and Ying Chen. Strong oxidation resistance of atomically thin boron nitride nanosheets. *ACS nano*, 8(2):1457–1462, 2014.
- [17] Qiran Cai, Declan Scullion, Wei Gan, Alexey Falin, Shunying Zhang, Kenji Watanabe, Takashi Taniguchi, Ying Chen, Elton JG Santos, and Lu Hua Li. High thermal conductivity of high-quality monolayer boron nitride and its thermal expansion. *Science advances*, 5(6):eaav0129, 2019.
- [18] CR Dean, AF Young, I Meric, C Lee, and L Wang. Ss, k. watanabe, t. taniguchi, p. kim, kl shepard, j. hone. *Nat. Nanotechnol.*, 5:722–726, 2010.
- [19] Noah Mendelson, Zai-Quan Xu, Toan Trong Tran, Mehran Kianinia, John Scott, Carlo Bradac, Igor Aharonovich, and Milos Toth. Engineering and tuning of quantum emitters in few-layer hexagonal boron nitride. *ACS nano*, 13(3):3132–3140, 2019.
- [20] Ah-Jin Cho and Jang-Yeon Kwon. Hexagonal boron nitride for surface passivation of two-dimensional van der waals heterojunction solar cells. *ACS applied materials & interfaces*, 11(43):39765–39771, 2019.
- [21] Han Zheng and Kuang Yu. First-principles calculations of the hydrolysis mechanism of hexagonal boron nitride nanosheets: Implications for preventing hydrolytic degradation. *ACS Applied Nano Materials*, 5(2):2501–2509, 2022.
- [22] Jia Zhang, Biying Tan, Xin Zhang, Feng Gao, Yunxia Hu, Lifeng Wang, Xiaoming Duan, Zhihua Yang, and PingAn Hu. Atomically thin hexagonal boron nitride and its heterostructures. *Advanced Materials*, 33(6):2000769, 2021.
- [23] Xue Yang, Renhui Zhang, Jibin Pu, Zhongyi He, and Liping Xiong. 2d graphene and h-bn layers application in protective coatings. *Corrosion Reviews*, 39(2):93–107, 2021.

- [24] Jing Li, S Majety, R Dahal, WP Zhao, JY Lin, and HX Jiang. Dielectric strength, optical absorption, and deep ultraviolet detectors of hexagonal boron nitride epilayers. *Applied physics letters*, 101(17), 2012.
- [25] S Dai, Q Ma, T Andersen, AS Mcleod, Z Fei, MK Liu, M Wagner, K Watanabe, T Taniguchi, MJNC Thiemens, et al. Subdiffractional focusing and guiding of polaritonic rays in a natural hyperbolic material. *Nature communications*, 6(1):6963, 2015.
- [26] Joshua D Caldwell, Andrey V Kretinin, Yiguo Chen, Vincenzo Giannini, Michael M Fogler, Yan Francescato, Chase T Ellis, Joseph G Tischler, Colin R Woods, Alexander J Giles, et al. Sub-diffractional volume-confined polaritons in the natural hyperbolic material hexagonal boron nitride. *Nature communications*, 5(1):5221, 2014.
- [27] Snežana Lazić, André Espinha, Sergio Pinilla Yanguas, Carlos Gibaja, Félix Zamora, Pablo Ares, Manish Chhowalla, Wendel S Paz, Juan José Palacios Burgos, Alberto Hernández-Mínguez, et al. Dynamically tuned non-classical light emission from atomic defects in hexagonal boron nitride. *Communications physics*, 2(1):113, 2019.
- [28] Pablo Ares, Tommaso Cea, Matthew Holwill, Yi Bo Wang, Rafael Roldán, Francisco Guinea, Daria V Andreeva, Laura Fumagalli, Konstantin S Novoselov, and Colin R Woods. Piezoelectricity in monolayer hexagonal boron nitride. *Advanced Materials*, 32(1):1905504, 2020.
- [29] Babak Anasori and Yury Gogotsi. Mxenes: trends, growth, and future directions. *Graphene and 2D Materials*, 7(3):75–79, 2022.
- [30] Paweł P Michałowski, Mark Anayee, Tyler S Mathis, Sylwia Kozdra, Adrianna Wójcik, Kanit Hantanasirisakul, Iwona Jóźwik, Anna Piątkowska, Małgorzata Moździońek, Agnieszka Malinowska, et al. Oxycarbide mxenes and max phases identification using monoatomic layer-by-layer analysis with ultralow-energy secondary-ion mass spectrometry. *Nature Nanotechnology*, 17(11):1192–1197, 2022.
- [31] Michael Naguib, Murat Kurtoglu, Volker Presser, Jun Lu, Junjie Niu, Min Heon, Lars Hultman, Yury Gogotsi, and Michel W Barsoum. Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 . *Advanced materials*, 23(37):4248–4253, 2011.
- [32] Olha Mashtalir, Michael Naguib, Vadym N Mochalin, Yohan Dall’Agnese, Min Heon, Michel W Barsoum, and Yury Gogotsi. Intercalation and delamination of layered carbides and carbonitrides. *Nature communications*, 4(1):1716, 2013.
- [33] Michael Ghidui, Maria R Lukatskaya, Meng-Qiang Zhao, Yury Gogotsi, and Michel W Barsoum. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. *Nature*, 516(7529):78–81, 2014.
- [34] G Murali, Jeevan Kumar Reddy Modigunta, Young Ho Park, Jong-Hoon Lee, Jishu Rawal, Seul-Yi Lee, Insik In, and Soo-Jin Park. A review on mxene synthesis, stability, and photocatalytic applications. *ACS nano*, 16(9):13370–13429, 2022.
- [35] Peng Zhang, Yanmeng Peng, Qizhen Zhu, Razium Ali Soomro, Ning Sun, and Bin Xu. 3d foam-based mxene architectures: Structural and electrolytic engineering for advanced potassium-ion storage. *Energy & Environmental Materials*, 2022.

- [36] Peng Zhang, Qizhen Zhu, Yi Wei, and Bin Xu. Achieving stable and fast potassium storage of Sb_2S_3 @ mxene anode via interfacial bonding and electrolyte chemistry. *Chemical Engineering Journal*, 451:138891, 2023.
- [37] Sheng Yong, Chengning Yao, Nicholas Hillier, Hyunho Kim, Martin Holicky, Sihui Liu, Regan Doherty, Felice Torrissi, and Stephen Beeby. Ti_3C_2 mxene as additive for low-cost textile supercapacitors with enhanced electrical performance. *Advanced Materials Technologies*, 9(2):2301266, 2024.
- [38] Fangwang Ming, Hanfeng Liang, Gang Huang, Zahra Bayhan, and Husam N Alshareef. Mxenes for rechargeable batteries beyond the lithium-ion. *Advanced Materials*, 33(1):2004039, 2021.
- [39] Razium A Soomro, Peng Zhang, Baomin Fan, Yi Wei, and Bin Xu. Progression in the oxidation stability of mxenes. *Nano-Micro Letters*, 15(1):108, 2023.
- [40] Jizhou Jiang, Saishuai Bai, Jing Zou, Song Liu, Jyh-Ping Hsu, Neng Li, Guoyin Zhu, Zechao Zhuang, Qi Kang, and Yizhou Zhang. Improving stability of mxenes. *Nano Research*, 15(7):6551–6567, 2022.
- [41] Fangcheng Cao, Ye Zhang, Hongqing Wang, Karim Khan, Ayesha Khan Tareen, Wenjing Qian, Han Zhang, and Hans Ågren. Recent advances in oxidation stable chemistry of 2d mxenes. *Advanced Materials*, 34(13):2107554, 2022.
- [42] Andrew E Naclerio and Piran R Kidambi. A review of scalable hexagonal boron nitride (h-bn) synthesis for present and future applications. *Advanced Materials*, 35(6):2207374, 2023.
- [43] Vigneshwaran Shanmugam, Rhoda Afriyie Mensah, Karthik Babu, Sidique Gawusu, Avishek Chanda, Yongming Tu, Rasoul Esmaeely Neisiany, Michael Försth, Gabriel Sas, and Oisik Das. A review of the synthesis, properties, and applications of 2d materials. *Particle & Particle Systems Characterization*, 39(6):2200031, 2022.
- [44] Jeongho Park, William C Mitchel, Lawrence Grazulis, Howard E Smith, Kurt G Eyink, John J Boeckl, David H Tomich, Shanee D Pacley, and John E Hoelscher. Epitaxial graphene growth by carbon molecular beam epitaxy (cmbe). *Advanced Materials*, 22(37):4140–4145, 2010.
- [45] YI Zhang, Luyao Zhang, and Chongwu Zhou. Review of chemical vapor deposition of graphene and related applications. *Accounts of chemical research*, 46(10):2329–2339, 2013.
- [46] Gang Hee Han, Hyeon-Jin Shin, Eun Sung Kim, Seung Jin Chae, Jae-Young Choi, and Young Hee Lee. Poly (ethylene co-vinyl acetate)-assisted one-step transfer of ultra-large graphene. *Nano*, 6(01):59–65, 2011.
- [47] Xuesong Li, Weiwei Cai, Jinho An, Seyoung Kim, Junghyo Nah, Dongxing Yang, Richard Piner, Aruna Velamakanni, Inhwa Jung, Emanuel Tutuc, et al. Large-area synthesis of high-quality and uniform graphene films on copper foils. *science*, 324(5932):1312–1314, 2009.

- [48] ATT Koh, YM Foong, and Daniel HC Chua. Cooling rate and energy dependence of pulsed laser fabricated graphene on nickel at reduced temperature. *Applied Physics Letters*, 97(11), 2010.
- [49] I Navas, R Vinodkumar, and VP Mahadevan Pillai. Self-assembly and photoluminescence of molybdenum oxide nanoparticles. *Applied Physics A*, 103:373–380, 2011.
- [50] Kyung Yeol Ma, Leining Zhang, Sunghwan Jin, Yan Wang, Seong In Yoon, Hyuntae Hwang, Juseung Oh, Da Sol Jeong, Meihui Wang, Shahana Chatterjee, et al. Epitaxial single-crystal hexagonal boron nitride multilayers on ni (111). *Nature*, 606(7912):88–93, 2022.
- [51] Andre Konstantin Geim. Graphene: status and prospects. *science*, 324(5934):1530–1534, 2009.
- [52] Madeline S Stark, Kaci L Kuntz, Sean J Martens, and Scott C Warren. Intercalation of layered materials from bulk to 2d. *Advanced Materials*, 31(27):1808213, 2019.
- [53] Yingchang Yang, Hongshuai Hou, Guoqiang Zou, Wei Shi, Honglei Shuai, Jiayang Li, and Xiaobo Ji. Electrochemical exfoliation of graphene-like two-dimensional nanomaterials. *Nanoscale*, 11(1):16–33, 2019.
- [54] Damien Hanlon. *Liquid phase exfoliation of novel 2D nanomaterials*. PhD thesis, Trinity College Dublin, 2016.
- [55] Felice Torrisi and Tian Carey. Graphene, related two-dimensional crystals and hybrid systems for printed and wearable electronics. *Nano Today*, 23:73–96, 2018.
- [56] Kostya S Novoselov, Da Jiang, F Schedin, TJ Booth, VV Khotkevich, SV Morozov, and Andre K Geim. Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences*, 102(30):10451–10453, 2005.
- [57] Kostya S Novoselov, Da Jiang, F Schedin, TJ Booth, VV Khotkevich, SV Morozov, and Andre K Geim. Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences*, 102(30):10451–10453, 2005.
- [58] Daniela Pacile, JC Meyer, ÇÖ Girit, and AJAPL Zettl. The two-dimensional phase of boron nitride: Few-atomic-layer sheets and suspended membranes. *Applied Physics Letters*, 92(13), 2008.
- [59] Roman V Gorbachev, Ibtisam Riaz, Rahul R Nair, Rashid Jalil, Liam Britnell, Branson D Belle, Ernie W Hill, Kostya S Novoselov, Kenji Watanabe, Takashi Taniguchi, et al. Hunting for monolayer boron nitride: optical and raman signatures. *arXiv preprint arXiv:1008.2868*, 2010.
- [60] Lu Hua Li, Ying Chen, Gavin Behan, Hongzhou Zhang, Mladen Petravic, and Alexey M Glushenkov. Large-scale mechanical peeling of boron nitride nanosheets by low-energy ball milling. *Journal of materials chemistry*, 21(32):11862–11866, 2011.

- [61] Yagang Yao, Ziyin Lin, Zhuo Li, Xiaojuan Song, Kyoung-Sik Moon, and Ching-ping Wong. Large-scale production of two-dimensional nanosheets. *Journal of Materials Chemistry*, 22(27):13494–13499, 2012.
- [62] Soumyabrata Roy, Xiang Zhang, Anand B Puthirath, Ashokkumar Meiyazhagan, Sohini Bhattacharyya, Muhammad M Rahman, Ganguli Babu, Sandhya Susarla, Sreehari K Saju, Mai Kim Tran, et al. Structure, properties and applications of two-dimensional hexagonal boron nitride. *Advanced Materials*, 33(44):2101589, 2021.
- [63] Thanh-Hai Le, Yuree Oh, Hyungwoo Kim, and Hyeonseok Yoon. Exfoliation of 2d materials for energy and environmental applications. *Chemistry—A European Journal*, 26(29):6360–6401, 2020.
- [64] Francesco Bonaccorso and Zhipei Sun. Solution processing of graphene, topological insulators and other 2d crystals for ultrafast photonics. *Optical Materials Express*, 4(1):63–78, 2014.
- [65] Yenny Hernandez, Valeria Nicolosi, Mustafa Lotya, Fiona M Blighe, Zhenyu Sun, Sukanta De, Ignatius T McGovern, Brendan Holland, Michele Byrne, Yurii K Gun'Ko, et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, 3(9):563–568, 2008.
- [66] Wei Cao, Jin Wang, and Ming Ma. Exfoliation of two-dimensional materials: the role of entropy. *The journal of physical chemistry letters*, 10(5):981–986, 2019.
- [67] Ning Wang, Guang Yang, Haixu Wang, Changzeng Yan, Rong Sun, and Ching-Ping Wong. A universal method for large-yield and high-concentration exfoliation of two-dimensional hexagonal boron nitride nanosheets. *Materials Today*, 27:33–42, 2019.
- [68] Yi Lin, Tiffany V Williams, and John W Connell. Soluble, exfoliated hexagonal boron nitride nanosheets. *The Journal of Physical Chemistry Letters*, 1(1):277–283, 2010.
- [69] Aamar F Khan, Dale AC Brownson, Christopher W Foster, Graham C Smith, and Craig E Banks. Surfactant exfoliated 2d hexagonal boron nitride (2d-hbn) explored as a potential electrochemical sensor for dopamine: Surfactants significantly influence sensor capabilities. *Analyst*, 142(10):1756–1764, 2017.
- [70] Xianlei Li, Xiaopeng Hao, Mingwen Zhao, Yongzhong Wu, Jiayang Yang, Yupeng Tian, and Guodong Qian. Exfoliation of hexagonal boron nitride by molten hydroxides. *Advanced Materials (Deerfield Beach, Fla.)*, 25(15):2200–2204, 2013.
- [71] Neha Mittal, Garima Kedawat, Kanika, Sarika Gupta, and Bipin Kumar Gupta. An innovative method for large-scale synthesis of hexagonal boron nitride nanosheets by liquid phase exfoliation. *ChemistrySelect*, 5(40):12564–12569, 2020.
- [72] Yi Lin, Tiffany V Williams, and John W Connell. Soluble, exfoliated hexagonal boron nitride nanosheets. *The Journal of Physical Chemistry Letters*, 1(1):277–283, 2010.

- [73] Hyunho Kim, Adrees Arbab, Benji Fenech-Salerno, Chengning Yao, Ryan Macpherson, Jong Min Kim, and Felice Torrisi. Barium titanate-enhanced hexagonal boron nitride inks for printable high-performance dielectrics. *Nanotechnology*, 33(21):215704, 2022.
- [74] Felice Torrisi, Tawfique Hasan, Weiping Wu, Zhipei Sun, Antonio Lombardo, Tero S Kulmala, Gen-Wen Hsieh, Sungjune Jung, Francesco Bonaccorso, Philip J Paul, et al. Inkjet-printed graphene electronics. *ACS nano*, 6(4):2992–3006, 2012.
- [75] Panagiotis G Karagiannidis, Stephen A Hodge, Lucia Lombardi, Flavia Tomarchio, Nicolas Decorde, Silvia Milana, Ilya Goykhman, Yang Su, Steven V Mesite, Duncan N Johnstone, et al. Microfluidization of graphite and formulation of graphene-based conductive inks. *ACS nano*, 11(3):2742–2755, 2017.
- [76] Keith R Paton, Eswaraiah Varra, Claudia Backes, Ronan J Smith, Umar Khan, Arlene O’Neill, Conor Boland, Mustafa Lotya, Oana M Istrate, Paul King, et al. Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nature materials*, 13(6):624–630, 2014.
- [77] Jonathan N Coleman, Mustafa Lotya, Arlene O’Neill, Shane D Bergin, Paul J King, Umar Khan, Karen Young, Alexandre Gaucher, Sukanta De, Ronan J Smith, et al. Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science*, 331(6017):568–571, 2011.
- [78] Nicholas R Glavin, Rahul Rao, Vikas Varshney, Elisabeth Bianco, Amey Apte, Ajit Roy, Emilie Ringe, and Pulickel M Ajayan. Emerging applications of elemental 2d materials. *Advanced Materials*, 32(7):1904302, 2020.
- [79] Adrees Arbab. *Charge transport mechanism within 2D material films and its role on field effect transistor and capacitor technology*. PhD thesis, University of Cambridge, 2023.
- [80] Tian Carey, Adrees Arbab, Luca Anzi, Helen Bristow, Fei Hui, Sivasambu Bohm, Gwenhivir Wyatt-Moon, Andrew Flewitt, Andrew Wadsworth, Nicola Gasparini, et al. Inkjet printed circuits with two-dimensional semiconductor inks for high-performance electronics. *arXiv preprint arXiv:2011.12359*, 2020.
- [81] Tian Carey. *Two-dimensional material inks and composites for printed electronics and energy*. PhD thesis, 2018.
- [82] Weifeng Li, Yanmei Yang, Gang Zhang, and Yong-Wei Zhang. Ultrafast and directional diffusion of lithium in phosphorene for high-performance lithium-ion battery. *Nano letters*, 15(3):1691–1697, 2015.
- [83] Xiao Zhang, Wei Tan, Tian Carey, Bo Wen, Delong He, Adrees Arbab, Alex Groombridge, Fiona Smail, Jean de La Verpilliere, Chengning Yao, et al. Enhanced composite thermal conductivity by percolated networks of in-situ confined-grown carbon nanotubes. *Nano Research*, 16(11):12821–12829, 2023.
- [84] Benji Fenech-Salerno, Martin Holicky, Chengning Yao, Anthony EG Cass, and Felice Torrisi. A sprayed graphene transistor platform for rapid and low-cost chemical sensing. *Nanoscale*, 15(7):3243–3254, 2023.

- [85] S Anirudh, Satheesh Krishnamurthy, Balasubramanian Kandasubramanian, and Praveen Kumar. Probing into atomically thin layered nano-materials protective coating for aerospace and strategic defence application—a review. *Journal of alloys and compounds*, page 172203, 2023.
- [86] Feng Ru Fan, Ruoxing Wang, Hua Zhang, and Wenzhuo Wu. Emerging beyond-graphene elemental 2d materials for energy and catalysis applications. *Chemical Society Reviews*, 50(19):10983–11031, 2021.
- [87] Tofik Ahmed Shifa, Fengmei Wang, Yang Liu, and Jun He. Heterostructures based on 2d materials: A versatile platform for efficient catalysis. *Advanced Materials*, 31(45):1804828, 2019.
- [88] Harneet Kaur and Jonathan N Coleman. Liquid-phase exfoliation of nonlayered non-van-der-waals crystals into nanoplatelets. *Advanced Materials*, 34(35):2202164, 2022.
- [89] Liyong Niu, Jonathan N Coleman, Hua Zhang, Hyeonsuk Shin, Manish Chhowalla, and Zijian Zheng. Production of two-dimensional nanomaterials via liquid-based direct exfoliation. *Small*, 12(3):272–293, 2016.
- [90] Mohammad Hamidul Islam, Shaila Afroj, Mohammad Abbas Uddin, Daria V Andreeva, Kostya S Novoselov, and Nazmul Karim. Graphene and cnt-based smart fiber-reinforced composites: a review. *Advanced Functional Materials*, 32(40):2205723, 2022.
- [91] Eswaraiiah Varrla, Claudia Backes, Keith R Paton, Andrew Harvey, Zahra Gholamvand, Joe McCauley, and Jonathan N Coleman. Large-scale production of size-controlled mos2 nanosheets by shear exfoliation. *Chemistry of Materials*, 27(3):1129–1139, 2015.
- [92] Eswaraiiah Varrla, Keith R Paton, Claudia Backes, Andrew Harvey, Ronan J Smith, Joe McCauley, and Jonathan N Coleman. Turbulence-assisted shear exfoliation of graphene using household detergent and a kitchen blender. *Nanoscale*, 6(20):11810–11819, 2014.
- [93] Sonia Biccai, Sebastian Barwich, Daniel Boland, Andrey Harvey, Damien Hanlon, Niall McEvoy, and Jonathan N Coleman. Exfoliation of 2d materials by high shear mixing. *2D Materials*, 6(1):015008, 2018.
- [94] Weiran Zheng and Lawrence Yoon Suk Lee. Beyond sonication: Advanced exfoliation methods for scalable production of 2d materials. *Matter*, 5(2):515–545, 2022.
- [95] Dinh-Tuan Nguyen, Hsiang-An Ting, Yen-Hsun Su, Mario Hofmann, and Ya-Ping Hsieh. Additive-enhanced exfoliation for high-yield 2d materials production. *Nanomaterials*, 11(3):601, 2021.
- [96] Stanley Goldberg. Mechanical/physical methods of cell disruption and tissue homogenization. *2D PAGE: Sample preparation and fractionation*, pages 3–22, 2008.

- [97] T Panagiotou, SV Mesite, JM Bernard, KJ Chomistek, and RJ Fisher. Production of polymer nanosuspensions using microfluidizer processor based technologies. In *Proceedings of the nanotechnology conference and trade show*, pages 688–691, 2008.
- [98] Qingwei Yan, Wen Dai, Jingyao Gao, Xue Tan, Le Lv, Junfeng Ying, Xiaoxin Lu, Jibao Lu, Yagang Yao, Qiuping Wei, et al. Ultrahigh-aspect-ratio boron nitride nanosheets leading to superhigh in-plane thermal conductivity of foldable heat spreader. *Acs Nano*, 15(4):6489–6498, 2021.
- [99] Qing Zhang, Wenzhong Bao, Amy Gong, Tao Gong, Dakang Ma, Jiayu Wan, Jiaqi Dai, Jeremy N Munday, Jr-Hau He, Liangbing Hu, et al. A highly sensitive, highly transparent, gel-gated mos 2 phototransistor on biodegradable nanopaper. *Nanoscale*, 8(29):14237–14242, 2016.
- [100] Jamileh Shojaeiarani, Dilpreet Bajwa, and Greg Holt. Sonication amplitude and processing time influence the cellulose nanocrystals morphology and dispersion. *Nanocomposites*, 6(1):41–46, 2020.
- [101] Kenneth S Suslick. Effects of ultrasound on surfaces and solids. *Advances in sonochemistry*, 1:197–230, 1990.
- [102] Yanyan Xu, Huizhe Cao, Yanqin Xue, Biao Li, and Weihua Cai. Liquid-phase exfoliation of graphene: an overview on exfoliation media, techniques, and challenges. *Nanomaterials*, 8(11):942, 2018.
- [103] Gaurav Kumar, Srishti Upadhyay, Dhiraj Kumar Yadav, Santanu Malakar, Priyanka Dhurve, and Shweta Suri. Application of ultrasound technology for extraction of color pigments from plant sources and their potential bio-functional properties: A review. *Journal of Food Process Engineering*, 46(6):e14238, 2023.
- [104] Khuyen Viet Bao Tran, Takahide Kimura, Takashi Kondo, and Shinobu Koda. Quantification of frequency dependence of mechanical effects induced by ultrasound. *Ultrasonics sonochemistry*, 21(2):716–721, 2014.
- [105] Rakhee Durge, RV Kshirsagar, and Pankaj Tambe. Effect of sonication energy on the yield of graphene nanosheets by liquid-phase exfoliation of graphite. *Procedia Engineering*, 97:1457–1465, 2014.
- [106] Hugo Miguel Santos, Carlos Lodeiro, and José-Luis Capelo-Martínez. Ultrasonic energy as a tool for sample treatment for the analysis of elements and elemental speciation. *Ultrasound in Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, pages 17–54, 2009.
- [107] Clésia C Nascentes, Mauro Korn, Clarivaldo S Sousa, and Marco AZ Arruda. Use of ultrasonic baths for analytical applications: a new approach for optimisation conditions. *Journal of the Brazilian Chemical Society*, 12:57–63, 2001.
- [108] NP Dhanalakshmi and R Nagarajan. Ultrasonic intensification of the chemical degradation of methyl violet: an experimental study. *International Journal of Chemical and Molecular Engineering*, 5(11):1033–1038, 2011.

- [109] Konstantinos Kouroupis-Agalou, Andrea Liscio, Emanuele Treossi, Luca Ortolani, Vittorio Morandi, Nicola Maria Pugno, and Vincenzo Palermo. Fragmentation and exfoliation of 2-dimensional materials: a statistical approach. *Nanoscale*, 6(11):5926–5933, 2014.
- [110] MM Chivate and AB Pandit. Quantification of cavitation intensity in fluid bulk. *Ultrasonics Sonochemistry*, 2(1):S19–S25, 1995.
- [111] Jonathan N Coleman. Liquid exfoliation of defect-free graphene. *Accounts of chemical research*, 46(1):14–22, 2013.
- [112] Artur Ciesielski and Paolo Samorì. Graphene via sonication assisted liquid-phase exfoliation. *Chemical Society Reviews*, 43(1):381–398, 2014.
- [113] J Scott Bunch, Yuval Yaish, Markus Brink, Kirill Bolotin, and Paul L McEuen. Coulomb oscillations and hall effect in quasi-2d graphite quantum dots. *Nano letters*, 5(2):287–290, 2005.
- [114] Yenny Hernandez, Valeria Nicolosi, Mustafa Lotya, Fiona M Blighe, Zhenyu Sun, Sukanta De, Ignatius T McGovern, Brendan Holland, Michele Byrne, Yurii K Gun’Ko, et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, 3(9):563–568, 2008.
- [115] Dmitri Golberg, Yoshio Bando, Yang Huang, Takeshi Terao, Masanori Mitome, Chengchun Tang, and Chunyi Zhi. Boron nitride nanotubes and nanosheets. *ACS nano*, 4(6):2979–2993, 2010.
- [116] Chunyi Zhi, Yoshio Bando, Chengchun Tang, Hiroaki Kuwahara, and Dimitri Golberg. Large-scale fabrication of boron nitride nanosheets and their utilization in polymeric composites with improved thermal and mechanical properties. *Advanced materials*, 21(28):2889–2893, 2009.
- [117] Valeria Nicolosi, Manish Chhowalla, Mercouri G Kanatzidis, Michael S Strano, and Jonathan N Coleman. Liquid exfoliation of layered materials. *Science*, 340(6139):1226419, 2013.
- [118] Yenny Hernandez, Mustafa Lotya, David Rickard, Shane D Bergin, and Jonathan N Coleman. Measurement of multicomponent solubility parameters for graphene facilitates solvent discovery. *Langmuir*, 26(5):3208–3213, 2010.
- [119] J Marguerite Hughes, Damian Aherne, and Jonathan N Coleman. Generalizing solubility parameter theory to apply to one-and two-dimensional solutes and to incorporate dipolar interactions. *Journal of Applied Polymer Science*, 127(6):4483–4491, 2013.
- [120] Chen-Xia Hu, Yuyoung Shin, Oliver Read, and Cinzia Casiraghi. Dispersant-assisted liquid-phase exfoliation of 2d materials beyond graphene. *Nanoscale*, 13(2):460–484, 2021.
- [121] Aideen Griffin, Katharina Nisi, Joshua Pepper, Andrew Harvey, Beata M Szydłowska, Jonathan N Coleman, and Claudia Backes. Effect of surfactant choice and concentration on the dimensions and yield of liquid-phase-exfoliated nanosheets. *Chemistry of Materials*, 32(7):2852–2862, 2020.

- [122] Zahra Rafiei-Sarmazdeh, Seyed Hassan Jafari, Seyed Javad Ahmadi, and Seyed Morteza Zahedi-Dizaji. Large-scale exfoliation of hexagonal boron nitride with combined fast quenching and liquid exfoliation strategies. *Journal of materials science*, 51:3162–3169, 2016.
- [123] Jacob N Israelachvili. Van der waals forces. *Intermolecular and surface forces*, pages 107–132, 2011.
- [124] Charles M Hansen. *Hansen solubility parameters: a user's handbook*. CRC press, 2007.
- [125] Hélène Launay, Charles M Hansen, and Kristoffer Almdal. Hansen solubility parameters for a carbon fiber/epoxy composite. *Carbon*, 45(15):2859–2865, 2007.
- [126] Abhijit Biswas, Rui Xu, Joyce Christiansen-Salameh, Eugene Jeong, Gustavo A Alvarez, Chenxi Li, Anand B Puthirath, Bin Gao, Arushi Garg, Tia Gray, et al. Phase stability of hexagonal/cubic boron nitride nanocomposites. *Nano Letters*, 23(15):6927–6936, 2023.
- [127] Graeme Cunningham, Mustafa Lotya, Clotilde S Cucinotta, Stefano Sanvito, Shane D Bergin, Robert Menzel, Milo SP Shaffer, and Jonathan N Coleman. Solvent exfoliation of transition metal dichalcogenides: dispersibility of exfoliated nanosheets varies only weakly between compounds. *ACS nano*, 6(4):3468–3480, 2012.
- [128] Min Yi, Zhigang Shen, Shulin Ma, and Xiaojing Zhang. A mixed-solvent strategy for facile and green preparation of graphene by liquid-phase exfoliation of graphite. *Journal of Nanoparticle Research*, 14:1–9, 2012.
- [129] Dimitrios Tasis, Kostas Papagelis, Panagiotis Spiliopoulos, and Costas Galiotis. Efficient exfoliation of graphene sheets in binary solvents. *Materials Letters*, 94:47–50, 2013.
- [130] Guoxiu Wang, Xiaoping Shen, Jane Yao, and Jinsoo Park. Graphene nanosheets for enhanced lithium storage in lithium ion batteries. *Carbon*, 47(8):2049–2053, 2009.
- [131] Rekha Narayan and Sang Ouk Kim. Surfactant mediated liquid phase exfoliation of graphene. *Nano Convergence*, 2:1–19, 2015.
- [132] Onofrio M Maragó, Francesco Bonaccorso, Rosalba Saija, Giulia Privitera, Pietro G Gucciardi, Maria Antonia Iatì, Giuseppe Calogero, Philip H Jones, Ferdinando Borghese, Paolo Denti, et al. Brownian motion of graphene. *ACS nano*, 4(12):7515–7523, 2010.
- [133] Xiaoxi Zhu, Leonard WT Ng, Guohua Hu, Tien-Chun Wu, Doo-Seung Um, Nasiruddin Macadam, and Tawfique Hasan. Hexagonal boron nitride-enhanced optically transparent polymer dielectric inks for printable electronics. *Advanced Functional Materials*, 30(31):2002339, 2020.
- [134] Joohoon Kang, Jung-Woo T Seo, Diego Alducin, Arturo Ponce, Miguel Jose Yacamán, and Mark C Hersam. Thickness sorting of two-dimensional transition metal dichalcogenides via copolymer-assisted density gradient ultracentrifugation. *Nature communications*, 5(1):5478, 2014.

- [135] Tatsuo Sato and Richard Ruch. Stabilization of colloidal dispersions by polymer adsorption. 1980.
- [136] Sheena S Sukumaran, KB Jinesh, and KG Gopchandran. Liquid phase exfoliated graphene for electronic applications. *Materials Research Express*, 4(9):095017, 2017.
- [137] Xin-Gui Li, Mei-Rong Huang, and He Bai. Thermal decomposition of cellulose ethers. *Journal of Applied Polymer Science*, 73(14):2927–2936, 1999.
- [138] Athanasios B Bourlinos, Vasilios Georgakilas, Radek Zboril, Theodore A Steriotis, Athanasios K Stubos, and Christos Trapalis. Aqueous-phase exfoliation of graphite in the presence of polyvinylpyrrolidone for the production of water-soluble graphenes. *Solid State Communications*, 149(47-48):2172–2176, 2009.
- [139] C Backes, AM Abdelkader, C Alonso, A Andrieux-Ledier, R Arenal, J Azpeitia, N Balakrishnan, L Banszerus, J Barjon, R Bartali, et al. Production and processing of graphene and related materials, 2d mater., 2020, 7, 022001. DOI, 10:2053–1583.
- [140] Claudia Backes, Amr M Abdelkader, Concepción Alonso, Amandine Andrieux-Ledier, Raul Arenal, Jon Azpeitia, Nilanthi Balakrishnan, Luca Banszerus, Julien Barjon, Ruben Bartali, et al. Production and processing of graphene and related materials. *2D Materials*, 7(2):022001, 2020.
- [141] Anthony Hutin and Marcio S Carvalho. Effect of contamination from direct sonication on characterization of nanofluid stability. *Powder Technology*, 399:117157, 2022.
- [142] Umar Khan, Arlene O’Neill, Harshit Porwal, Peter May, Khalid Nawaz, and Jonathan N Coleman. Size selection of dispersed, exfoliated graphene flakes by controlled centrifugation. *Carbon*, 50(2):470–475, 2012.
- [143] Celeste L Todaro. Centrifugation. In *Fermentation and biochemical engineering handbook*, pages 558–589. Elsevier, 1996.
- [144] Theodor Svedberg, Kai Oluf Pedersen, et al. The ultracentrifuge. *The Ultracentrifuge.*, 1940.
- [145] Xingke Cai, Yuting Luo, Bilu Liu, and Hui-Ming Cheng. Preparation of 2d material dispersions and their applications. *Chemical Society Reviews*, 47(16):6224–6266, 2018.
- [146] Fuad I Alzakia, Wanxin Sun, Stephen J Pennycook, and Swee Ching Tan. Introducing normalized centrifugation for a more accurate thermodynamic analysis of molybdenum disulfide dispersions: A study on mixed solvents of alcohols and amines with water. *ACS applied materials & interfaces*, 12(2):3096–3103, 2019.
- [147] Arlene O’Neill, Umar Khan, and Jonathan N Coleman. Preparation of high concentration dispersions of exfoliated mos2 with increased flake size. *Chemistry of Materials*, 24(12):2414–2421, 2012.
- [148] Umar Khan, Arlene O’Neill, Mustafa Lotya, Sukanta De, and Jonathan N Coleman. High-concentration solvent exfoliation of graphene. *small*, 6(7):864–871, 2010.

- [149] Stephen Olaribigbe Majekodunmi. A review on centrifugation in the pharmaceutical industry. *Am. J. Biomed. Eng.*, 5(2):67–78, 2015.
- [150] Subhasree Panda, Kalim Deshmukh, SK Khadheer Pasha, Jayaraman Theerthagiri, Sivakumar Manickam, and Myong Yong Choi. Mxene based emerging materials for supercapacitor applications: Recent advances, challenges, and future perspectives. *Coordination Chemistry Reviews*, 462:214518, 2022.
- [151] Hyunho Kim. *Two-Dimensional Transition Metal Carbides (MXenes) for Electronic and Energy Harvesting Applications*. PhD thesis, 2020.
- [152] Kang Rui Garrick Lim, Mikhail Shekhirev, Brian C Wyatt, Babak Anasori, Yury Gogotsi, and Zhi Wei Seh. Fundamentals of mxene synthesis. *Nature Synthesis*, 1(8):601–614, 2022.
- [153] Mohamed Alhabeb, Kathleen Maleski, Babak Anasori, Pavel Lelyukh, Leah Clark, Saleesha Sin, and Yury Gogotsi. Guidelines for synthesis and processing of two-dimensional titanium carbide ($\text{Ti}_3\text{C}_2\text{Tx}$ mxene). *Chemistry of Materials*, 29(18):7633–7644, 2017.
- [154] Joseph Halim, Sankalp Kota, Maria R Lukatskaya, Michael Naguib, Meng-Qiang Zhao, Eun Ju Moon, Jeremy Pitock, Jagjit Nanda, Steven J May, Yury Gogotsi, et al. Synthesis and characterization of 2d molybdenum carbide (mxene). *Advanced Functional Materials*, 26(18):3118–3127, 2016.
- [155] Mykola Seredych, Christopher Eugene Shuck, David Pinto, Mohamed Alhabeb, Eliot Precetti, Grayson Deysher, Babak Anasori, Narendra Kurra, and Yury Gogotsi. High-temperature behavior and surface chemistry of carbide mxenes studied by thermal analysis. *Chemistry of Materials*, 31(9):3324–3332, 2019.
- [156] Kun Wang, Youfu Zhou, Wentao Xu, Decai Huang, Zhiguang Wang, and Maochun Hong. Fabrication and thermal stability of two-dimensional carbide Ti_3C_2 nanosheets. *Ceramics International*, 42(7):8419–8424, 2016.
- [157] Alexey Lipatov, Mohamed Alhabeb, Maria R Lukatskaya, Alex Boson, Yury Gogotsi, and Alexander Sinitskii. Effect of synthesis on quality, electronic properties and environmental stability of individual monolayer Ti_3C_2 mxene flakes. *Advanced Electronic Materials*, 2(12):1600255, 2016.
- [158] Bilal Ahmed, Dalaver H Anjum, Mohamed N Hedhili, Yury Gogotsi, and Husam N Alshareef. H_2O_2 assisted room temperature oxidation of Ti_3C_2 mxene for li-ion battery anodes. *Nanoscale*, 8(14):7580–7587, 2016.
- [159] Tian Zhang, Limei Pan, Huan Tang, Fei Du, Yanhua Guo, Tai Qiu, and Jian Yang. Synthesis of two-dimensional $\text{Ti}_3\text{C}_2\text{Tx}$ mxene using $\text{HCl} + \text{LiF}$ etchant: enhanced exfoliation and delamination. *Journal of Alloys and Compounds*, 695:818–826, 2017.
- [160] Subhasree Panda, Kalim Deshmukh, SK Khadheer Pasha, Jayaraman Theerthagiri, Sivakumar Manickam, and Myong Yong Choi. Mxene based emerging materials for supercapacitor applications: Recent advances, challenges, and future perspectives. *Coordination Chemistry Reviews*, 462:214518, 2022.

- [161] Sheng Yang, Panpan Zhang, Faxing Wang, Antonio Gaetano Ricciardulli, Martin R Lohe, Paul WM Blom, and Xinliang Feng. Fluoride-free synthesis of two-dimensional titanium carbide (mxene) using a binary aqueous system. *Angewandte Chemie*, 130(47):15717–15721, 2018.
- [162] Tengfei Li, Lulu Yao, Qinglei Liu, Jiajun Gu, Ruichun Luo, Jinghan Li, Xudong Yan, Weiqiang Wang, Pan Liu, Bin Chen, et al. Fluorine-free synthesis of high-purity $\text{Ti}_3\text{C}_2\text{Tx}$ ($\text{t} = \text{oh}, \text{o}$) via alkali treatment. *Angewandte Chemie International Edition*, 57(21):6115–6119, 2018.
- [163] Lu-Yang Xiu, Zhi-Yu Wang, and Jie-Shan Qiu. General synthesis of mxene by green etching chemistry of fluoride-free lewis acidic melts. *Rare Metals*, 39(11):1237–1238, 2020.
- [164] Wanmei Sun, SA Shah, Yexiao Chen, Z Tan, H Gao, T Habib, M Radovic, and MJ Green. Electrochemical etching of Ti_2AlC to Ti_2CTx (mxene) in low-concentration hydrochloric acid solution. *Journal of Materials Chemistry A*, 5(41):21663–21668, 2017.
- [165] Jinnan Xuan, Zhiqiang Wang, Yuyan Chen, Dujuan Liang, Liang Cheng, Xiaojing Yang, Zhuang Liu, Renzhi Ma, Takayoshi Sasaki, and Fengxia Geng. Organic-base-driven intercalation and delamination for the production of functionalized titanium carbide nanosheets with superior photothermal therapeutic performance. *Angewandte Chemie*, 128(47):14789–14794, 2016.
- [166] Gengnan Li, Li Tan, Yumeng Zhang, Binghan Wu, and Liang Li. Highly efficiently delaminated single-layered mxene nanosheets with large lateral size. *Langmuir*, 33(36):9000–9006, 2017.
- [167] Mohammad Khazaei, Ahmad Ranjbar, Masao Arai, Taizo Sasaki, and Seiji Yunoki. Electronic properties and applications of mxenes: a theoretical review. *Journal of Materials Chemistry C*, 5(10):2488–2503, 2017.
- [168] Michael Ghidui, Joseph Halim, Sankalp Kota, David Bish, Yury Gogotsi, and Michel W Barsoum. Ion-exchange and cation solvation reactions in Ti_3C_2 mxene. *Chemistry of Materials*, 28(10):3507–3514, 2016.
- [169] Alaa Abdellah, Daniela Baierl, Bernhard Fabel, Paolo Lugli, and Giuseppe Scarpa. Spray-coating deposition for large area organic thin-film devices. In *Technical proceedings of the 2009 NSTI Nanotechnology Conference and Expo: Nanotech Conference & Expo 2009; Volume 2*, pages 447–450. CRC Press, 2009.
- [170] Arthur H Lefebvre. Properties of sprays. *Particle & Particle Systems Characterization*, 6(1-4):176–186, 1989.
- [171] F Schmelz and Peter Walzel. Breakup of liquid droplets in accelerated gas flows. *Atomization and Sprays*, 13(4), 2003.
- [172] D Jakubczyk, M Kolwas, G Derkachov, K Kolwas, and M Zientara. Evaporation of micro-droplets: the "radius-square-law" revisited. *Acta Physica Polonica A*, 122(4):709–716, 2012.

- [173] Francesco Bonaccorso, Antonino Bartolotta, Jonathan N Coleman, and Claudia Backes. 2d-crystal-based functional inks. *Advanced Materials*, 28(29):6136–6166, 2016.
- [174] Jack W Owen, Natalia A Azarova, Marsha A Loth, Markos Paradinas, Mariona Coll, Carmen Ocal, John E Anthony, Oana D Jurchescu, et al. Effect of processing parameters on performance of spray-deposited organic thin-film transistors. *Journal of Nanotechnology*, 2011, 2011.
- [175] Byung-Kwan Yu, Doojin Vak, Jang Jo, Seok-In Na, Seok-Soon Kim, Mi-Kyoung Kim, and Dong-Yu Kim. Factors to be considered in bulk heterojunction polymer solar cells fabricated by the spray process. *IEEE Journal of Selected Topics in Quantum Electronics*, 16(6):1838–1846, 2010.
- [176] Jack W Owen, Natalia A Azarova, Marsha A Loth, Markos Paradinas, Mariona Coll, Carmen Ocal, John E Anthony, Oana D Jurchescu, et al. Effect of processing parameters on performance of spray-deposited organic thin-film transistors. *Journal of Nanotechnology*, 2011, 2011.
- [177] Lori Zimmer. *The art of spray paint: inspirations and techniques from masters of aerosol*. Rockport Publishers, 2017.
- [178] Atieh Moridi, SEYYED MOSTAFA Hassani-Gangaraj, Mario Guagliano, and Ming Dao. Cold spray coating: review of material systems and future perspectives. *Surface Engineering*, 30(6):369–395, 2014.
- [179] Pierre L Fauchais, Joachim VR Heberlein, and Maher I Boulos. *Thermal spray fundamentals: from powder to part*. Springer Science & Business Media, 2014.
- [180] Verawati Tjoa, Julianto Chua, Stevin S Pramana, Jun Wei, Subodh G Mhaisalkar, and Nripan Mathews. Facile photochemical synthesis of graphene-pt nanoparticle composite for counter electrode in dye sensitized solar cell. *ACS applied materials & interfaces*, 4(7):3447–3452, 2012.
- [181] Scott Gilje, Song Han, Minsheng Wang, Kang L Wang, and Richard B Kaner. A chemical route to graphene for device applications. *Nano letters*, 7(11):3394–3398, 2007.
- [182] Viet Hung Pham, Tran Viet Cuong, Seung Hyun Hur, Eun Woo Shin, Jae Seong Kim, Jin Suk Chung, and Eui Jung Kim. Fast and simple fabrication of a large transparent chemically-converted graphene film by spray-coating. *Carbon*, 48(7):1945–1951, 2010.
- [183] Zhimin Zhu, Joyce Lowes, John Berron, Brian Smith, and Dan Sullivan. Spin-coating defect theory and experiments. *ECS Transactions*, 60(1):293, 2014.
- [184] Un Gi Lee, Woo-Byoung Kim, Do Hyung Han, and Hyun Soo Chung. A modified equation for thickness of the film fabricated by spin coating. *Symmetry*, 11(9):1183, 2019.
- [185] Kion Norrman, Afshin Ghanbari-Siahkali, and NB Larsen. 6 studies of spin-coated polymer films. *Annual Reports Section" C"(Physical Chemistry)*, 101:174–201, 2005.

- [186] Y Chang, WC Wu, and WC Chen. Theoretical analysis on spin coating of polyimide precursor solutions. *Journal of The Electrochemical Society*, 148(4):F77, 2001.
- [187] Edward D Cohen and Edgar B Gutoff. Modern coating and drying technology. (*No Title*), 1992.
- [188] Abhilasha Mishra, Neha Bhatt, and AK Bajpai. Nanostructured superhydrophobic coatings for solar panel applications. In *Nanomaterials-Based Coatings*, pages 397–424. Elsevier, 2019.
- [189] Yiwen Wang, Joel Luke, Alberto Privitera, Nicolas Rolland, Chiara Labanti, Giacomo Londi, Vincent Lemaure, Daniel TW Toolan, Alexander J Sneyd, Soyeong Jeong, et al. The critical role of the donor polymer in the stability of high-performance non-fullerene acceptor organic solar cells. *Joule*, 7(4):810–829, 2023.
- [190] Francesco Bonaccorso, Antonio Lombardo, Tawfique Hasan, Zhipei Sun, Luigi Colombo, and Andrea C Ferrari. Production and processing of graphene and 2d crystals. *Materials today*, 15(12):564–589, 2012.
- [191] E Kymakis, E Stratakis, MM Stylianakis, E Koudoumas, and C Fotakis. Spin coated graphene films as the transparent electrode in organic photovoltaic devices. *Thin Solid Films*, 520(4):1238–1241, 2011.
- [192] Xi Yang, Weifei Fu, Wenqing Liu, Jinghua Hong, Yu Cai, Chuanhong Jin, Mingsheng Xu, Haibo Wang, Deren Yang, and Hongzheng Chen. Engineering crystalline structures of two-dimensional mos 2 sheets for high-performance organic solar cells. *Journal of Materials Chemistry A*, 2(21):7727–7733, 2014.
- [193] Mohammed Aziz Ibrahim, Tian-wei Lan, Jing Kai Huang, Yang-Yuan Chen, Kung-Hwa Wei, Lain-Jong Li, and Chih Wei Chu. High quantity and quality few-layers transition metal disulfide nanosheets from wet-milling exfoliation. *RSC advances*, 3(32):13193–13202, 2013.
- [194] Zhong-Shuai Wu, Khaled Parvez, Xinliang Feng, and Klaus Müllen. Graphene-based in-plane micro-supercapacitors with high power and energy densities. *Nature communications*, 4(1):2487, 2013.
- [195] Goki Eda, H Emrah Unalan, Nalin Rupesinghe, Gehan AJ Amaratunga, and Manish Chhowalla. Field emission from graphene based composite thin films. *Applied Physics Letters*, 93(23), 2008.
- [196] Mikhail Shekhirev, Jeffrey Busa, Christopher E Shuck, Angel Torres, Saman Bagheri, Alexander Sinitskii, and Yury Gogotsi. Ultralarge flakes of ti3c2t x mxene via soft delamination. *ACS nano*, 16(9):13695–13703, 2022.
- [197] John R Ferraro. *Introductory raman spectroscopy*. Elsevier, 2003.
- [198] Herman A Szymanski. *Raman spectroscopy: theory and practice*. Springer Science & Business Media, 2012.
- [199] Shu-Lin Zhang. *Raman spectroscopy and its application in nanostructures*. John Wiley & Sons, 2012.

- [200] Peter Vandenabeele. *Practical Raman spectroscopy: an introduction*. John Wiley & Sons, 2013.
- [201] Pei-San Hung, Yi-Chun Kuo, He-Guei Chen, Hui-Hua Kenny Chiang, and Oscar Kuang-Sheng Lee. Detection of osteogenic differentiation by differential mineralized matrix production in mesenchymal stromal cells by raman spectroscopy. *PloS one*, 8(5):e65438, 2013.
- [202] Andrea C Ferrari, Jannik C Meyer, Vittorio Scardaci, Cinzia Casiraghi, Michele Lazzeri, Francesco Mauri, Stefano Piscanec, Dingde Jiang, Konstantin Sergeevich Novoselov, Siegmund Roth, et al. Raman spectrum of graphene and graphene layers. *Physical review letters*, 97(18):187401, 2006.
- [203] Roman V Gorbachev, Ihtsam Riaz, Rahul R Nair, Rashid Jalil, Liam Britnell, Branson D Belle, Ernie W Hill, Kostya S Novoselov, Kenji Watanabe, Takashi Taniguchi, et al. Hunting for monolayer boron nitride: optical and raman signatures. *arXiv preprint arXiv:1008.2868*, 2010.
- [204] Mikhail Shekhirev, Christopher E Shuck, Asia Sarycheva, and Yury Gogotsi. Characterization of mxenes at every step, from their precursors to single flakes and assembled films. *Progress in Materials Science*, 120:100757, 2021.
- [205] John F Watts and John Wolstenholme. *An introduction to surface analysis by XPS and AES*. John Wiley & Sons, 2019.
- [206] John C Vickerman and Ian S Gilmore. *Surface analysis: the principal techniques*. John Wiley & Sons, 2011.
- [207] Jill Chastain and Roger C King Jr. Handbook of x-ray photoelectron spectroscopy. *Perkin-Elmer Corporation*, 40:221, 1992.
- [208] Joseph Halim, Kevin M Cook, Michael Naguib, Per Eklund, Yury Gogotsi, Johanna Rosen, and Michel W Barsoum. X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (mxenes). *Applied Surface Science*, 362:406–417, 2016.
- [209] George F Harrington and José Santiso. Back-to-basics tutorial: X-ray diffraction of thin films. *Journal of Electroceramics*, 47(4):141–163, 2021.
- [210] Kaimin Shih. *X-ray diffraction: Structure, principles and applications*. Nova Science Publishers, Inc., 2013.
- [211] Myeongkyu Lee. *X-Ray diffraction for materials research: from fundamentals to applications*. CRC Press, 2017.
- [212] Flavien Pillet, Louise Chopinet, Cécile Formosa, and Étienne Dague. Atomic force microscopy and pharmacology: from microbiology to cancerology. *Biochimica et Biophysica Acta (BBA)-General Subjects*, 1840(3):1028–1050, 2014.
- [213] Guanghong Zeng, Yusheng Duan, Flemming Besenbacher, and Mingdong Dong. Nanomechanics of amyloid materials studied by atomic force microscopy. *Atomic Force Microscopy Investigations into Biology-From Cell to Protein*, 2012.

- [214] Nuno C Santos and Filomena A Carvalho. Atomic force microscopy. *Meth Mol biol*, 1886, 2019.
- [215] Wesley C Sanders. *Atomic Force Microscopy: Fundamental Concepts and Laboratory Investigations*. CRC Press, 2019.
- [216] Alexey Lipatov, Mohamed Alhabeab, Maria R Lukatskaya, Alex Boson, Yury Gogotsi, and Alexander Sinitskii. Effect of synthesis on quality, electronic properties and environmental stability of individual monolayer Ti_3C_2 mxene flakes. *Advanced Electronic Materials*, 2(12):1600255, 2016.
- [217] Phuong Nguyen-Tri, Payman Ghassemi, Pascal Carriere, Sonil Nanda, Aymen Amine Assadi, and Dinh Duc Nguyen. Recent applications of advanced atomic force microscopy in polymer science: A review. *Polymers*, 12(5):1142, 2020.
- [218] Fabio Variola. Atomic force microscopy in biomaterials surface science. *Physical Chemistry Chemical Physics*, 17(5):2950–2959, 2015.
- [219] Hang Zhang, Junxiang Huang, Yongwei Wang, Rui Liu, Xiulan Huai, Jingjing Jiang, and Chantelle Anuso. Atomic force microscopy for two-dimensional materials: A tutorial review. *Optics Communications*, 406:3–17, 2018.
- [220] Nanoscience Instruments. Schematic of a scanning electron microscope, 2024. [Online; accessed 25-March-2024].
- [221] Weilie Zhou, Robert Apkarian, Zhong Lin Wang, and David Joy. Fundamentals of scanning electron microscopy (sem). *Scanning microscopy for nanotechnology: techniques and applications*, pages 1–40, 2007.
- [222] Sobarwiki. Schematic of uv-visible spectrophotometer, 2013. [Wikipedia online; accessed 21-March-2024].
- [223] Challa SSR Kumar. *UV-VIS and photoluminescence spectroscopy for nanomaterials characterization*, volume 111. Springer, 2013.
- [224] Leonard Ng Wei Tat. *2d Material Inks for Printed Electronics*. PhD thesis, University of Cambridge, 2019.
- [225] Xiong Liu, Mark Atwater, Jinhai Wang, and Qun Huo. Extinction coefficient of gold nanoparticles with different sizes and different capping ligands. *Colloids and Surfaces B: Biointerfaces*, 58(1):3–7, 2007.
- [226] Jianfeng Shen, Yongmin He, Jingjie Wu, Caitian Gao, Kuntal Keyshar, Xiang Zhang, Yingchao Yang, Mingxin Ye, Robert Vajtai, Jun Lou, et al. Liquid phase exfoliation of two-dimensional materials by directly probing and matching surface tension components. *Nano letters*, 15(8):5449–5454, 2015.
- [227] Jeon-Hong Kang, Sang-Hwa Lee, Hyun Ruh, and Kwang-Min Yu. Development of a thickness meter for conductive thin films using four-point probe method. *Journal of Electrical Engineering & Technology*, 16:2265–2273, 2021.

- [228] Dieter K Schroder. *Semiconductor material and device characterization*. John Wiley & Sons, 2015.
- [229] Lydon J Swartzendruber. *Calculations for comparing two-point and four-point probe resistivity measurements on rectangular bar-shaped semiconductor samples*, volume 13. US Department of Commerce, National Bureau of Standards, 1964.
- [230] Francesco Del Giudice. A review of microfluidic devices for rheological characterisation. *Micromachines*, 13(2):167, 2022.
- [231] Taghi Miri. Viscosity and oscillatory rheology. *Practical food rheology: An interpretive approach*, pages 7–28, 2011.
- [232] Alexander J Jing, Anqiu Zhang, and Zongquan Wu. Thermal analysis of polymer fibers. *Handbook of Thermal Analysis and Calorimetry*, 3:409–490, 2002.
- [233] Barbara Lothenbach, Pawel Durdzinski, and Klaartje De Weerd. Thermogravimetric analysis. *A practical guide to microstructural analysis of cementitious materials*, 1:177–211, 2016.
- [234] R Bruce Prime, Harvey E Bair, Sergey Vyazovkin, Patrick K Gallagher, and Alan Riga. Thermogravimetric analysis (tga). *Thermal analysis of polymers: Fundamentals and applications*, pages 241–317, 2009.
- [235] Sina Ebnesajjad. Surface and material characterization techniques. In *Handbook of adhesives and surface preparation*, pages 31–48. Elsevier, 2011.
- [236] Particle Technology Labs. Thermogravimetric analysis, 2024. [online; accessed 29-March-2024].
- [237] Joseph D Menczel, Lawrence Judovits, R Bruce Prime, Harvey E Bair, Mike Reading, and Steven Swier. Differential scanning calorimetry (dsc). *Thermal analysis of polymers: Fundamentals and applications*, pages 7–239, 2009.
- [238] Hayden Johnson. Heat capacity by the sapphire method, 2024. [Online © 2024 Materials Characterization Lab, Department of Materials Science Engineering at the University of Utah; accessed 29-March-2024].
- [239] Plastics — determination of thermal conductivity and thermal diffusivity — part 1: General principles. [online; accessed 29-March-2024].
- [240] Xutong Yang, Chaobo Liang, Tengbo Ma, Yongqiang Guo, Jie Kong, Junwei Gu, Minjiao Chen, and Jiahua Zhu. A review on thermally conductive polymeric composites: classification, measurement, model and equations, mechanism and fabrication methods. *Advanced composites and hybrid materials*, 1:207–230, 2018.
- [241] Martin Rides, Junko Morikawa, Lars Halldahl, Bruno Hay, Hubert Lobo, Angela Dawson, and Crispin Allen. Intercomparison of thermal conductivity and thermal diffusivity methods for plastics. *Polymer Testing*, 28(5):480–489, 2009.
- [242] Quantum Design. *Physical Property Measurement System-Thermal Transport Option User’s Manual*.

- [243] Plastics — determination of thermal conductivity and thermal diffusivity — part 4: Light flash method. [online; accessed 29-March-2024].
- [244] Plastics — determination of thermal conductivity and thermal diffusivity — part 2: Transient plane heat source (hot disc) method. [online; accessed 29-March-2024].
- [245] Refractory materials — determination of thermal conductivity — part 1: Hot-wire methods (cross-array and resistance thermometer). [online; accessed 29-March-2024].
- [246] Roberto Li Voti, Grigore Leahu, Emilija Petronijevic, Alessandro Belardini, Tiziana Cesca, Carlo Scian, Giovanni Mattei, and Concita Sibilia. Characterization of chirality in diffractive metasurfaces by photothermal deflection technique. *Applied Sciences*, 12(3):1109, 2022.
- [247] Sophie McArdle, Quang Anh Dang, Daniel Holland, and Aaron T Marshall. Assessing the feasibility of implementing porous carbon foam electrodes derived from coal in redox flow batteries. *Journal of The Electrochemical Society*, 2024.
- [248] Seokho Moon, Jiye Kim, Jeonghyeon Park, Semi Im, Jawon Kim, Inyong Hwang, and Jong Kyu Kim. Hexagonal boron nitride for next-generation photonics and electronics. *Advanced Materials*, 35(4):2204161, 2023.
- [249] Darshana Wickramaratne, Leigh Weston, and Chris G Van de Walle. Monolayer to bulk properties of hexagonal boron nitride. *The Journal of Physical Chemistry C*, 122(44):25524–25529, 2018.
- [250] Akash Laturia, Maarten L Van de Put, and William G Vandenberghe. Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. *npj 2D Materials and Applications*, 2(1):6, 2018.
- [251] Jeroen Brebels, Jean V Manca, Laurence Lutsen, Dirk Vanderzande, and Wouter Maes. High dielectric constant conjugated materials for organic photovoltaics. *Journal of Materials Chemistry A*, 5(46):24037–24050, 2017.
- [252] Faisal Ahmed, Sunwoo Heo, Zheng Yang, Fida Ali, Chang Ho Ra, Ho-In Lee, Takashi Taniguchi, James Hone, Byoung Hun Lee, and Won Jong Yoo. Dielectric dispersion and high field response of multilayer hexagonal boron nitride. *Advanced Functional Materials*, 28(40):1804235, 2018.
- [253] Sung Kyu Jang, Jiyoun Youn, Young Jae Song, and Sungjoo Lee. Synthesis and characterization of hexagonal boron nitride as a gate dielectric. *Scientific reports*, 6(1):30449, 2016.
- [254] Sung Kyu Jang, Jiyoun Youn, Young Jae Song, and Sungjoo Lee. Synthesis and characterization of hexagonal boron nitride as a gate dielectric. *Scientific reports*, 6(1):30449, 2016.
- [255] Jun-Ho Lee, Dong Hoon Shin, Heejun Yang, Nae Bong Jeong, Do-Hyun Park, Kenji Watanabe, Takashi Taniguchi, Eunah Kim, Sang Wook Lee, Sung Ho Jhang, et al. Semiconductor-less vertical transistor with i on/i off of 106. *Nature Communications*, 12(1):1000, 2021.

- [256] Liam Britnell, RV Gorbachev, Rashid Jalil, BD Belle, Fredrik Schedin, Artem Mishchenko, Thanasis Georgiou, MI Katsnelson, Laurence Eaves, SV Morozov, et al. Field-effect tunneling transistor based on vertical graphene heterostructures. *Science*, 335(6071):947–950, 2012.
- [257] He Li, Lulu Ren, Yao Zhou, Bin Yao, and Qing Wang. Recent progress in polymer dielectrics containing boron nitride nanosheets for high energy density capacitors. *High Voltage*, 5(4):365–376, 2020.
- [258] You Li, Yongxin Qian, Qinghui Jiang, Abubakar Yakubu Haruna, Yubo Luo, and Jun-you Yang. Thermally conductive polymer-based composites: fundamentals, progress and flame retardancy/anti-electromagnetic interference design. *Journal of Materials Chemistry C*, 10(39):14399–14430, 2022.
- [259] Intel. Moore’s law, 2023. [Online; accessed 16-June-2024].
- [260] Zhihao Zhang, Xuehui Wang, and Yuying Yan. A review of the state-of-the-art in electronic cooling. *e-Prime-Advances in Electrical Engineering, Electronics and Energy*, 1:100009, 2021.
- [261] D Dan, C Yao, Y Zhang, Y Qian, and W Zhuge. Research progress and future prospects of battery thermal management system based on heat pipe technology. *Chin. Sci. Bull.*, 64(7):682–693, 2019.
- [262] Chengning Yao, Dan Dan, Yangjun Zhang, Yueqi Wang, Yuping Qian, Yuying Yan, and Weilin Zhuge. Thermal performance of a micro heat pipe array for battery thermal management under special vehicle-operating conditions. *Automotive Innovation*, 3:317–327, 2020.
- [263] M Hamidnia, Y Luo, and XD Wang. Application of micro/nano technology for thermal management of high power led packaging—a review. *Applied Thermal Engineering*, 145:637–651, 2018.
- [264] Arden L Moore and Li Shi. Emerging challenges and materials for thermal management of electronics. *Materials today*, 17(4):163–174, 2014.
- [265] Ibtissam Afaynou, Hamza Faraji, Khadija Choukairy, Adeel Arshad, and Müslüm Arıcı. Heat transfer enhancement of phase-change materials (pcms) based thermal management systems for electronic components: A review of recent advances. *International Communications in Heat and Mass Transfer*, 143:106690, 2023.
- [266] Kafil M Razeeb, Eric Dalton, Graham Lawrence William Cross, and Anthony James Robinson. Present and future thermal interface materials for electronic devices. *International Materials Reviews*, 63(1):1–21, 2018.
- [267] Clemens JM Lasance, Robert E Simons, et al. Advances in high-performance cooling for electronics. *Electronics Cooling*, 11(4):22–39, 2005.
- [268] M Grujicic, CL Zhao, and EC Dusel. The effect of thermal contact resistance on heat management in the electronic packaging. *Applied surface science*, 246(1-3):290–302, 2005.

- [269] Jia Zhang, Han Zhai, Zihua Wu, Yuanyuan Wang, Huaqing Xie, and Mengjun Zhang. Enhanced performance of photovoltaic–thermoelectric coupling devices with thermal interface materials. *Energy reports*, 6:116–122, 2020.
- [270] Cong Guo, Yuhan Li, JianHua Xu, Qin Zhang, Kai Wu, and Qiang Fu. A thermally conductive interface material with tremendous and reversible surface adhesion promises durable cross-interface heat conduction. *Materials Horizons*, 9(6):1690–1699, 2022.
- [271] Chang-Ping Feng, Lu-Yao Yang, Jie Yang, Lu Bai, Rui-Ying Bao, Zheng-Ying Liu, Ming-Bo Yang, Hong-Bo Lan, and Wei Yang. Recent advances in polymer-based thermal interface materials for thermal management: A mini-review. *Composites Communications*, 22:100528, 2020.
- [272] Qingxia He, Mengmeng Qin, Heng Zhang, Junwei Yue, Lianqiang Peng, Gejun Liu, Yiyu Feng, and Wei Feng. Patterned liquid metal embedded in brush-shaped polymers for dynamic thermal management. *Materials Horizons*, 11(2):531–544, 2024.
- [273] Haoqi Ma, Bin Gao, Meiyu Wang, Zhenye Yuan, Jingbo Shen, Jingqi Zhao, and Yakai Feng. Strategies for enhancing thermal conductivity of polymer-based thermal interface materials: A review. *Journal of Materials Science*, 56:1064–1086, 2021.
- [274] Tianle Zhou, Xin Wang, Xiaoheng Liu, and Dangsheng Xiong. Improved thermal conductivity of epoxy composites using a hybrid multi-walled carbon nanotube/micro-sic filler. *Carbon*, 48(4):1171–1176, 2010.
- [275] Yongcun Zhou, Siqu Wu, Yuheng Long, Pengli Zhu, Feixiang Wu, Feng Liu, Vignesh Murugadoss, Williams Winchester, Amit Nautiyal, Zhe Wang, et al. Recent advances in thermal interface materials. *ES Materials & Manufacturing*, 7(7):4–24, 2020.
- [276] Zhenye Yuan, Haoqi Ma, Mohammed A Hussien, and Yakai Feng. Development and challenges of thermal interface materials: a review. *Macromolecular Materials and Engineering*, 306(11):2100428, 2021.
- [277] Yongcun Zhou, Siqu Wu, Yuheng Long, Pengli Zhu, Feixiang Wu, Feng Liu, Vignesh Murugadoss, Williams Winchester, Amit Nautiyal, Zhe Wang, et al. Recent advances in thermal interface materials. *ES Materials & Manufacturing*, 7(7):4–24, 2020.
- [278] Yingyan Zhang, Jun Ma, Ning Wei, Jie Yang, and Qing-Xia Pei. Recent progress in the development of thermal interface materials: a review. *Physical Chemistry Chemical Physics*, 23(2):753–776, 2021.
- [279] Seran Choi and Jooheon Kim. Thermal conductivity of epoxy composites with a binary-particle system of aluminum oxide and aluminum nitride fillers. *Composites Part B: Engineering*, 51:140–147, 2013.
- [280] Tsuneyuki Yamane, Naoto Nagai, Shin-ichiro Katayama, and Minoru Todoki. Measurement of thermal conductivity of silicon dioxide thin films using a 3ω method. *Journal of applied physics*, 91(12):9772–9776, 2002.
- [281] Haoran Li, Li Wang, Yurong He, Yanwei Hu, Jiaqi Zhu, and Baocheng Jiang. Experimental investigation of thermal conductivity and viscosity of ethylene glycol based zno nanofluids. *Applied Thermal Engineering*, 88:363–368, 2015.

- [282] Yimin Yao, Xiaoliang Zeng, Guiran Pan, Jiajia Sun, Jiantao Hu, Yun Huang, Rong Sun, Jian-Bin Xu, and Ching-Ping Wong. Interfacial engineering of silicon carbide nanowire/cellulose microcrystal paper toward high thermal conductivity. *ACS applied materials & interfaces*, 8(45):31248–31255, 2016.
- [283] Hua-qing Xie, Jin-chang Wang, Tong-geng Xi, and Yan Liu. Thermal conductivity of suspensions containing nanosized sic particles. *International Journal of Thermophysics*, 23:571–580, 2002.
- [284] Zhongqi Shi, Mohamed Radwan, Soshu Kirihara, Yoshinari Miyamoto, and Zhihao Jin. Enhanced thermal conductivity of polymer composites filled with three-dimensional brushlike aln nanowhiskers. *Applied physics letters*, 95(22), 2009.
- [285] Yuan Ji, Shi-Da Han, Hong Wu, Shao-Yun Guo, Feng-Shun Zhang, and Jian-Hui Qiu. Understanding the thermal impedance of silicone rubber/hexagonal boron nitride composites as thermal interface materials. *Chinese Journal of Polymer Science*, 42(3):352–363, 2024.
- [286] John M Hutchinson and Sasan Moradi. Thermal conductivity and cure kinetics of epoxy-boron nitride composites—a review. *Materials*, 13(16):3634, 2020.
- [287] Ying Cui, Zihao Qin, Huan Wu, Man Li, and Yongjie Hu. Flexible thermal interface based on self-assembled boron arsenide for high-performance thermal management. *Nature communications*, 12(1):1284, 2021.
- [288] Wenkui Xing, Yue Xu, Chengyi Song, and Tao Deng. Recent advances in thermal interface materials for thermal management of high-power electronics. *Nanomaterials*, 12(19):3365, 2022.
- [289] Xingcun Colin Tong. *Advanced materials for thermal management of electronic packaging*, volume 30. Springer Science & Business Media, 2011.
- [290] Chengru Wang, Jie Guo, Lan Dong, Adili Aiyiti, Xiangfan Xu, and Baowen Li. Superior thermal conductivity in suspended bilayer hexagonal boron nitride. *Scientific reports*, 6(1):25334, 2016.
- [291] Gustavo Grinblat, Michael P Nielsen, Paul Dichtl, Yi Li, Rupert F Oulton, and Stefan A Maier. Ultrafast sub–30-fs all-optical switching based on gallium phosphide. *Science advances*, 5(6):eaaw3262, 2019.
- [292] Tao Ouyang, Yuanping Chen, Yuee Xie, Kaike Yang, Zhigang Bao, and Jianxin Zhong. Thermal transport in hexagonal boron nitride nanoribbons. *Nanotechnology*, 21(24):245701, 2010.
- [293] Chao Yuan, Jiahan Li, Lucas Lindsay, David Cherns, James W Pomeroy, Song Liu, James H Edgar, and Martin Kuball. Modulating the thermal conductivity in hexagonal boron nitride via controlled boron isotope concentration. *Communications physics*, 2(1):43, 2019.
- [294] Puqing Jiang, Xin Qian, and Ronggui Yang. Time-domain thermorefectance (tdtr) measurements of anisotropic thermal conductivity using a variable spot size approach. *Review of Scientific Instruments*, 88(7), 2017.

- [295] Zheng-Bai Zhao, Cheng Hu, Yang Wang, Hong-Min Cong, Yong Ma, Ding-Duo Lin, Wei-Li Li, and Chao Yan. Fabrication of environment-friendly and flexible waterborne epoxy/pvp/h-bn composites for thermal interface material. *Ceramics International*, 48(19):28030–28037, 2022.
- [296] Chemtronics. Circuitworks boron nitride heat sink grease. [Online; accessed 16-March-2024].
- [297] Laird Technologies. T-flex™ 600 series thermal gap filler. [Online; accessed 16-March-2024].
- [298] 3M Advanced Materials Division. 3mtm bornitrid cooling fillers, for thermally conductive and electrically insulating plastics and adhesives. [Online; accessed 16-March-2024].
- [299] Xinwei Xu, Renchao Hu, Meiyu Chen, Jiufeng Dong, Bin Xiao, Qing Wang, and Hong Wang. 3d boron nitride foam filled epoxy composites with significantly enhanced thermal conductivity by a facial and scalable approach. *Chemical Engineering Journal*, 397:125447, 2020.
- [300] Kiho Kim and Jooheon Kim. Vertical filler alignment of boron nitride/epoxy composite for thermal conductivity enhancement via external magnetic field. *International Journal of Thermal Sciences*, 100:29–36, 2016.
- [301] Jingkai Han, Gaolai Du, Weiwei Gao, and Hao Bai. An anisotropically high thermal conductive boron nitride/epoxy composite based on nacre-mimetic 3d network. *Advanced Functional Materials*, 29(13):1900412, 2019.
- [302] Zhi-Guo Wang, Ming-Zhao Chen, Ya-Hui Liu, Hong-Ji Duan, Ling Xu, Li Zhou, Jia-Zhuang Xu, Jun Lei, and Zhong-Ming Li. Nacre-like composite films with high thermal conductivity, flexibility, and solvent stability for thermal management applications. *Journal of Materials Chemistry C*, 7(29):9018–9024, 2019.
- [303] Ri-Chao Zhang, Zirui Huang, Zhihuan Huang, Meiling Zhong, Dongmian Zang, Ai Lu, Yuanfei Lin, Bronagh Millar, Graham Garet, Josh Turner, et al. Uniaxially stretched polyethylene/boron nitride nanocomposite films with metal-like thermal conductivity. *Composites Science and Technology*, 196:108154, 2020.
- [304] Yei Hwan Jung, Tzu-Hsuan Chang, Huilong Zhang, Chunhua Yao, Qifeng Zheng, Vina W Yang, Hongyi Mi, Munho Kim, Sang June Cho, Dong-Wook Park, et al. High-performance green flexible electronics based on biodegradable cellulose nanofibril paper. *Nature communications*, 6(1):7170, 2015.
- [305] Qing-Fang Guan, Huai-Bin Yang, Zi-Meng Han, Li-Chuan Zhou, Yin-Bo Zhu, Zhang-Chi Ling, He-Bin Jiang, Peng-Fei Wang, Tao Ma, Heng-An Wu, et al. Lightweight, tough, and sustainable cellulose nanofiber-derived bulk structural materials with low thermal expansion coefficient. *Science advances*, 6(18):eaaz1114, 2020.
- [306] Evon Foo, Mariatti Jaafar, Azizan Aziz, and Lim Chong Sim. Properties of spin coated epoxy/silica thin film composites: Effect of nano-and micron-size fillers. *Composites Part A: Applied Science and Manufacturing*, 42(10):1432–1437, 2011.

- [307] Hongli Zhu, Zhiqiang Fang, Colin Preston, Yuanyuan Li, and Liangbing Hu. Transparent paper: fabrications, properties, and device applications. *Energy & Environmental Science*, 7(1):269–287, 2014.
- [308] Guillermo Angeles, Maite Lascurain, Raymundo Davalos-Sotelo, Reyna Paula Zarate-Morales, and Fernando Ortega-Escalona. Anatomical and physical changes in leaves during the production of tamales. *American Journal of Botany*, 100(8):1509–1521, 2013.
- [309] Anja Lund, Yunyun Wu, Benji Fenech-Salerno, Felice Torrisi, Tricia Breen Carmichael, and Christian Müller. Conducting materials as building blocks for electronic textiles. *MRS bulletin*, 46(6):491–501, 2021.
- [310] Xiaoliang Zeng, Jiajia Sun, Yimin Yao, Rong Sun, Jian-Bin Xu, and Ching-Ping Wong. A combination of boron nitride nanotubes and cellulose nanofibers for the preparation of a nanocomposite with high thermal conductivity. *ACS nano*, 11(5):5167–5178, 2017.
- [311] Xiaojuan Tian, Ni Wu, Bing Zhang, Yifan Wang, Zishuo Geng, and Yongfeng Li. Glycine functionalized boron nitride nanosheets with improved dispersibility and enhanced interaction with matrix for thermal composites. *Chemical Engineering Journal*, 408:127360, 2021.
- [312] Roghayyeh Lotfi, Michael Naguib, Dundar E Yilmaz, Jagjit Nanda, and Adri CT Van Duin. A comparative study on the oxidation of two-dimensional $\text{Ti}_3\text{C}_2\text{Tx}$ mxene structures in different environments. *Journal of Materials Chemistry A*, 6(26):12733–12743, 2018.
- [313] Michael Naguib, Olha Mashtalir, Maria R Lukatskaya, Boris Dyatkin, Chuanfang Zhang, Volker Presser, Yury Gogotsi, and Michel W Barsoum. One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphitic carbon by oxidation of mxenes. *Chemical communications*, 50(56):7420–7423, 2014.
- [314] Xinliang Li, Xiaowei Yin, Meikang Han, Changqing Song, Xinnan Sun, Hailong Xu, Laifei Cheng, and Litong Zhang. A controllable heterogeneous structure and electromagnetic wave absorption properties of Ti_2CTx mxene. *Journal of Materials Chemistry C*, 5(30):7621–7628, 2017.
- [315] Raghavan B Rakhi, Bilal Ahmed, Mohamed N Hedhili, Dalaver H Anjum, and Husam N Alshareef. Effect of postetch annealing gas composition on the structural and electrochemical properties of Ti_2CTx mxene electrodes for supercapacitor applications. *Chemistry of Materials*, 27(15):5314–5323, 2015.
- [316] Jingxiao Li, Yulei Du, Chengxue Huo, Shun Wang, and Chong Cui. Thermal stability of two-dimensional Ti_2C nanosheets. *Ceramics International*, 41(2):2631–2635, 2015.
- [317] Chuanfang John Zhang, Sergio Pinilla, Niall McEvoy, Conor P Cullen, Babak Anasori, Edmund Long, Sang-Hoon Park, Andrés Seral-Ascaso, Aleksey Shmeliov, Dileep Krishnan, et al. Oxidation stability of colloidal two-dimensional titanium carbides (mxenes). *Chemistry of Materials*, 29(11):4848–4856, 2017.

- [318] Jiebo Li, Ruzhan Qin, Li Yan, Zhen Chi, Zhihao Yu, Naitao Li, Mingjun Hu, Hailong Chen, and Guangcun Shan. Plasmonic light illumination creates a channel to achieve fast degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. *Inorganic Chemistry*, 58(11):7285–7294, 2019.
- [319] Shuohan Huang and Vadym N Mochalin. Understanding chemistry of two-dimensional transition metal carbides and carbonitrides (mxenes) with gas analysis. *ACS nano*, 14(8):10251–10257, 2020.
- [320] Jizhen Zhang, Na Kong, Dylan Hegh, Ken Aldren S Usman, Guangwu Guan, Si Qin, Izabela Jurewicz, Wenrong Yang, and Joselito M Razal. Freezing titanium carbide (mxenes) aqueous dispersions for ultra-long-term storage. *ACS Applied Materials and Interfaces*.
- [321] Sehyun Doo, Ari Chae, Daesin Kim, Taegon Oh, Tae Yun Ko, Seon Joon Kim, Dong-Yeun Koh, and Chong Min Koo. Mechanism and kinetics of oxidation reaction of aqueous $\text{Ti}_3\text{C}_2\text{T}_x$ suspensions at different pHs and temperatures. *ACS Applied Materials & Interfaces*, 13(19):22855–22865, 2021.
- [322] Xingyu Wang, Zhiyu Wang, and Jieshan Qiu. Stabilizing mxene by hydration chemistry in aqueous solution. *Angewandte Chemie*, 133(51):26791–26795, 2021.
- [323] Jie Zhou, Xianhu Zha, Fan Y Chen, Qun Ye, Per Eklund, Shiyu Du, and Qing Huang. A two-dimensional zirconium carbide by selective etching of Al_3C_3 from nanolaminated $\text{Zr}_3\text{Al}_3\text{C}_5$. *Angewandte Chemie International Edition*, 55(16):5008–5013, 2016.
- [324] Jun Lu, Ingemar Persson, Hans Lind, Justinas Palisaitis, M Li, Y Li, K Chen, Jie Zhou, S Du, Z f Chai, et al. $\text{Ti}_{n+1}\text{C}_n$ mxenes with fully saturated and thermally stable Cl terminations. *Nanoscale Advances*, 1(9):3680–3685, 2019.
- [325] Mian Li, Jun Lu, Kan Luo, Youbing Li, Keke Chang, Ke Chen, Jie Zhou, Johanna Rosen, Lars Hultman, Per Eklund, et al. Element replacement approach by reaction with lewis acidic molten salts to synthesize nanolaminated max phases and mxenes. *Journal of the American Chemical Society*, 141(11):4730–4737, 2019.
- [326] Justinas Palisaitis, Ingemar Persson, Joseph Halim, Johanna Rosen, and Per OÅ Persson. On the structural stability of mxene and the role of transition metal adatoms. *Nanoscale*, 10(23):10850–10855, 2018.
- [327] Babak Anasori, Maria R Lukatskaya, and Yury Gogotsi. 2d metal carbides and nitrides (mxenes) for energy storage. *Nature Reviews Materials*, 2(2):1–17, 2017.
- [328] Tyler S Mathis, Kathleen Maleski, Adam Goad, Asia Sarycheva, Mark Anayee, Alexandre C Foucher, Kanit Hantanasirisakul, Christopher E Shuck, Eric A Stach, and Yury Gogotsi. Modified max phase synthesis for environmentally stable and highly conductive Ti_3C_2 mxene. *ACS nano*, 15(4):6420–6429, 2021.
- [329] Erik Piatti, Adrees Arbab, Francesco Galanti, Tian Carey, Luca Anzi, Dahnan Spurling, Ahin Roy, Ainur Zhussupbekova, Kishan A Patel, Jong M Kim, et al. Charge transport mechanisms in inkjet-printed thin-film transistors based on two-dimensional materials. *Nature Electronics*, 4(12):893–905, 2021.

- [330] Touseef Habib, Xiaofei Zhao, Smit A Shah, Yexiao Chen, Wanmei Sun, Hyosung An, Jodie L Lutkenhaus, Miladin Radovic, and Micah J Green. Oxidation stability of $\text{Ti}_3\text{C}_2\text{Tx}$ mxene nanosheets in solvents and composite films. *npj 2D Materials and Applications*, 3(1):8, 2019.
- [331] Kathleen Maleski, Vadym N Mochalin, and Yury Gogotsi. Dispersions of two-dimensional titanium carbide mxene in organic solvents. *Chemistry of Materials*, 29(4):1632–1640, 2017.
- [332] Christopher E Shuck, Meikang Han, Kathleen Maleski, Kanit Hantanasirisakul, Seon Joon Kim, Junghoon Choi, William EB Reil, and Yury Gogotsi. Effect of Ti_3AlC_2 max phase on structure and properties of resultant $\text{Ti}_3\text{C}_2\text{T}_x$ mxene. *ACS Applied Nano Materials*, 2(6):3368–3376, 2019.
- [333] Yanan Jiang, Tao Sun, Xi Xie, Wei Jiang, Jia Li, Bingbing Tian, and Chenliang Su. Oxygen-functionalized ultrathin $\text{Ti}_3\text{C}_2\text{Tx}$ mxene for enhanced electrocatalytic hydrogen evolution. *ChemSusChem*, 12(7):1368–1373, 2019.
- [334] Vladislav Kamysbayev, Alexander S Filatov, Huicheng Hu, Xue Rui, Francisco Lagunas, Di Wang, Robert F Klie, and Dmitri V Talapin. Covalent surface modifications and superconductivity of two-dimensional metal carbide mxenes. *Science*, 369(6506):979–983, 2020.
- [335] Yoonjeong Chae, Seon Joon Kim, Soo-Yeon Cho, Junghoon Choi, Kathleen Maleski, Byeong-Joo Lee, Hee-Tae Jung, Yury Gogotsi, Yonghee Lee, and Chi Won Ahn. An investigation into the factors governing the oxidation of two-dimensional Ti_3C_2 mxene. *Nanoscale*, 11(17):8387–8393, 2019.
- [336] Fanjie Xia, Junchao Lao, Ruohan Yu, Xiaohan Sang, Jiayan Luo, Yu Li, and Jinsong Wu. Ambient oxidation of Ti_3C_2 mxene initialized by atomic defects. *Nanoscale*, 11(48):23330–23337, 2019.
- [337] Zhirong Zhang, Zhongping Yao, Xiao Zhang, and Zhaohua Jiang. 2d carbide mxene under postetch low-temperature annealing for high-performance supercapacitor electrode. *Electrochimica Acta*, 359:136960, 2020.
- [338] Ingemar Persson, Joseph Halim, Thomas W Hansen, Jakob B Wagner, Vanya Darakchieva, Justinas Palisaitis, Johanna Rosen, and Per OÅ Persson. How much oxygen can a mxene surface take before it breaks? *Advanced Functional Materials*, 30(47):1909005, 2020.
- [339] Xiaofei Zhao, Dustin E Holta, Zeyi Tan, Ju-Hyun Oh, Ian J Echols, Muhammad Anas, Huaixuan Cao, Jodie L Lutkenhaus, Miladin Radovic, and Micah J Green. Annealed $\text{Ti}_3\text{C}_2\text{T}_z$ mxene films for oxidation-resistant functional coatings. *ACS Applied Nano Materials*, 3(11):10578–10585, 2020.
- [340] Alexey Lipatov, Adam Goad, Michael J Loes, Nataliia S Vorobeva, Jehad Abourahma, Yury Gogotsi, and Alexander Sinitskii. High electrical conductivity and breakdown current density of individual monolayer $\text{Ti}_3\text{C}_2\text{Tx}$ mxene flakes. *Matter*, 4(4):1413–1427, 2021.

- [341] Alexey Lipatov, Saman Bagheri, and Alexander Sinitskii. Metallic conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ mxene confirmed by temperature-dependent electrical measurements. *ACS Materials Letters*, 6(1):298–307, 2023.
- [342] Joseph Halim, Maria R Lukatskaya, Kevin M Cook, Jun Lu, Cole R Smith, Lars-Åke Naslund, Steven J May, Lars Hultman, Yury Gogotsi, Per Eklund, et al. Transparent conductive two-dimensional titanium carbide epitaxial thin films. *Chemistry of Materials*, 26(7):2374–2381, 2014.
- [343] A Miranda, Joseph Halim, MW Barsoum, and A Lorke. Electronic properties of freestanding $\text{Ti}_3\text{C}_2\text{T}_x$ mxene monolayers. *Applied Physics Letters*, 108(3), 2016.
- [344] Joseph Halim, Ingemar Persson, Eun Ju Moon, Philipp Kühne, Vanya Darakchieva, Per O Å Persson, Per Eklund, Johanna Rosen, and Michel W Barsoum. Electronic and optical characterization of 2d Ti_2C and Nb_2C (mxene) thin films. *Journal of Physics: Condensed Matter*, 31(16):165301, 2019.
- [345] J Ongena, M Istvan, R Koch, and A Debeil. Hidden consequences of intermittent electricity production. *Eur J Soc Sci*, 2(2), 2017.
- [346] Patrice Simon and Yury Gogotsi. Materials for electrochemical capacitors. *Nature materials*, 7(11):845–854, 2008.
- [347] Isabelle Dumé. Lithium-ion batteries break energy density record, 2023. [Online; accessed 18-April-2024].
- [348] Kriti Sharma, Anmol Arora, Surya Kant Tripathi, et al. Review of supercapacitors: Materials and devices. *Journal of Energy Storage*, 21:801–825, 2019.
- [349] Yuqi Jiang and Jinping Liu. Definitions of pseudocapacitive materials: a brief review. *Energy & Environmental Materials*, 2(1):30–37, 2019.
- [350] Patrice Simon, Yury Gogotsi, and Bruce Dunn. Where do batteries end and supercapacitors begin? *Science*, 343(6176):1210–1211, 2014.
- [351] Brian E Conway. *Electrochemical supercapacitors: scientific fundamentals and technological applications*. Springer Science & Business Media, 2013.
- [352] Dhruva P Chatterjee and Arun K Nandi. A review on the recent advances in hybrid supercapacitors. *Journal of Materials Chemistry A*, 9(29):15880–15918, 2021.
- [353] G Murali, Jishu Rawal, Jeevan Kumar Reddy Modigunta, Young Ho Park, Jong-Hoon Lee, Seul-Yi Lee, Soo-Jin Park, and Insik In. A review on mxenes: new-generation 2d materials for supercapacitors. *Sustainable Energy & Fuels*, 5(22):5672–5693, 2021.
- [354] Lu Li, Jing Wen, and Xitian Zhang. Progress of two-dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ in supercapacitors. *ChemSusChem*, 13(6):1296–1329, 2020.
- [355] Ying Tao, Xiaoying Xie, Wei Lv, Dai-Ming Tang, Debin Kong, Zhenghong Huang, Hiroto Nishihara, Takafumi Ishii, Baohua Li, Dmitri Golberg, et al. Towards ultrahigh volumetric capacitance: graphene derived highly dense but porous carbons for supercapacitors. *Scientific reports*, 3(1):2975, 2013.

- [356] Mehdi Ghaffari, Yue Zhou, Haiping Xu, Minren Lin, Tae Young Kim, Rodney S Ruoff, and QM Zhang. High-volumetric performance aligned nano-porous microwave exfoliated graphite oxide-based electrochemical capacitors. *Advanced Materials*, 25(35):4879–4885, 2013.
- [357] Xinliang Li, Zhaodong Huang, Christopher E Shuck, Guojin Liang, Yury Gogotsi, and Chunyi Zhi. Mxene chemistry, electrochemistry and energy storage applications. *Nature Reviews Chemistry*, 6(6):389–404, 2022.
- [358] Yohan Dall’Agnese, Maria R Lukatskaya, Kevin M Cook, Pierre-Louis Taberna, Yury Gogotsi, and Patrice Simon. High capacitance of surface-modified 2d titanium carbide in acidic electrolyte. *Electrochemistry Communications*, 48:118–122, 2014.
- [359] Yury Gogotsi and Reginald M Penner. Energy storage in nanomaterials—capacitive, pseudocapacitive, or battery-like?, 2018.
- [360] Gil Bergman, Elad Ballas, Qiang Gao, Amey Nimkar, Bar Gavriel, Mikhael D Levi, Daniel Sharon, Fyodor Malchik, Xuehang Wang, Netanel Shpigel, et al. Elucidation of the charging mechanisms and the coupled structural–mechanical behavior of $\text{Ti}_3\text{C}_2\text{Tx}$ (mxenes) electrodes by in situ techniques. *Advanced Energy Materials*, 13(8):2203154, 2023.
- [361] Hui Shao, Zifeng Lin, Kui Xu, Pierre-Louis Taberna, and Patrice Simon. Electrochemical study of pseudocapacitive behavior of $\text{Ti}_3\text{C}_2\text{Tx}$ mxene material in aqueous electrolytes. *Energy Storage Materials*, 18:456–461, 2019.
- [362] G Murali, Jishu Rawal, Jeevan Kumar Reddy Modigunta, Young Ho Park, Jong-Hoon Lee, Seul-Yi Lee, Soo-Jin Park, and Insik In. A review on mxenes: new-generation 2d materials for supercapacitors. *Sustainable Energy & Fuels*, 5(22):5672–5693, 2021.
- [363] Minmin Hu, Tao Hu, Zhaojin Li, Yi Yang, Renfei Cheng, Jinxing Yang, Cong Cui, and Xiaohui Wang. Surface functional groups and interlayer water determine the electrochemical capacitance of $\text{Ti}_3\text{C}_2\text{Tx}$ mxene. *ACS nano*, 12(4):3578–3586, 2018.
- [364] Jeremy Come, Jennifer M Black, Maria R Lukatskaya, Michael Naguib, Majid Beidaghi, Adam J Rondinone, Sergei V Kalinin, David J Wesolowski, Yury Gogotsi, and Nina Balke. Controlling the actuation properties of mxene paper electrodes upon cation intercalation. *Nano Energy*, 17:27–35, 2015.
- [365] Minmin Hu, Zhaojin Li, Tao Hu, Shihao Zhu, Chao Zhang, and Xiaohui Wang. High-capacitance mechanism for $\text{Ti}_3\text{C}_2\text{Tx}$ mxene by in situ electrochemical raman spectroscopy investigation. *ACS nano*, 10(12):11344–11350, 2016.
- [366] Two-Dimensional Titanium Carbide. Cation intercalation and high volumetric capacitance of. *science*, 1241488(1502):341, 2013.
- [367] Xuehang Wang, Tyler S Mathis, Ke Li, Zifeng Lin, Lukas Vlcek, Takeshi Torita, Naresh C Osti, Christine Hatter, Patrick Urbankowski, Asia Sarycheva, et al. Influences from solvents on charge storage in titanium carbide mxenes. In *MXenes*, pages 783–810. Jenny Stanford Publishing, 2023.

- [368] Masashi Okubo, Akira Sugahara, Satoshi Kajiyama, and Atsuo Yamada. Mxene as a charge storage host. *Accounts of chemical research*, 51(3):591–599, 2018.
- [369] Subhasree Panda, Kalim Deshmukh, SK Khadheer Pasha, Jayaraman Theerthagiri, Sivakumar Manickam, and Myong Yong Choi. Mxene based emerging materials for supercapacitor applications: Recent advances, challenges, and future perspectives. *Coordination Chemistry Reviews*, 462:214518, 2022.
- [370] Christopher Eames and M Saiful Islam. Ion intercalation into two-dimensional transition-metal carbides: global screening for new high-capacity battery materials. *Journal of the American Chemical Society*, 136(46):16270–16276, 2014.
- [371] Xianwu Huang, Jiahui Huang, Dong Yang, and Peiyi Wu. A multi-scale structural engineering strategy for high-performance mxene hydrogel supercapacitor electrode. *Advanced Science*, 8(18):2101664, 2021.
- [372] Yu Xia, Tyler S Mathis, Meng-Qiang Zhao, Babak Anasori, Alei Dang, Zehang Zhou, Hyesung Cho, Yury Gogotsi, and Shu Yang. Thickness-independent capacitance of vertically aligned liquid-crystalline mxenes. *Nature*, 557(7705):409–412, 2018.
- [373] Zhimin Fan, Yuqi Yang, Haoxiang Ma, Youshan Wang, Zhimin Xie, and Yuyan Liu. High-volumetric capacitance and high-rate performance in liquid-mediated densified holey mxene film. *Carbon*, 186:150–159, 2022.
- [374] Gang Wang, Sung-Kon Kim, Michael Cai Wang, Tianshu Zhai, Siddhanth Munukutla, Gregory S Girolami, Peter J Sempstrott, SungWoo Nam, Paul V Braun, and Joseph W Lyding. Enhanced electrical and mechanical properties of chemically cross-linked carbon-nanotube-based fibers and their application in high-performance supercapacitors. *ACS nano*, 14(1):632–639, 2019.
- [375] Zhaoyuan Liu, Lidong Wang, Guizhi Ma, Yinan Yuan, Henan Jia, and Weidong Fei. A supercapacitor with ultrahigh volumetric capacitance produced by self-assembly of reduced graphene oxide through phosphoric acid treatment. *Journal of Materials Chemistry A*, 8(36):18933–18944, 2020.
- [376] Yunfeng Guan, Rong Zhao, Ye Cong, Kai Chen, Jingsong Wu, Hui Zhu, Zhijun Dong, Qin Zhang, Guanming Yuan, Yanjun Li, et al. Flexible ti₂c mxene film: synthesis, electrochemical performance and capacitance behavior. *Chemical Engineering Journal*, 433:133582, 2022.
- [377] Kai Zhu, Yuming Jin, Fei Du, Shuang Gao, Zhongmin Gao, Xing Meng, Gang Chen, Yingjin Wei, and Yu Gao. Synthesis of ti₂ctx mxene as electrode materials for symmetric supercapacitor with capable volumetric capacitance. *Journal of energy chemistry*, 31:11–18, 2019.
- [378] Qingmin Shan, Xinpeng Mu, Mohamed Alhabeb, Christopher E Shuck, Di Pang, Xin Zhao, Xue-Feng Chu, Yingjin Wei, Fei Du, Gang Chen, et al. Two-dimensional vanadium carbide (v₂c) mxene as electrode for supercapacitors with aqueous electrolytes. *Electrochemistry Communications*, 96:103–107, 2018.

- [379] Jian Yang, Weizhai Bao, Pauline Jaumaux, Songtao Zhang, Chengyin Wang, and Guoxiu Wang. Mxene-based composites: synthesis and applications in rechargeable batteries and supercapacitors. *Advanced Materials Interfaces*, 6(8):1802004, 2019.
- [380] Yue Li, Canping Pan, Pascal Kamdem, and Xiao-Juan Jin. Binder-free two-dimensional mxene/acid activated carbon for high-performance supercapacitors and methylene blue adsorption. *Energy & Fuels*, 34(8):10120–10130, 2020.
- [381] Sunil Kumar, Malik Abdul Rehman, Sungwon Lee, Minwook Kim, Hyeryeon Hong, Jun-Young Park, and Yongho Seo. Supercapacitors based on $\text{Ti}_3\text{C}_2\text{Tx}$ mxene extracted from supernatant and current collectors passivated by cvd-graphene. *Scientific reports*, 11(1):649, 2021.
- [382] Shuaikai Xu, Guodong Wei, Junzhi Li, Wei Han, and Yury Gogotsi. Flexible mxene–graphene electrodes with high volumetric capacitance for integrated co-cathode energy conversion/storage devices. *Journal of materials chemistry A*, 5(33):17442–17451, 2017.
- [383] Meng-Qiang Zhao, Chang E Ren, Zheng Ling, Maria R Lukatskaya, Chuanfang Zhang, Katherine L Van Aken, Michel W Barsoum, and Yury Gogotsi. Flexible mxene/carbon nanotube composite paper with high volumetric capacitance. *Advanced materials*, 27(2), 2014.
- [384] Yi Tang, JianFeng Zhu, ChenHui Yang, and Fen Wang. Enhanced supercapacitive performance of manganese oxides doped two-dimensional titanium carbide nanocomposite in alkaline electrolyte. *Journal of Alloys and Compounds*, 685:194–201, 2016.
- [385] Fen Wang, Minjuan Cao, Yi Qin, Jianfeng Zhu, Lei Wang, and Yi Tang. ZnO nanoparticle-decorated two-dimensional titanium carbide with enhanced supercapacitive performance. *RSC advances*, 6(92):88934–88942, 2016.
- [386] Minjuan Cao, Fen Wang, Lei Wang, Wenling Wu, Wenjing Lv, and Jianfeng Zhu. Room temperature oxidation of Ti_3C_2 mxene for supercapacitor electrodes. *Journal of The Electrochemical Society*, 164(14):A3933, 2017.
- [387] Muhammad Boota, Babak Anasori, Cooper Voigt, Meng-Qiang Zhao, Michel W Barsoum, and Yury Gogotsi. Pseudocapacitive electrodes produced by oxidant-free polymerization of pyrrole between the layers of 2d titanium carbide (mxene). *Adv. Mater.*, 28(7):1517–1522, 2016.
- [388] Armin VahidMohammadi, Jorge Moncada, Hengze Chen, Emre Kayali, Jafar Orangi, Carlos A Carrero, and Majid Beidaghi. Thick and freestanding mxene/pani pseudocapacitive electrodes with ultrahigh specific capacitance. *Journal of Materials Chemistry A*, 6(44):22123–22133, 2018.
- [389] Lu Li, Na Zhang, Mingyi Zhang, Xitian Zhang, and Zhiguo Zhang. Flexible $\text{Ti}_3\text{C}_2\text{Tx}/\text{PEDOT}$ PSS films with outstanding volumetric capacitance for asymmetric supercapacitors. *Dalton Transactions*, 48(5):1747–1756, 2019.

- [390] Zheng Ling, Chang E Ren, Meng-Qiang Zhao, Jian Yang, James M Giammarco, Jieshan Qiu, Michel W Barsoum, and Yury Gogotsi. Flexible and conductive mxene films and nanocomposites with high capacitance. *Proceedings of the National Academy of Sciences*, 111(47):16676–16681, 2014.
- [391] Raghavan Baby Rakhi, Bilal Ahmed, Dalaver Anjum, and Husam N Alshareef. Direct chemical synthesis of mno₂ nanowhiskers on transition-metal carbide surfaces for supercapacitor applications. *ACS applied materials & interfaces*, 8(29):18806–18814, 2016.
- [392] Yangyang Wen, Thomas E Rufford, Xingzhu Chen, Neng Li, Miaoqiang Lyu, Liming Dai, and Lianzhou Wang. Nitrogen-doped ti₃c₂tx mxene electrodes for high-performance supercapacitors. *Nano energy*, 38:368–376, 2017.
- [393] Zehang Zhou, Weerapha Panatdasirisuk, Tyler S Mathis, Babak Anasori, Canhui Lu, Xinxing Zhang, Zhiwei Liao, Yury Gogotsi, and Shu Yang. Layer-by-layer assembly of mxene and carbon nanotubes on electrospun polymer films for flexible energy storage. *Nanoscale*, 10(13):6005–6013, 2018.
- [394] Xian-Yang Li, Jia-Kang Qu, and Hua-Yi Yin. Electrolytic alloy-type anodes for metal-ion batteries. *Rare Metals*, 40:329–352, 2021.
- [395] Panpan Zhang, Faxing Wang, Minghao Yu, Xiaodong Zhuang, and Xinliang Feng. Two-dimensional materials for miniaturized energy storage devices: from individual devices to smart integrated systems. *Chemical Society Reviews*, 47(19):7426–7451, 2018.
- [396] Dhruva P Chatterjee and Arun K Nandi. A review on the recent advances in hybrid supercapacitors. *Journal of Materials Chemistry A*, 9(29):15880–15918, 2021.
- [397] Deepak P Dubal, Omar Ayyad, Vanesa Ruiz, and Pedro Gomez-Romero. Hybrid energy storage: the merging of battery and supercapacitor chemistries. *Chemical Society Reviews*, 44(7):1777–1790, 2015.
- [398] Matteo Stoppa and Alessandro Chiolerio. Wearable electronics and smart textiles: A critical review. *sensors*, 14(7):11957–11992, 2014.
- [399] Qi Xue, Jinfeng Sun, Yan Huang, Minshen Zhu, Zengxia Pei, Hongfei Li, Yukun Wang, Na Li, Haiyan Zhang, and Chunyi Zhi. Recent progress on flexible and wearable supercapacitors. *Small*, 13(45):1701827, 2017.
- [400] Jianmin Li, Jianmei Chen, Hao Wang, and Xu Xiao. All-mxene cotton-based supercapacitor-powered human body thermal management system. *ChemElectroChem*, 8(4):648–655, 2021.
- [401] Yuanming Wang, Xue Wang, Xifei Li, Xiaolong Li, Yang Liu, Yang Bai, Huanhao Xiao, and Guohui Yuan. A high-performance, tailorable, wearable, and foldable solid-state supercapacitor enabled by arranging pseudocapacitive groups and mxene flakes on textile electrode surface. *Advanced Functional Materials*, 31(7):2008185, 2021.

- [402] Kim Alfonsi, Juan Colberg, Peter J Dunn, Thomas Fevig, Sandra Jennings, Timothy A Johnson, H Peter Kleine, Craig Knight, Mark A Nagy, David A Perry, et al. Green chemistry tools to influence a medicinal chemistry and research chemistry based organisation. *Green Chemistry*, 10(1):31–36, 2008.
- [403] Titas Kumar Mukhopadhyay and Ayan Datta. Deciphering the role of solvents in the liquid phase exfoliation of hexagonal boron nitride: A molecular dynamics simulation study. *the Journal of Physical Chemistry C*, 121(1):811–822, 2017.
- [404] Gonzalo Vazquez, Estrella Alvarez, and Jose M Navaza. Surface tension of alcohol water+ water from 20 to 50. degree. c. *Journal of chemical and engineering data*, 40(3):611–614, 1995.
- [405] Ali Yazdan, Jizhe Wang, Ce-Wen Nan, and Liangliang Li. Rheological behavior and thermal conductivities of emulsion-based thermal pastes. *Journal of Electronic Materials*, 49:2100–2109, 2020.
- [406] Xiang Nie, Guo Li, Zhao Jiang, Wei Li, Ting Ouyang, and Jianfeng Wang. Co-solvent exfoliation of hexagonal boron nitride: effect of raw bulk boron nitride size and co-solvent composition. *Nanomaterials*, 10(6):1035, 2020.
- [407] Siyu Qiang, Tian Carey, Adrees Arbab, Weihua Song, Chaoxia Wang, and Felice Torrisi. Wearable solid-state capacitors based on two-dimensional material all-textile heterostructures. *Nanoscale*, 11(20):9912–9919, 2019.
- [408] Yenny Hernandez, Valeria Nicolosi, Mustafa Lotya, Fiona M Blighe, Zhenyu Sun, Sukanta De, Ignatius T McGovern, Brendan Holland, Michele Byrne, Yurii K Gun'Ko, et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, 3(9):563–568, 2008.
- [409] Chenping Wu, Abdul Majid Soomro, Feipeng Sun, Huachun Wang, Youyang Huang, Jiejun Wu, Chuan Liu, Xiaodong Yang, Na Gao, Xiaohong Chen, et al. Large-roll growth of 25-inch hexagonal bn monolayer film for self-release buffer layer of free-standing gan wafer. *Scientific reports*, 6(1):34766, 2016.
- [410] Pankaj Kumar Rastogi, Krishna Rani Sahoo, Pallavi Thakur, Rahul Sharma, Sumit Bawari, Ramakrishna Podila, and Tharangattu N Narayanan. Graphene–hbn non-van der waals vertical heterostructures for four-electron oxygen reduction reaction. *Physical Chemistry Chemical Physics*, 21(7):3942–3953, 2019.
- [411] Dongju Lee and Sung Ho Song. Ultra-thin ultraviolet cathodoluminescent device based on exfoliated hexagonal boron nitride. *RSC advances*, 7(13):7831–7835, 2017.
- [412] Tiantian Shen, Song Liu, Wenjun Yan, and Jigang Wang. Highly efficient preparation of hexagonal boron nitride by direct microwave heating for dye removal. *Journal of materials science*, 54(12):8852–8859, 2019.
- [413] Oded Hod. Graphite and hexagonal boron-nitride have the same interlayer distance. why? *Journal of chemical theory and computation*, 8(4):1360–1369, 2012.
- [414] Ki Kang Kim, Soo Min Kim, and Young Hee Lee. A new horizon for hexagonal boron nitride film. *Journal of the Korean physical society*, 64:1605–1616, 2014.

- [415] Adam G Kelly, Toby Hallam, Claudia Backes, Andrew Harvey, Amir Sajad Esmaeily, Ian Godwin, João Coelho, Valeria Nicolosi, Jannika Lauth, Aditya Kulkarni, et al. All-printed thin-film transistors from networks of liquid-exfoliated nanosheets. *Science*, 356(6333):69–73, 2017.
- [416] Claudia Backes, Ronan J Smith, Niall McEvoy, Nina C Berner, David McCloskey, Hannah C Nerl, Arlene O’Neill, Paul J King, Tom Higgins, Damien Hanlon, et al. Edge and confinement effects allow in situ measurement of size and thickness of liquid-exfoliated nanosheets. *Nature communications*, 5(1):4576, 2014.
- [417] NovaCentrix. Nanosilver ink – aqueous dispersions for inkjet printing, 2018. [Wikipedia online; accessed 21-March-2024].
- [418] Adam G Kelly, David Finn, Andrew Harvey, Toby Hallam, and Jonathan N Coleman. All-printed capacitors from graphene-bn-graphene nanosheet heterostructures. *Applied Physics Letters*, 109(2), 2016.
- [419] J Sandler, MSP Shaffer, T Prasse, W Bauhofer, K Schulte, and AH Windle. Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties. *Polymer*, 40(21):5967–5971, 1999.
- [420] Akash Laturia, Maarten L Van de Put, and William G Vandenberghe. Author correction: Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. *npj 2D Materials and Applications*, 4(1):28, 2020.
- [421] Siti Machmudah, Hideki Kanda, Motonobu Goto, et al. Hydrolysis of biopolymers in near-critical and subcritical water. In *Water extraction of bioactive compounds*, pages 69–107. Elsevier, 2017.
- [422] RL Angle and HE Talley. Electrical and charge storage characteristics of the tantalum oxide-silicon dioxide device. *IEEE Transactions on Electron Devices*, 25(11):1277–1283, 1978.
- [423] Ying Cao, Jiatian Zhang, Dandan Zhang, Yan Lv, Jie Li, Yiting Xu, Kaibin He, Guorong Chen, Conghui Yuan, Birong Zeng, et al. A novel shape memory-assisted and thermo-induced self-healing boron nitride/epoxy composites based on diels–alder reaction. *Journal of Materials Science*, 55:11325–11338, 2020.
- [424] Asja Pettignano, Aurélia Charlot, and Etienne Fleury. Solvent-free synthesis of amidated carboxymethyl cellulose derivatives: Effect on the thermal properties. *Polymers*, 11(7):1227, 2019.
- [425] Rolf Landauer. The electrical resistance of binary metallic mixtures. *Journal of applied physics*, 23(7):779–784, 1952.
- [426] Rajesh Kumar, Sagar Kumar Nayak, Swarnalata Sahoo, Bishnu P Panda, Smita Mohanty, and Sanjay K Nayak. Study on thermal conductive epoxy adhesive based on adopting hexagonal boron nitride/graphite hybrids. *Journal of Materials Science: Materials in Electronics*, 29:16932–16938, 2018.
- [427] Sukhvinder S Kang. Advanced cooling for power electronics. In *2012 7th international conference on integrated power electronics systems (cips)*, pages 1–8. IEEE, 2012.

- [428] Dongliang Zhao, Xin Qian, Xiaokun Gu, Saad Ayub Jajja, and Ronggui Yang. Measurement techniques for thermal conductivity and interfacial thermal conductance of bulk and thin film materials. *Journal of Electronic Packaging*, 138(4):040802, 2016.
- [429] Roberto Li Voti, Grigore Leahu, Emilija Petronijevic, Alessandro Belardini, Tiziana Cesca, Carlo Scian, Giovanni Mattei, and Concita Sibilica. Characterization of chirality in diffractive metasurfaces by photothermal deflection technique. *Applied Sciences*, 12(3):1109, 2022.
- [430] Abid Hussanan and Nguyen Thoi Trung. Heat transfer analysis of sodium carboxymethyl cellulose based nanofluid with titania nanoparticles. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 56(2):248–256, 2019.
- [431] SA Svetlov, NS Levina, and AS Pivovarov. Determination of thermal conductivity coefficient of moist sodium carboxymethyl cellulose. *Chemical and Petroleum Engineering*, 54(9):723–727, 2019.
- [432] IY Forero-Sandoval, F Cervantes-Alvarez, JA Ramirez-Rincon, JD Macias, Nelson Wilbur Pech-May, Jose Ordonez-Miranda, and JJ Alvarado-Gil. Percolation threshold of the thermal, electrical and optical properties of carbonyl-iron microcomposites. *Applied Composite Materials*, 28:447–463, 2021.
- [433] Shuaishuai Zhou, Tongle Xu, Liyuan Jin, Na Song, and Peng Ding. Ultraflexible polyamide-imide films with simultaneously improved thermal conductive and mechanical properties: Design of assembled well-oriented boron nitride nanosheets. *Composites Science and Technology*, 219:109259, 2022.
- [434] Taku Goto, Masaki Iida, Helen Tan, Chang Liu, Koichi Mayumi, Rina Maeda, Koichi Kitahara, Kazuto Hatakeyama, Tsuyohito Ito, Yoshiki Shimizu, et al. Thermally conductive tough flexible elastomers as composite of slide-ring materials and surface modified boron nitride particles via plasma in solution. *Applied Physics Letters*, 112(10), 2018.
- [435] Md Golam Rasul, Alper Kiziltas, Christos D Malliakas, Ramin Rojaee, Soroosh Sharifi-Asl, Tara Foroozan, Reza Shahbazian-Yassar, and Babak Arfaei. Polyethylene-bn nanosheets nanocomposites with enhanced thermal and mechanical properties. *Composites Science and Technology*, 204:108631, 2021.
- [436] Jaehyun Wie and Jooheon Kim. Thermal properties of binary filler hybrid composite with graphene oxide and pyrolyzed silicon-coated boron nitride. *Polymers*, 12(11):2553, 2020.
- [437] Kennedy C Onyelowe and Denise-Penelope N Kontoni. A critical review of rheological models in self-compacting concrete for sustainable structures. *Scientific Reports*, 13(1):21296, 2023.
- [438] Sayan Ganguly and Narayan Ch Das. Rheological properties of polymer-carbon composites. *Carbon-Containing Polymer Composites*, pages 271–294, 2019.
- [439] Chuangang Lin and DDL Chung. Rheological behavior of thermal interface pastes. *Journal of electronic materials*, 38:2069–2084, 2009.

- [440] Chuangang Lin, Timothy A Howe, and DDL Chung. Electrically nonconductive thermal pastes with carbon as the thermally conductive component. *Journal of electronic materials*, 36:659–668, 2007.
- [441] Ali Yazdan, Jizhe Wang, Ce-Wen Nan, and Liangliang Li. Rheological behavior and thermal conductivities of emulsion-based thermal pastes. *Journal of Electronic Materials*, 49:2100–2109, 2020.
- [442] JR Stokes and JH Telford. Measuring the yield behaviour of structured fluids. *Journal of Non-Newtonian Fluid Mechanics*, 124(1-3):137–146, 2004.
- [443] Electrolube. Tcor, thermally conductive rtv (oxime), 2013. [Online; accessed 21-March-2024].
- [444] Vakefield-vette. Thermal compounds, adhesives and interface materials, 2007. [Online; accessed 21-March-2024].
- [445] Gregory Nellis and Sanford Klein. *Heat transfer*. Cambridge university press, 2008.
- [446] Ozlem Ipek Kalaoglu-Altan, Burcak Karaguzel Kayaoglu, and Levent Trabzon. Improving thermal conductivities of textile materials by nanohybrid approaches. *Iscience*, 25(3), 2022.
- [447] Abdul Samad Farooq and Peng Zhang. Fundamentals, materials and strategies for personal thermal management by next-generation textiles. *Composites Part A: Applied Science and Manufacturing*, 142:106249, 2021.
- [448] Yucan Peng and Yi Cui. Advanced textiles for personal thermal management and energy. *Joule*, 4(4):724–742, 2020.
- [449] Amir Abbas, Yan Zhao, Xungai Wang, and Tong Lin. Cooling effect of mwcnt-containing composite coatings on cotton fabrics. *Journal of The Textile Institute*, 104(8):798–807, 2013.
- [450] Kai Wu, Luping Yu, Chuxin Lei, Jiexin Huang, Dingyao Liu, Yang Liu, Yangsu Xie, Feng Chen, and Qiang Fu. Green production of regenerated cellulose/boron nitride nanosheet textiles for static and dynamic personal cooling. *ACS applied materials & interfaces*, 11(43):40685–40693, 2019.
- [451] Michael A Hope, Alexander C Forse, Kent J Griffith, Maria R Lukatskaya, Michael Ghidui, Yury Gogotsi, and Clare P Grey. Nmr reveals the surface functionalisation of ti₃c₂mxene. *Physical Chemistry Chemical Physics*, 18(7):5099–5102, 2016.
- [452] Jehad K El-Demellawi, Sergei Lopatin, Jun Yin, Omar F Mohammed, and Husam N Alshareef. Tunable multipolar surface plasmons in 2d ti₃c₂t_x mxene flakes. *ACS nano*, 12(8):8485–8493, 2018.
- [453] Kanit Hantanasirisakul and Yury Gogotsi. Electronic and optical properties of 2d transition metal carbides and nitrides (mxenes). *Advanced materials*, 30(52):1804779, 2018.

- [454] Jong Woo Park, Dong Yeop Lee, Hyunsoo Kim, Jae Sang Hyeon, Monica Jung de Andrade, Ray H Baughman, and Seon Jeong Kim. Highly loaded mxene/carbon nanotube yarn electrodes for improved asymmetric supercapacitor performance. *Mrs Communications*, 9(1):114–121, 2019.
- [455] Junyeong Yun, Ian Echols, Paraskevi Flouda, Yijun Chen, Shaoyang Wang, Xiaofei Zhao, Dustin Holta, Miladin Radovic, Micah J Green, Mohammad Naraghi, et al. Layer-by-layer assembly of reduced graphene oxide and mxene nanosheets for wire-shaped flexible supercapacitors. *ACS Applied Materials & Interfaces*, 13(12):14068–14076, 2021.
- [456] Ruiyang Kang, Zhenyu Zhang, Liangchao Guo, Junfeng Cui, Yapeng Chen, Xiao Hou, Bo Wang, Cheng-Te Lin, Nan Jiang, and Jinhong Yu. Enhanced thermal conductivity of epoxy composites filled with 2d transition metal carbides (mxenes) with ultralow loading. *Scientific reports*, 9(1):9135, 2019.
- [457] Volker Presser, Michael Naguib, Laurent Chaput, Atsushi Togo, Gilles Hug, and Michel W Barsoum. First-order raman scattering of the max phases: Ti_2AlN , Ti_2AlC , Ti_3AlC_2 , Ti_3AlC_2 , and Ti_3AlC_2 . *Journal of Raman Spectroscopy*, 43(1):168–172, 2012.
- [458] Sharona A Melchior, Kumar Raju, Innocent S Ike, Rudolph M Erasmus, Guy Kabongo, Iakovos Sigalas, Sunny E Iyuke, and Kenneth I Ozoemena. High-voltage symmetric supercapacitor based on 2d titanium carbide (mxene, Ti_2CTx)/carbon nanosphere composites in a neutral aqueous electrolyte. *Journal of The Electrochemical Society*, 165(3):A501–A511, 2018.
- [459] Fei-Fei Liu, Jian Zhao, Shuguang Wang, and Baoshan Xing. Adsorption of sulfonamides on reduced graphene oxides as affected by ph and dissolved organic matter. *Environmental pollution*, 210:85–93, 2016.
- [460] Shen Lai, Jaeho Jeon, Sung Kyu Jang, Jiao Xu, Young Jin Choi, Jin-Hong Park, Euyheon Hwang, and Sungjoo Lee. Surface group modification and carrier transport properties of layered transition metal carbides (Ti_2CTx , Ti_2OH , Ti_2F and Ti_2O). *Nanoscale*, 7(46):19390–19396, 2015.
- [461] Hongjun Fang, Yusong Pan, Minyuan Yin, and Chengling Pan. Enhanced visible light photocatalytic activity of cds with alkalized Ti_3C_2 nano-sheets as co-catalyst for degradation of rhodamine b. *Journal of Materials Science: Materials in Electronics*, 30:14954–14966, 2019.
- [462] Fanfan Liu, Aiguo Zhou, Jinfeng Chen, Heng Zhang, Jianliang Cao, Libo Wang, and Qianku Hu. Preparation and methane adsorption of two-dimensional carbide Ti_2C . *Adsorption*, 22:915–922, 2016.
- [463] S Myhra, JAA Crossley, and MW Barsoum. Crystal-chemistry of the Ti_3AlC_2 and Ti_4AlN_3 layered carbide/nitride phases—characterization by xps. *Journal of Physics and Chemistry of Solids*, 62(4):811–817, 2001.
- [464] Chiranjit Roy, Subhra Kanti De, Pritam Banerjee, Soumen Pradhan, and Somnath Bhattacharyya. Investigating suitable medium for the long-duration storage of Ti_2CTx mxene. *Journal of Alloys and Compounds*, 938:168471, 2023.

- [465] Sukanta De, Paul J King, Philip E Lyons, Umar Khan, and Jonathan N Coleman. Size effects and the problem with percolation in nanostructured transparent conductors. *ACS nano*, 4(12):7064–7072, 2010.
- [466] Paul M Kogut and Joseph P Straley. Distribution-induced non-universality of the percolation conductivity exponents. *Journal of Physics C: Solid State Physics*, 12(11):2151, 1979.
- [467] Niklaus Johner, Claudio Grimaldi, Isaac Balberg, and Peter Ryser. Transport exponent in a three-dimensional continuum tunneling-percolation model. *Physical Review B—Condensed Matter and Materials Physics*, 77(17):174204, 2008.
- [468] Alexey Lipatov and Alexander Sinitskii. Electronic and mechanical properties of mxenes derived from single-flake measurements. *2D Metal Carbides and Nitrides (MXenes) Structure, Properties and Applications*, pages 301–325, 2019.
- [469] Shaohong Luo, Shashikant Patole, Shoaib Anwer, Baosong Li, Thomas Delclos, Oleksiy Gogotsi, Veronika Zahorodna, Vitalii Balitskyi, and Kin Liao. Tensile behaviors of ti3c2tx (mxene) films. *Nanotechnology*, 31(39):395704, 2020.
- [470] Suvdanchimeg Sunderiya, Selengesuren Suragtkhuu, Solongo Purevdorj, Tumentsereg Ochirkhuyag, Munkhjargal Bat-Erdene, Purevlkham Myagmarsereejid, Ashley D Slattey, Abdulaziz SR Bati, Joseph G Shapter, Dorj Odkhuu, et al. Understanding the oxidation chemistry of ti3c2tx (mxene) sheets and their catalytic performances. *Journal of Energy Chemistry*, 88:437–445, 2024.
- [471] IS Beloborodov, AV Lopatin, VM Vinokur, and Konstantin B Efetov. Granular electronic systems. *Reviews of Modern Physics*, 79(2):469–518, 2007.
- [472] Tzung-I Su, Cheng-Ren Wang, Shui-Tien Lin, and Ralph Rosenbaum. Magnetoresistance of al 70 pd 22.5 re 7.5 quasicrystals in the variable-range hopping regime. *Physical Review B*, 66(5):054438, 2002.
- [473] Shayan Seyedin, Tian Carey, Adrees Arbab, Ladan Eskandarian, Sivasambu Bohm, Jong Min Kim, and Felice Torrisi. Fibre electronics: towards scaled-up manufacturing of integrated e-textile systems. *Nanoscale*, 13(30):12818–12847, 2021.
- [474] Poonam Sundriyal and Shantanu Bhattacharya. Textile-based supercapacitors for flexible and wearable electronic applications. *Scientific reports*, 10(1):13259, 2020.
- [475] Jie Wang, Xiuhan Li, Yunlong Zi, Sihong Wang, Zhaoling Li, Li Zheng, Fang Yi, Shengming Li, and Zhong Lin Wang. A flexible fiber-based supercapacitor-triboelectric-nanogenerator power system for wearable electronics. *Advanced Materials*, 27(33):4830–4836, 2015.
- [476] Md Rashedul Islam, Shaila Afroj, Christopher Beach, Mohammad Hamidul Islam, Carinna Parraman, Amr Abdelkader, Alexander J Casson, Kostya S Novoselov, and Nazmul Karim. Fully printed and multifunctional graphene-based wearable e-textiles for personalized healthcare applications. *IScience*, 25(3), 2022.

- [477] Yixue Duan, Gongchuan You, Kaien Sun, Zhe Zhu, Xiaoqiao Liao, Linfeng Lv, Hui Tang, Bin Xu, and Liang He. Advances in wearable textile-based micro energy storage devices: structuring, application and perspective. *Nanoscale Advances*, 3(22):6271–6293, 2021.
- [478] Md Rashedul Islam, Shaila Afroj, Kostya S Novoselov, and Nazmul Karim. Smart electronic textile-based wearable supercapacitors. *Advanced Science*, 9(31):2203856, 2022.
- [479] Awais Sattar Ghouri, Rabya Aslam, Muhammad Saqib Siddiqui, and Syed Kamran Sami. Recent progress in textile-based flexible supercapacitor. *Frontiers in Materials*, 7:58, 2020.
- [480] Nick Hillier, Sheng Yong, and Stephen Beeby. Optimization of carbon electrodes for solid-state e-textile supercapacitors. In *Journal of Physics: Conference Series*, volume 1407, page 012059. IOP Publishing, 2019.
- [481] Anthony G Pandolfo and Anthony F Hollenkamp. Carbon properties and their role in supercapacitors. *Journal of power sources*, 157(1):11–27, 2006.
- [482] Sheng Yong, Nicholas Hillier, and Stephen Paul Beeby. Phase-inverted copolymer membrane for the enhancement of textile supercapacitors. *Polymers*, 14(16):3399, 2022.
- [483] Changsoon Choi, Jong Woo Park, Keon Jung Kim, Duck Weon Lee, Monica Jung De Andrade, Shi Hyeong Kim, Sanjeev Gambhir, Geoffrey M Spinks, Ray H Baughman, and Seon Jeong Kim. Weavable asymmetric carbon nanotube yarn supercapacitor for electronic textiles. *RSC advances*, 8(24):13112–13120, 2018.
- [484] Litty V Thekkekara and Min Gu. Large-scale waterproof and stretchable textile-integrated laser-printed graphene energy storages. *Scientific reports*, 9(1):11822, 2019.
- [485] Taegun Kim, Edmund P Samuel, Chanwoo Park, Yong-II Kim, Ali Aldalbahi, Faisal Alotaibi, and Sam S Yoon. Wearable fabric supercapacitors using super-sonically sprayed reduced graphene and tin oxide. *Journal of Alloys and Compounds*, 856:157902, 2021.
- [486] Yu V Surovikin, AV Syrieva, and AV Lavrenov. The effect of superconductive carbon black on the properties of supercapacitor electrode. In *AIP Conference Proceedings*, volume 2285. AIP Publishing, 2020.
- [487] Amrita Jain, Monika Michalska, Angelika Zaszczynska, and Piotr Denis. Surface modification of activated carbon with silver nanoparticles for electrochemical double layer capacitors. *Journal of Energy Storage*, 54:105367, 2022.
- [488] Jie Li and Zhou Xu. Few-walled carbon nanotube-enhanced activated carbon supercapacitor performance in organic electrolyte at 4 v. *RSC advances*, 9(33):18863–18867, 2019.

- [489] N Jäckel, D Weingarth, M Zeiger, M Aslan, I Grobelsek, and V Presser. Comparison of carbon onions and carbon blacks as conductive additives for carbon supercapacitors in organic electrolytes. *Journal of Power Sources*, 272:1122–1133, 2014.
- [490] Yao Chen, Xiong Zhang, Haitao Zhang, Xianzhong Sun, Dacheng Zhang, and Yanwei Ma. High-performance supercapacitors based on a graphene-activated carbon composite prepared by chemical activation. *Rsc Advances*, 2(20):7747–7753, 2012.
- [491] Lanshu Xu, Yue Li, Mengying Jia, Qiang Zhao, Xiaojuan Jin, and Chunli Yao. Synthesis and characterization of free-standing activated carbon/reduced graphene oxide film electrodes for flexible supercapacitors. *RSC advances*, 7(71):45066–45074, 2017.
- [492] Sheng Yong, John Owen, and Stephen Beeby. Solid-state supercapacitor fabricated in a single woven textile layer for e-textiles applications. *Advanced Engineering Materials*, 20(5):1700860, 2018.
- [493] Yuanming Wang, Xue Wang, Xifei Li, Xiaolong Li, Yang Liu, Yang Bai, Huanhao Xiao, and Guohui Yuan. A high-performance, tailorable, wearable, and foldable solid-state supercapacitor enabled by arranging pseudocapacitive groups and mxene flakes on textile electrode surface. *Advanced Functional Materials*, 31(7):2008185, 2021.
- [494] Goki Eda, Giovanni Fanchini, and Manish Chhowalla. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature nanotechnology*, 3(5):270–274, 2008.
- [495] Weisheng Li, Jian Zhou, Songhua Cai, Zhihao Yu, Jialin Zhang, Nan Fang, Taotao Li, Yun Wu, Tangsheng Chen, Xiaoyu Xie, et al. Uniform and ultrathin high- κ gate dielectrics for two-dimensional electronic devices. *Nature Electronics*, 2(12):563–571, 2019.
- [496] María Mercedes Velázquez, Teresa Alejo, David López-Díaz, Beatriz Martin-Garcia, and María Dolores Merchán. Langmuir-blodgett methodology: A versatile technique to build 2d material films. *Two-dimensional Materials-Synthesis, Characterization and Potential Applications*, pages 22–42, 2016.
- [497] Sanjib Biswas and Lawrence T Drzal. A novel approach to create a highly ordered monolayer film of graphene nanosheets at the liquid- liquid interface. *Nano letters*, 9(1):167–172, 2009.
- [498] A Sikora, H Ftouni, J Richard, C Hébert, D Eon, F Omnès, and O Bourgeois. Highly sensitive thermal conductivity measurements of suspended membranes (sin and diamond) using a 3ω -völklein method. *Review of Scientific Instruments*, 83(5), 2012.
- [499] Xinhe Yang, Peng Liu, Duanliang Zhou, Feng Gao, Xinhe Wang, Shiwei Lv, Zi Yuan, Xiang Jin, Wei Zhao, Haoming Wei, et al. High temperature performance of coaxial h-bn/cnt wires above 1,000° c: Thermionic electron emission and thermally activated conductivity. *Nano Research*, 12:1855–1861, 2019.
- [500] Rina Ibragimova, Paul Erhart, Patrick Rinke, and Hannu-Pekka Komsa. Surface functionalization of 2d mxenes: trends in distribution, composition, and electronic properties. *The journal of physical chemistry letters*, 12(9):2377–2384, 2021.

- [501] Qiye Guan, Hejin Yan, and Yongqing Cai. Flatten the li-ion activation in perfectly lattice-matched mxene and 1t-mos2 heterostructures via chemical functionalization. *Advanced Materials Interfaces*, 9(7):2101838, 2022.
- [502] Di Wang, Chenkun Zhou, Alexander S Filatov, Wooje Cho, Francisco Lagunas, Mingzhan Wang, Suriyanarayanan Vaikuntanathan, Chong Liu, Robert F Klie, and Dmitri V Talapin. Direct synthesis and chemical vapor deposition of 2d carbide and nitride mxenes. *Science*, 379(6638):1242–1247, 2023.
- [503] Jack W Owen, Natalia A Azarova, Marsha A Loth, Markos Paradinas, Mariona Coll, Carmen Ocal, John E Anthony, and Oana D Jurchescu. Effect of processing parameters on performance of spray-deposited organic thin-film transistors. *Journal of Nanotechnology*, 2011(1):914510, 2011.
- [504] Natalia A Azarova, Jack W Owen, Claire A McLellan, Marsha A Grimminger, Eric K Chapman, John E Anthony, and Oana D Jurchescu. Fabrication of organic thin-film transistors by spray-deposition for low-cost, large-area electronics. *Organic Electronics*, 11(12):1960–1965, 2010.
- [505] Yu Xie, Siyi Gao, and Morteza Eslamian. Fundamental study on the effect of spray parameters on characteristics of p3ht: Pcbm active layers made by spray coating. *Coatings*, 5(3):488–510, 2015.
- [506] Chao Yuan, Jiahan Li, Lucas Lindsay, David Cherns, James W Pomeroy, Song Liu, James H Edgar, and Martin Kuball. Modulating the thermal conductivity in hexagonal boron nitride via controlled boron isotope concentration. *Communications physics*, 2(1):43, 2019.
- [507] A Franck. Understanding rheology of structured fluids. *Book of TA instruments*, pages 1–17, 2004.

Appendix A

h-BN based characterisation

A.1 Spray coating optimisation

The film made in this work is a network of 2D flakes. The uniformity of the dielectric film affects the I-V characteristics of the fabricated capacitor [503]. The lower the roughness of the film is, the average thickness of the film is less overestimated, thus the dielectric constant and breakdown strength are more accurate.

The spray coating protocol has been optimised to achieve the best uniformity of the film, via adjusting the nitrogen pressure [503], the ink concentration [504], the substrate temperatures [505], the nozzle-substrate distances [503] and the nozzle-substrate angles. The nozzle-substrate angle is set between 30-45 °C to meet the best holding gesture of human beings since the spray coating was done manually in this work. The film roughness is measured by a profilometer (Detak 150) and calculated in root mean square roughness (R_q) and aiming for $R_q \sim 6.1$ nm, as the average thickness of the FLh-BN flakes is 6.1 nm based on AFM statistics.

The film roughness can be reduced from 41.1 nm to 26.7 nm if the ink concentration declines from 3.0 to 1.0 mg mL⁻¹. The substrate temperature set at 40 °C exhibits the optimal film roughness at 12.3 nm, compared to that at 25 °C (26.7 nm) and 60 °C (30.9 nm), which gives the best evaporation rate of the solvent and minimise the coffee ring effect and the too-early evaporation. The pressure of N₂ was optimised at 20 psi with a nozzle-substrate distance of 15-20 cm, showing the best film roughness at 3.0-3.4 nm. The literature has proved that a high carrier gas mobility will help to spray the ink into the fine aerosol, leading to a uniform thin film [503]. However, the carrier gas mobility cannot be too large for a certain nozzle

distance. Otherwise, the deposited ink droplets may be blown away and cause non-uniformity [173]. If further increasing the nozzle distance to avoid this, some droplets may evaporate before reaching the substrate since the ink solvent used here contains highly volatile ethanol. Therefore, the group "d2" is the optimal spray coating parameters set for this work.

Table A.1 Summary of spray coating parameters before and after optimisation

	Spray coating parameters				
	ink concentration (mg mL ⁻¹)	temperature (°C)	pressure of N ₂ (psi)	nozzle-substrate distance (cm)	film roughness (nm)
a	3.0	25	40	20	41.1
b1	1.0	25	40	20	26.7
b2	1.0	40	40	20	12.3
b3	1.0	60	40	20	30.9
c1	1.0	40	20	20	3.4
c2	1.0	40	5	15	7.9
d1	1.0	40	20	5	16.1
d2	1.0	40	20	15	3.0

A.2 Tunneling model fittings of capacitors

A.3 The thermal conductivity of h-BN

A.3.1 Sample preparation

Bh-BN powders, purchased from Goodfellows (B516011, < 10 μm size), were compressed at 15 tons for 30 minutes using a hydraulic press (Specac® Atlas 15T) to form a thick pellet.

A.3.2 Thermal properties of h-BN

The robust pellet was then measured for density (ρ), specific heat capacity (C_p), and thermal diffusivity (D).

Figure A.4(a) plots the thermal diffusion length (l_t) as a function of the inverse square root of frequency ($F^{-0.5}$) via the PDT method (Section 2.6.6). By fitting the linear trend correlated

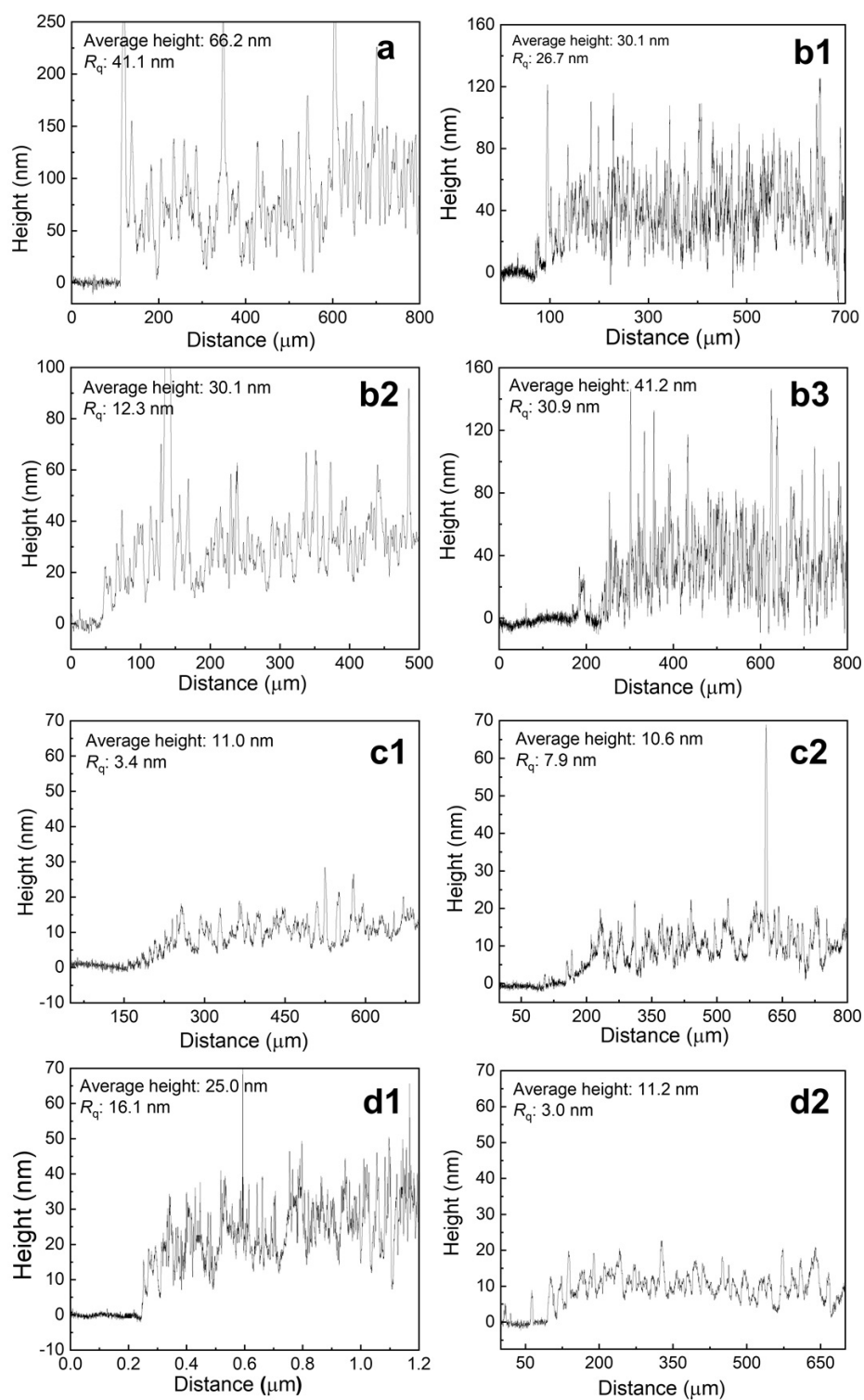


Fig. A.1 Optimisation of spray coating parameters.

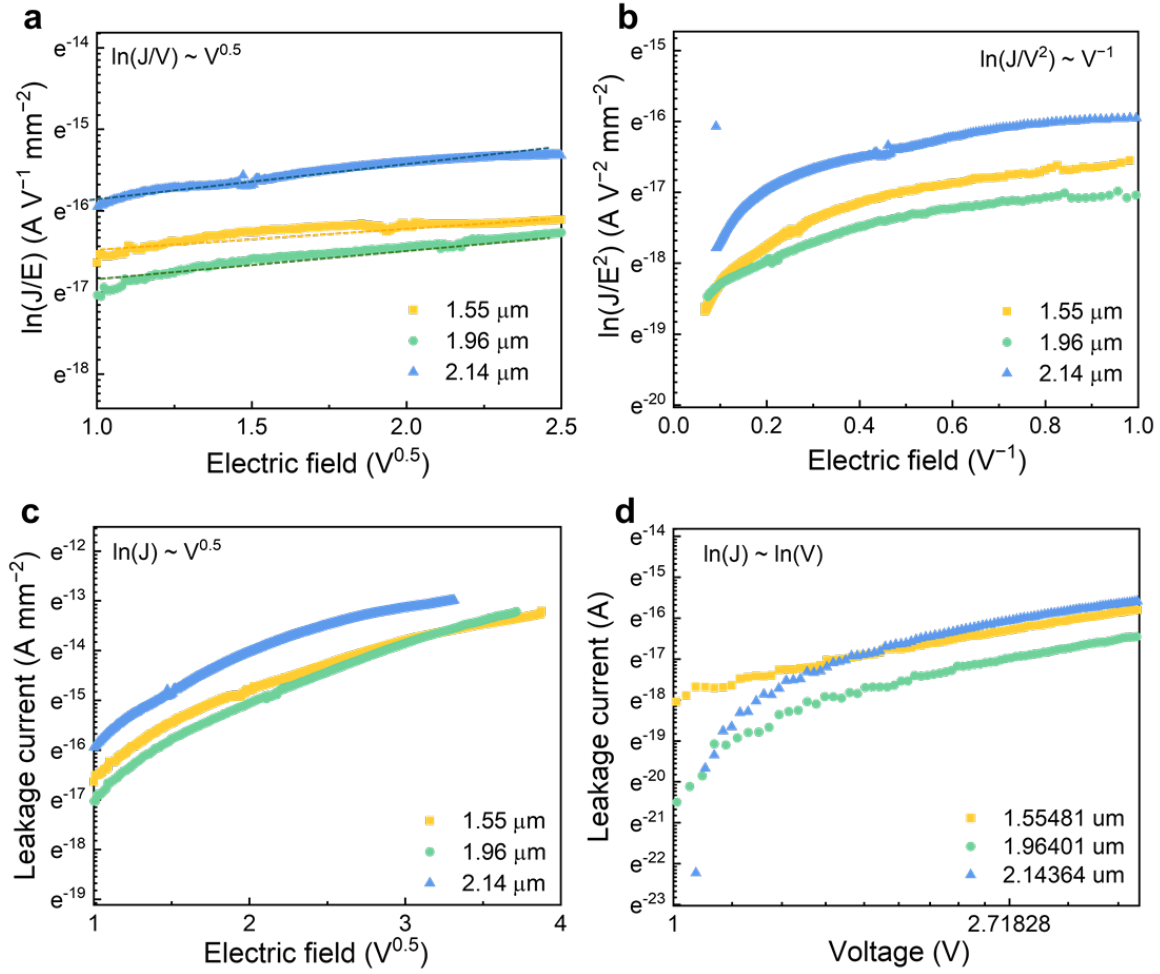


Fig. A.2 Electrical property analysis, described by the field-assisted tunnelling models: (a) the Poole-Frenkel model fitting by plotting J/V versus $V^{0.5}$, and (b) the Fowler-Nordheim model fitting by plotting J/V^2 versus $1/V$, (c) the Schottky emission model fitting by plotting J versus $V^{0.5}$, and (d) the Ohmic conduction fitting by plotting $\ln J$ versus $\ln V$.

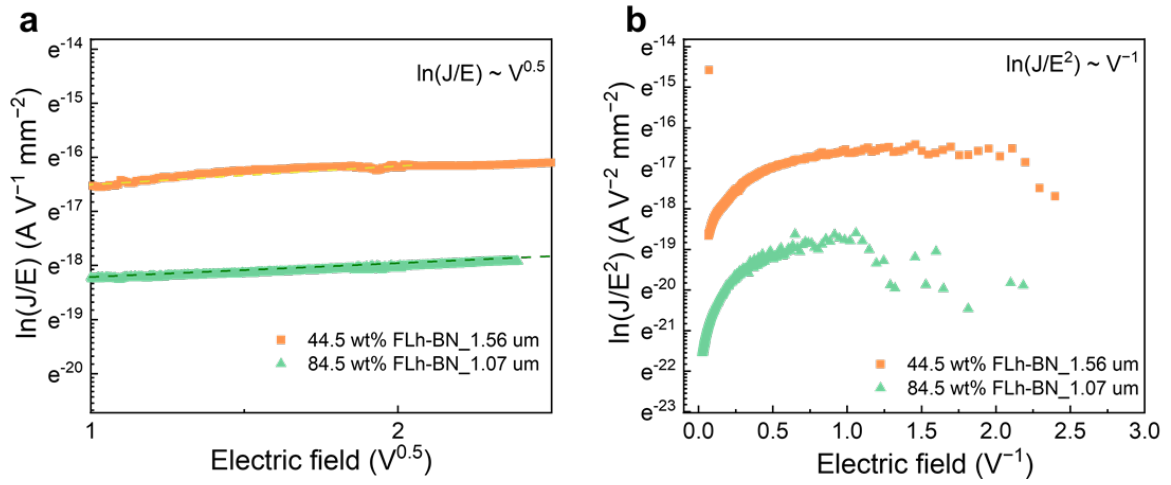


Fig. A.3 Electrical property analysis of FLh-BN/CMC capacitors with different mass loadings of FLh-BN, described by the field-assisted tunnelling models: (a) the Poole-Frenkel model fitting by plotting J/V versus $V^{0.5}$, and (b) the Fowler-Nordheim model fitting by plotting J/V^2 versus $1/V$.

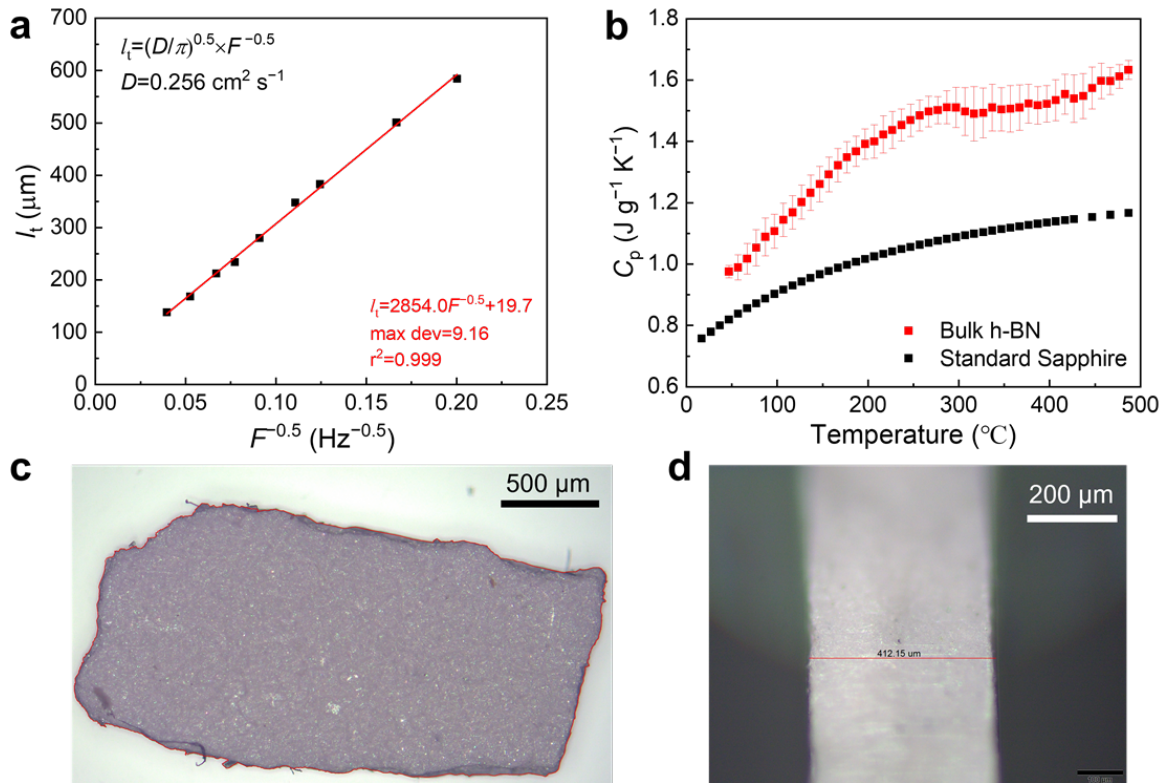


Fig. A.4 Determination of the κ of Bh-BN via PDT, DSC, and density measurement. (a) The thermal diffusion length as a function of the inverse square root of frequency; (b) the C_p as a function of temperatures; and the ρ calculation from the surface area (c) and sample thickness (d) determination via optical microscopy.

to the Equation 2.25, I found the D value of the Bh-BN material is $0.256 \text{ cm}^2 \text{ s}^{-1}$. Figure A.4(b) plots the C_p as a function of temperatures via the DSC technique (Section 2.6.5). I found the C_p value of the Bh-BN material is $0.97 \text{ g}^{-1} \text{ K}^{-1}$ at RT.

Figure A.4(c-d) shows the surface area (c) and thickness (d) determination via optical microscopy. By knowing both m and V , the ρ of the Bh-BN pellet is 1.69 g cm^{-3} . Compared to the published ρ of h-BN at a ρ of 2.1 g cm^{-3} , the Bh-BN pellet I characterised gave a lower ρ value due to the porosity (nanopore size: 1.8-2.0 nm) of the pellet.

Table A.2 summarised the key thermal properties of Bh-BN. Based on our characterisation, Bh-BN exhibited a κ value of $51 \text{ W m}^{-1} \text{ K}^{-1}$ at RT, which is one order of magnitude lower than the highest reported in-plane κ of $480 \text{ W m}^{-1} \text{ K}^{-1}$ for the modulated and optimized Bh-BN [506]. That can be attributed to the porosity and randomly oriented h-BN flakes in the pellet, which makes it difficult to state the κ to be in-plane or out-of-plane values. The presence of nanopores in the pellet leads to a porosity of 0.195 for the Bh-BN pellet, which increases the thermal contact resistance between Bh-BN flakes and reduces the κ of the material.

Table A.2 The κ of Bh-BN tested

Sample	D	ρ	C_p	Porosity	κ
Units	$\text{cm}^2 \text{ s}^{-1}$	g cm^{-3}	$\text{J g}^{-1} \text{ K}^{-1}$	/	$\text{W m}^{-1} \text{ K}^{-1}$
Bh-BN	0.25	1.69	0.97	0.195	51

A.4 Homogeneity characterisation of the composites

CMC can act as a stabilizer with regions of markedly different polarity since the polymer chain owns a hydrophilic group and a hydrophobic tail separately. When present with h-BN in dispersions, its hydrophobic tail physically contacts the basal plane of Bh-BN/FLh-BN flakes because of the Van-der Waals force, while its hydrophilic group protrudes into the solvent and interacts with the solvent molecules. When the Bh-BN/FLh-BN flakes tend to approach each other in the dispersions due to the unbalanced forces, the CMC polymer chains begin to collide with each other in the same space. The resulting repulsion force between the chains prevents the Bh-BN/FLh-BN flakes from aggregation, thus enabling a homogeneous mixture [135, 134].

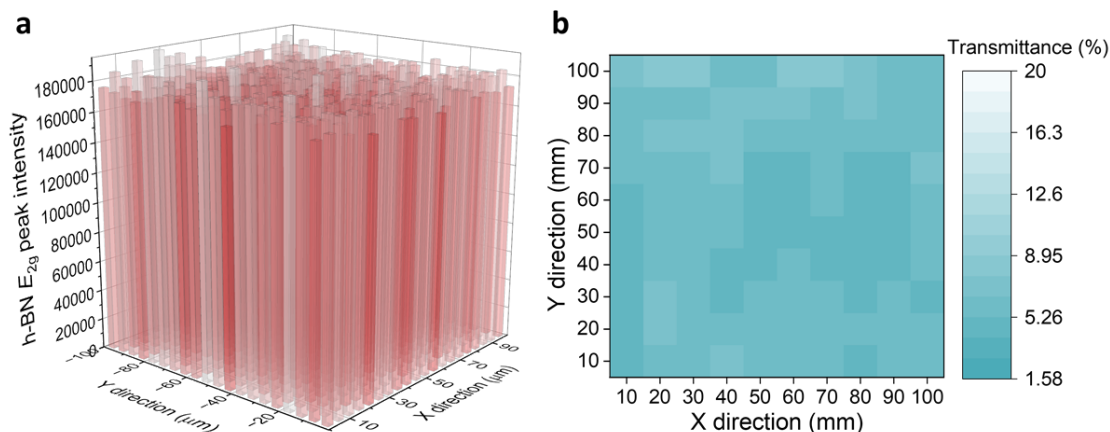


Fig. A.5 Characterisation of homogeneity of the dispersed h-BN flakes in the FLh-BN/CMC composite. (a) The distribution of Raman peak intensities of h-BN along a $60 \times 120 \mu\text{m}$ size film via Raman mapping; (b) Transmittance ($T\%$) distribution along a $100 \times 100 \text{ mm}$ size film at a wavelength of 600 nm.

Take the FLh-BN/CMC composite film as an example, we characterized the homogeneity of a $20.6 \mu\text{m}$ thick film, using statistical analysis of the h-BN E_{2g} Raman peak intensity via Raman mapping spectroscopy and statistical analysis of UV transmittance via a UV-Vis-NIR spectrophotometer. Raman spectra were collected across the film surface with a step size of $5 \mu\text{m}$, and the transmittance ($T\%$) distribution of the film was measured along a $100 \times 100 \text{ mm}$ size at 600 nm with a light aperture of 1 cm^2 .

Figure A.5 (a) demonstrates the uniform distribution of the h-BN E_{2g} Raman peak (1365 cm^{-1}) intensities relative to the baseline, indicating a homogeneous distribution of FLh-BN in the FLh-BN/CMC composite film. Figure A.5 (b) draws the distribution of $T\%$ across the measured FLh-BN/CMC film. We observed the average transmittance of the film was $5.84 \pm 0.79 \%$ with a standard deviation of 0.79% . For comparison, we measured the $T\%$ on an equivalent pure CMC film and a pure FLh-BN film. The $T\%$ of the equivalent pure CMC film was $\sim 86 \%$ and the $T\%$ of the equivalent pure FLh-BN film was $\sim 1.58 \%$, respectively. This indicates that most of the $T\%$ of the FLh-BN/CMC film is lost due to the FLh-BN filler. Therefore, we could claim that the uniform $T\%$ distribution across the composite film indicates the homogeneous distribution of FLh-BN flakes in the CMC matrix.

A.5 Visco-elasticity of the composite

The storage modulus (G') and loss modulus (G'') are used to describe the visco-elastic behaviour of materials. The G' represents the elastic portion of a material's response to

deformation, while the G'' represents the viscous portion. The G' measures the energy stored in the material during each deformation cycle, which is recoverable upon removing the stress. High G' indicates that the material behaves more like a solid and can store more energy elastically. On the contrary, the G'' measures the energy dissipated as heat in each deformation cycle. High G'' indicates that the material behaves more like a liquid and dissipates more energy as heat. The strength of the colloidal forces is reflected by $\tan(\delta) = G''/G'$, with $\tan(\delta) < 1$ suggesting the materials are highly associated while a higher $\tan(\delta)$ suggesting the materials are largely un-associated.

Through the strain sweep test, the two moduli as a function of strain can be obtained to establish the extent of the material's linearity [507]. Usually, a visco-elastic material is independent of strain up to a critical strain level. Beyond this critical strain level, the material's behaviour is non-linear, and the G' declines. Figure A.6 plots the strain sweeps for (a) the 60 wt.% FLh-BN/CMC and (b) the 60 wt.% Bh-BN/CMC pastes.

In the case of the 60 wt.% FLh-BN/CMC paste, the critical strain is 0.05%. Below 0.05%, the structure of the paste is intact, and the paste behaves solid-like with a $\tan(\delta) < 1$, indicating the paste is structured and associated [507]. However, increasing the strain above the critical value disrupts the paste's internal network structure, making the paste becomes progressively more fluid-like. Both moduli decline and the G'' exceeds G' eventually, resulting in the $\tan(\delta)$ going beyond 1, suggesting the paste structure was disrupted and the material lost internal association. The 60 wt.% Bh-BN/CMC paste reveals a similar visco-elastic behaviour, with a higher critical strain at 6.7%. The linear portion of the moduli lasts to a stronger strain compared to that of the 60 wt.% FLh-BN/CMC paste, indicating that the 60 wt.% Bh-BN/CMC paste behaves more solid-like at the same strain level.

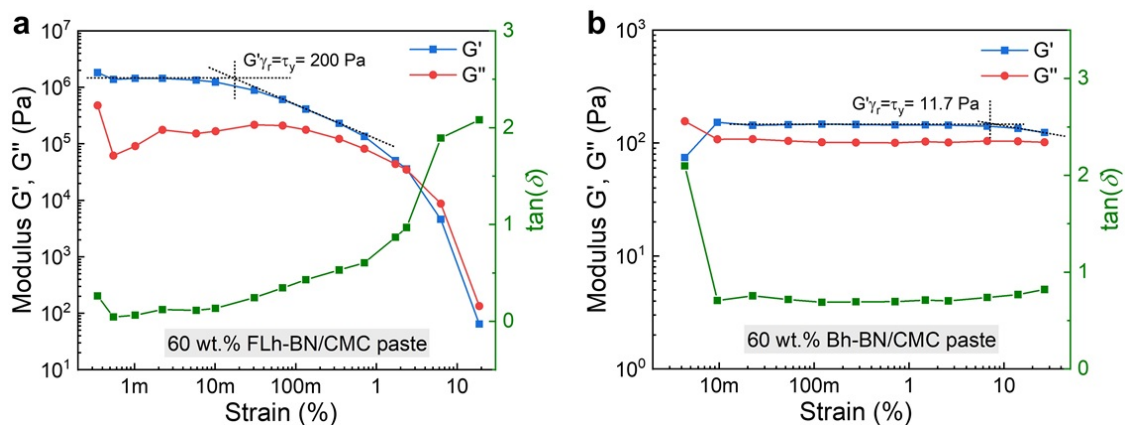


Fig. A.6 Rheological analysis via strain sweep for (a) the 60 wt.% FLh-BN/CMC and (b) the 60 wt.% Bh-BN/CMC pastes.

A.6 Case studies of the composites for heat dissipation

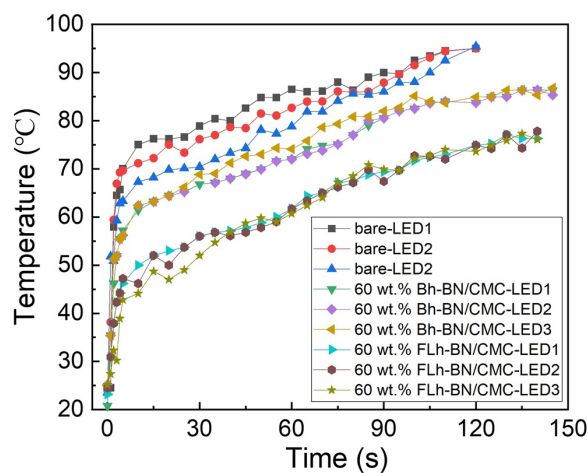


Fig. A.7 The 3 replicates showing the recorded LED core temperature evolution over time without (red) or with (green: Bh-BN/CMC; blue: FLh-BN/CMC) the pastes.

Set temperature	44 °C	55 °C	66 °C	76 °C
Coated cotton	40.6	48.9	56.7	61.0
	±2.7	±3.4	±3.5	±4.2
Uncoated cotton	43.8	53.3	64.6	73.9
	±1.1	±1.6	±2.8	±2.1

Fig. A.8 The 3 replicates showing the equilibrium temperature comparison between a coated textile and an uncoated textile above the same heater at different temperatures (b-44 °C; c-55 °C; d-66 °C; e-76 °C).

Appendix B

Ti₃C₂T_x/AC electrodes for textile supercapacitors

B.1 Explore the electrochemical potential of supercapacitor D

Given supercapacitor D's superior performance, we further explored its electrochemical potential at higher current densities, higher voltage scan rates, and wider operating voltage windows.

B.1.1 GC and CV performance

Figure B.1(a) shows the GC plots of supercapacitor D between 0 to 1.8 V at 0.25, 0.5, 1, 2, 3, 4 and 5 mA cm⁻². The curves are all linear and symmetrical at various current densities, demonstrating the device's reversibility with an electrostatic electrical double-layer property.

Figure B.1(b) shows the GC results of supercapacitor D charged up to 2.6 V at 1 mA cm⁻², without being short-circuited. It suggests that the Ti₃C₂T_x-infused carbon textile supercapacitor with DMSO as its electrolyte can be reliably charged to 2.6 V, compared to that most aqueous-based supercapacitors are restrained with a voltage limit of < 1 V.

Figure B.1(c) reports the CV plots of supercapacitor D tested between ± 1.8 V at a scan rate of 25, 50, 100 and 200 mV s⁻¹. The plots show no redox peak at all scan rates, indicating the supercapacitor D operates in an electrostatic electrical double-layer way and is electrochemically stable at the high scan rate up to 200 mV s⁻¹.

Figure B.1(d) plots the CV curves of supercapacitor D between ± 1.8 V to ± 2.6 V at 50 mV s^{-1} . It can stably operate over a wider voltage window (± 2.6 V), with no noticeable destructive redox reactions in both positive and negative voltage ranges.

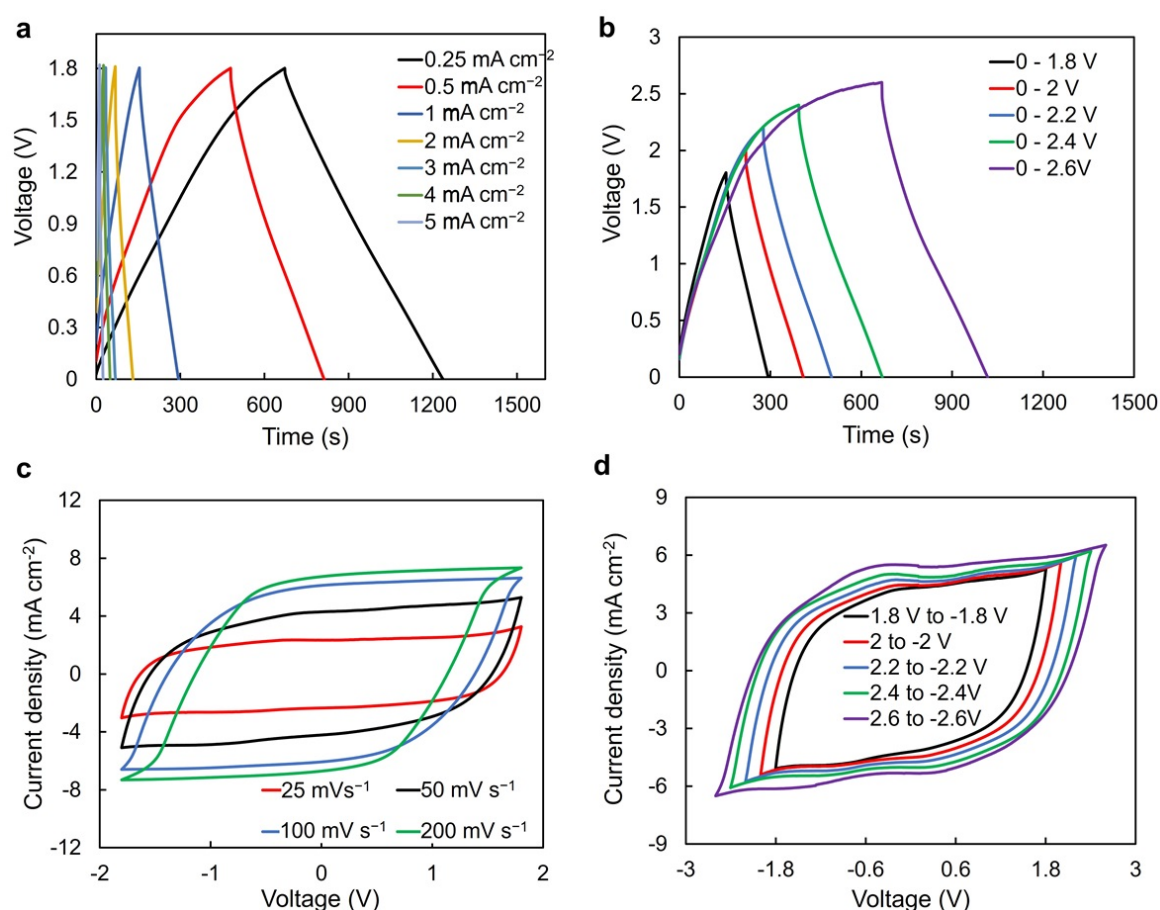


Fig. B.1 Electrical performance of supercapacitor D: (a) the GC plots tested at cycling currents varies at 0.25, 0.5, 1, 2, 3, 4, 5 mA cm⁻², (b) the GC plots tested between 0 and 1.8, 2.0, 2.2, 2.4, and 2.6 V, at 1 mA cm⁻², (c) the CV plots tested at a scan rate of 25, 50, 100, 200 mV s⁻¹, and (d) the CV plots tested between ± 1.8 V to ± 2.6 V at 50 mV s^{-1} , and (d) the Ragone plot and capacitance of supercapacitor D at different tested voltages.

B.1.2 Expanded capacitance, power density and energy density

Figure B.2 shows the C_A change as a function of voltage (black axes). The C_A of the supercapacitor D increases from 84.2 mF cm^{-2} (0–1.8 V) to 148.7 mF cm^{-2} (0–2.6 V), suggesting that increasing the voltage limit from 1.8 V to 2.6 V, there is more electrical energy stored in the textile supercapacitor D. The red axes show the Ragone plot, with the

power density increasing from 0.8 to 1.06 mW cm^{-2} and also the energy density increasing from 30.3 to 92.1 $\mu\text{Wh cm}^{-2}$.

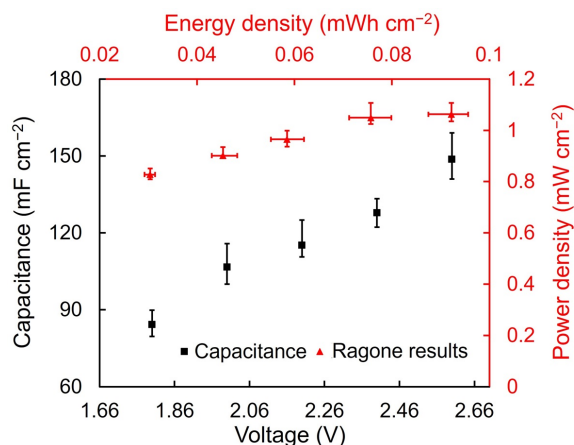


Fig. B.2 The C_A and Ragone plot of supercapacitor D at different tested voltages.

B.1.3 Device flexibility

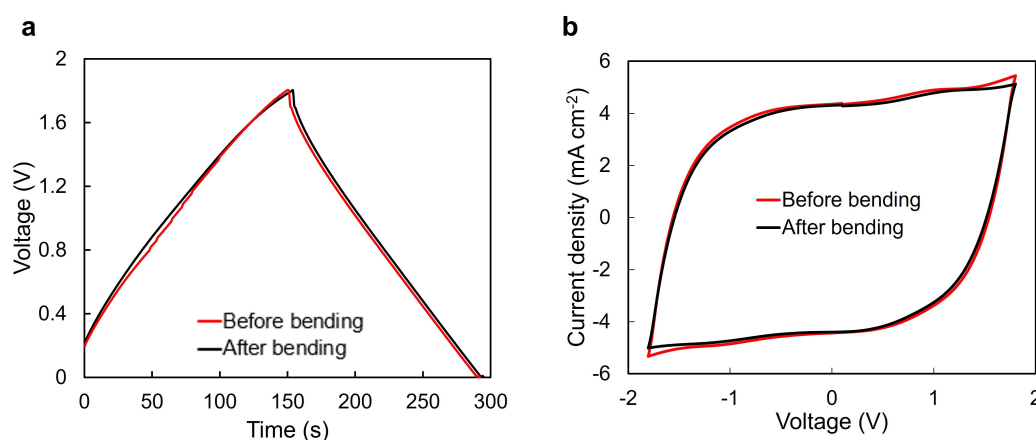


Fig. B.3 The flexibility of supercapacitor D. (a) The GC plot tested at 1 mA cm^{-2} , and (b) the CV plot tested at 50 mV s^{-1} to demonstrate the flexibility of supercapacitor D before and after bending (2000 cycles).

The mechanical durability of the textile supercapacitors was also investigated by the cyclical bending experiment. After obtaining the initial CV and GC results of the textile supercapacitor, the textile supercapacitors were taken out from the tube fitting, sealed in a plastic bag, and bent around the mandrel with a diameter of 3.2 mm 2000 times, the rotational speed was 60 rpm. After the bending experiment, the textile supercapacitors were then put into a tube cell for testing.

Figure B.3 shows the GC (a) and CV (b) plots of the supercapacitor D before (red curve) and after (black curve) cyclically bending the supercapacitor 2000 times around a mandrel (a diameter of 3.2 mm). There is no noticeable change in the shape of the curves, and only a small ($\sim 0.7\%$) drop of C_A is observed. It suggests that the electrochemical performance of the supercapacitor D is not impacted by the mechanical strain by the repeated bending cycles, and the bonding between the electrode and the textile is mechanically stable.

B.2 θ_c of Ti₃C₂T_x/AC electrodes



Fig. B.4 The wettability of supercapacitor electrodes using different materials. Water θ_c tests of supercapacitor A (a), B (b), C (c), and D (d); and the absorption of DMSO into the textile supercapacitor of supercapacitor A (a), B (b), C (c) and D (d).