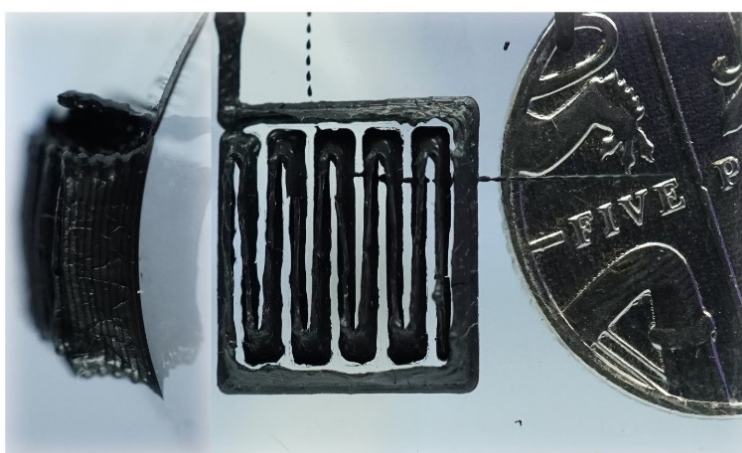


Direct ink writing of two-dimensional materials for electrochemical energy storage devices

Apostolos Panagiotopoulos



A thesis submitted in part fulfilment of the requirements for the degree of
Doctor of Philosophy at Imperial College London.

Main Supervisor
Prof Cecilia Mattevi
Co-supervisor
Prof Eduardo Saiz

Department of Materials
IMPERIAL

Cover Image – MoS₂ 30%wt inks 3D printed with a 250 microns nozzle as 10 layered serpentine architectures on ITO-PET flexible substrates from side(left) and top(right) views. Five pence coin for scale as the denomination of five one-hundredths of a British Pound Sterling, circulated in 2019 by the Royal Mint of the United Kingdom of Great Britain and Northern Ireland.

Declaration

The content written and presented herein is a result of my own work.

Information derived from the published and unpublished work of others has been acknowledged appropriately in the text and relevant sources given.

Apostolos Panagiotopoulos
London, July 2024

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Abstract

Extrusion-based 3D printing offers a novel approach for creating intricate device geometries unachievable by other manufacturing techniques. This study introduces a method for fabricating miniaturised energy storage devices using robocasting and viscoelastic inks made from atomically thin transition metal dichalcogenide (TMD) sheets. The focus is on scaling up TMD-based ink processing for industrial viability to manufacture 3D electrodes with optimised architectures. This is achieved through a solid-state bulk-powder intercalation and direct hydration process, with a 100% material yield, unlike other exfoliation methods requiring sedimentation, filtration, and reincorporation into ink.

Extensive material characterisation was performed from bulk to exfoliated inks to 3D printed electrodes, including rheological assessment, surface and crystallographic analyses, imaging, tomographic microscopies, and novel electrochemical techniques were proposed. For the first time, a high-capacitive combination of mono to few-layered MoS_2 and TiS_2 were directly exfoliated and suspended in a hydrogel carrier. By adjusting the ink's rheological properties to enhance shear-induced extrusion flow, microelectrodes for symmetric supercapacitors were 3D printed. The rational design of 3D electrodes exposed highly capacitive 2D nanosheets, enabling rapid surface electrostatic charges and continuous charge transfer reactions, leading to higher capacitance and cyclability.

The optimised devices demonstrated state-of-the-art performance in non-carbonaceous TMD-only supercapacitors with a two-step ink processing, 3D printing of complex architectures, and remarkable performance metrics: 0.63 F/cm^2 areal capacitance at 90 mg/cm^2 , 6.5 F/g gravimetric capacitance, and 4.5 F/cm^3 volumetric capacitance at 35 mg/cm^2 . The 3D electrodes exhibited excellent cycling stability and coulombic efficiency over 100,000 cycles. This high performance is attributed to the metallic conductivity of lithiated TMDs and their crystallographic phase engineering.

Overall, this study presents a viable method for fabricating miniaturised energy storage devices using TMD-based inks and Direct Ink Writing technology, providing detailed characterisation and insights into the performance factors of TMD-based 3D printed supercapacitor electrodes.

Acknowledgements

With this, I would like to acknowledge the entirety of the Mattevi Group, past and present group members, the department of Materials and the Imperial College community for the collective knowledge in Materials Science, Engineering, Chemistry (among other things) and constant inspiration. Special recognition goes to Prof Cecilia Mattevi for her immense support and for upholding a stimulating working environment. Mr Stefano Tagliaferri who joined the group curious and thirsty for knowledge, may he long stay that way. Dr Maria Sokolikova for the constant support and endless scientific discussions. Dr Mauro Och and Dr Peter Sherrell, for questioning my thinking process, Mr Gang Cheng for his calm composure, Dr Nagaraju Goli for electrochemistry discussions, Dr Chiara Grotta and Dr Federico Pesci for their head start in material processing and particular bulk powder lithium exfoliation. Of course, any of this wouldn't be possible without the EPSRC departmental doctoral training programme 16-17 and ERC Consolidator Grant 2018 that Cecilia secured.

Special thanks also go to Prof Eduardo Saiz for his calm and assertive presence, Additive Manufacturing discussions and business ideas along with the whole of CASC group, the Imperial College Electrochemistry Network for providing a platform to discuss, champion best practices and challenge electrochemical concepts and methodologies. People sitting in RSM 1.10, we've seen joy and despair throughout these years and lived to tell the tale. Dr Alba Maria Matas Adams, Dr Annalisa Neri and Mrs Darakshan Khan for helping take care of me during my entire studies, keeping me punctual and listening to all my concerns. Dr Ainara Aguadero, Dr Andrea Cavallaro and people in the Electroceramics group for discussions related from science to nutrition. Dr Sarah Fearn for endless discussions and queries regarding everything and anything with a lot of SIMS in between. Prof Emmanuel Topoglidis, Prof Tony Cass, Dr Jess Wade and Dr Julianna Panidi for being the best mentors anyone could ask for and inspiring me to pursue academic excellence, all these years. Mr George Elder for keeping me moving mentally and physically.

I would also like to acknowledge everyone at Imperial College Union, Move Imperial, Imperial College Fencing Club and Imperial College Yacht Club, you've given me so many memories, friendships, acquaintances, carried me across the country on land and water without holding back on the thrills and sweats, making sure there was balance in body and mind. Lots of medals, trophies, and memories may they be long cherished.

Lastly, I would also like to acknowledge all my friends and family, for the constant and endless support, always lending an ear to listen to all of it, challenging my knowledge and bearing with my intermittent absences, whilst I buried myself in the world of (self)discovery. For always being there, sharing stories under sail, waves, cycles and living life with me.

I owe and dedicate (it all) to you.

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Nomenclature and abbreviations

k	Dielectric Constant
q_1	Charge
r	Distance
ϵ_0	Permittivity of the vacuum
ϵ_r	Permittivity of the substance
C	Capacitance
Q	Charge
V	Potential
d	Approaching Distance
A	Surface of the Planar Electrode

Ox	Oxidisation
e^{-}	Electrons
Red	Reduction
t_0	Time where potential is applied
t_1	Time where potential is stopped being applied
E	Energy Density
DV	Potential Difference
P	Power Density
Δt	Discharging Time
μ	Viscosity (Engineering)
η	Viscosity (Scientific)
τ	Shear stress
$\dot{\gamma}$	Shear strain rate or shear rate
K	Flow consistency index
n	Power-law index
τ_y	Minimum shear stress
K	Flow consistency index
m	Dimensionless thixotropic index
$\dot{Q}$	Volumetric flow index
S	Printing speed
R	Nozzle Radius
ΔP	Pressure difference applied to the nozzle
L	Nozzle Length
σ_y^{dyn}	Dynamic Yield Stress
γ	Suspension Surface Tension or ink specific weight
ρgh	Self-weight of the material
G'	Storage Modulus
G''	Loss Modulus
ΔV	Voltage Window
v	Scanrate
AC	Alternating Current
AFM	Atomic Force Microscopy
AgNPs	Silver Nanoparticles
AM	Additive Manufacturing
CASC	Centre for Advanced Structural Ceramics
CCD	Cyclic Charge Discharge
CGIS	Coarse Grained Implicit Solvent
CGT	Coil Globule Transition
CMT	Critical Micelle Temperature
CNC	Cellulose Nanocrystal Concentration
CPC	Controlled Potential Coulometry
CV	Cyclic Voltammetry
DC	Direct Current
DIW	Direct Ink Writing
DSC	Differential Scanning Calorimetry
EDL	Electrical Double Layer

EDLC	Electrical Double Layer Capacitance
EDM	Electrical Discharge Machining
EDX	Energy Dispersive X-Ray Spectroscopy
EES	Electrochemical Energy Storage Devices
EIS	Electrochemical Impedance Spectroscopy
EO	Electro Optic
FDM	Fused Deposition Modelling
GCD	Galvanostatic Charge Discharge
hBN	Hexagonal Boron Nitride
HER	Hydrogen Evolution Reaction
LAOS	Large Amplitude Oscillatory Shear
LAOS	Large Amplitude Oscillatory Shear
LFP	Lithium Iron Phosphate
LLC	Lyotropic Liquid Crystallisation
LTO	Lithium Titanium Oxide
OCP	Open Circuit Potential
PEG or PEO	Poly Ethylene Glycol
PLA	Poly Lactic Acid
PO	Polyolefin
PPO	Poly Phenylene Oxide
PVDF	Poly Vinylidene Fluoride
SANS	Small Angle Neutron Scattering
SAXS	Small Angle X-Ray Scattering
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SLM	Selective Layer Melting
SLS	Selective Layer Sintering
TBA	Tetrabutylammonium
TEA	Tetraethylammonium
TEM	Transmission Electron Microscopy
THA	Tacrine
TMA	Tetramethylammonium
TMD	Transition Metal Dichalcogenide
TPA	Triphenylamine
XCT	X-Ray Computed Tomography
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Thesis Introduction

The expansion of the world population and the increasing ubiquity of personal electronic devices have led to an inevitable rise in demand for new energy storage technologies and their device implementation. On the other hand, traditional manufacturing and assembly-line methods are becoming saturated and cannot keep up with the demand for increasingly miniaturised electronic devices. To address this challenge, novel manufacturing methodologies must be explored.

One such methodology is 3D printing, which enables the fabrication of complex, customisable geometries with unprecedented precision. Unlike traditional subtractive manufacturing techniques, 3D printing adds material in a layer-by-layer fashion, which can reduce material waste and lead to more efficient use of resources. Furthermore, 3D printing allows for rapid prototyping and the creation of bespoke designs that can be tailored to specific applications, without the need for expensive tooling or moulds.

3D printing can facilitate the manufacture of devices with enhanced performance characteristics by allowing the integration of different materials, such as metals, polymers, and ceramics, into a single structure. This approach can overcome the limitations of conventional manufacturing techniques, which often require multiple steps and assembly processes, leading to increased costs and decreased performance. 3D printing of microscale devices holds great promise for energy storage applications, as it enables the fabrication of complex electrode architectures with high surface area and low ionic tortuosity, which can enhance the performance of microsupercapacitors and other energy storage devices.

This thesis will explore the potential of 3D printing as a manufacturing methodology for micro energy storage devices based on Transition Metal Dichalcogenides (TMDs). By leveraging the benefits of 3D printing, scalable and cost-effective methods for fabricating TMD-based microsupercapacitors with enhanced performance characteristics were developed.

Thesis Aims and Objectives

The main aim of this thesis is to upscale processing and exfoliation of Transition Metal Dichalcogenide (TMD) inks to formulate rheologically adaptable inks for extrusion-based Additive Manufacturing (AM).

The objectives are:

To develop a consistent and reliable protocol to successfully 3D print microsupercapacitor devices utilising highly concentrated water-based inks of chemically exfoliated TMD nanosheets. Already established exfoliation routes result in low-concentration suspensions, usually in organic solvents which are unsuitable for 3D printing.

To investigate the factors that affect the printability of TMD inks, including their rheological properties, surface tension, intrinsic shear and plug flow and adhesion to different substrates.

To identify the optimum viscosity ratio for successful and continuous dispensing and largest quantity of exfoliated material.

To demonstrate the printability of various TMD ink architectures with different resolutions and evaluate the effect of printing parameters on the quality of the printed structures. After a printing strategy is established, to explore, identify, and compare various designs of 3D printed TMD microsupercapacitors, including device geometries, type of conductive substrate, electrolyte composition towards high performance metrics.

To assemble 3D-printed TMD-based microsupercapacitor devices and evaluate their performance in terms of capacitance, energy density, power density, and cycling stability. From these, the most promising device design architecture will be selected as a viable solution for 3D printed microsupercapacitors. To characterise these devices in terms of nanomorphology and link the electrode and device characteristics to electrode performance.

This research aims to pave the way for the development of novel, scalable, and cost-effective manufacturing methods for energy storage devices based on nanomaterials.

Chapter 1: Introduction

Introduction

3D printing brings the possibility to additively manufacture from the bottom-up full supercapacitor devices in a scalable, fast, and precise manner. However, when adding more material in the 3rd dimension with amorphous bulk materials such as carbon¹, significant electrochemical performance limitations arise, due to the low ionic tortuosity. 2D materials, when exfoliating and templating limitations have been addressed, can bring a unique solution due to their earth-abundance, high surface area and intercalation properties. However, this brings further limitations for the widespread commercial utilisation, due to safety concerns. By exploring rheologically adaptable water-based colloid chemistries for scalable few-step exfoliation and exploiting the inherent dynamic properties of shear forces in Direct Ink Writing, could realise the vision of creating next-generation energy storage devices with unparalleled efficiency and functionality.

1.1 3D supercapacitors with 2D materials towards high performance metrics

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, are a type of energy storage device that utilise both Faradaic and Non-Faradaic electrochemical reactions. These devices can store charges that are comparable to batteries while still delivering charges as fast as capacitors¹(Figure 1a). To assemble a functioning device, two charge storing electrodes must be ionically linked with an intermediate electrolyte(Figure 1b). The electronic conductance of the electrode can be enhanced in a circuit, with the use of a current collector. The design of structures must be optimised to direct an optimum amount of charge storage packing per area, volume, or gravimetric performance for the material. Additionally, architectural elements need to be fine-tuned to promote fast ionic travel and avoid short-circuiting. An ion-permeable separator can also be used in case electrodes need to be packed in tight formations, as per the battery conventional paradigm. Finally, all these components must be held in place and operate consistently for very high amounts of cycling, that for applications is expected to exceed 100,000 cycles.

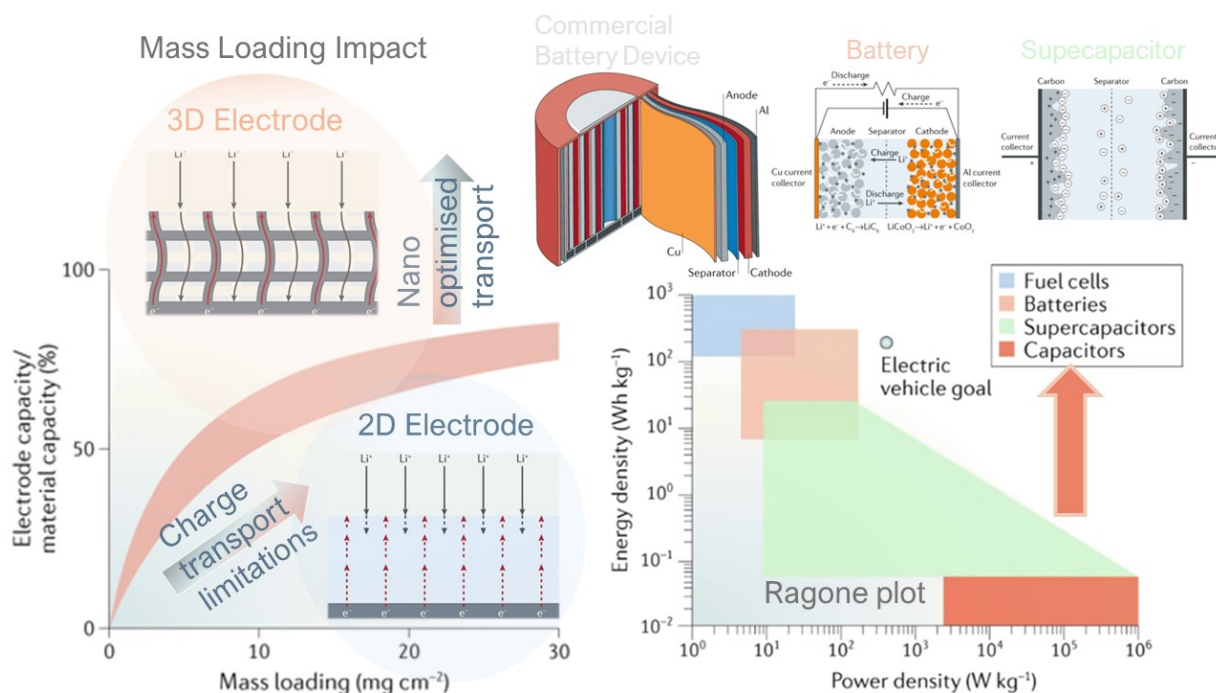


Figure 1 3D supercapacitors based on 2D materials offer high-performance metrics. The Ragone plot compares energy storage technologies, highlighting the performance of supercapacitors, batteries, fuel cells, and capacitors. The basic configuration and working mechanisms of supercapacitors and batteries are illustrated, alongside the typical configuration of a commercial battery device. The capacity of an electrode is shown to be positively proportional to the mass loading of active materials, indicating that higher loadings allow a greater electrode area to store charges, with less space devoted to current collectors. Conventional electrodes with 2D current collectors exhibit limited charge penetration depth, whereas 3D thick electrodes demonstrate efficient charge delivery throughout their entire thickness. Adapted with permission from Springer Nature Limited 2019 ².

Understanding the complex electrochemical mechanisms that occur within supercapacitors is crucial to design and advance energy storage technology. Non-Faradaic mechanisms, such as Surface Ion Adsorption, Solvated Ion Adsorption, and Electrosorption, involve the adsorption of ions onto the surface and near-surface of an electrode, forming an electrical double layer that stores energy. Conversely, Faradaic mechanisms, like pseudocapacitance, involve charge storage through reversible redox reactions on the surface, near-surface or within the bulk of electrode materials. While traditionally viewed as discrete entities, recent developments suggest these processes exist on a continuum, influenced by variables such as ion solvation, ion-host interaction, and the operating timeframe^{3,3-9}. Finally, the level of uniformity and elemental composition between the two electrodes categorises the supercapacitor as symmetric (identical) and asymmetric (different).

Performance metrics in supercapacitors are measured with charge, capacitance, energy density and power density. Charge is dictating the electromagnetic behaviour of electrons and protons and enabling the flow of electricity in material. Charge can be directly integrated from the current that is generated at a fixed potential over the time that is applied. Capacitance (C) describes the capability of a material to store electric charge, whereas Energy Density is a measure of the amount of energy stored in a system per unit volume or mass. The energy density of a supercapacitor determines how much energy it can store, which is an important parameter for many applications where high energy density is required, such as electric vehicles, portable electronics, and renewable energy systems.

Table 1 Performance metrics for supercapacitors and definitions.

Charge Q (C)	$Q = \int_{t_0}^{t_1} i(t)dt$	t_0 = Time where potential is applied, t_1 = Time where potential application is stopped. $i(t)$ = current that is applied at a fixed potential over time. Charge is measured in Coulombs	Charge is dictating the electro-magnetic behaviour of electrons and protons enabling flow of electricity.
Capacitance C (F)	$C = \frac{Q}{V}$	Where Q are the charges stored, over a specific voltage point. Capacitance is measured in Farads (F).	Capacitance (C) describes the capability of a material to store electric charge
Energy Density E (Wh)	$E = \frac{1}{2} * C * DV^2$	C is the capacitance calculated from Cyclic Charge Discharge DV is the discharge potential window. ($V_{in}-V_{final}$) In Volts.	Energy density is a measure of the amount of energy stored in a system per unit volume or mass.
Power Density P (W)	$P = \frac{E}{\Delta t}$	Where E is the Energy Density and Δt is the discharging time, at a constant discharge rate.	Power density is the amount of power that can be delivered per unit volume or unit mass of the device.

In comparison to batteries, supercapacitors generally have lower energy density but higher power density, meaning they can release energy more quickly. The higher the energy density,

the more energy the device can store, and the longer it can operate before needing to be recharged. The energy density (E) is determined by several factors, such as: the electrode material, the thickness of the electrode, the operating voltage, and the electrolyte. The electrode material affects the device capacitance. The electrode thickness should be chosen to optimise the surface area and maximise energy storage. Higher operating voltages generally lead to higher energy density. There is a trade-off between energy density and device reliability since higher voltages increase the risk of device failure due to electrode breakdown or degradation. The electrolyte affects the capacitance and the operating voltage. Aqueous electrolytes offer low cost and high conductivity, but they have lower operating voltages compared to non-aqueous electrolytes. Non-aqueous electrolytes have higher operating voltages and therefore can achieve higher energy densities, but they are more expensive, chemically volatile and have lower ionic conductivity.

Supercapacitors can deliver high power output due to their ability to rapidly charge and discharge. This makes them particularly useful in applications that require high power bursts, such as regenerative braking in electric vehicles or providing backup power to critical systems during power outages.

1.1.2 3D printing advances in supercapacitors

To achieve high energy and power densities, nanostructured electrode materials have been developed. However, the exceptional performance of these materials is typically limited to laboratory devices using ultrathin electrodes with very low mass loadings. To realise the potential of active materials in commercial devices, the mass loading must be no less than $\sim 10 \text{ mg cm}^{-2}$ ². This challenge can be overcome by developing 3D electrode architectures that contain a 3D conductive scaffold acting as a 3D current collector and a 3D porous network for efficient ion transport. This structure ensures efficient charge delivery throughout the bulk volume of a thick electrode, which is desirable for the utilisation of all electrode materials regardless of the electrode thickness and for the realisation of high-rate and high-capacity energy storage. The development of these 3D electrodes can be enabled with 3D printing technology. Hierarchical 3D electrodes with a continuous conductive network for electron transport and a fully interconnected hierarchical porosity for ion transport have emerged as a promising solution. With the advent of 3D printing and the expansion of all-printable

electrochemical energy storage devices, it is now possible to manufacture these 3D electrodes with specific design to optimise macro and nanomorphology. A thick electrode with high mass loading will only actively use only a portion of the active material with insufficient charge delivery for energy (charge) storage, thus it is key to introduce and optimise porosity.

The design of a 3D electrode should enable an efficient charge delivery (kinetic) throughout the entire electrode volume, enabling the utilisation of all electrode materials regardless of the thickness. An example of this intra-electrode optimised kinetics is represented by the creation of a 'holey graphene' ¹⁰ in Figure 2. Figure 2 contrasts the performance and processing challenges of 3D frameworks derived from 2D materials at both nano and macro scales. At the nano scale, the engineering of pores or 'holes' in the graphene framework exhibit superior electrochemical properties compared to the same framework with no holes, with faster kinetics and higher capacitance. At the macroscale, methods vary in the complexity and ease of patterning nano-optimised 3D hierarchical architectures, with some approaches being more difficult to pattern and process (e.g. CVD growth on Ni Foam) compared to others.

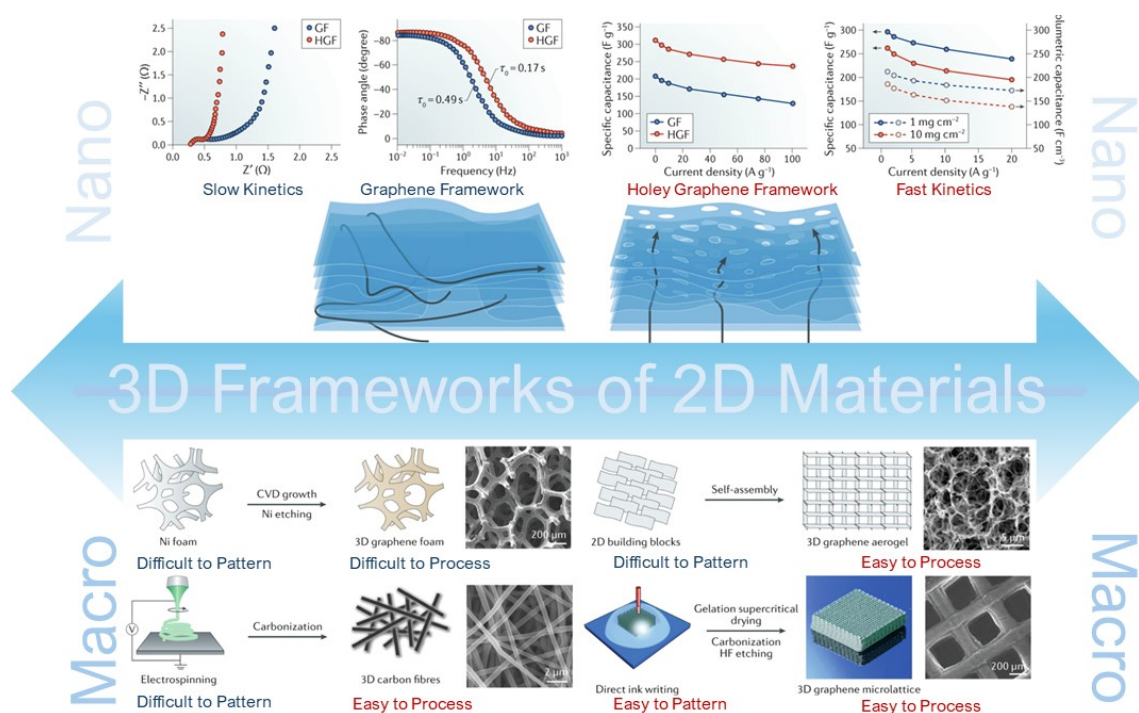


Figure 2 Direct Ink Writing 3D Frameworks of 2D Material patterned in Macro-Architectures with optimised nanomorphology as a viable solution of advancing Supercapacitors. Illustration of a compressed film of a solvated graphene framework (GF) with arrows depicting the ion transport pathways and Illustration of a compressed film of a solvated holey graphene framework (HGF) with arrows depicting the ion transport pathways. The ions in the GF film

must travel long distances to find the broken edge of the graphene sheet and, hence, to cross into another graphene sheet, while the nanopores in the HGF function as shortcuts between neighbouring graphene sheets to greatly increase the speed of ion transport across the HGF film. EIS showing improved ionic kinetics form in the 'holey' graphene framework Improved ionic kinetics reflection in the capacitance. Manufacturing of various 3D architectures with carbon as the exemplar. Adapted with permission from Springer Nature Limited 2019².

1.2. DIW 3D Architectures of 2D Materials for Supercapacitors

Additive Manufacturing has revolutionised the way electronic devices are manufactured. It offers great advantages such as rapid prototyping, increased design flexibility, and reduced material waste. In the field of printed electronics and electrochemical energy storage devices, a lot of printing techniques have been explored, including inkjet printing, fused deposition modelling, selective laser melting/sintering, stereolithography, and direct ink writing (DIW). Each of these techniques has its own advantages and limitations, and the choice of technique depends on the specific requirements of the application. From additive manufacturing, all-polymer RC filter circuits were the first to use inkjet printing techniques in 2003 to inkjet print PEDOT:PSS and polyaniline RC filters¹¹. Additive in nature, inkjet printing however is limited in the material that it can dispense in the Z dimension, as the inks used have very low viscosity, usually around a few mg mL⁻¹¹². Ultimately, the printed electrode will present a low material density.

The processability of functional ink formulation, ease of manufacturing, unparalleled control over geometrical dispensing precision, fast printing speed and low costs, makes Direct Ink Writing the most attractive for EES devices. Direct Ink Writing (DIW¹³) or Robocasting, is an additive manufacturing technique that uses rheologically adaptable highly concentrated inks extruded from an impinging electrical, mechanical, or pneumatic plunger or screw in a layer-by-layer fashion. This process allows for the dispensing of very fine geometries ranging from microns up to a meter size struts, with the z dimension defined by the radius of the nozzle. DIW is now widely considered the go-to method for dispensing EES materials¹², along with all their device components. A series of all-printable devices can be seen in Figure 3.

Examples of DIW EES devices include all printed batteries^{14,15} as well as battery components¹⁶, all-printed supercapacitors¹⁷⁻¹⁹ and a variety of electrodes and electrolytes²⁰⁻²². These devices are made possible by the combination of fast printing of high active material

concentration and the ability to fine-tune the morphological elements of the extruded struts through the ink formulation and the inherent forces that arise from the plunger.

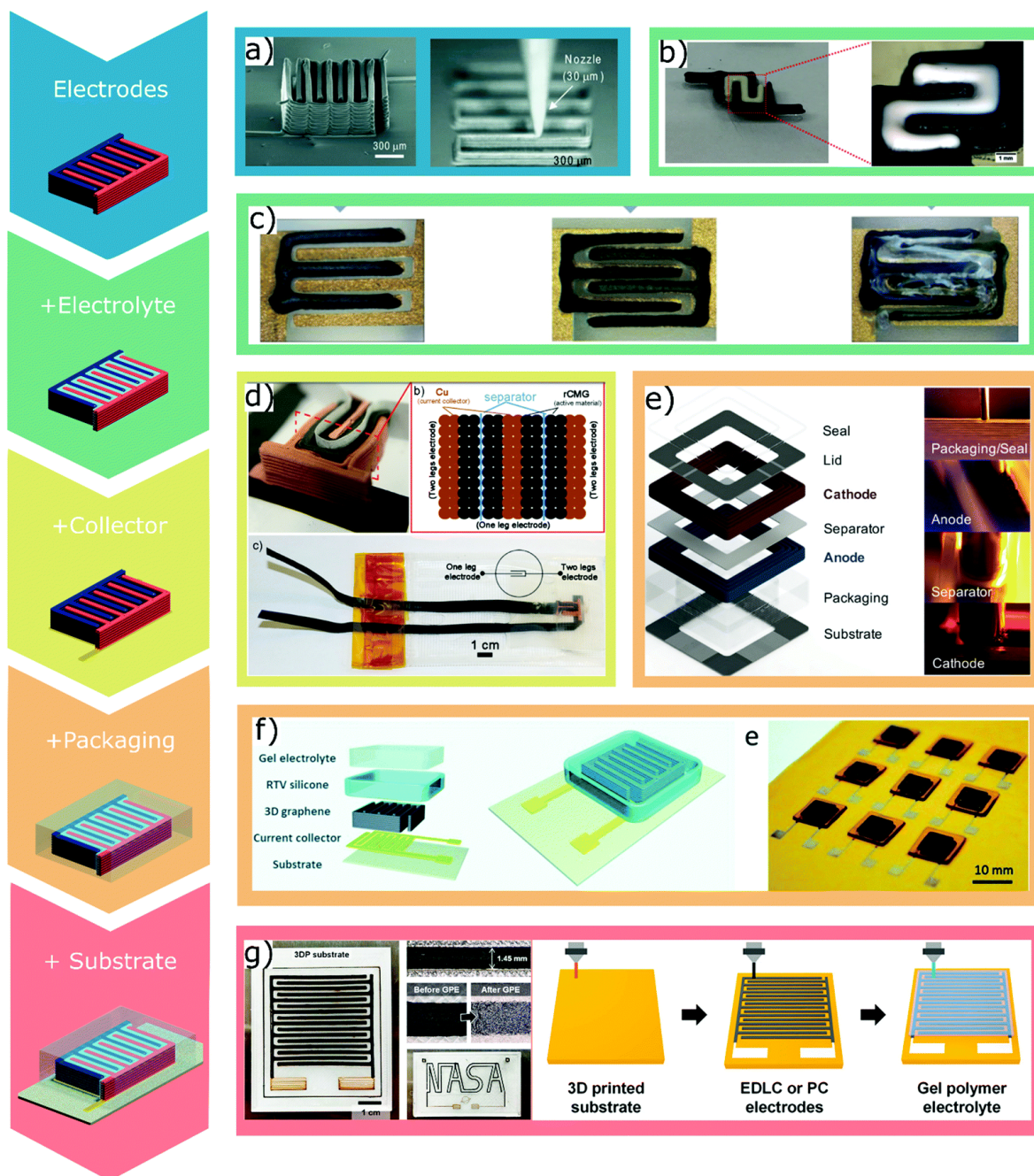


Figure 3 All 3D printed components to assemble electrochemical energy storage devices. A) printed electrodes, b) and c) printed electrodes and electrolyte, d) printed electrodes and current collector, e) and f) printed electrodes, electrolyte and packaging (encasing). Reproduced from ¹² with permission from the Royal Society of Chemistry.

DIW is able to produce hierarchical²³ 3D electrodes with tailored porosity and materials composition which makes it an attractive method for improving energy storage device performance. A wide array of formulation strategies has been already reported and by applying multi-nozzle elements^{24,25} with different materials as well as adaptive technologies, one can virtually build complete devices from the bottom up²⁴. Figure 3 shows a variety of printable device components from electrodes, electrolytes, current collectors, packaging seal and even substrates. Since the first demonstration of all-printable battery components (electrodes & electrolyte) in 2013²⁶, there has been a significant effort to manufacture all printable electrochemical EES devices with a wide array of materials and processes using DIW^{18,27,28}. So far, most examples are focused on enhancing performance rather than proposing readily functional inks and utilising the rheological elements to template the morphologies of the electrodes.

1.2.1. Direct Ink Writing of 2D materials

The growing field of 3D printing, or additive manufacturing, has catalysed a paradigm shift in materials science, enabling the fabrication of structures with intricate geometries and multi-functionalities. A first example of 3D printed 2D materials was demonstrated where graphene oxide sheets formed non-covalent networks with optimised rheological properties, for DIW of supercapacitors²⁹. This inspired a variety of 3D printed structures based on 2D materials such as Graphene^{30,31}, MXenes^{32,33}, hexagonal Boron Nitride (S-hBN) platelets^{34,35}, and TMDs^{36,37}.

Graphene along with intermediate products such as graphene oxide, has inspired a tremendous progress in structural design³⁸, templating³⁹ and optimisation of electrodes for electrochemical energy storage^{40,41}, because of the abundance, stability, electrical conductivity and hydrophilicity. The latter can enable the formulation of aqueous inks which is desirable for future scalability^{42,43}.

MXenes have attracted significant attention due to their very high conductivity, practically eliminating conductive additives and/or current collectors and for their hydrophilicity. Since their discovery, they have been extensively studied for their electrochemical energy storage properties. Additionally, the electrostatic charge of hydrophilic Titanium Carbide nanosheets was utilised to demonstrate stable aqueous inks⁴⁴ that can be used for inkjet printing. To

increase the viscosity of MXenes inks and make them printable, four organic solvents were used, introducing further processing steps in the handling of the materials⁴⁵. MXenes are notoriously synthesised by aggressive etching methods, conventionally with LiF and HCl to etch the Ti_3AlC_2 precursor to get the metallic MAX phase of $\text{Ti}_3\text{C}_2\text{T}_x$. This method was also used to produce MAX phase Titanium Carbide nanosheets and then disperse them into aqueous inks of neutral pH to produce viscoelastic inks with shear-thinning properties⁴⁵. A variety of architectures were printed in current-collector free interdigitated devices, exploiting the MAX phase Titanium Carbide conductive properties for supercapacitors with MXene clay processing^{46,47} along with further tuning the porosity of the 3D structure by aligning voids and interlayer boundaries⁴⁸.

Hexagonal Boron Nitride is another family of 2D materials that the printability has been explored. Specifically, the Direct Ink Writing of PEO polymer composite electrolytes embedded with silane-treated hexagonal boron nitride (S-hBN) platelets³⁴. These structures were 3D printed with a composition of up to 60% vol hBN³⁵. However, hBN is an electrical insulator, thus it is not suitable as electrode material.

TMDs are layered materials that have a lamellar structure similar to that of graphite. They are semiconductors with sizable bandgaps, making them attractive for various applications. In contrast to graphene, TMDs are chemically versatile and can be chemically functionalised. Additionally, they can present either semiconducting or metallic electrical properties. The generalised formula for TMDs is MX_2 , where M is a transition metal of Groups 4 – 10, and X is a chalcogen (Figure 5a).

Bulk TMDs have many polymorphs and stacking polytypes. Individual MX_2 monolayers can exist in one of two phases, leading to a wide variety of polymorphs and stacking sequences. The most common polymorphs are 1T, 2H, (Figure 5b and c) and 3R, where the letters stand for trigonal, hexagonal and rhombohedral⁴⁹. A single TMD can have multiple polymorphs or polytypes, depending on how it was synthesised. For example, natural MoS_2 is commonly found in the 2H phase, while synthetic MoS_2 often contains the 3R phase. Group 4 TMDs such as TiS_2 have inherently 1T phase. Monolayer TMDs exhibit only two polymorphs: trigonal prismatic and octahedral phases. MoS_2 presents distinct electronic properties in the 1T phase versus the 2H phase; the first phase is related to metallic properties while the second phase to semiconducting properties⁴⁹. These crystal phases can be differentiated using several

techniques including high-resolution scanning transmission electron microscopy in annular dark field mode, Raman spectroscopy and XPS⁴⁹.

Additionally, 2H MoS₂ presents layer-dependent electronic properties, presenting an indirect band gap in the bulk form while a direct band gap in the monolayer form⁴⁹. The direct bandgap can enable string photoluminescence⁵⁰ and therefore applications in photonics and optoelectronics. In contrast, the bulk forms of these materials have indirect bandgaps and lower photoluminescence efficiency.

Ever since the processing and high volumetric performance of the metallic 1T phase of MoS₂⁵¹ nanosheets as a supercapacitor electrode along with the ability to intercalate a variety of ions in aqueous and organic electrolytes, inspired the community to investigate rigorously in the potential of processing and 3D printing of structures based on TMD electrodes. As highlighted on a 2022 progress review in additive manufacturing of MoS₂-based structures for energy storage applications³⁶, the processing of TMDs include several and complex pre-processing stages hinder large-scale production, templating and dispensing of 3D structures based on TMD active material electrodes. So far, solution processed, liquid exfoliation^{50,52} is the most viable route when upscaling production to mass-produce ink solutions in high concentrations. This way, liquid exfoliated graphene and semiconducting MoS₂ nanosheets were dispensed firstly by inkjet printing of interdigitated electrodes for transistors^{53,54}, memristors⁵⁵, supercapacitors⁵⁶ and solar cells^{57,58}.

1.2.2 Importance of 3D printing of TMDs

3D printed demonstrated results with TMD inks for any application are scarce and almost always are combined with other conductive materials or spray-painted/deposited on other architectures. Most attempts functionalise MoS₂ whereas the only notable exception is the 3D printing of thermoelectric modules based on TiS₂/hexylamine structures⁵⁹. However, resolution using this method is relatively poor as extruded films are only dispensed in 'thermoelectric legs'.

From literature observations(Figure 4), it becomes apparent that a true upscalable, few-step processing method to additively manufacture electrochemical energy storage devices based on TMDs has yet to be realised, which makes the content of this work even more important. Additionally, the use of inherent semimetallic phased in TMDs have yet to be 3D printed for

energy storage applications. Therefore, future research in this area should focus on developing simple and scalable methods for processing TMDs with metallic electronic phases to enable their widespread use in 3D printed energy storage devices.

3D printing TMDs

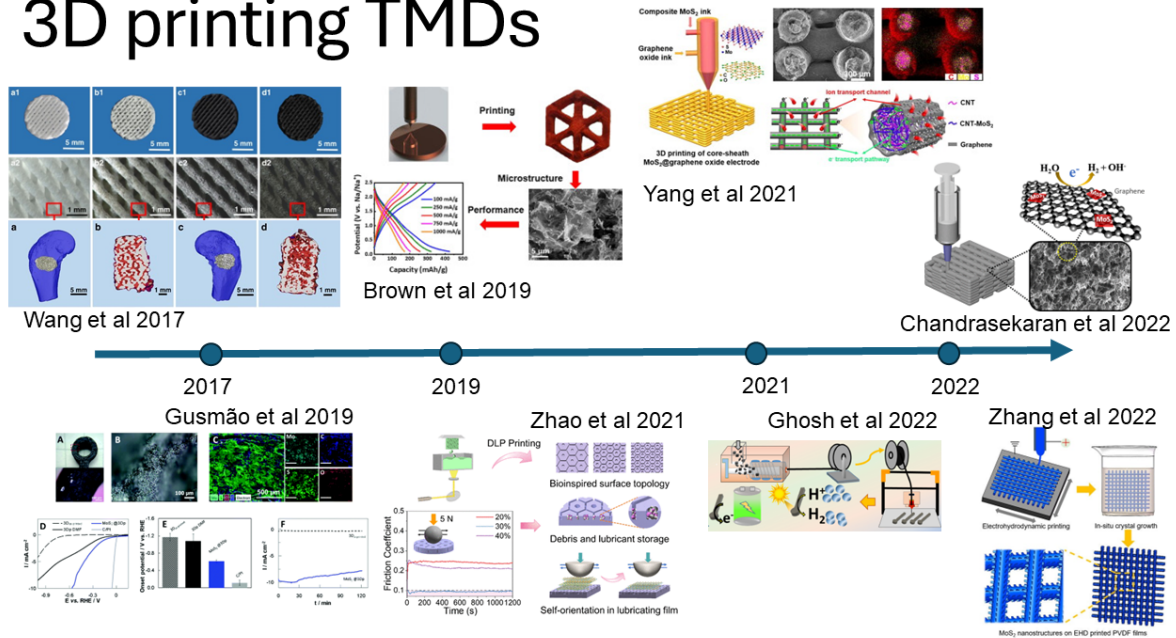


Figure 4 Chronology of 3D printing TMDs. Wang et al 2017, 3D printed bioceramic scaffold enriched via hydrothermal growth of MoS₂ nanosheets⁶⁰ to promote photothermal effects. Gusmão et al 2019, MoS₂ spray coating on 3D printed carbon-based structures for hydrogen evolution reaction⁶¹. Brown et al 2019, MoS₂-graphene aerogels via inkjet loading for sodium batteries⁶². Zhao et al 2021, ceramic digital light printing and hydrothermal growth of MoS₂/MoSe₂ heterostructures for macroscale superlubricity⁶³. Yang et al 2021, Direct Ink Writing of core-sheath 3D architectures of conductive MoS₂-loaded pseudocapacitor⁶⁴. This recipe was the first demonstration of DIW of TMDs with 5 processing steps. Ghosh et al 2022, Fused Deposition modelling and embedding of 2D MoS₂/carbon in PLA/PEG filaments for 3D printing of electrodes towards photo and electrochemical energy conversion and storage⁶⁵. Chandrasekaran et al 2022, DIW of graphene/MoS₂ aerogels for Hydrogen Evolution Reaction⁶⁶. Zhang et al 2022, Electro Hydro Dynamic printing, which is considered as a subcategory of inkjet printing, was used to print PVDF fibres and then MoS₂⁶⁷ was coated on these fibres as negligible MoS₂ nanostructures for potential electrochemical energy storage. (Adapted for the purposes of this Thesis with permissions from Springer Nature Limited, Royal Society of Chemistry, Elsevier and Creative Commons Attribution)

Figure 5 illustrates the general formula of TMDs, and the possible combinations along with the thermodynamically stable trigonal prismatic and octahedral phase coordinations.

1.2.3 Intercalation in TMDs for 3D processing and phase conversion for energy storage

Intercalation with alkali metals can cause phase changes in some TMDs. For example, lithium intercalation in 2H-MoS₂ transforms it to the 1T polymorph, and the reverse transition from 1T to 2H has been observed in TaS₂ on Li intercalation. Partial phase transformation can also produce a 2H-1T hybrid structure. Lithiation and delithiation of MoS₂ and other transition metal dichalcogenides (TMDs) occurs through a process of intercalation, which leads to the formation of a metallic 1T-Li_xMoS₂ lattice structure from a semiconducting 2H-MoS₂ structure. The intercalation process is almost isotropic, but the rate of intercalation is slightly higher along the edges of the TMDs due to lower energy for interlayer expansion near the edges^{68–70}.

A general formula for the lithiation can be given below:

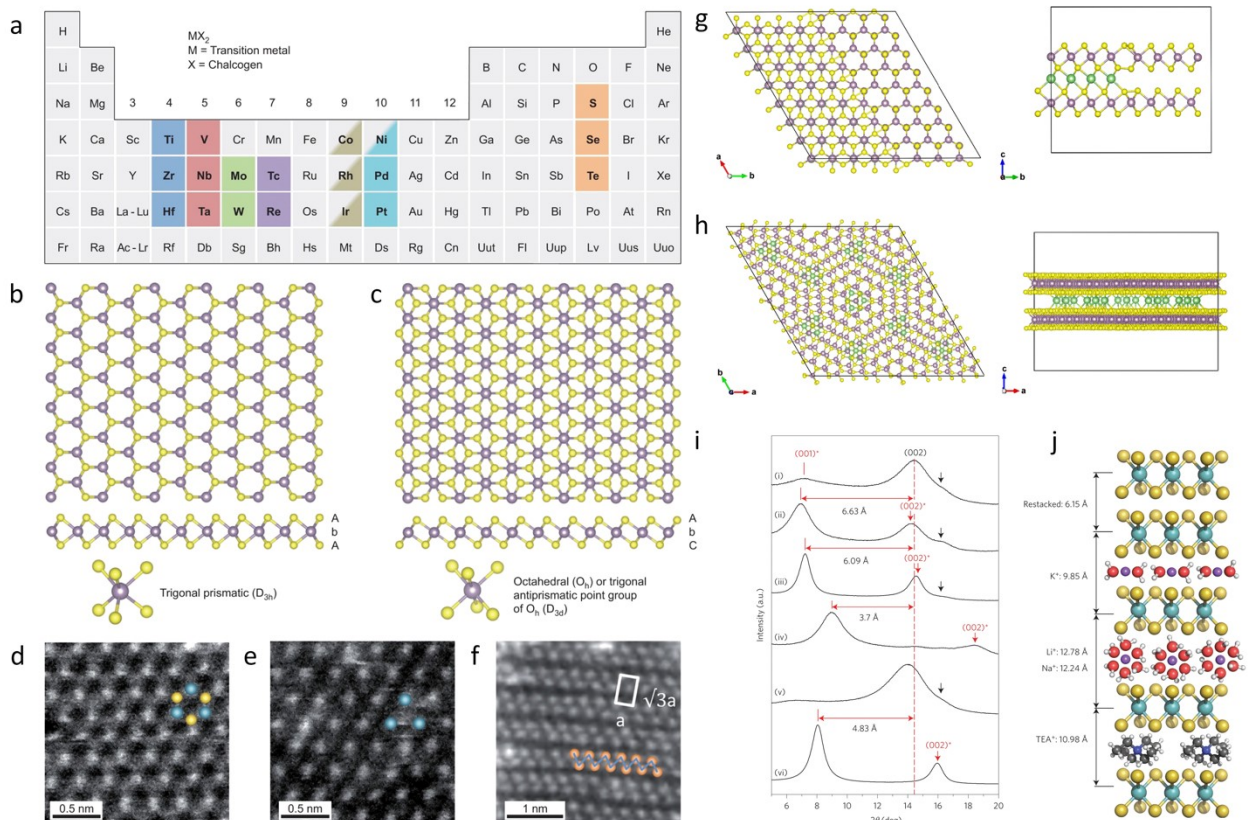
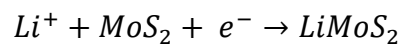


Figure 5 Structure of monolayered TMDs. a) About 40 different layered TMD compounds exist. Partial highlights indicate that only some of the dichalcogenides form layered structures. b)c) 1T and 2H phases. Atom colour code: purple, metal; yellow, chalcogen. d),e) TEM of single-layer MoS₂ showing the contrast variation of 1H (d) and 1T (e) phases. Blue and yellow balls

indicate Mo and S atoms, respectively. f, Zigzag chain clusterisation of W atoms due to Jahn–Teller distortion in single layer WS_2 . The clustered W atoms are represented by orange balls. The $\sqrt{3}a \times a$ unit cell of the superstructure is indicated with a white rectangle. g) Lithium intercalation in bilayer 2H-MoS₂ through the edge, resulting a phase separation (left side: top view (view along the c-axis), right side: cross-section view) and h) Lithium intercalation in twisted bilayer MoS₂ (left side: top view (view along the c-axis), right side: cross-section view). i) XRD Spectra from as-exfoliated 1T phase MoS₂ nanosheets (i) and cycled MoS₂ film (ii–vi) in different sulphate-based electrolytes. The characteristic (002) peak from restacked MoS₂ nanosheets is found at 14.4° for as-exfoliated 1T MoS₂. After intercalation, new peaks labelled (001)* and (002)* are detected indicating different spacing between the MoS₂ nanosheets. j) Schematics of restacked non-intercalated and intercalated 1T MoS₂ nanosheets. (a–f) Adapted with permission from Springer Nature Chem 5, 263–275 (2013)⁴⁹. g)h) Adapted as an open access article under the terms of the Creative Commons CC BY⁷¹ i)j) Adapted for the purposes of this thesis with permission from Springer Nature Limited⁵¹.

Figure 5 illustrates the lithium intercalation in twisted bilayer MoS₂, resulting in an intermediate state without a distinct phase boundary. It was therefore discovered that TMDs can develop a periodic distortion of their crystal lattice due to instability in their electronic structure. This CDW-like lattice distortion has been observed at low temperatures in some TMDs but also at room temperature in intercalated TMDs. The formation of a superlattice by chain clusterisation of metal atoms has been observed in Li-intercalated MoS₂ and WS₂, resulting in a distorted phase that can be metastable even after the intercalant is removed. This phase is believed to be caused by the "Jahn-Teller instability" that reduces the free energy by splitting partially filled degenerate orbitals^{49,72}.

Since the discovery in 1983⁷³ that a phase transition occurs in Li_xMoS_2 when $0.2 < x < 1$, both electrochemical and chemical methods have been developed for lithium intercalation of MoS₂. Electrochemical methods offer dynamical and reversible control of the process, while chemical intercalation provides a simpler approach using highly reducible lithium solutions. It was previously believed that lithium diffused into MoS₂ through the edge, but recent studies highlighted in Figure 6 have shown that lithium can also cross layers via defects in thin flakes⁷⁴. Differential optical microscopy has revealed that intercalation starts from the edge with distinct phase separation observed in both electrochemical and chemical intercalation processes^{68–70,75,76}. The phase separation in chemical intercalation occurs within a very narrow boundary region of a few hundred nanometres. Wu et al⁷⁴, reported the stabilisation of the intermediate state cross the entire flake of twisted bilayer MoS₂, which allows lithium

intercalation from the top surface and enables fast Li-ion diffusion due to reduced interlayer interaction (Figure 6).

The 1T(1T') polymorph of TMDs is thermodynamically metastable under ambient conditions but is kinetically stable for a few days to a few months depending on the material morphology and environment⁷⁷. The study of 1T' transition metal dichalcogenides is of great importance for electrochemical energy storage devices due to their unique electronic and structural properties. 1T' phase materials possess metallic conductivity, which enables them to efficiently store and transport charge. Additionally, the presence of structural defects in 1T' TMDs can create additional active sites for electrochemical reactions, leading to enhanced performance as electrode materials in supercapacitors. The ability to control and optimise the synthesis of 1T' TMDs is therefore critical in the development of high-performance energy storage devices.

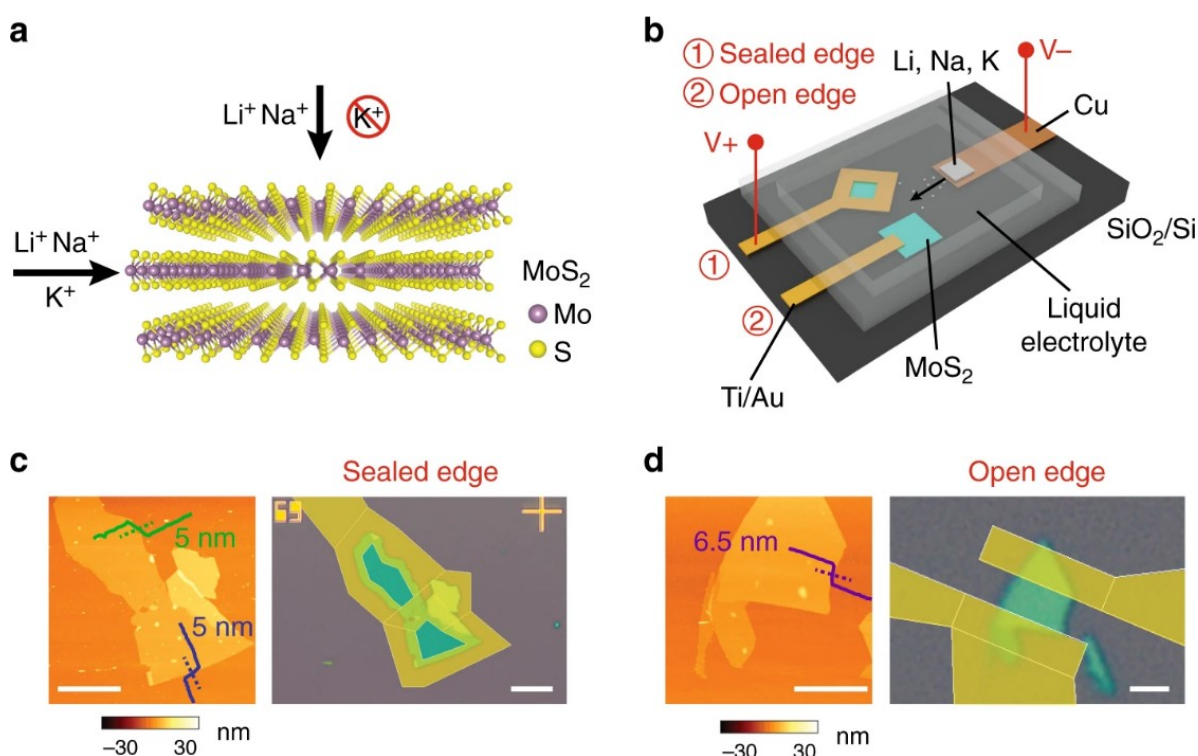


Figure 6 Intercalation from the top and the side. a) Li⁺, Na⁺, and K⁺ intercalation into MoS₂ through top and edge channels. b) An electrochemical cell used to perform intercalation of Li⁺, Na⁺, and K⁺ into MoS₂ with sealed and open edge. c-d AFM and optical microscopy images of typical MoS₂ flakes designed for sealed edge measurement and open edge measurement, respectively. The thicknesses are typically < 10 nm, measured across three edges indicated by the dash lines. Scale bars in c and d, 5 μm. Open access article reproduced under the terms of the Creative Commons Attribution⁷⁴

Adding to the high capacitance of 1T' MoS₂ electrodes, the ability to accommodate a wide range of solvated ions makes them promising candidates for energy storage applications⁵¹. Figure 5i) shows XRD analysis of intercalated electrodes revealed that the spacing between the nanosheets increased as cations or protons were intercalated, indicating that the 1T' MoS₂ electrodes can dynamically expand to accommodate different ions. The observed expansion values are higher than the hydrated cation sizes, which suggests that the solvated ions may be partially desolvated during intercalation. This phenomenon is currently investigated and has been called 'ion sieving'⁴. Figure 5 i) shows interestingly, the absence of the (001) peak after proton intercalation in zero pH electrolytes suggests that smaller protons can easily diffuse between the interlayer spacings in restacked MoS₂ without causing substantial expansion. These findings suggest that 1T' MoS₂ electrodes have great potential for accommodating a wide range of ions in different electrolytes, which is a desirable feature for high-performance energy storage applications.

The two-dimensional nature of TMDs provides a large surface area, which is advantageous for the storage of charge making them attractive candidate electrodes for use in supercapacitors. Studies have shown that exfoliated 1T' MoS₂ nanosheets exhibit very high specific capacitance and excellent cycling stability in supercapacitor applications⁵¹.

1.2.4 Intercalation based Exfoliation of TMDs from bulk for 3D processing

High-quality monolayered samples of TMDs, can be traditionally obtained by mechanical exfoliation using the Scotch-tape method. This technique is ideal for demonstrating high-performance devices and condensed-matter phenomena⁴⁹. However, for applications where large quantities of materials are required, such as electrochemical energy storage, catalysis, sensing, or fillers for composites, chemical exfoliation methods are proved to be more suitable. TMD layered compounds, such as WS₂, MoS₂, MoSe₂ and MoTe₂, have been successfully exfoliated in mainly organic solvents such as, dimethylformamide, and N-methyl-2-pyrrolidone⁴⁹. Direct sonication in a surfactant-coated aqueous solution has been used to disperse the nanosheets, and the yield of single-layer sheets has been optimised by adjusting the starting mass, sonication time, and centrifugation conditions. However, sonication may break the nanosheets and reduce their lateral dimensions. The challenges faced in exfoliating TMDs are similar to those encountered with graphene, and further progress is possible.

Intercalation-based exfoliation is a widely applicable strategy for the scalable production of atomically thin sheets, including TMDs⁷⁸. This method involves the intercalation of foreign species into the interlayer spaces of layered materials, followed by an exfoliation process to obtain nanosheets. Factors such as the intercalating species, concentration, and exfoliation method can affect the quality of the resulting nanosheets. The phase-transition phenomena involved in intercalation-based exfoliation can also induce differences in the electronic and structural properties of the nanosheets compared to their bulk counterparts. The type of intercalant and solvent used in intercalation-based exfoliation plays a critical role in the success of the process.

The current exfoliation landscape reviewed on a recent article, as shown in Figure 7, consists mainly of solvent intercalation processes. Specifically, TMD exfoliation strategies including intercalation and subsequent phase transition from 2H to 1T/1T' can be achieved through *n*-butyllithium⁷⁹, Lithium and Sodium Naphthalenide⁸⁰, Lithium-Ion Anode^{81,82}, and Sulphate Ions^{83,81,82}. However, as these processes include solvents, the exfoliated nanosheets need to be carefully centrifuged, collected from supernatants, sedimented, purified and redispersed in ink formulations, making them lengthy processes with little yield.

Intercalation-based exfoliation using lithium borohydride (LiBH₄) is the only solvent-free process that can act as a Li⁺ intercalant in bulk powder, and requires an intercalation time of ~2-3 days in an inert environment at 300°C. This method has been demonstrated for the exfoliation of WS₂ and MoS₂, producing 1T-WS₂⁸⁴ and 1T-MoS₂⁸⁵ monolayers, respectively. After hydration, atomically thin sheets can be produced in a very high-concentrated ink that could be further processed for the dispensing of 3D printed electrochemical energy storage devices.

This is highly significant, as a 3D printable strategy for dispensing large quantities of TMD active materials towards high performance metrics has yet to be realised. As TMD metallic phases are not thermodynamically stable in water, a stabilising agent needs to be introduced that could potentially also exploit its inherent properties to make the highly concentrated ink printable.

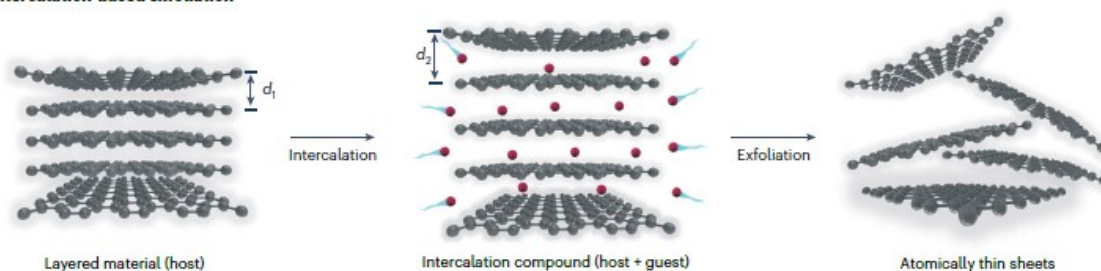
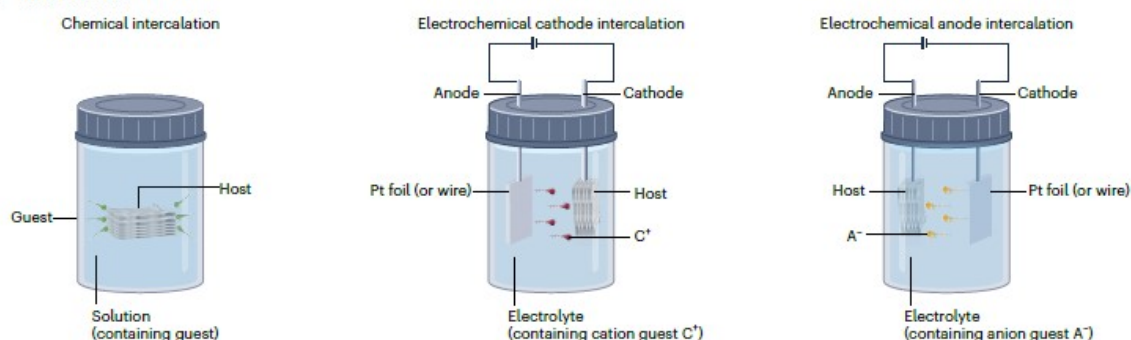
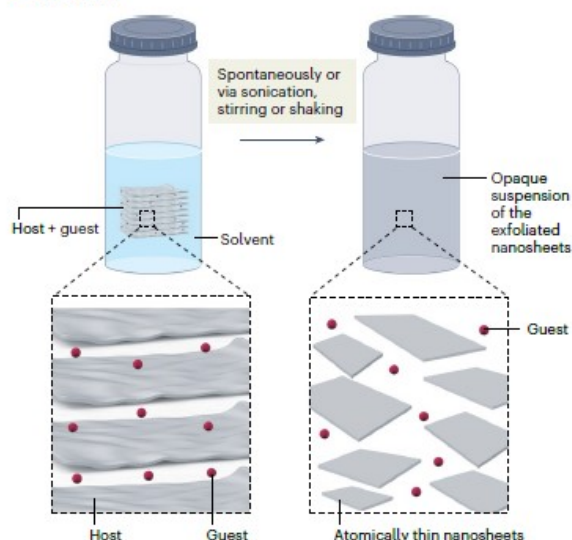
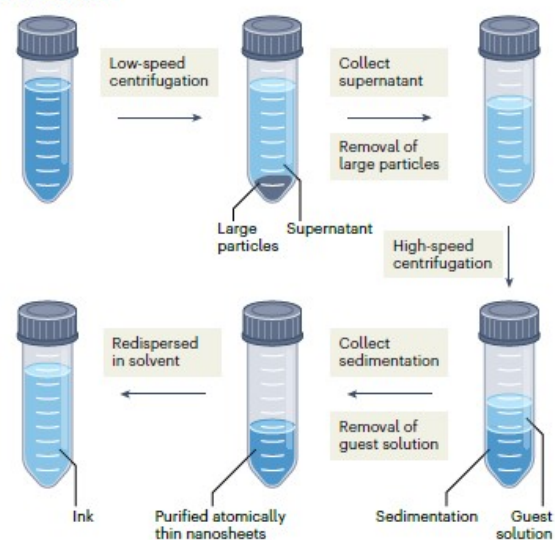
a Intercalation-based exfoliation**b Intercalation****c Exfoliation****d Purification**

Figure 7 - Schematic Illustration of intercalation-based exfoliation. a) Typical procedure of intercalation-based exfoliation. The red spheres represent the intercalant species b) Intercalation routes (chemical intercalation, electrochemical cathode intercalation and electrochemical anode intercalation). c) Exfoliation process. After full intercalation, the intercalation compound (host + guest) is transferred into water or other solvent, and sonication, stirring or shaking is performed, isolating the atomic layers and forming an opaque suspension of the exfoliated nanosheets. d) Purification treatment, performed via low-speed centrifugation in series with high-speed centrifugation (with several cycles) to purify and collect the exfoliated nanosheets. Reproduced with permission from⁷⁸. Springer Nature 2023.

1.3 DIW extrusion principles for 3D printing 2D material inks

To achieve high-quality and functional printed structures, it is crucial to carefully design and control the properties of the inks used for DIW. Ink properties play a crucial role in each of the three key steps of the DIW deposition process: flow, ejection, and deposition.

During flow, the ink needs to be able to smoothly pass through the syringe barrel and nozzle, without forming agglomerates that can cause clogging. During ejection, the ink should rapidly transition from a shear-thinning fluid, which refers to a reduction in viscosity over increasing shear rate, to a solid-like material to retain its shape after deposition. During deposition, the printed structure must retain its shape until full solidification has occurred, usually by solvent removal. Moreover, the ejection properties should avoid microstructural changes and filament stretching during ejection to ensure the accurate deposition of the ink.

In Direct Ink Writing (DIW) the diameter of the deposition nozzle is the main factor that controls printing resolution. Ink flow properties must be carefully tailored to promote the smooth flow of ink through the nozzle, without forming large and hard agglomerates that can jam the deposition nozzle, resulting in failed prints. An example of this property can be seen in Figure 8.

Inks employed in DIW printing are usually yield stress fluids, which behave as elastic or viscoelastic solids under a threshold value of stress known as the yield stress while they flow when the yield stress is exceeded. Ideally, yield-stress inks should possess rapid recovery properties to maintain their shape after deposition. However, ink properties are often influenced by shear history as well, indicating that inks are thixotropic. In thixotropic materials, the rest properties are only retrieved after a finite recovery time, which can be relatively long compared to the deposition time. During DIW, the recovery process should be adequately fast to achieve good shape accuracy and avoid slumping of the structure and efficient printing times.

The challenges associated with ink ejection properties include microstructural changes and filament stretching. During DIW, the ink filament is subjected to bending and stretching before final deposition, which can result in inaccurate deposition of the ink. However, the degree of stretching can be controlled by altering the ratio between the extrusion rate and

printing speed. Techniques such as altering the nozzle geometry and the use of Non-Newtonian inks can be employed to minimise the stretching and maintain accurate deposition of the ink.

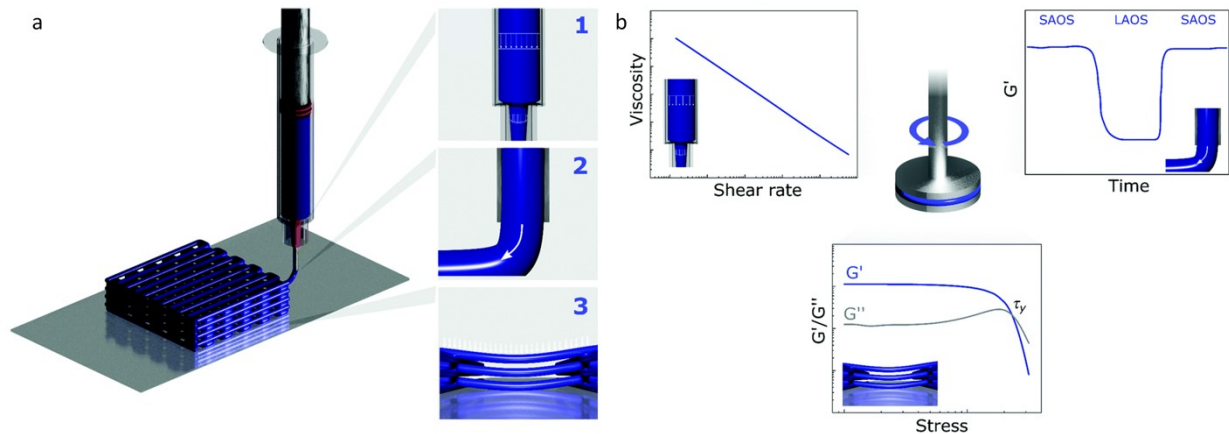


Figure 8- a) Three steps of bottom-up architecture deposition in Direct Ink Writing. b) The archetypal ink properties for 3D shape extrusion can be demonstrated rheologically by Viscosity Flow Ramp, Oscillation Amplitude tests, Three Interval Thixotropy Tests. Adapted from¹² with permission from the Royal Society of Chemistry.

In conclusion, the rheological properties desired for successful ink deposition include a high storage modulus at rest, which limits the bending of suspended parts. Additionally, a high yield stress is necessary to prevent the structure from collapsing. Space-filling structures on the other hand, require a lower storage modulus and yield stress to avoid excessive elasticity, which may hinder the fusion of neighbouring filaments, while dense and thick structures are rare in energy storage, and a high storage modulus ($>10^4$ Pa)¹² is typically desirable. The ink must also solidify quickly to maintain its shape and structural integrity.

1.3.1 Ink design for DIW of supercapacitors

Ink design for Direct Ink Writing (DIW) is therefore a crucial part of energy device fabrication, as it impacts the rheological behaviour, printability, and functional properties of the final product. Ink formulation involves balancing the need for optimal rheological behaviour with desirable functional properties, such as high energy density, electrical conductivity, and mechanical integrity. Two primary objectives guide ink formulation: meeting rheological criteria for printability and developing the desired functional properties for the final device.

The fundamental components of an ink include functional fillers, binders, additives, and solvents. Functional fillers provide the functional properties of the final device and can range from carbonaceous materials to ceramics and metals. Nanoparticles are often used as they present unique electronic properties and avoid clogging due to their small size. Binders, usually polymeric materials, are added to bind particles together and promote adhesion with the substrate. Inorganic or electroactive binders can also be used but must be minimised to limit their impact on electrochemical performance. Solvents are necessary to give fluidity to the ink during extrusion and deposition processes, with aqueous inks typically preferred for sustainability reasons. Additives are included in the ink formulation to control specific properties such as particle dispersion, drying rate, and rheology.

Careful ink design is necessary for printable ink to have suitable flow behaviour, adhesion, stability, and electrochemical performance, including high power and energy densities, long cycle stability, and high electrical conductivity. The ideal ink should be prepared as simply as possible, with fewer components, a straightforward preparation process, non-toxic, and low-cost. Ink microstructure and rheological properties must be considered in the ink design to ensure successful 3D printing and desirable electrochemical performance. Attractive networks, such as colloidal gels, are considered suitable for DIW due to their percolated network of attracting particles, which are either formed directly by the particles of active material or promoted by the addition of inactive additives. However, careful tailoring must be applied to prevent thixotropic behaviour, influenced by shear history, as it may be detrimental for printing.

1.3.2 Ink rheology and relation to printability in DIW for Supercapacitors

Rheometry typically determines the viscosity or viscoelasticity of a material. Viscosity, a measure of material internal flow resistance due to friction, depends on microscopic properties such as particle size. On the other hand, viscoelasticity quantifies the material response to a deforming force. Purely elastic materials do not dissipate energy after a load is applied, while viscoelastic materials exhibit some hysteresis in the stress-strain relationship due to material deformation.

Rheology is the study of deformation and flow of matter. In order to comprehend the flow and demonstrate the deformation, a series of tests can be measured. Results can then be

quantified and fitted into mathematical models that approximate and express their behaviour. As a general distinction, matter can be separated into one that responds plastically or reacts elastically. One that dissipates energy or one that stores it and everything in between.

Colloid Inks in DIW, can be broadly characterised as fluids and can be distinguished as Newtonian and Non-Newtonian fluids. Newtonian Fluids will hold a linear correlation of viscosity with the strain rate, whereas non-Newtonian fluids do not. When colloids are formulated with the precise dispensing of EES active materials in mind typically non-Newtonian are used. These can vary their viscosity to reach a yield point and can revert between solid-like and liquid-like behaviour depending on the shear strain rate. On the contrary, simpler colloid formulations that need no shape formation and are used as space-filling liquids (like electrolytes) can be Newtonian.

Typically, shear rheology using a rotational rheometer is used to assess rheological properties. Common rheological tests include flow ramps to evaluate the degree of shear thinning of inks and oscillatory tests to provide information on viscoelastic properties at rest. Shear thinning is the rheological behaviour of an ink to drop their viscosity while stress is applied. The opposite effect is called shear thickening. Both behaviours are non-Newtonian. The yield stress of inks is often determined from oscillatory tests, as the stress value at which the storage modulus equals the loss modulus. Flow stress can be measured using Large and Small Amplitude Oscillatory Stress (SAOS & LAOS) measurements and the recovery time between them⁸⁶. The ratio of yield stress to flow stress provides an indication of the brittleness of the ink, which can be related to ink printability^{12,86}.

The three-interval thixotropy tests (3ITT) are another method for studying thixotropy in inks¹². During 3ITTs, the ink is first sheared at a low stress to stabilise its microstructure. A high-stress interval follows to destroy the microstructure, mimicking the flow inside the nozzle. Finally, a low shear stress is applied again, and the recovery kinetics of the material is measured. Extensional rheology has also been used to assess printability, although yield-stress fluids do not form cylindrical filaments in capillary break-up extensional tests, and the filament thinning strongly depends on the initial deformation applied to the material.

The archetypal ink properties for 3D shape extrusion can be rheologically tested as shown in Figure 8 b and their behaviour demonstrated through:

- Viscosity Flow Ramp
- Oscillation Amplitude tests
- Three Interval Thixotropy Tests

To summarise, the ink viscosity needs to drop by several orders of magnitude in response to the applied shear rate to flow inside the syringe and into the nozzle. Subsequently, the ink needs to change from solid-to-liquid like behaviour, with an inversion of the storage and loss moduli past the yield point, to extrude from the nozzle and avoid clogging. Finally, after extrusion the storage and loss moduli need to revert to the initial solid-like behaviour, to retain the shape and support the weight from the subsequent layer. This behaviour can be expressed in rheology as shear-thinning, viscoelastic pseudoplastic.

1.3.3 The concept of extrusion-based printability

Extrusion-based printability is the capability of an ink to be extruded from a nozzle in a continuous filament to shape a model accurately representing the CAD file. To quantify the printability in terms of flow and deformation, inks need to follow the below mathematical expressions.

Viscosity: μ (engineering) or η (scientific)

$$\eta = \frac{\tau}{\dot{\gamma}} \quad Eq(1.11)$$

Where τ (Pa) is the shear stress applied to the fluid and $\dot{\gamma}$ (s^{-1}) is the shear strain rate. Viscosity (Pa.s) is a measure of fluid resistance to flow.

The power-law viscosity model is generally used to represent the non-linear relationship between shear stress and viscosity and is described by,

$$\eta = K\dot{\gamma}^{n-1} \quad Eq(1.12)$$

Where η is the viscosity (Pa.s), K is the flow consistency index(Pa.sⁿ), $\dot{\gamma}$ is the shear rate (s^{-1}), n *power-law index*. Please note, that in the power-law viscosity model the yield stress is not incorporated, so a more accurately model needs to describe these materials. Yield point is the

point on the stress-strain curve that indicates the limit of elastic behaviour and the beginning of plastic behaviour or the inversion of Storage and Elastic Moduli during and Oscillation-Amplitude rheological test.

An important index is the power law index, that is going to distinguish the fluid behaviour as Newtonian($n=1$) or non-Newtonian ($0<n<1$ i.e. shear thinning or Pseudoplastic and $n>1$ i.e. shear thickening or Dilatant), along with the τ (shear stress in Pa) and τ_y (minimum shear stress in Pa required for the sample fluid to yield) values which indicate if the sample fits the Power-Law or Herschel-Bulkley fluid models.

The below table, aims to summarise these distinctions:

Table 2.1 Distinctions of Matter based on their power-law index and minimum shear stress to reach the yield point. (Adapted from Dr Ezra Feilden, PhD thesis ⁸⁷)

	$0<n<1$	$n = 1$	$n > 1$
$\tau_y = 0$	Shear-Thinning Pseudoplastic Power-Law Fluid	Newtonian Fluid	Shear-Thickening Dilatant Power-Lay Fluid
$\tau_y > 0$	Shear-Thinning Pseudoplastic Hershel-Bulkley Fluid	Bingham Plastic	Shear-Thickening Dilatant Herschel-Bulkley Fluid

As such, different mathematical models apply to different fluids. When yield stress is also considered, the power law is adapted to represent this behaviour better in the Herschel-Bulkley model.

$$\tau = \tau_y + K \dot{\gamma}^n \quad Eq(1.13)$$

τ is the shear stress (Pa), τ_y (minimum shear stress in Pa required for the sample fluid to yield), K is the flow consistency index, $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the power-law or flow index. When the shear stresses in the form of $(\tau - \tau_y)$ are plotted with respect to the estimated shear rates on a log-log graph, the values of n and K from the Hershel-Bulkley model can be determined. These values distinguish and optimise ink compositions based on their shear-

thinning capability and viscosity and thus help to determine the ideal printable ink for Direct Ink Writing⁸⁸.

However, thixotropic materials are influenced by the shear history and shear rate⁸⁶, so the Hershel-Bulkley model can be modified by incorporating a thixotropic index.

$$\tau = K |\dot{\gamma}|^n t^{-m} + \tau_0 \quad Eq(1.14)$$

Where, τ is the shear stress (Pa), K is the flow consistency index, $\dot{\gamma}$ is the shear rate (s^{-1}), n is the power-law or flow index, t is the shearing time(s), and m is a dimensionless thixotropic index (a.u). Approximation is limited when considering very slow timeframes and how material recovers once shear stress is removed⁸⁹.

The maximum shear stress(yield stress) for some fluids, can be separated in the static which is the stress required to flow from a rest state and the dynamic, which is the minimum stress required for a fluid in motion to continue flowing. As the inks flow through the nozzle tip, it induces a shear rate that is maximal at the walls and be estimated by:

$$\dot{\gamma} = \frac{4\dot{Q}}{\pi r^3} \quad Eq(1.15)$$

$\dot{\gamma}$ is the shear rate (s^{-1}), $\dot{Q}$ is the volumetric flow rate as calculated from $\dot{Q} = S r^2$ where S is the printing speed and r the nozzle radius⁹⁰. While the shear stress τ , assuming radial nozzle, can be estimated from:

$$\tau = \frac{\Delta P}{2L} r \quad Eq(1.16)$$

ΔP pressure difference applied at the nozzle, r is the radius of the nozzle, and L the nozzle length⁹¹.

M'Barki et al.⁹² have proposed a mathematical relationship to calculate the minimum yield stress required to avoid sagging due to self-weight capillary forces, expressed as:

$$\sigma_y^{dyn} \geq \gamma R^{-1} + \rho g h \quad Eq(1.17)$$

σ_y^{dyn} is the dynamic yield stress provided that this support the printed object's own weight, γ is the suspension surface tension, R the nozzle diameter, and $\rho g h$ the self-weight of the material.

Smay et al.⁹³ have applied elastic beam theory on the spanning ink filaments to calculate the minimum storage modulus, therefore the minimum ink elasticity required to assemble a given periodic structure therefore the maximum acceptance of deflection.

$$G' \geq 1.4\gamma \left(\frac{L}{D}\right)^4 D \quad Eq(1.18)$$

G' is the minimum storage modulus, γ is the ink's specific weight ($=0.25[\rho_{gel} - \rho_{oil}]g_0$, L is the length of the spanning element and D is its diameter. The ink Poisson ratio was assumed to be 0.5 (incompressible).

All these mathematical equations approximate the ink behaviour for DIW but are not absolute, as each ink attributes may add variability in these equations.

1.3.4 Mass loading and nozzle dynamics in 3D printing 2D Materials for Supercapacitors

When accounting the printability, it is evident that the rheological properties and the nozzle dynamics are intertwined. One is directly linked with the other and both need to be carefully considered when deciding a dispensing strategy for Direct Ink Writing. Depending on the nature of the ink materials and the interactions between them, different physical interactions occur that ultimately are going to influence the extrusion dynamics. Further to this, the geometry combination of the syringe barrel/nozzle is also going to play a role in this equation. A simple model of the velocity profile of a fluid flowing through a pipe is the plug flow model. In plug flow model, the velocity of the fluid is assumed to be constant across any cross-section point of the pipe perpendicular to the axis of the pipe, which is true in flat ended pistons. This model also assumes that there is no boundary layer adjacent to the inner wall of the pipe as well as that the fluid is perfectly mixed in the radial direction.

Increasing the concentration of active material in an ink composition directly affects the rheological behaviour of the ink, resulting in an increase in viscosity, storage modulus, and yield point, as seen in Figure 9. Hausmann et al⁹⁴. have studied the yield stress point of cellulose nanocrystal inks at concentrations ranging from 10-40%. Higher mass loading requires higher pressures to extrude from fine nozzles. This dynamic effect on anisotropic

particles such as Cellulose Nano Crystal(CNC) inks has been mapped with *in-situ* polarisation rheology⁹⁴.

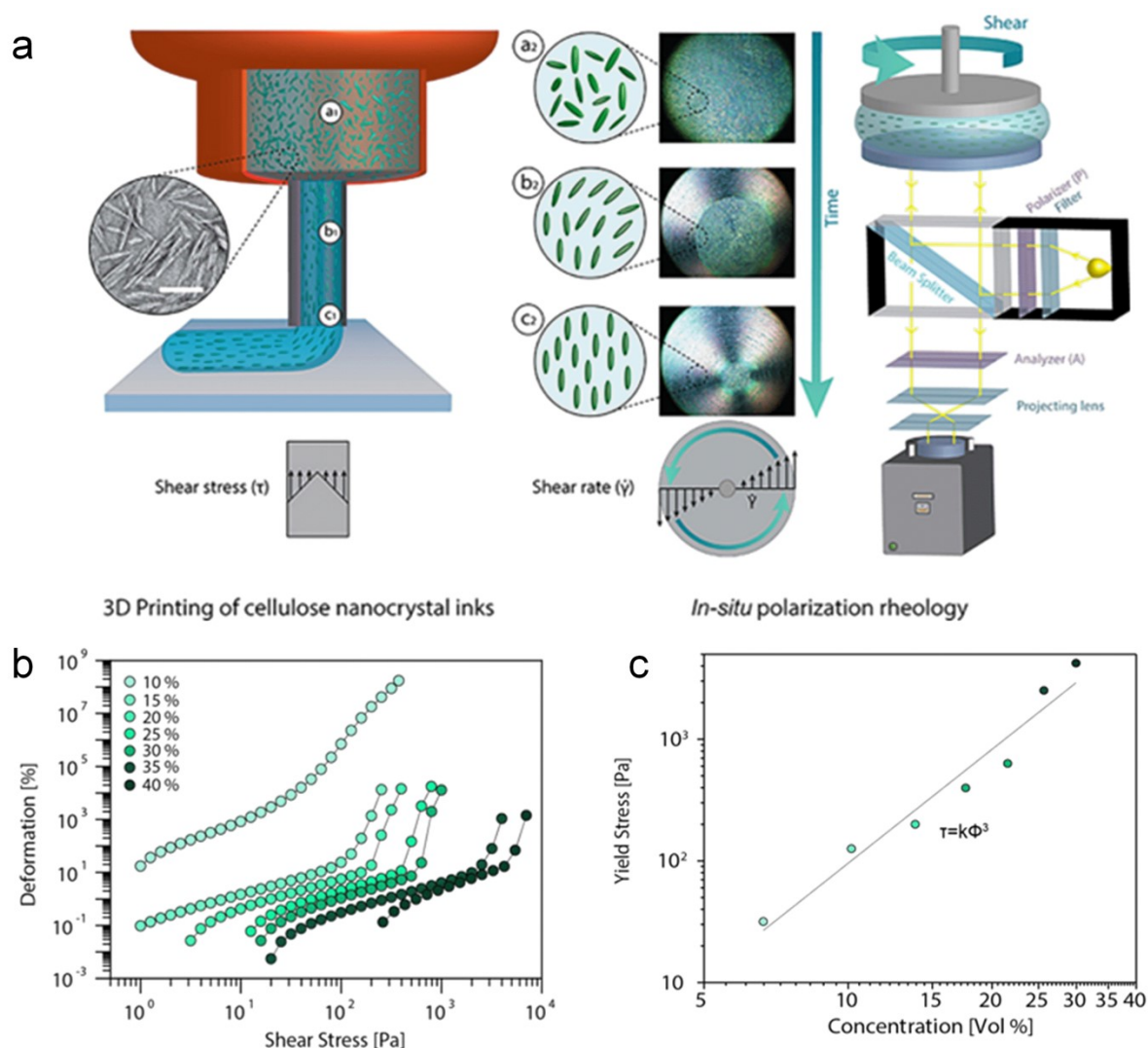


Figure 9 a) Dynamic alignment of anisotropic cellulose nanocrystals during Direct Ink Writing. b) c) Yield stress measurements for 10-40% concentration of cellulose nanocrystals. Adapted with permission from⁹⁴. Copyright 2018, American Chemical Society.

It was found that the particle alignment timeframe scales inversely with the applied shear stress and directly with the particle concentration. While the alignment of particles in diluted suspensions is well described by analytical and numerical models, the dynamics of particle orientation in highly concentrated inks typically used for direct ink writing is only recently being explored. The experiments show that the alignment of the particles transiently orients from the rim toward the centre of the disc in response to the linear gradient in shear rate. The evolution of the alignment quality in cellulose nanocrystal suspensions can be tracked over time for well-defined shear deformations or shear rates. Another example of the use of

anisotropic particles to increase the young's modulus has been shown with the 3D printing of Lightweight Cellular Composites⁹⁵. By controlling the composition and architecture over multiple length scales, the resulting structures can achieve remarkable properties, such as Young modulus values up to 10 times higher than existing commercially available polymers for 3Dprinting, while maintaining comparable strength values. The alignment of high aspect ratio fillers occurs along the print direction, allowing for spatial control of their orientation within the part, adding an entirely new dimension to engineering design and optimisation.

The compaction and arrangement of nanosheets during and after extrusion play a significant role in determining the mechanical and electrochemical properties of printed materials and therefore the performance of the printed device. As the range of materials that can be 3D printed with Direct Ink Writing is expanding. For example, it was observed by that anisotropic particles like ceramic fibres, were aligned in the printing direction⁹⁶. The velocity profile and gradient, nozzle length, and relative core radius are among the factors that influence particle alignment⁹⁴, among others⁹⁷. In principle, it is demonstrated that particle orientation occurs when the applied stress is higher than the yield stress of the ink. Tagliaferri et al⁴³ have reported alignment of graphene nanoplatelets in the outer region due to velocity gradient, while the inner core is randomly oriented due to the solid-plug flow behaviour. This could be explained by the different flow experienced from the two regions during printing, as it's subjected to both shear and elongational forces. By quantifying the gradient structure tensor of the tomographic image in the central and outer region of the filament, the orientation maps presented in Figure 10 e) indicate that they align parallel to the surface in the region close to the walls, whereas randomly oriented in the inner core, possibly because of small residence time of around a second inside the nozzle.

This has tremendous impact on the applicability of extruded particles as microfeatures can be further tailored to enhance the mechanical or electrochemical properties. For instance, the porosity and the local disposition of platelets directly influence the electronic and ionic transport of devices^{43,98}.

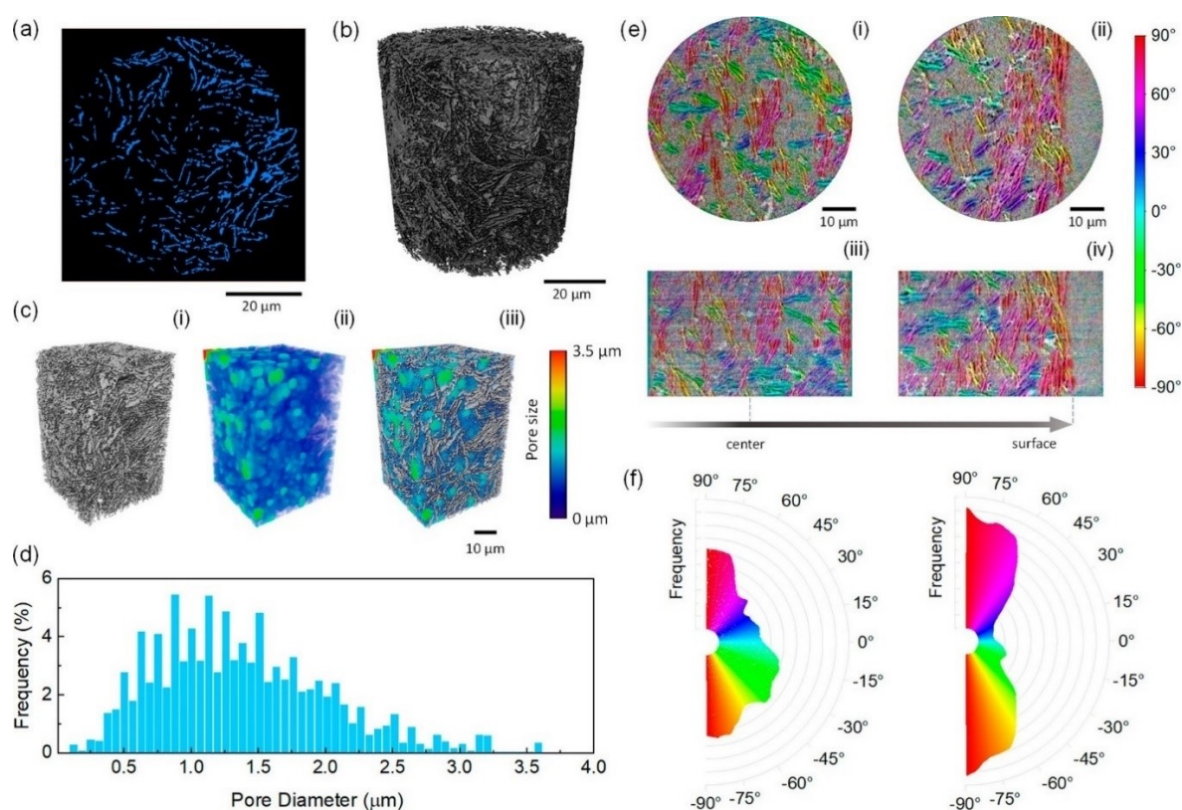


Figure 10 a,b) Reconstruction of a printed filament obtained from X-ray Nano-Computed Tomography: (a) slice perpendicular to the filament axis and (b) 3D rendering of the central region of the filament. c) 3D visualization of the region considered to calculate porosity: (i) PG platelets, (ii) pores, and (iii) simultaneous visualization of PG platelets and pores. d) Pore size distribution in the printed filament. e) Orientation of the platelets in the central (i), (iii) and outer (ii), (iv) regions of the filament: (i) and (ii) represent slices perpendicular to the filament axis, while (iii) and (iv) represent slices along the filament axis. f) Radial histograms presenting the orientation of platelets in the central (left) and outer (right) regions of the printed filament, respectively. Reproduced with permission from⁴³. Copyright 2021, American Chemical Society. (CC By 4.0)

1.3.5 DIW enabled by the colloid chemistry of triblock co polymer hydrogels

Colloid chemistry is an integral part of several chemical disciplines. Ranging from physical chemistry to inorganic chemistry, colloids offer various possibilities due to their dimensionality. The choice, design, synthesis of building blocks as well as the self-assembly, through the preparation, modification, and gelation, has profound effects on their utility. Since the discovery of DIW as an Additive Manufacturing technique, colloids have been

utilised to exploit the inherent dynamic properties⁹³ of the syringe barrel/nozzle to enable printing strategies not possible with other techniques. More specifically, the amphiphilic properties of polymers in water form highly versatile hydrogels.

Interactions of amphiphilic hydrogels with other colloids or particles, form a very dynamic environment that can be further exploited either for enhancing the printability, their functionality or both. Additionally, these can be further tuned in response to an external stimulus, where the hydrophobic to hydrophilic balance can be changed with the temperature, pressure, pH, ionic strength among others. This flexibility in tunability allows for the design of hydrogels with specific properties to achieve desired ink performance, making them ideal candidates for DIW technology.

1.3.5.1 3D templating from hydrogels and their response to external stimuli

A hydrogel is a three-dimensional network of interconnected molecules with a high density of functional groups that enable the absorption and retention of large amounts of water (typically at least 10% by overall weight or volume of interstitial fluid). This network structure allows for the maintenance of both bound and free water, resulting in swelling of the hydrogel in the presence of water. This ability to mimic biological structures in terms of water content and diffusion of solutes through the network makes hydrogels suitable for various applications, particularly in the biomedical field.

The choice of hydrogel material influences the method of crosslinking used to create a 3D structure. Hydrogels can be chemically crosslinked, which tend to offer greater mechanical stability but lack reversibility, or physically crosslinked, which are formed through a variety of intermolecular interactions and can provide self-healing properties and rapid assembly or disassembly. Hydrogels can also provide a wide range of stimuli responses, such as swelling, shrinking, or degrading, through stimuli such as heat, pH, ionic strength, light, electric fields, ultrasound, magnetic fields, solvents, mechanical forces, hydrolysis, enzymes, and redox reactions. These stimuli can be tailored by modifying the hydrogel network or by entrapping responsive components such as magnetic nanoparticles.

A schematic representation of hydrogel stimuli responses can be seen in Figure 11b). The density of crosslinked chains and hydrophilic groups can be used to modulate pore size and

diffusion rates. In this manner, molecules or particles can be dynamically encapsulated or released selectively in a hydrogel environment. Additionally, in the case of shrinking, the collapse of the 3D crosslinked network to a small enough size enables fast expulsion of molecules out of the network owing to mechanical squeezing. These mechanical properties can influence the Young modulus and the network response to external influences. Hydrogels offer a vast range of stimuli responses that can be tailored to meet specific needs.

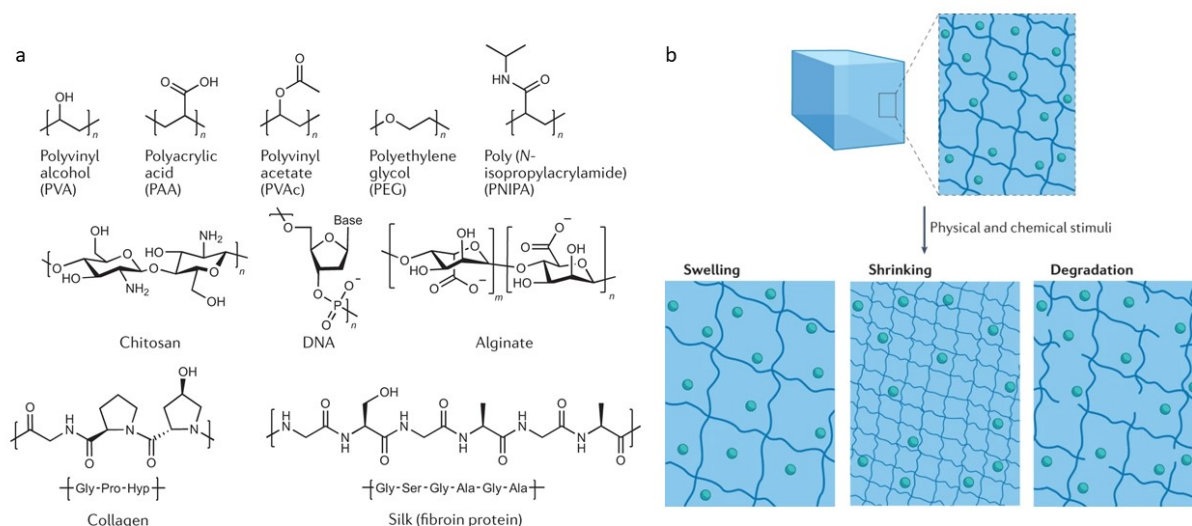


Figure 11 a) Chemical structures of the repeat units or primary sequences of common polymers used within hydrogel formation. b) A schematic representation of Hydrogel Stimuli responses. Swelling, Shrinking, Degradation. Adapted with permission from Springer Nature Limited⁹⁹.

Specifically, Triblock copolymer hydrogels have emerged as effective templating systems in recent years, owing to their unique ability to form self-assembled structures. These structures have been widely studied and utilised in various fields, including drug delivery, tissue engineering, and nanotechnology. The self-assembly of triblock copolymers is governed by the interplay between hydrophobic and hydrophilic interactions, which results in the formation of various ordered and disordered structures.

Triblock copolymers, such as Pluronic and Poloxamer, exhibit unique properties due to their hydrophilic and hydrophobic nature, allowing them to form cage-like structures to minimise exposure of hydrophobic segments to water. Micellisation, a process where dispersed solutions self-assemble, can be achieved by increasing concentration to the critical micelle concentration (CMC) or by increasing temperature to the critical micelle temperature (CMT). The resulting micelles have a PPO core and a PEO corona, and the size, aggregation number,

and structure depend on various factors including molecular weight, distribution of EO and PO segments, and the ratio of hydrophilic to hydrophobic blocks¹⁰⁰.

Micellisation is entropically driven due to the hydrophobic effect and highly concentrated solutions of PEO-b-PPO-b-PEO exhibit a thermoreversible gelation at temperatures close to ambient, where micelles increase in size and order into liquid crystalline lattices. The gelation process is believed to involve hard-sphere crystallisation aqueous solution¹⁰¹, where the micelles form ordered phases in close-packed arrays to maximise intermicellar distance. Gel formation is dependent on the volume fraction occupied by the micelles and the repulsive force between them. Several techniques have been used to study micelle formation, structure, and gelation, including SANS, SAXS, fluorescence, DSC, and rheological methods^{100,102–104}.

1.3.5.2 Pluronic f127 hydrophilic/hydrophobic blocks as a templating system

Pluronic F127 is the commercial name of Poloxamer 407 which is a triblock amphiphilic non-ionic surfactant of the general class of copolymers known also as poloxamers. It consists of three blocks of Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol). Poly propylene glycol, which is the centre hydrophobic block, flanked by two hydrophilic blocks of polyethylene glycol. The approximate lengths of the two hydrophilic blocks are 101 repeat units, while the hydrophobic approximate length is 56 repeat units. Pluronic f127 is the BASF commercial name, while other names have been known, signifying the manufacturer or purity grades. It is a common additive surfactant found in toothpastes precisely due to the biocompatibility and rheological properties¹⁰⁰. During the recent years, these properties have been extensively exploited as a templating method for drug delivery^{105,106}, scaffolding^{93,107–110}, and energy materials^{42,111–114}, among others. In aqueous media it forms a thermoresponsive hydrogel with unique phase-change properties.

The phase diagram of Pluronic F127 is compared in different temperatures for gel boundaries measured by tube inversion and rheometry along with the temperature dependence of the elastic modulus can be seen Figure 12 a Lyotropic phases formed by Pluronic f127 has been studied when in contact with glycerol, ethanol¹¹⁵, Tween 80¹¹⁶, as well as monoolein, capric acid and saturated diacyl phosphatidylcholines¹¹⁷.

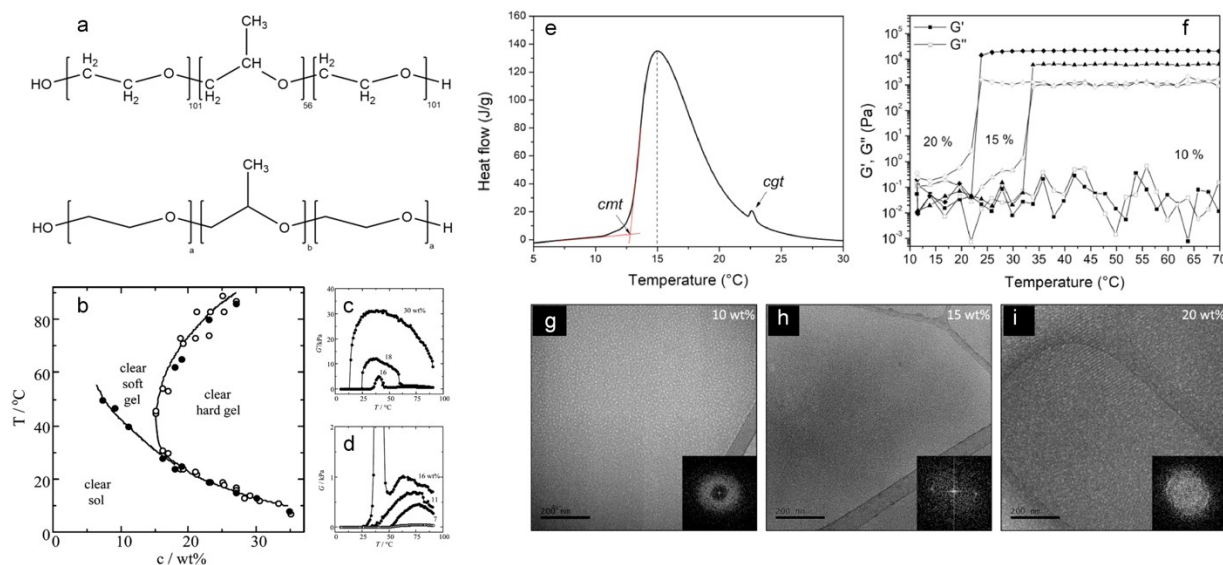


Figure 12 a) Chemical Structure of Pluronic F127 variant(top) and poloxamer 407 (bottom) skeleton formula. b) Gel diagram for aqueous solutions of copolymer F127: (○) gel boundary by tube inversion; (—) gel boundary by rheometry. c,d) Temperature dependence of the elastic modulus (filled symbols) for solutions of copolymer F127. Concentrations (wt %) are indicated: frequency 1 Hz, strain amplitude 0.5%. For clarity, the plot includes the viscous modulus only for the 7 wt % solution (unfilled symbols): note that the values of G' are larger than those of G'' in the soft gel region. Reproduced with permission from ¹¹⁸ Copyright 2007 American Chemical Society. (e) Micro differential scanning calorimetry curve of a 20 wt% Pluronic® F127 hydrogel performed at a 0.5 °C min⁻¹ heating rate in a VP-DSC Microcalorimeter (Microcal Inc). Critical micelle temperature (cmt) and critical gelation temperature (cgt) are indicated by arrows. The dashed line shows the temperature of the highest micellization rate. (f) G' (elastic modulus) and G'' (viscous modulus) of the 10 wt%, 15 wt% and 20 wt% samples obtained from a temperature sweep measured in a Mars III (Thermo Scientific) rheometer. The cgt occurs when G' becomes higher than G'' and is followed by a significant increase of both G' and G'' . (Bottom) (g) 10 wt%, (h) 15 wt% and (i) 20 wt% samples were prepared under the exact same conditions in order to observe the morphological evolution as a function of concentration of Pluronic® F127 solutions at 55 °C. Adapted with permission from ¹¹⁹. Creative Commons CC-BY, Elsevier 2020

These investigate the lyotropic liquid crystalline (LLC) phases formed by different block copolymers and lipid nanoparticulate systems. The addition of different solvents to the LLC systems led to changes in the lattice parameters and phase behaviour. Additionally, the use of different surfactants, such as Tween 80, influenced the formation of different bulk and dispersed LLC phases in selachyl alcohol-based systems. Cryo-TEM and synchrotron small-angle X-ray scattering were used to investigate the nanoparticle structure and revealed a wide range of mesophases ¹¹⁹.

The large amplitude oscillatory shear (LAOS) test method is highly sensitive to microstructure and is useful in rheologically classifying complex fluids into four types based on their behaviour under strain. The LAOS response of PEO-b-PPO-b-PEO triblock copolymer gels shows a transition from type I (strain thinning) to a combination of types I and IV (initially increasing then decreasing) in the soft gel region, with type III (weak strain overshoot) behaviour observed in the hard gel region. Oscillatory shear testing has also been used to investigate self-assembly and shear alignment¹²⁰ in Pluronic colloidal systems, with rheolight scattering, time-resolved small-angle neutron and Xray scattering (SAXS, SANS) techniques useful for studying the microstructural changes of colloidal particles exposed to LAOS¹⁰⁰.

Conclusions

Throughout this chapter, a comprehensive exploration of the multifaceted domain of supercapacitor devices has taken place, emphasising the role that DIW could play in shaping the future of this field. The potential that DIW offers in fabricating intricate hierarchical structures with precise control over geometry and material properties in enhanced performance and cost reductions is undeniable. With the incorporation of 2D materials into 3D architectures, the vision of creating highly efficient, versatile, integrated supercapacitors is swiftly becoming tangible. However, significant challenges related to scalability and manufacturing processes need to be addressed. This is especially relevant for materials such as TMDs, where intricate pre-processing stages impede mass-scale production. The exploration of scalable exfoliation techniques, particularly intercalation-based exfoliation from bulk powder, has underscored the potential to generate atomically thin flakes with desirable properties all while eliminating post processing steps.

The unique attributes of TMDs offer a plethora of opportunities for applications in energy storage, catalysis, and opto-electronics. Although challenges in synthesising-controlled structures and functionalities of TMD nanosheets remain, their potential contribution to the future is significant and must be explored. The investigation of ink rheology in DIW and its impact on the mechanical and electrochemical properties of printed materials has yielded key insights. Leveraging the inherent dynamics of the extrusion process can lead to enhanced properties of the 3D printed device, such as the alignment of anisotropic particles for optimal electrochemical energy storage.

Chapter 2:

Materials, methodologies and characterisation

Introduction

Lithium borohydride intercalation strategy and TMD exfoliation via direct hydration is identified as the most viable method to result in 100% TMD yield in the final ink. TMDs chosen for this study are MoS_2 and TiS_2 . The specifics of these reactions follow along with all methodologies employed in this study. All the characterisation techniques will then be analysed along with the thinking process behind identifying and selecting these.¹²¹

2.1 Materials characteristics

The ideal supercapacitor strikes a balance between battery-like energy storage and capacitor-like energy release. To achieve this balance, it needs to combine a very high surface area to exploit the electrostatic double layer capacitance in the Helmholtz plane¹²¹, charge exchange electrochemical attributes in this electrode-electrolyte interface^{122,123} but also as bulk exchange processes^{123–126}. Exfoliated layered two-dimensional materials (TMDs) are able to maximise their surface area and hence double-layer capacitance. Furthermore, they facilitate electrochemical charge exchange in the form of charged ionic species and can successfully adsorb and/or intercalate various solvated ions successfully, due to their atomic lattices^{74,123,125,127–135}.

Among such layered two-dimensional materials, Titanium Disulphide (TiS_2) with its inherent metallic 1T phase, meets all the aforementioned criteria^{136–138} and has been widely studied as a prototypical electrode material for its ability to intercalate a variety of ionic species in between the layers.^{130,139,140} However, this applicability in aqueous energy storage systems have been severely limited, due to the very high catalytic activity of the edges¹⁴¹ and spontaneous oxidation¹⁴². This inherent susceptibility to oxidation, particularly in water-based systems, poses a significant challenge for utilising TiS_2 as an effective electrode material in such environments and so far, has not been effectively stabilised in aqueous-based

systems, making the exploration of this material as supercapacitor electrode even more important.

Molybdenum Disulphide (MoS_2) atomic lattice of the basal plane can either be hexagonal or 2H which is semiconducting or (distorted) trigonal prismatic ($1T'$) with a semimetallic behaviour¹⁴³. This makes it quite an attractive material choice for microelectronics, as the conductivity can be further tailored to suit the application, without necessarily altering the chemical composition. In its metallic phase $1T(1T')$, MoS_2 has also demonstrated ultra – high-rate electrochemical capacitance^{51,144} as supercapacitor electrode material, delivering $0.63\text{F}/\text{cm}^2$ areal capacitance and up to $700\text{F}/\text{cm}^2$ of volumetric capacitance for nanofilms of concentrated MoS_2 . The abundance, low cost, processability and high-performance of Molybdenum and Titanium Disulphide has been identified as the most promising amongst TMDs.

Lithium borohydride (LiBH_4) is used to achieve lithium intercalation of transition metal dichalcogenides (TMDs) such as MoS_2 and TiS_2 , due to the solid-state intercalation allowing the high yield of exfoliated TMDs. The underlying principle of its usage relies on its reactivity as a lithium-ion donor. During intercalation, LiBH_4 is utilised to insert lithium ions between the layers of the TMDs, thereby expanding the interlayer spacing. This increase in interlayer spacing is advantageous for two key reasons: it facilitates the subsequent exfoliation process, and, in the context of electrochemical energy storage, it allows for enhanced ion mobility within the material. These factors combined contribute to improved energy storage performance of the TMD-based supercapacitors.

Pluronic F127 plays a crucial role in additive manufacturing as a carrier hydrogel for exfoliated transition metal dichalcogenides (TMDs), enabling the efficient production of intricate three-dimensional structures. Another key feature of Pluronic F127 hydrogel is the rapid inversion of the storage and loss moduli upon cessation of extrusion and yield forces. This characteristic ensures that the extruded layers maintain their shape and quickly recover their mechanical properties, enabling them to support the weight of the subsequent layers added during the 3D printing process. The combination of these rheological properties allows for the successful incorporation of exfoliated TMDs into a 3D printable ink, resulting in the fabrication of high-quality and robust aqueous-based electrochemical energy storage devices.

2.2 Methodologies, Results & Discussion

2.2.1 Lithium Borohydride Intercalation (LiBH_4)

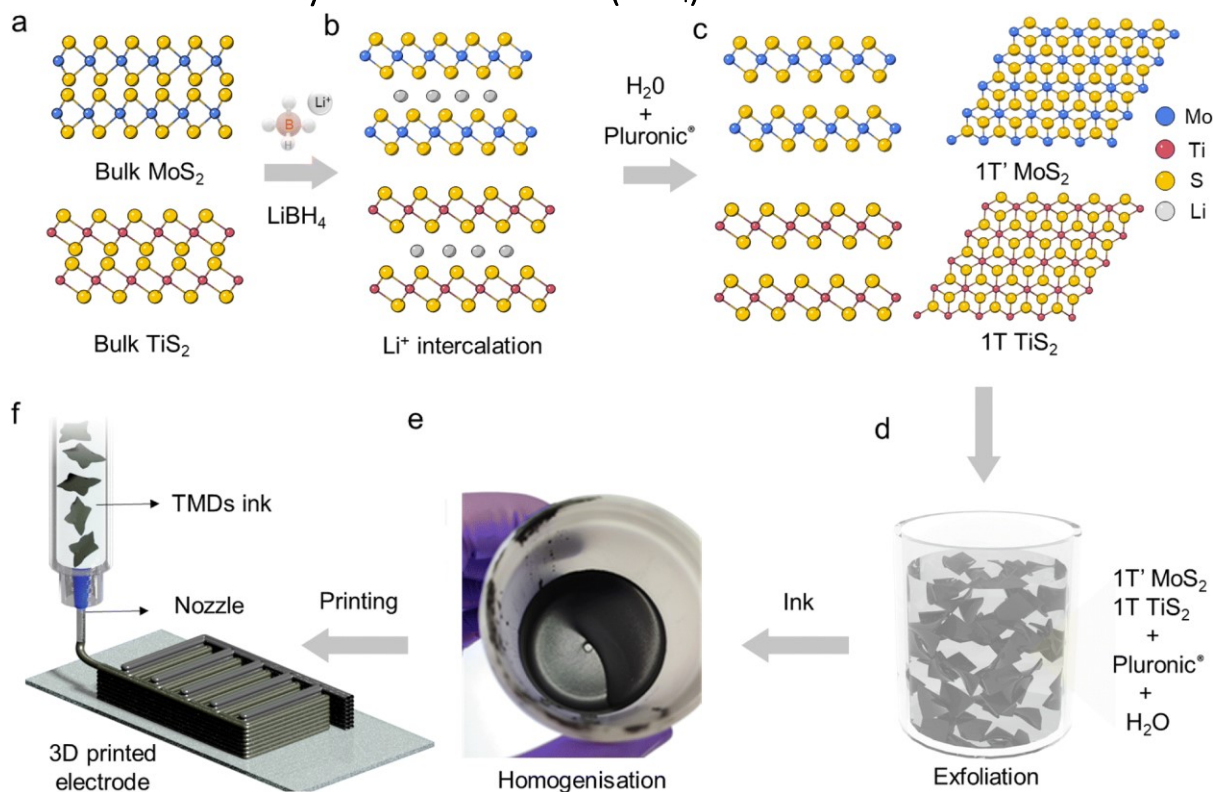


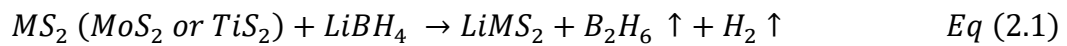
Figure 13 Schematic representation of the synthesis process, exfoliation mechanism and 3D printing of 1T'/1T $\text{MoS}_2/\text{TiS}_2$ inks. (a) Atomic structures of bulk MoS_2 and TiS_2 and (b) atomic lattices of lithiated MoS_2 and TiS_2 . (c) and (d) Pluronic-water exfoliation process of MoS_2 and TiS_2 . (e) Homogenization of 1T'/1T $\text{MoS}_2/\text{TiS}_2$ inks and (f) extrusion of the corresponding inks through a nozzle. Reproduced from ¹⁴⁵ with permission from the Royal Society of Chemistry.

In this solid-state intercalation process, the lithiated species will induce a phase change in TMD powders with 2H crystallinity but will also react exothermically with water during the exfoliation and provide the necessary energy to break the weak van der Waals bonds. The exact intercalation procedure was adapted from previous reports^{84,85} to produce lithiated TMD compounds^{85,146} and was carried in an Ar inert glovebox environment.

TMD powders were used as received and mixed in a ceramic beaker. TMD blend inks were combined in a 50:50 molar ratio and mixed with LiBH_4 in a 1:2.5 TMDs/ LiBH_4 ratio. The mixed powders in the ceramic beaker are covered with aluminium foil pierced with tweezers to free

any potential gas build-up, during the heating. The ceramic beaker containing the powders was then submerged in a beaker full of alumina beads for even heat transfer then subjected to a gradual heating process. Starting from room temperature and slowly increased until reaching 350°C. This heating process should be carried out over a span of 12 hours. After reaching the target temperature, maintain the powders at 350°C for a duration of 72 hours. This allows for the intercalation of the lithium ions into the TMD lattice to take place. Following the intercalation step, a cooling process was initiated, again spread over a span of 12 hours, to bring the temperature back down.

The intercalation process is expressed:



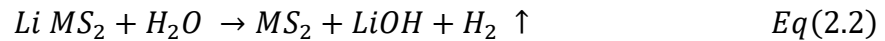
The purpose of this process is to induce a strong thermodynamic driving force, which facilitates the intercalation of lithium ions into the TMDs, resulting in the formation of lithiated species. The introduction of lithium ions occupies the space in between the layers leads to a phase change of the thermodynamically stable 2H MoS₂ into 1T' LiMoS₂ phase^{123,147}. while TiS₂ is inherently 1T and gets lithiated¹³⁷ in LiTiS₂.

Direct exfoliation with hydrogel serves a two-fold purpose. On the one hand, the water in the hydrogel system will react exothermically with Lithium metal ions intercalated in between the van der Waals sheets, releasing Hydrogen and providing the necessary energy to break the van der Waal bonds into atomically thin films. On the other hand, the Pluronic micellisation will encapsulate water molecules with the rearrangement of hydrophobic/hydrophilic blocks in order to stabilise the sensitive catalytic edges of TiS₂. Notably, Lithiated species are also stabilised in this regime as evidenced from ToF-SIMS measurements. This step is crucial to utilise all the intercalated powders with a very high yield. The exact procedure for the direct exfoliation of intercalated powders in a Pluronic F127 hydrogel system is as follows:

Pluronic F127 powders were gradually dispersed in deionised water (DI) in an ice bath. The optimal Pluronic concentration for exfoliation used to produce TMD inks was 25% w/v for the carrier hydrogel throughout. Pluronic 25%w/V mixtures were produced in bulk and conditioned at 4°C overnight. Intercalated powders were removed from the glovebox and transferred to a fire-proof polytetrafluoroethylene (PTFE) container. In a fumehood, the exfoliation reaction is initiated by pouring one third of conditioned Pluronic hydrogel while

stirring to initiate a vigour exothermic reaction. This reaction is then quenched with the other two-thirds of Pluronic hydrogel, while stirring continuously. With the same method, ink batches of 30%wt and 50%wt have been produced. The goal is to create a stable formulation with well-dispersed, exfoliated nanosheets that can be used as is for additive manufacturing.

The exfoliation reaction is expressed below¹⁴⁸:



The purpose of the exfoliation is to make a printable ink with the minimum amount of processing steps, without yield losses. This way, a high concentration of exfoliated sheets can be produced with thickness of a few nanometres and lateral size in the range of 200nm-1micron typically. Finally, the ink can be transferred to a sealed container and stored at 4°C.

2.2.3 Ink homogenisation

The subsequent formulation was then homogenised to reorient the exfoliated nanosheets, saturate hydrolysis, remove air bubbles and ensure optimum dispensing flow during 3D printing using a Thinky ARE -250 commercial planetary mixer purchased from Intertronics.

Exfoliated ink formulations were loaded into Thinky 300ml HDPE thick-walled jars with inner lids and caps, conditioned at 2000 rpm for 2 min to evenly disperse the exfoliated nanosheets in the formulation and defoamed at 2200 for another 2 mins to remove air bubbles.

2.2.4 Ink rheological assessment

Inks were then rheologically assessed in a TA Instruments HR1 Discovery Hybrid Rheometer equipped with a 40mm parallel Peltier Plate Steel for rotational mapping. It can accommodate various modes of deformation, including controlled stress, strain, or rate; steady shear or oscillation; rotational, tensile, compressive, or extensional deformation. Friction and temperature calibration were carried out before each step and the inks were loaded with a spatula and measured at a fixed gap of 1000 microns and a temperature of 25°C using a solvent trap to minimise water loss. TMD inks were then loaded using a spatula and Oscillatory tests were performed at 10 rad s⁻¹ and flow measurements, at a shear rate from 10–3 to 102 s⁻¹. Each measurement was performed three times with a cleaning and

recalibrating stage in between. The flow behaviour under different conditions was assessed using this methodology.

2.2.5 Architecture Design and .cad file production

This study explores two distinctive designs for the purposes of 3D printing supercapacitor electrodes. Serpentine and woodpile, each offering unique benefits and characteristics. While different architectures in various nozzle resolution were designed as proof-of-concept architectures to demonstrate the versatility and mechanical robustness of the TMD ink formulations as 3D supercapacitor electrodes. Figure 14 showcases the two designs that were designed in Robocad which is the proprietary software of the 3D printer manufacturer 3D Inks LLC and systematically compared in this study.

The serpentine design is characterised by its precise layering, where each extruded filament sits directly on top of the preceding layer. This architecture results in an optimised mass-to-surface area coverage ratio, particularly noticeable as the layers are increased. The resulting design promotes efficient utilisation of the active material, which is crucial for the electrochemical performance of the 3D printed $\text{MoS}_2/\text{TiS}_2$ 50wt% ink electrodes in supercapacitors.

The woodpile design, as its name suggests, resembles a stack of parallel and perpendicular extruded filaments, forming a lattice-like structure. It is one of the easiest architectures to print, as the weight of subsequent layers is distributed evenly across the previous layer's frame, reducing the risk of structural collapse. The woodpile design also boasts the highest amount of mass per layer, and since each layer is just one extruded filament thick, it theoretically provides the largest electrostatically active surface area. Given its widespread application in various 3D printing projects, the woodpile design serves as an excellent benchmark for evaluating the performance of supercapacitor electrodes.

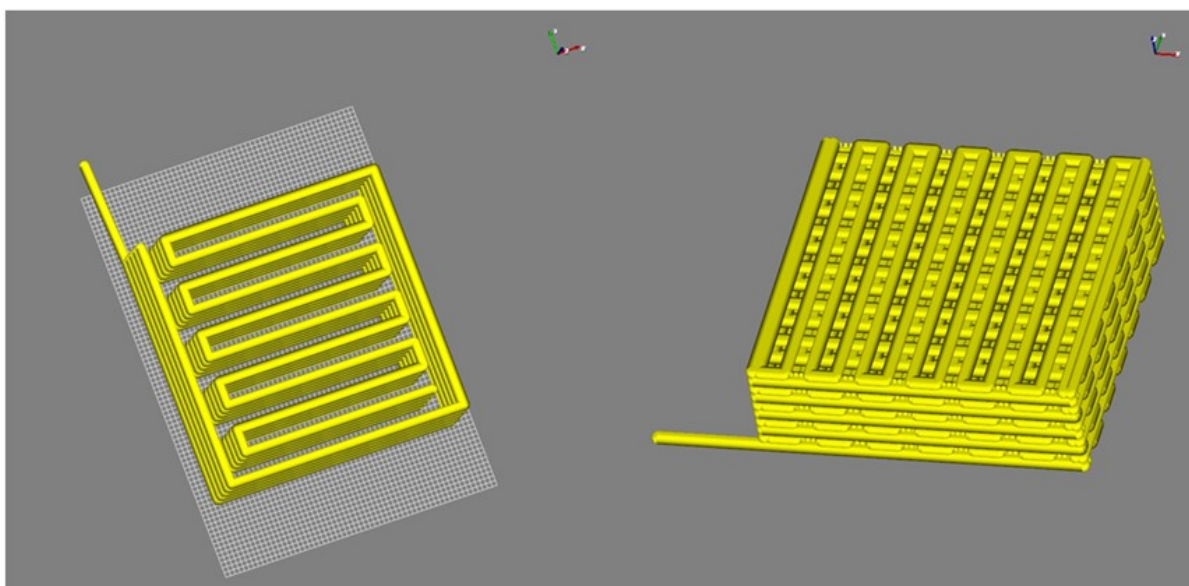


Figure 14 3D CAD Designs of 10layered serpentine (left)(1x1cm) and woodpile (right)(1x1cm) with 410 microns nozzle(blue) used for this study.

The effect of the structure thickness on the electrochemical performance of the 3D printed electrodes will be investigated, considering variations from 2 to 10 printed layers. These architectural choices underscore the importance of design in the additive manufacturing of energy storage devices, allowing for the manipulation of mass distribution, surface area exposure, and structural integrity to optimise electrochemical performance.

For reference, the 10-layer Woodpile .CAD file design produced here using the 410 microns nozzle has 184.70 cubic millimetres of volume and a surface area of 1803.97 square millimetres, whereas the 10-layer Serpentine design has 158.51 cubic millimetres of volume and a surface area of 1548.40 square millimetres. These values were extracted from the proprietary software and AutoCAD.

2.2.6 Syringe Loading and Nozzle choice Methodology.

After homogenisation, TMD inks were loaded in Nordson 3ml syringes using a spatula. To ensure no air bubbles are introduced during the loading of the syringes, TMD inks can be extruded from a syringe into another syringe without a nozzle on. Once loaded, syringes were sealed with the proprietary cap or loaded with Nordson EFD General Purpose Dispense Tips. For the purposes of this study 6.35 mm / 0.25", 100 microns (Yellow - PN 7018462), 250 microns (Red – PN 7018333), and 410 microns (Blue – PN 7018260) nozzles were used. After

the nozzle is securely attached, optimum dispensing was verified by extruding the ink from the nozzle. The ink should come out smoothly and evenly. If the loaded syringes were not used immediately, they were stored upright in a syringe holder properly to prevent the ink from drying out or being contaminated.

2.2.7 Substrate effect and preparation

The selection of an appropriate substrate is crucial in the manufacturing of supercapacitor electrodes and other electrochemical energy storage devices. Parameters under consideration for the ideal substrate are low-cost, processability, conductivity and electrochemical activity. Based on all these parameters ITO-Glass, Carbon Foil and Gold Foil substrates were considered as platforms for dispensing, templating, processing, assembling and operating supercapacitor devices. ITO-Glass can be easily cut and handled; however, its semiconducting nature makes it resistive, and it exhibits relatively low electrochemical activity. Carbon Foil is also a low-cost material that can be easily mass-produced. It provides an optimal surface for depositing continuous filaments in 3D objects and can be processed, cut, and handled with ease. It offers excellent electrical conductivity and is electrostatically active, albeit electrochemically inert. All substrates were purchased from Merck Sigma-Aldrich and can be thermally annealed at 470°C to remove the polymeric part of the electrodes. However, it should be noted that thermal annealing will cause ITO-Glass to lose its conductivity. Based on these considerations, the best substrate to template, process, assemble and operate supercapacitor devices was Carbon Foil, so was used as received, with no conditioning steps throughout when benchmarking the performance of TMD-based electrodes and devices.

ITO-Glass was purchased from Merck/Sigma-Aldrich 578274. Carbon foil was purchased from Merck/Sigma-Aldrich GF23879009. Gold Foil of 0.10mm was purchased from Merck/Sigma-Aldrich GF55563699. Gold Foil 0.125mm from Merck/Sigma-Aldrich GF13495349.

2.2.8 Thin Film patterning

The process of thin film patterning plays an integral role in the creation of supercapacitor electrodes. This process primarily involves the precise application and formation of thin layers of formulated TMD ink onto the selected substrate. Thin films were patterned with a

cylindrical rod, using the Doctor Blade technique to ensure a controlled and uniform distribution of the ink, imitating roll – to –roll production.

Graphite foil sheets were first prepared by masking off areas to create dimensions of 1 x 10 cm. This was accomplished using a single layer of 3M Scotch Magic tape adhesive type 810, with a thickness of 62.5 microns. The tape served as an effective mask to confine the TMD ink to the specified dimensions and prevent unintentional spreading. Following the masking process, TMD inks were spread onto the unmasked area of the Graphite foil. This technique allowed us to regulate the thickness of the thin films, resulting in a post-drying thickness of 40 microns. After the spreading and drying processes were complete, the patterned films were then cut into 1 x 1 cm squares for the active material. The precise patterning and uniform thickness of these films are crucial factors as a standardised approach in achieving consistent and reliable performance in supercapacitor devices.

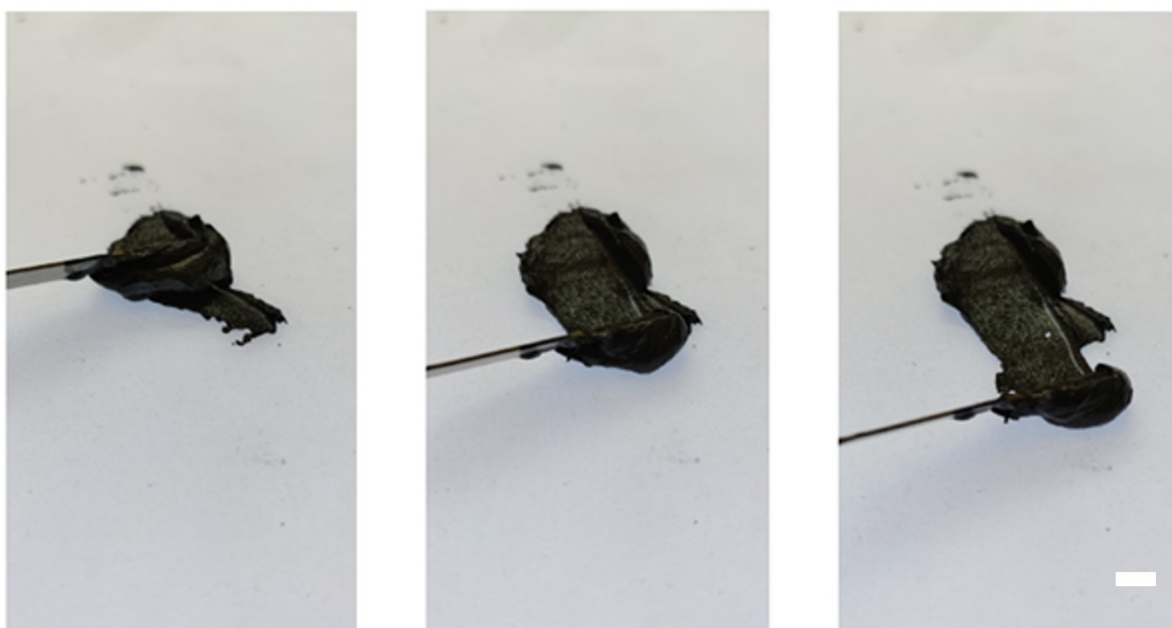


Figure 15 Spreading of an MoS₂ 30%wt with a metal spatula. When no-force is applied the material behaves as a solid and is spreading while pressure is applied. This behaviour is characteristic of shear-thinning (scale bar 0.5cm).

Figure 15 shows the shear-thinning behaviour of the ink when spread with a spatula.

2.2.9 3D printing of TMD inks

TMD inks with 30% wt and 50%wt of active material versus the total weight of ink were loaded in syringes and a plethora of architectures were 3D printed in various resolutions. Generally, thicker nozzles accommodate higher mass loading and finer nozzles allow for lower mass loading of active materials due to the pressure generated as the yield point increases.

The 3D printing methodology after designing the .cad file in the appropriate nozzle diameter, loading the syringe and nozzle combination is followed by mounting the Syringes onto the three-axis stage of the Robocasting printer which is loaded on a conventional gantry crane. After initiating, the Computer-Aided-Designs were then translated into G-code using the manufacturer proprietary software and TMD inks are then dispensed in the respective 3D shapes onto the flat substrates with the syringe displacement actuators forcing the plunger resulting in a 6mm/s feed rate. The printing process was then monitored during printing to ensure TMD inks are being dispensed in the correct 3D shapes. In some cases, micro adjustments of the z dimensions were carried out by manually lowering or rising the three-axis stage on the gantry crane to ensure contact between subsequent printing layers with the previous ones ensuring a continuous dispensing and successful prints in different architectures and substrate combinations.

2.2.10 Thermal annealing

Thermal annealing was used to decompose the polymeric content and study the exposed exfoliated sheets without the hydrogel support, as well as the effect of phase conversion between 1T' and 2H in MoS₂ containing inks.

Thermal annealing was carried out in Vacuum Tube furnace under an argon flux. First, a vacuum stage was initiated with the samples in the tube in order to reach a vacuum of 10⁻⁷ mbar for 30 minutes. Heating process was carried out with a heating rate of 25°C/min reaching 470°C and held for 3h.

2.2.11 In-house Hydrogel Electrolyte formulation

The primary goal of engineering an energy storage device is to maximise its efficiency while ensuring stability and safety. One innovative approach towards achieving this involves the use

of hydrogel electrolytes. Hydrogel electrolytes possess unique properties that make them ideal for electrochemical applications, especially in supercapacitor devices. They can provide high ionic conductivity, low internal resistance, and maintain a high electroactive surface area, all critical factors for efficient electrochemical charge storage.

In this context, a bespoke formulation of a hydrogel electrolyte was developed, specifically tailored for the unique requirements. The formulation is based on a 27%w/V Pluronic f127 hydrogel and sulfuric acid to reach 1M H₂SO₄ Pluronic f127 27%w/V taking advantage of the amphiphilic properties of the poloxamer, and its thermoresponsiveness, a key characteristic that provides the hydrogel electrolyte with its distinctive advantages.

In the bespoke hydrogel electrolyte formulation, this thermoresponsive behaviour of the poloxamer is exploited to achieve a balance between fluidity for electrode wetting and solidity for device stability. At low temperatures (4°C), the electrolyte exists in a liquid phase, enabling it to readily infiltrate the electrode material and maximise the electroactive surface area. Upon transitioning to room temperature, the electrolyte undergoes gelation, solidifying to form a quasi-solid-state device that exhibits superior stability and safety compared to its liquid counterparts. Meanwhile, the inclusion of 1M H₂SO₄ serves to provide the necessary ionic conductivity for charge transport. The combination of these components results in an electrolyte system that effectively enables high electrochemical charge storage, thereby simplifying the device assembly process and reducing the overall cost of the device.

The Hydrogel electrolyte was formulated by gradually dropping Sulfuric Acid to a 27%w/V Pluronic solution conditioned in liquid state at 4°C, to reach an overall concentration of 1M of sulphuric acid versus the water volume in the 27% w/V Pluronic solution. In some cases, solidification of the hydrogel arbitrarily occurs when the pH is locally very acidic, but by conditioning of the electrolyte at 4°C for a few days, the electrolyte homogenises.

For comparison aqueous electrolytes of 1M H₂SO₄, Li₂SO₄, Na₂SO₄, Zn₂SO₄, and K₂SO₄ were used by dissolving powders purchased from Sigma-Aldrich in DI to result in 1M solutions.

2.3 Materials Characterisation

In the context of this work, a broad spectrum of material characterisation techniques have been employed, including scanning electron microscopy (SEM), energy-dispersive X-ray

spectroscopy (EDX), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), atomic force microscopy (AFM), X-ray computed tomography (XCT), electrochemical microscopy techniques such as scanning electrochemical microscopy and thermoanalytical techniques such as differential scanning calorimetry (DSC).

Each of these techniques provides distinct and essential information about the materials under study. For example, SEM provides insights into the material surface topography, while ToF-SIMS can determine the ionic composition of the material. Raman spectroscopy offers details about the vibrational modes within the material, which can reveal chemical bonding and phase information. XPS and XRD can provide insights into the chemical states and crystallographic structure of the material, respectively. The combination of these techniques allows for a thorough and detailed characterisation of materials, revealing the complex interplay between material composition, structure, and properties.

2.3.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a powerful analytical tool used for obtaining high-resolution images of a material surface topography. The technique hinges on the principles of electron scattering, which occurs when an electron beam is directed and scanned over the surface of a sample. The first step in SEM analysis involves preparing the sample. This generally includes the careful cleaning and mounting of the sample onto a suitable SEM stub. If the sample is not conductive, it may also require coating with a thin layer of a conductive material, such as gold or platinum to prevent the accumulation of static charge during imaging. Once the sample is prepared, it is placed in the SEM vacuum chamber. The SEM operates by producing a focused beam of electrons from an electron gun at the top of the microscope. This electron beam is rastered, or scanned back and forth, across the surface of the sample. When the electron beam hits the sample surface, it interacts with the atoms in the sample. This interaction results in the emission of secondary electrons, backscattered electrons and X-rays. Secondary Electrons are ejected from the atoms in the sample due to the interaction with the incoming electron beam. Secondary electrons are low energy and therefore can only escape from a very small volume near the sample surface. As a result, they provide information about the surface morphology and topography of the sample.

Backscattered Electrons are incident electrons that are reflected back from the sample, usually without losing any energy. The intensity of backscattered electrons depends on the atomic number of the atom they hit, so these electrons can provide information about the elemental composition of the sample. The emitted secondary and backscattered electrons are detected and converted into an image. The brightness in the image corresponds to the intensity of the electron signal, with higher intensities translating to brighter areas. In this case, SEM is combined with Energy Dispersive X-ray Spectroscopy (EDX), which provides elemental and chemical information about the sample. When the electron beam hits the sample, it can also cause the emission of characteristic X-rays, which can be detected and analysed by EDX. Each element has a unique set of X-ray energies, allowing for the identification and quantification of the elements present in the sample. The surface morphology of as-printed 3D printed structures was investigated with a Zeiss Auriga 45-25 Cross Beam Electron Microscope using a Shottky field emission gun with Gemini electron column. High-resolution images were obtained with the standard in-chamber ET electron detector operating between 5-20 kV of accelerating voltage. It is worth noting that for the imaging of as printed and thermally annealed 3D printed architectures and thin films, no gold sputtering was required. However, in 30%wt blends, charging of the surface was observed when prolonged imaging and in some cases local decomposition of the hydrogel.

2.3.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a powerful analytical technique that provides a wealth of information about a sample's morphological, chemical, and crystallographic characteristics. Unlike Scanning Electron Microscopy (SEM) which analyses the electrons scattered from the surface of the specimen, TEM operates by directing a high-energy electron beam through an ultra-thin sample. It then analyses the transmitted electrons — those that have passed through the specimen — to derive detailed insights about the sample's structure and composition. TEM works on the principle of electron scattering. When the incident electron beam interacts with the sample, electrons are scattered due to their interactions with the electrostatic field of nuclei or the electron clouds of specimen atoms. Scattering can be elastic (where the electron retains its energy) or inelastic (where there is a measurable energy loss). The scattered electrons provide valuable information about the sample. For

instance, those that pass through the sample without deviation — known as the direct beam — provide data about the sample's morphology, chemistry, and crystal structure. The scattered electrons, on the other hand, provide details about the sample's electron density, crystallography, and more. The interaction of the incident electron wave with the crystal lattice of the specimen can result in changes in its amplitude and phase. These changes contribute to the formation of amplitude and phase contrast in TEM images. By tuning imaging conditions, one can optimise for either type of contrast, allowing for more focused investigation of the sample. In the study of atomically thin Transition Metal Dichalcogenides (TMDs), TEM proves to be an indispensable tool. The ability of TEM to probe their structure and composition at the atomic level offers an unparalleled depth of understanding, especially in determining monolayer between few-layer exfoliated flakes. The phase contrast mechanism of TEM allows the imaging of lattice fringes, which can be used to characterise the local crystal structure and orientation of TMDs. This detailed understanding can guide the design and optimisation of TMD-based devices.

In the context of this work, samples for TEM were prepared by drop-casting diluted dispersions of MoS₂/TiS₂ inks on carbon-coated copper grids. The grids were dried overnight under ambient conditions. Low-magnification bright-field TEM images and selected area electron diffraction (SAED) patterns were acquired on a JEOL JEM-2100Plus microscope. High-resolution TEM (HRTEM) imaging was performed using a JEOL JEM-2100F microscope with a field-emission gun operated at 200 kV accelerating voltage.

2.3.2 Raman Spectroscopy

Raman Spectroscopy is an analytical tool in materials science, providing detailed information about the molecular composition and crystal structure of a sample. It is based on the principle of inelastic scattering, or Raman scattering, of monochromatic light from a laser source. Once the sample is prepared, it is illuminated with a monochromatic laser beam. The laser light can be in the visible, near infrared or near ultraviolet range, depending on the sample and the information sought. As the laser light interacts with the sample, most of the light is scattered elastically, meaning the scattered photons have the same energy as the incoming photons. However, a small fraction of light undergoes inelastic scattering, where the energy of the scattered photon is different from the incident photon. This inelastic scattering is known as

Raman scattering. The energy difference between the incoming and scattered photon corresponds to the energy of a vibrational mode in the sample. This is known as the Raman shift and is specific to the chemical bonds and symmetry of the molecules in the sample. When the scattered photon has less energy than the incident photon, it corresponds to a vibrational excitation in the sample and the process is known as Stokes Raman scattering. When the scattered photon has more energy, it corresponds to a vibrational de-excitation and is known as Anti-Stokes Raman scattering. The scattered light is then collected and passed through a monochromator to produce a Raman spectrum, which plots the intensity of the scattered light (y-axis) against the Raman shift (x-axis). Each peak in the Raman spectrum corresponds to a specific vibrational mode in the sample, providing detailed information about the molecular structure, chemical composition, and crystallographic orientation of the sample. In this work, Raman spectra of architectures, thin films and ink blends were collected using a Renishaw inVia spectrometer equipped with a 532 nm laser. Maps were collected under a 100x objective with a grating of 1800 line mm⁻¹, with a spectral resolution 1.5 cm⁻¹

2.3.3 X-Ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a highly sensitive, surface analysis technique that provides both qualitative and quantitative information about the elemental composition, chemical state, and electronic structure of materials. The technique is based on the photoelectric effect, wherein X-ray radiation causes the emission of electrons from a material. The sample is prepared and placed in a high-vacuum chamber to eliminate interference from atmospheric gases. The sample is then irradiated with a beam of X-rays with a specific wavelength. This radiation excites the atoms in the sample, causing them to emit electrons. The emitted electrons, known as photoelectrons, have kinetic energies that depend on the binding energies of the original atomic orbitals from which they were ejected. These photoelectrons are detected, and their kinetic energies are measured. Analysis of the XPS Spectrum: The number of photoelectrons emitted at each kinetic energy level is plotted to produce an XPS spectrum. This plot shows peaks corresponding to the different elements present in the sample. The position of these peaks on the energy scale reveals the elements atomic or ionic state, while the area under each peak provides a measure of the amount of that element present. By using a beam of ions to etch away layers of the material, XPS can

also provide depth profiling of the sample. This reveals changes in composition and chemical state with depth, with a typical depth resolution in the range of $\sim 10\text{nm}$. XPS can detect all elements except for hydrogen and helium, and its sensitivity extends to concentrations as low as 1 atomic percent. Therefore, XPS is an indispensable tool in many fields such as materials science, chemistry, and surface engineering, offering detailed insights into the surface and near-surface regions of a wide range of materials. In this work, XPS spectra of as printed, thermally annealed and electrochemically cycled architectures a and thin films were recorded on a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer system. Data were collected at 29 eV passing energy for both core level (S 2p, C1s and Mo 3d) and valence spectra.

2.3.4 X-Ray Diffraction (XRD)

X-ray Diffraction (XRD) is a non-destructive, analytical technique used to identify and quantify the crystalline phases present in a sample. It is a powerful tool in crystallography, the study of crystal structure and properties. The technique is based on the principle of wave-particle duality and the concept of Bragg's law. A powdered or single-crystal sample is mounted onto a goniometer, a device that allows precise orientation of the sample. An X-ray beam is directed at the sample. As X-rays are electromagnetic waves with a wavelength similar to the spacing of atoms in a crystal, they interact strongly with the electron cloud of the atoms in the sample. As the X-rays interact with the atoms, they are scattered in various directions. Some of these scattered waves interfere constructively, producing a pattern of bright spots known as a diffraction pattern. The angles and intensities of these diffracted beams are measured with a detector that rotates around the sample. The data collected from the diffraction pattern are used to produce an XRD spectrum. The positions and intensities of the peaks in this spectrum provide information about the crystal structure of the material, including atomic positions, chemical bonds, and any crystallographic disorder. By measuring the angles and intensities of the diffracted beams, XRD can provide detailed information about the crystallographic structure of the material. In this work, a Bruker D2 desktop XRD instrument was used to probe the possible intercalation of solvated ions between 7-20 diffraction angles, in TMD powders and thin films.

2.3.5 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a surface-sensitive technique used for the characterisation of material composition at a very fine scale. It uses an ion beam to sputter the surface of a sample, ejecting secondary ions that are then analysed based on their time-of-flight. As the technique is surface sensitive, the condition of the sample surface is critical. Once the sample is *in vacuo*, a focused primary ion beam (with energy ranging between 0.1-25 keV) is directed at the sample surface, causing sputtering, which is the ejection of surface atoms or molecules. This sputtering process results in the emission of a variety of particles, including monoatomic and polyatomic ions, electrons, and photons. The secondary ions (i.e., ions ejected from the sample surface due to the primary ion beam impact) are collected and directed towards the mass spectrometer. This is typically done using an electric field to accelerate the ions. The secondary ions are then analysed based on their time-of-flight, which is the time taken for the ions to travel a fixed distance. Because the ions are accelerated to the same kinetic energy, the time-of-flight depends on the mass-to-charge ratio of the ions. The data collected from the time-of-flight analysis can then be used to identify the elements, isotopes, and molecular species present in the sample.

ToF-SIMS offers high sensitivity, down to parts per million (ppm), and it can measure all elements in the periodic table, from hydrogen to uranium, along with isotopes and molecular species. It also provides high spatial resolution, allowing for the detection and identification of features on the sample surface at the micrometre to nanometre scale. This makes it a powerful tool for surface analysis in a wide range of fields, including materials science, semiconductor technology, geology, and biology.

In the experimental context of this work, as printed and annealed 3D electrodes were rastered and mapped over a predefined area of 50x50 microns with a 25 keV Bi⁺ primary ion beam, as well as depth profiled by surface milling utilising a 25keV Cs⁺ and Ar⁺ beam reaching up to 50 microns. All measurements were carried out in a Combined IONTOF TOF.SIMS5-Qtac100 LEIS instrument.

2.3.6 Atomic Force Microscopy and in-Operando Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a powerful high-resolution scanning probe microscopy technique, capable of measuring surface topography down to the nanometre scale. It operates by 'scanning' a sharp tip over a sample's surface, recording minute forces between the tip and the sample to produce an image. The in-Operando AFM allows for real-time monitoring of electrochemical processes. A sharp-tipped cantilever, typically made of silicon or silicon nitride, is brought close to the sample's surface. The cantilever is piezoelectrically oscillated at or near its resonance frequency. The sample is scanned by moving the cantilever in a raster pattern across the sample surface. This can be done by 'tapping' (where the cantilever gently oscillates against the surface) or 'dragging' (where the cantilever is dragged across the surface while maintaining a constant force). As the cantilever tip interacts with the surface, forces between the tip and the sample cause the cantilever to deflect. These forces can include mechanical contact forces, van der Waals forces, capillary forces, chemical bonding forces, electrostatic forces, magnetic forces, among others. The deflection is proportional to the force according to Hooke's law. A laser beam is reflected off the back of the cantilever and onto a photodetector, which tracks the changes in the cantilever's position as it scans the sample's surface. The deflection signal is then converted into an image of the surface topography. For in-operando AFM, the process is conducted within an electrochemical cell. Here, the AFM tip or the sample stage can be biased to measure changes in the microstructure or observe interfacial topographic reactions happening in real time during electrochemical processes. A potential is applied through the AFM probe, and the resulting current generated upon interacting with the surface of the working electrode is measured. This method allows for the direct observation of dynamic processes in real-time, providing insight into how the sample's topography changes under operation conditions to examine interfacial reactions. In this work, a Bruker PeakForce SECM instrument was used to probe the volumetric expansion of TMD layered sheets in a 50%wt MoS₂/TiS₂ thin film.

2.3.7 X-Ray Computed Tomography (XCT)

X-Ray Computed Tomography (XCT) is a non-destructive imaging technique that generates 3D models of a sample by piecing together 2D cross-sectional X-ray images. This technique is widely used in materials science, engineering, and medical applications for its ability to

visualise internal structures and features down to the nanometre scale. The sample to be analysed is mounted securely within the XCT system. The sample must be stable and fit within the field of view of the system. The XCT system emits X-rays which penetrate through the sample. The X-ray source and detector rotate around the sample, capturing X-ray images from various angles. The intensity of the transmitted X-rays depends on the material density and composition of the sample. As the X-rays pass through the sample, they are attenuated to different degrees based on the sample's internal structure. The detector captures these attenuations to create 2D projection images. Using a mathematical process called tomographic reconstruction, the 2D images are combined to form a 3D representation of the sample. This is done by compiling the images into a series of cross-sectional slices, which can then be digitally 'stacked' together to create a detailed 3D model. The resulting 3D model can be virtually sliced in any direction to reveal internal structures and features of the sample. Through image segmentation, different volumetric features with similar density thresholds can be isolated for further study. These structures can be visually added or removed to gain insights into the sample's microstructure in three dimensions. The data acquired from XCT can be used to analyse a sample's internal structure, density variations, porosity, and more. The information can be crucial in understanding the sample's composition, integrity, and potential defects.

In the experimental context of this work, Three-dimensional microstructure of the printed structures was investigated using X-ray microcomputed Tomography (Zeiss Versa 620) in a large-field-of-view mode for a complete map profiling of two 10x10mm electrodes in different architectures (woodpile and serpentine), acquiring phase-contrast images. The porosity of the filament was calculated from the scan in the central region, segmenting the MoS₂/TiS₂ flakes suspended in the polymeric hydrogel with Avizo software. The tomographic data were segmented into two domains (respectively MoS₂/TiS₂ and air) using Avizo software via a greyscale thresholding. The surface area and porosity of the printed woodpile structure were computed considering the surface of the MoS₂/TiS₂ domain. (Thermo Fisher Scientific, USA).

2.3.8 Thermoanalytical techniques : Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a robust thermoanalytical technique that measures the heat flow associated with transitions in materials as a function of temperature. It has

broad applications in various fields, including polymer chemistry, pharmaceuticals, and food science, due to its ability to provide insights into material properties such as melting temperature, heat capacity, enthalpy changes, and glass transition temperature. A small amount of the material to be tested is placed in a DSC sample pan. A reference sample, typically an inert material with a well-characterised heat capacity over the desired temperature range, is placed in a separate pan. The sample and reference pans are loaded into the DSC instrument. The instrument is then set to heat the pans at a specific rate, usually a few degrees per minute. As the temperature increases, both the sample and reference materials will absorb heat. The DSC measures the differential heat flow required to keep both the sample and the reference at the same temperature. The DSC records the heat flow to the sample and reference over time, generating a DSC curve. This curve can provide information about exothermic (heat-releasing) and endothermic (heat-absorbing) processes in the sample. Analysis of the DSC curve can reveal a range of material characteristics. For instance, endothermic peaks correspond to temperatures at which the sample undergoes phase changes, such as melting or glass transition. Exothermic peaks may indicate crystallisation or oxidative degradation reactions.

To optimise thermal annealing temperature and holding times, Differential Scanning Calorimetry studies were carried out as a first tool to gauge the transitions occurring in response to an increasing temperature. The experiments were performed under N₂ atmosphere with a heating rate of 10°C/min in a Mettler Toledo DSC700 instrument.

2.4 Electroanalytical tools for supercapacitors

Principles of electrochemical energy storage

Electrochemical energy storage devices consist of four main components which are: electrodes, separators, substrates, and electrolytes. Each of them, plays a crucial role in the device's overall performance. These components can be assembled in a variety of configurations to create devices that exploit different energy storage mechanisms. To thoroughly understand these mechanisms, it is crucial to examine both the individual components and their synergistic interactions within the full device assembly.

In the context of experimental investigation, these devices can be studied as two, three, or four electrode systems. Traditional two-electrode systems include a working electrode and a counter electrode, forming either symmetric or asymmetric full devices. Three-electrode systems add a reference electrode to the setup, such as a standard calomel electrode or a silver/silver chloride electrode, calibrated against a standard hydrogen electrode. Four-electrode systems are generally used when examining the properties of an electronic conductor (for instance, conductivity measurements of an electrode) or an ionic conductor (such as the effect of an applied current on the electrolyte itself or on some barrier within the electrolyte, like a separator).

The analysis of these systems is often conducted using various electroanalytical techniques. These include, but are not limited to, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy, Cyclic Charge Discharge, and Controlled Potential Coulometry. Each of these techniques provides valuable insights into the operation and performance of electrochemical energy storage devices.

The following sections will delve into these electroanalytical techniques, providing comprehensive protocol guides for their application in studying electrochemical energy storage systems.

2.4.1 Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) is a widely adopted potentiodynamic electroanalytical technique in electrochemical energy storage, due to its capability to distinguish different energy storage mechanisms based on the shape of the cyclic voltammogram. For instance, rectangular shapes are attributed to electrostatic energy storage, whereas quasi-rectangular shapes are indicative of resistive behaviour that can be attributed to surface and near-surface adsorption and/or solvated ion intercalation. The scan rate in mV/s is a critical parameter that can shed light on these mechanisms, as different processes necessitate varying timeframes to occur. Furthermore, CV can signal the presence of electrocatalytic influences from oxygen or hydrogen reduction via hydrolysis, which typically manifest as sharp current increases, or spikes, especially when nearing high voltages in aqueous systems. Broad peaks in the anodic or cathodic current may denote reversible or non-reversible reactions, such as reduction and oxidation. Despite the wealth of valuable information that CV can provide, there are some

limitations. One common issue is the susceptibility to hysteresis effects due to the technique's polarising nature¹⁴⁹. To mitigate this, researchers should empirically determine the location of the point of zero charge for each system under study, as this location varies across different systems. It is essential to avoid crossing the point of zero charge during operation.

By following the correct measuring protocol, stored charges can be directly integrated from the CV area using the below formula:

$$Q = \oint \frac{i}{2v} dV \quad Eq(2.3)$$

Where Q is the total number of charges, i is the current and v the scanrate. Furthermore, capacitance values can be extracted by integrating the area underneath a CV curve using the below formula:

$$C_{dev} = 4 * \frac{\oint i dV}{2 v \Delta V x} \quad Eq(2.4)$$

Where ΔV is the voltage window (0.5V), v the scanrate, x is the area of the device immersed in the electrolyte, i is the current

This formula is adjusted with a 4x multiplier for a symmetric device. The multiplier of 4 adjusts the capacitance of the cell and the combined mass of two electrodes to the capacitance and mass of a single electrode¹⁴⁹. One common issue is the susceptibility to hysteresis effects due to the technique's polarising nature¹⁴⁹. Generally, it is widely accepted that Cyclic Charge Discharge values are more accurate when determining the Capacitance values, the capacitance from CV can also be assumed and will be compared within.

2.4.2 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) provides information on interfacial phenomena. It operates by applying sinusoidal potentials or currents with varying frequencies and subsequently measuring the system's impedance. This impedance is complex, containing both a real (resistive) and an imaginary (reactive) component. EIS can provide a wealth of valuable insights about the interface between the electrode and the electrolyte and is routinely used to measure the ionic conductivity of a system. In an impedance spectrum, resistive elements are typically represented as semicircles, while capacitive elements are seen

as sloping regions. The behaviour of the system under investigation can be deduced by fitting the experimentally obtained EIS data to theoretical models. This fitting process can help approximate the various properties of the system, such as resistance, capacitance, and diffusion coefficients, among others. Furthermore, the principles of EIS can also be applied under conditions where a bias is applied to the system, enabling the study of evolving interfacial reactions during the operation of an energy storage device. This "in-operando" approach can provide valuable real-time information about the system's performance and stability under practical conditions.

2.4.3 Cyclic Charge Discharge (CCD)

Cyclic Charge Discharge is an important electroanalytical technique used to simulate the operational conditions of an electrochemical energy storage device. By applying a controlled current to the device, the corresponding change in potential (voltage) is measured over time, providing a charge-discharge profile for the device. The shape of the charge and discharge curves, as well as the time taken for these processes to occur, can reveal vital information about the device energy storage performance parameters. The slope of these curves is directly related to the internal resistance of the device. The steeper the slope, the lower the internal resistance and the more efficient the device is at storing and delivering energy. The total area under the charge-discharge curve provides a measure of the device capacitance or its ability to store charge. Furthermore, the time taken for each charge-discharge cycle provides insight into the energy density (energy stored per unit area, volume or weight) of the device. The power density (energy delivered per unit time) can be inferred from the rate at which the device can charge or discharge. Perhaps one of the most important aspects of CCD is its ability to assess the device cycling stability or longevity, which is a critical factor for practical applications. By continuously cycling the device through charging and discharging processes, one can study how the device performance parameters change over time, thereby providing an estimate of its lifetime before failure. CCD is widely accepted as the method to extract performance metrics for supercapacitors and batteries.

Capacitance was calculated from symmetric devices using the below formula.

$$C = 4 \frac{I * \Delta t}{x * DV} \quad Eq(2.5)$$

Where I is the discharge current, Δt is the discharging time. X is the area of the device immersed in the electrolyte or the weight of the active material and DV is the discharge potential window. The factor of 4 is put to reflect underestimations between two and three electrode systems¹⁴⁹.

Energy Density was calculated from symmetric devices using the below formula.

$$E = \frac{1}{8} * \frac{C * DV^2}{3600} \quad Eq(2.6)$$

Where E is energy density, C is the capacitance calculated from CCD and DV is the discharge potential window.

Power Density was calculated from symmetric devices using the below formula.

$$P = \frac{E}{\Delta t} \quad Eq(2.7)$$

2.4.4 Controlled Potential Coulometry (CPC)

Controlled Potential Coulometry is a potentiostatic electrochemical technique that measures the total charge passed in an electrochemical reaction at a working electrode held at a constant potential. It has been extensively used in corrosion studies, where it can provide a complete quantification of a working electrode's corrosion into an analyte. While its applications for energy storage are still emerging¹⁵⁰. This technique has the ability to measure the total flow of charge between the working and counter electrodes, which presents a promising avenue for quantifying stored charge in electrochemical energy storage devices.

Moreover, CPC provides a direct measure of the supercapacitor capacitance – through the relationship between charge storage and time under a controlled potential. For instance, a linear change vs. time profile might suggest a capacitive storage mechanism, while deviations from linearity could indicate contributions from other processes such as Faradaic reactions.

CPC is a direct integration from the current as measured from Chronoamperometry, so charges are quantified by integrating current that is generated at a fixed potential over the time that is applied:

$$Q = \int_{t_0}^{t_1} i(t) dt \quad Eq(2.8)$$

t_0 = Time where potential is applied, t_1 = Time where potential is stopped being applied. $i(t)$ = current that is applied at a fixed potential over time.

$$C = \frac{Q}{V} \quad Eq(2.9)$$

Capacitance in coulometric studies is calculated from the charges as extracted from controlled potential coulometry over the fixed potential that is applied.

2.5 Electrochemical Cell Assembly

The electrochemical cells were constructed using 3D printed electrodes with different number printed layers to create two-electrode symmetric systems. The printed electrodes with substrates measuring $2 \times 1 \text{ cm}^2$ were connected with copper clamps within 50 ml borosilicate glass cells. The inter-electrode distance was consistently maintained at 1 cm for all experiments to ensure uniformity in the test conditions.

The cell assembly was then completed by introducing 30 ml of the electrolyte formulation, (H_2SO_4 – Poloxamer) which was poured directly into the beaker at a temperature of 4°C , ensuring only the 1 cm^2 active electrode area was covered. The cell was then sealed with parafilm to prevent any external interference.

2.6 Electrochemical Measurements

The electrochemical methods utilised in this study consists of several key electroanalytical techniques, each of which contributes to a comprehensive characterisation of the electrodes. These techniques include Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD), and Chronoamperometric/Controlled Potential Coulometric measurements. These measurements were carried out at room temperature using Gamry1010E Interface electrochemical workstation.

The Open Circuit Potential was measured at $\pm 15 \text{ mV}$ after setting the electrochemical cell and measured before any experiment/conditioning, indicative of electrode symmetry. This

is a vital parameter in two-electrode systems and is indicative of the balance between the two electrodes.

CV curves were performed within a potential window of 0-0.5 V. The scan rate varied from 0.1 to 10,000 mV s⁻¹ and vice-versa. Five cycles were recorded for each scan rate, with the third one typically presented for visualisation. This technique provides valuable insight into the electrochemical reactions occurring within the electrodes.

EIS measurements were conducted over a frequency range from 0.02 Hz to 100,000 Hz and vice versa. The potential was kept constant across the entire device operating potential spectrum, ranging from 0.0 V to 0.5 V and back to 0.0 V, with a step size of 0.1 V. EIS measurements can reveal valuable information about resistive and capacitive elements within the system, providing further insight into the electrode/electrolyte interfaces.

GCD analysis was performed at a fixed current ranging from 0.1 to 1 mA/cm². Measurements were taken over 100 and 1,000 cycles for each current density and over 100,000 cycles for 1 mA. To provide a sense of scale, each charge/discharge cycle lasted for 40s, equivalent to 41 days of continuous cycling. The 50th cycle was visualised each time.

Chronoamperometric/Controlled Potential Coulometric Studies were conducted across the device operating potential window with a step size of 0.1 V. These measurements can reveal insights into the quantity of stored charge and help in discerning the underlying mechanisms.

2.7 Benchmarking Performance of Electrochemical Devices

A reliable, standardised benchmarking process allows for a fair comparison of different materials, electrode architectures, and energy storage devices. Multiple techniques are currently employed, leading to wide variations in reported results, as pointed out by Ruoff et al¹⁴⁹.

The following best practices and recommendations are proposed based on the literature in best practices for accurate benchmarking of EES^{9,121,149,151–153}, such as adoption of standardised measurement methods, consideration of the test cell configuration, electrolytes and charge/discharge rates in conditions that closely mimic actual device applications for accurate benchmarking. The report of performance metrics at the packaged cell level, noting

the mass of all components for a more accurate representation of performance. The accurate classification of electrode materials, understanding and probing of the charge storage mechanisms. The development of hybrid energy storage devices that combine the best features of charge storage. Addressing gaps in knowledge in terms of the surface chemistry on electrochemical properties, new electrolyte development, self-discharge and performance degradation mechanisms. Finally, while three-electrode tests are useful to distinguish material properties at the half-cell, two-electrode measurements must be used for performance evaluation so the closely simulate a packaged commercial cell. CCD is the go-to method for performance evaluation as CV can be subject to electrode polarisation and over-estimation when the point of zero is crossed.

Conclusions

In summary, conductive additive-free 3D printed supercapacitors were designed using lithium-ion intercalated MoS₂ and TiS₂ nanosheets. The exfoliated 2D MoS₂ and TiS₂ sheets were blended with Pluronic to obtain a viscoelastic ink, which is 3D printable in mechanically stable structure with excellent shape retention. To achieve 3D printing and rheological assessment, inks were homogenised to remove air bubbles and achieve optimum flow. Different architectures were designed to demonstrate the printability as well as to assess the electrode potentials for electrochemical supercapacitors. The advantage of 3D electrodes in elevating energy storage performance of supercapacitors was compared with thin film-based supercapacitors. The hydrogel electrolyte was synthesised to use as liquid-free and durable 3D supercapacitors, which is beneficial for commercial applications.

Different printed architectures and supercapacitor designs were proposed to evaluate the performance. A comprehensive range of electroanalytical tools were employed to systematically test performance metrics as well as the underlying energy storage mechanisms. Techniques such as CV, EIS, CCD, and CPC highlighted the complexity and interplay of factors influencing energy storage. This study examined electrostatic and electrochemical phenomena, applied currents and potentials, and dynamic transformations within devices. Insights from these analyses can improve the design and durability of energy storage devices and guide strategies to address material characterisation and operational issues, ensuring reliability and longevity. Benchmarking performance metrics is emphasised to assess and enhance the performance of fabricated supercapacitor materials.

Chapter 3: Formulation of printable inks of two-dimensional Transition Metal Dichalcogenides for 3D printing supercapacitors

Introduction

Formulating printable inks for Electrochemical Energy Storage (EES) devices requires a deep understanding of rheological behaviour to ensure smooth, continuous dispensing that accurately reflects the CAD. Key factors such as viscosity, yield point, storage modulus, and recovery point must be meticulously optimised to achieve mass production feasibility and high dispensing efficiency, while minimising post-printing processing steps to maximise device turnover.

This chapter explores the fundamentals of ink formulation, focusing on select ink examples to provide a comprehensive understanding of their properties and performance. It includes a detailed examination of thermal properties, the annealing process, and the presence of lithium post-hydrolysis.

3D printing of 2D materials has emerged as a promising approach for high-performance EES devices, particularly through 3D architectures based on 2D nanosheet microlattices. The 3D architecture also provides mechanical stability and prevents nanosheet restacking. Incorporating functional fillers into the 2D material inks allows for tailoring electrode properties to meet specific application requirements, showcasing the potential of 3D printed structures for developing high-performance supercapacitors.

Beyond rheological and topographical investigations, this chapter examines the ink materials using Raman, DSC, XPS, TEM, and ToF-SIMS analyses. Raman provides information related to the crystalline phase of MoS_2 , TiS_2 , and their blends, DSC assesses crystallographic phase transformation and the evaporation temperature water in hydrogel, XPS provides information about the atomic composition of the surface, and TEM provide atomic resolution and information about the crystallinity of the individual flakes while ToF-SIMS provides

information about the composition and in specific about the presence of lithiated species and phase changes during hydration and annealing.

3.1 In-Depth Examination of selected Ink Examples

3.1.1 Pluronic F127 rheology

In DIW, Pluronic F127 stands out due to its ability to form a gel phase above its critical micelle temperature (CMT). This behaviour allows it to transition from a more liquid state at low temperatures to a semi-solid state at elevated temperatures, providing a means of extruding the material while retaining its structure post-extrusion. This is particularly useful in direct ink writing (DIW) techniques, where the viscosity and yield strength of the ink play significant roles in the resolution and accuracy of the printed structures.

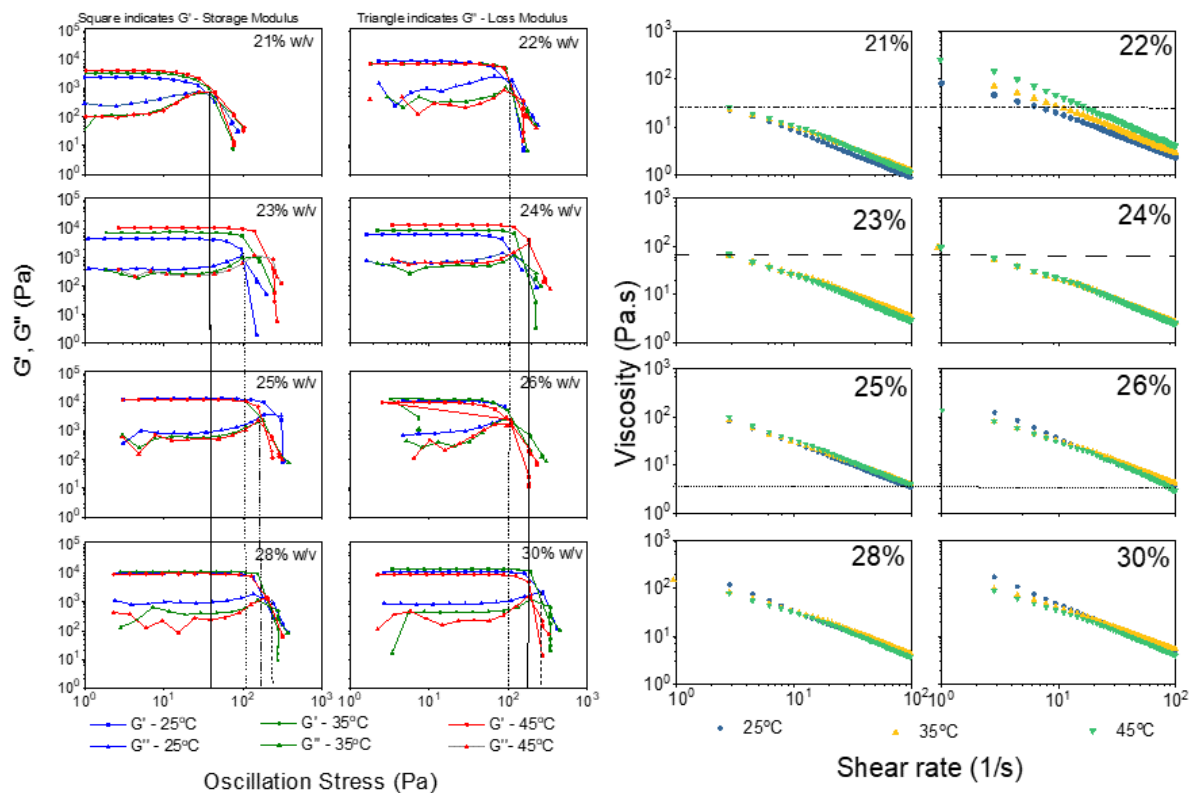


Figure 16 Oscillatory measurements (left) of storage (G') and loss moduli (G'') at different oscillation stresses at an angular frequency of 10rad/s and flow ramps (right) of different w/v% Pluronic F127 in water, at 25°C, 35°C and 45°C.

In-depth examination of Pluronic F127 was conducted with a focus on its rheological properties and temperature responses. Different weight/volume concentrations ranging from 21-30%w/v were evaluated at varying temperatures (25°C, 35°C, and 45°C) as shown in Figure 16. This study highlights the yield points of the hydrogel and its sensitivity to temperature changes. The collected data, particularly at temperatures exceeding 25°C, demonstrated satisfactory gelation, an optimal transformation from solid to liquid phase, as well as a yield point greater than 10^2 Pa, which suggests good printability.

The Pluronic F127 concentration of 25% weight/volume at 25°C was determined to be the optimum conditions for printing, as they present the best Yield Point to Oscillation Stress ratio through experimental testing. The yield points at an angular frequency of 10rad/s is shown on Table 3.

Table 3 List of storage moduli and oscillation stress at yield point extracted from rheological oscillatory measurements at an angular frequency of 10 rad/s, in response to the temperature (°C) and concentration of Pluronic hydrogels.

Storage Modulus (G') (Pa)	Oscillation Stress (Pa)	Temperature (°C)	Concentration (w/V)
640	35	25	21
570	41	35	21
653	46	45	21
2242	90	25	22
612	112	35	22
525	123	45	22
1044	99	25	23
1006	148	35	23
988	205	45	23
1083	116	25	24
661	156	35	24
3034	182	45	24
3595	265	25	25
2263	179	35	25
1224	189	45	25
1663	125	35	26
1705	109	45	26
1272	186	25	28
726	216	35	28
1401	205	45	28
2288	263	25	30
842	275	35	30
950	204	45	30

This study underlines the significance of understanding and optimising the rheological properties of the printing ink. For instance, the higher yield point means that the higher storage modulus overall for that ink and therefore better shape retention right after printing. Through meticulous examination and experimental refinement, Pluronic F127-based ink has been proven to offer reliable, efficient, and flexible solution for 3D printed EES applications. This highlights the profound impact that a well-designed ink formulation can have on the success of 3D printed energy storage devices.

3.2 Transition Metal Dichalcogenides (TMDs) – Based Ink Formulation Strategy

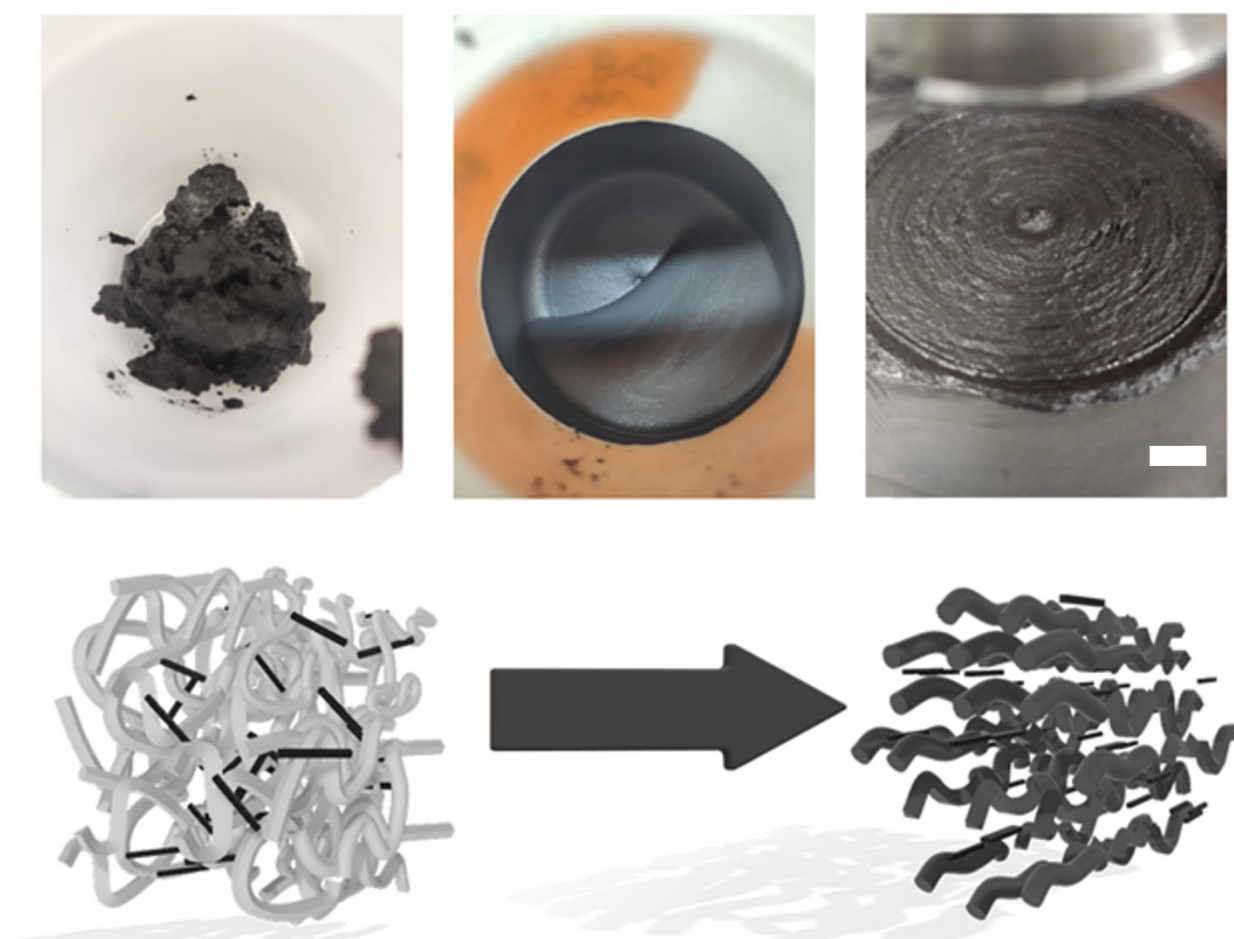


Figure 17 MoS₂/TiS₂ 50%wt ink after exfoliation (left), homogenisation (middle) and after rheological measurements (right). Simplistic representation (bottom). Nanosheets and polymeric compounds are randomly arranged after exfoliation, they reorient after homogenisation and align after oscillatory shear measurements (scalebar = 0.5cm).

The processing steps after exfoliation can be seen in Figure 17. Exfoliated hydrogel inks are homogenised and then are ready for testing or dispensing. In each individual step there is a thermodynamic evolution of the nanosheet suspension system that is directly influenced by the hydrogel w/v percentage and active material abundance. The hydrophobic and hydrophilic blocks of the copolymer are forming random sized micelles suspending a network of anisotropic nanosheets. The way that these reorganise directly influences all the reactions occurring. From hydrolysis, oxidation to electrochemical activity. As investigated from previous studies^{43,94,107}, there is a trend in alignment of anisotropic particles due to the shear forces applied on the ink.

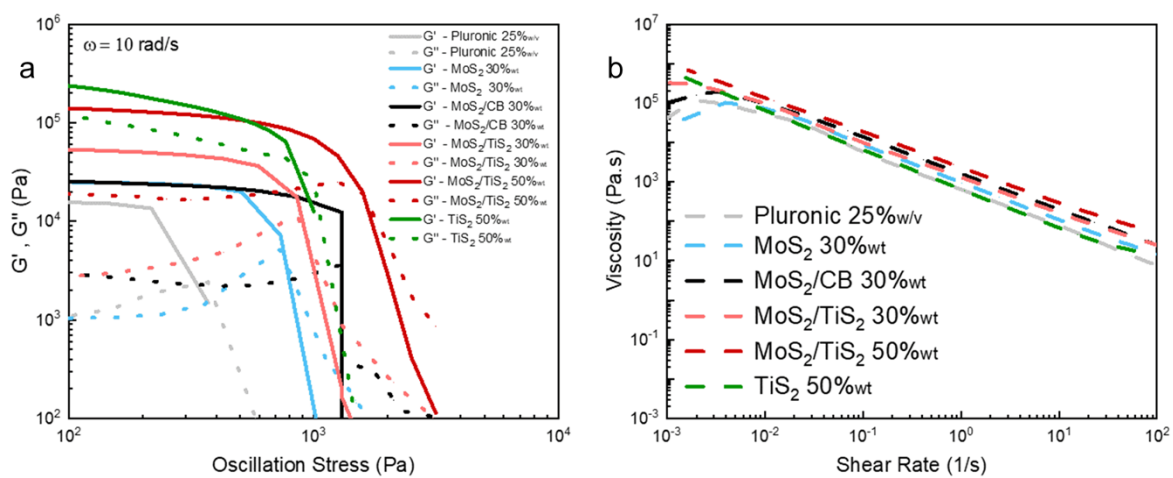


Figure 18 a) Oscillatory measurements and b) flow ramps for Pluronic 25%w/v and MoS_2 30%wt, MoS_2 30wt% + 5wt% Carbon Black, $\text{MoS}_2/\text{TiS}_2$ 30wt, $\text{MoS}_2/\text{TiS}_2$ 50wt and TiS_2 50wt%.

All these inks based on 25%w/v Pluronic hydrogel exhibit shear-thinning behaviour with a yield point around 10^3 Pa and a linear relation in viscosity, storage modulus and yield point as active materials are added to the blend. All inks except the TiS_2 in 50%wt are rheologically stable under oscillatory pressures shown in Figure 18. TiS_2 50%wt has the highest storage modulus and viscosity under rest but is quickly dissipating this energy as exfoliated nanosheets are rearranged with the Pluronic amphiphilic triblocks and subsequently hydrolysed as the edges encounter water molecules. This behaviour can be also experimentally observed when stirring and dispensing this ink.

Other inks behaviour fit into the Herschel-Bulkley generalised description of non-Newtonian fluids as the stress experienced by the fluid is related to the applied strain non-linearly, as shown in Figure 19. Furthermore, the storage modulus, yield point and viscosity of 30%wt is among the highest in reported in literature. Therefore, these inks exhibit high stability, making them suitable for precise and continuous dispensing of active materials.

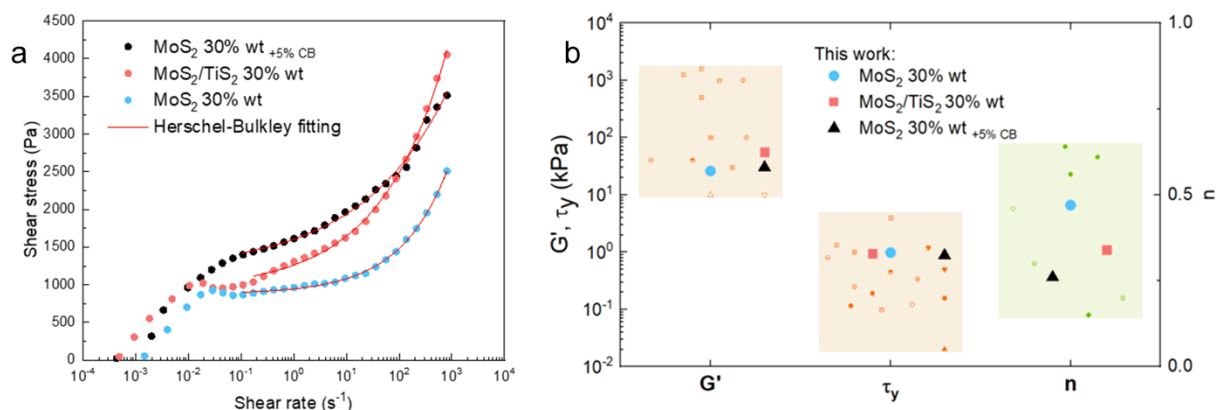


Figure 19 a) Shear Stress of the ink in response to the applied shear rate of MoS₂ 30%wt +5%wt Carbon Black, MoS₂ 30%wt and MoS₂/TiS₂ 30%wt. b) Storage Modulus (G'), Yield Point (τ_y) and flow index (n) of MoS₂ 30%wt +5%wt Carbon Black, MoS₂ 30%wt and MoS₂/TiS₂ 30%wt, compared to literature values^{14,15,154–164}.

However, it is notable that certain formulations such as TiS₂ 50%wt exhibit different characteristics. Despite having the highest storage modulus and viscosity under low oscillatory stresses, the ink quickly dissipates energy as exfoliated nanosheets are rearranged with the Pluronic amphiphilic triblocks and subsequently hydrolysed quite possibly as the electrocatalytically active edges encounter water molecules^{141,142}. This is evident in Figure 18, showcasing the unique rheological properties of each ink formulation.

All TMDs ink formulations were developed and tested using the described universal strategy, attempting to balance conductivity towards high performance metrics, and optimising the ratio between the catalytic activity of MoS₂ and the oxidation of TiS₂. This strategy ultimately demonstrates the significance of carefully selected ink formulations in producing high-performance, 3D printed EES devices.

The uniqueness of this scalable exfoliation of MoS₂/TiS₂ nanosheets relies on the non-hazardous and water-based amphiphilic properties of a thermoresponsive co-block polymer

(poloxamer). The latter enables the dispersion of the platelets and the achievement of high concentration ($>1 \text{ mg mL}^{-1}$) via steric and electrostatic stabilisation¹⁴². The resulting formulation is printable via continuous extrusion over three dimensions using a robocasting technique.

3.3 Raman characterisation of Pristine TMD inks

The intrinsic nature of TMD blends used in this work is characterised by Raman spectroscopy. Figure 20 presents the Raman profiles of three different inks - a $\text{MoS}_2/\text{TiS}_2$ blend, pure TiS_2 , and pure MoS_2 . The Raman spectra distinctly reveal the characteristic peaks associated with each of these materials, confirming their inherent presence within the respective printed and dried inks.

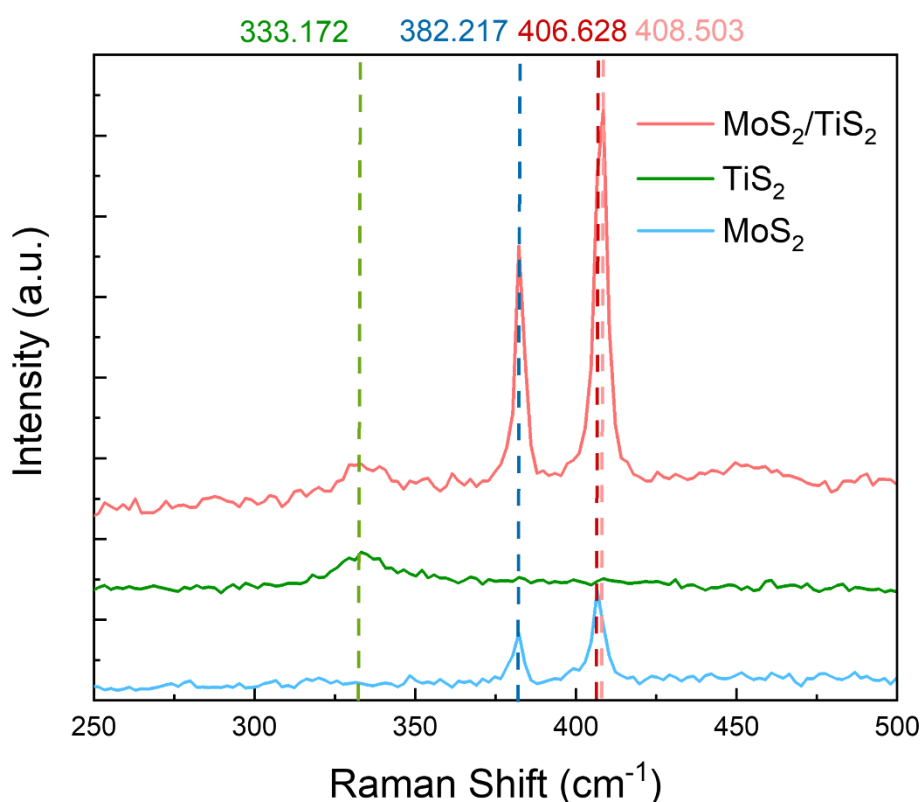


Figure 20 Raman profiles of three different inks. $\text{MoS}_2/\text{TiS}_2$ (red), TiS_2 (green) and MoS_2 (blue).

The red spectrum, representing the $\text{MoS}_2/\text{TiS}_2$ blend, shows combined peaks from both components, confirming the successful synthesis of the composite ink. Meanwhile, the green spectrum corresponds to pure TiS_2 , and the blue spectrum corresponds to pure MoS_2 . The Raman spectrum of MoS_2 consists of two modes, the E_{1g}^1 and the A_{1g} (at $\sim 383 \text{ cm}^{-1}$ and

$\sim 406\text{cm}^{-1}$ respectively) related to the in plane and out of plane vibrational modes. Both these spectra, when compared with the blend Raman profile, act as a testament to the unaltered, pristine nature of these TMDs in the blended ink. These findings underscore the successful incorporation of both MoS_2 and TiS_2 in the blended ink without altering their intrinsic properties.

3.4 Thermal annealing effect

Thermal annealing is a significant post-processing step in the realm of 3D printing in order to remove stagnant, electrochemically inactive components to improve electronic conductivity, isolate active material for study and characterisation. Its effectiveness hinges on a nuanced understanding of the material behaviour under varying heat levels, which can be explored through techniques like Differential Scanning Calorimetry (DSC).

To unravel the intricacies of the material thermal behaviour using DSC, one must consider the series of endothermic and exothermic reactions that occur at different temperatures. As observed from collected data in Figure 21, at temperatures above 80°C , an initial rise in the heat flow occurs as the water molecules bound in the polymeric parts are released in an endothermic reaction. Following that, at 95°C another endothermic reaction occurs which has been linked to phase conversion from the $1\text{T}'$ to the 2H^{165} phase. This conversion is speculated to occur due to the delithiation process from the interstitial lattices as delithiated $1\text{T}'$ species are not thermodynamically stable^{166,167}. Finally, a major exothermic reaction occurs at around 400°C , which is attributed to Pluronic f127 thermal degradation temperature¹⁶⁸.

After subsequent experiments, it was found that the optimum annealing temperature to ensure the effective removal of Pluronic and the exposure of conductive sheets was 470°C .

Figure 21 b) presents a high-resolution X-ray photoelectron spectrum of the molybdenum 3d region of an electrochemically cycled three-dimensional (3D) $\text{MoS}_2/\text{TiS}_2$ serpentine electrode. The spectral contributions of both 1T and 2H phase components within the MoS_2 's Mo 3d spectrum are illustrated by distinct blue and red curves, respectively. The figure reveals a prevalence of the 1T phase, in the as-printed material.

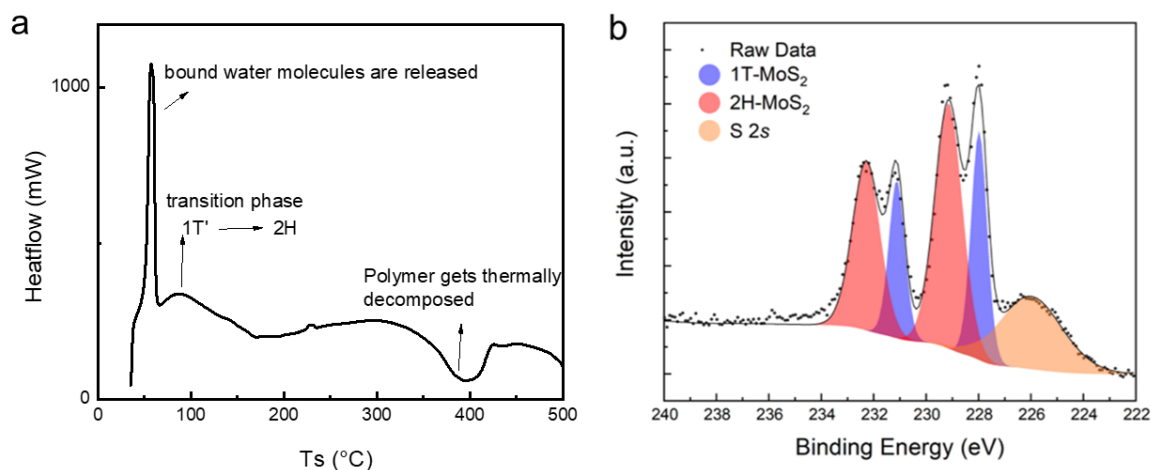


Figure 21 a) Differential Scanning Calorimetry (DSC) of MoS₂ 30%wt of as exfoliated ink. b) X-ray photoelectron spectrum from the Mo 3d region of an electrochemically cycled 3D MoS₂/TiS₂ serpentine electrode. Contributions from 1T and 2H phase components in the Mo 3d spectrum of MoS₂ are indicated by blue and red curves, respectively.

3.5 Topographical investigation of as spread MoS₂/TiS₂ nanosheet hydrogel inks and the impact of thermal annealing

Understanding the topography of as-spread MoS₂/TiS₂ nanosheet hydrogel inks can reveal vital insights into their structural characteristics and performance. The topographical characteristics of these nanosheet networks are primarily determined by the structural integrity of the nanoflakes and the percolating network they form.

These percolating networks composed of MoS₂ or MoS₂/TiS₂ nanosheets suspended in hydrogel environments constitute a crucial part of this investigation. Through Scanning Electron Microscopy (SEM) analysis (Figure 22), a complex and interconnected network of exfoliated flakes that form the electrodes, can be observed. These nanosheet hydrogel inks appear as an intricate lattice, formed by nanoflakes with lateral sizes ranging from 300nm to 1 micron.

Furthermore, a close look at the cross-sectional SEM imaging (Figure 22) reveals how the thermal annealing process, applied post-printing, impacts the nanostructure of the electrodes. This process aims to eliminate the Pluronic polymer (poloxamer), consequently the flake-like structure of the printed electrodes is visible.

This process also brings into focus the voids that were previously occupied by the polymer, potentially creating electrolyte-accessible spaces in the assembled device. These voids are essential to consider, as they may contribute to the overall performance of the material in its respective application.

This investigation shows the importance of meticulous SEM analysis in understanding the morphology of as-spread $\text{MoS}_2/\text{TiS}_2$ nanosheet hydrogel inks.

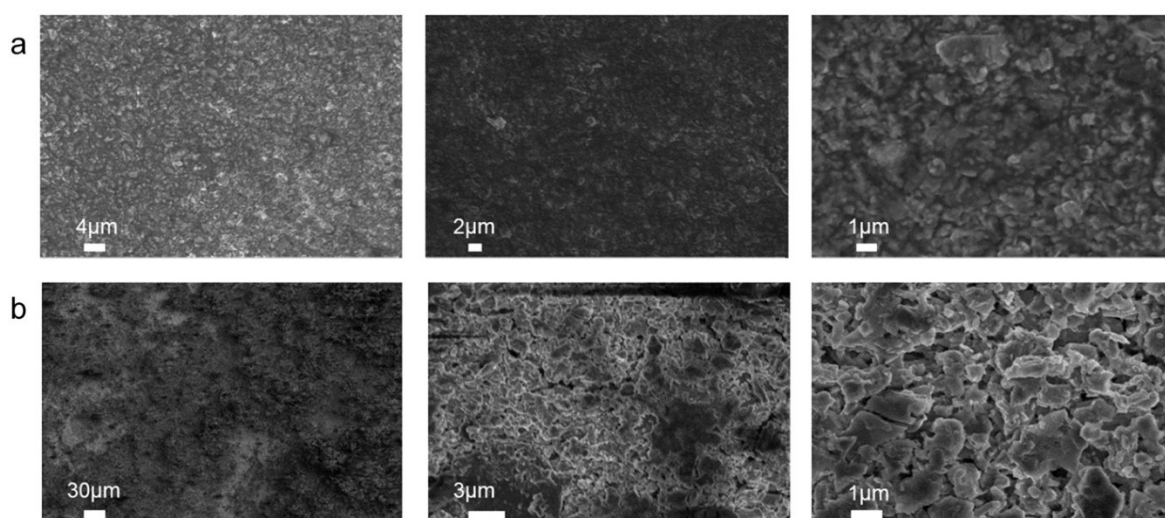


Figure 22 a) SEM images of $\text{MoS}_2/\text{TiS}_2$ 50%wt thin films as spread and b) annealed at 470°C .

3.6 Transmission Electron Microscopy of isolated few-layered $\text{MoS}_2/\text{TiS}_2$ sheets

Transmission Electron Microscopy (TEM) is an invaluable tool for examining the details of exfoliated inks. The technique is crucial in observing the exfoliated nanosheets after polymeric compounds are washed away, quite literally rinsed with DI water, allowing these flakes to be isolated on TEM grids. TEM imaging revealed the presence of both single and few-layered nanosheets. It is important to note, TiS_2 has an inherent semimetallic 1T phase throughout, while MoS_2 exhibited both 1T' and 2H phases.

Figure 23 reports a Selected Area Electron Diffraction (SAED) pattern (a) and its respective analysis (b). The SAED pattern showcases two superimposed 2×2 lattices of individual 1T' MoS_2 domains rotated by 120 degrees. These domains form the superstructure observed in

the diffraction patterns of exfoliated few-layer MoS₂. The formation of this superstructure is shown in greater detail in panel c.

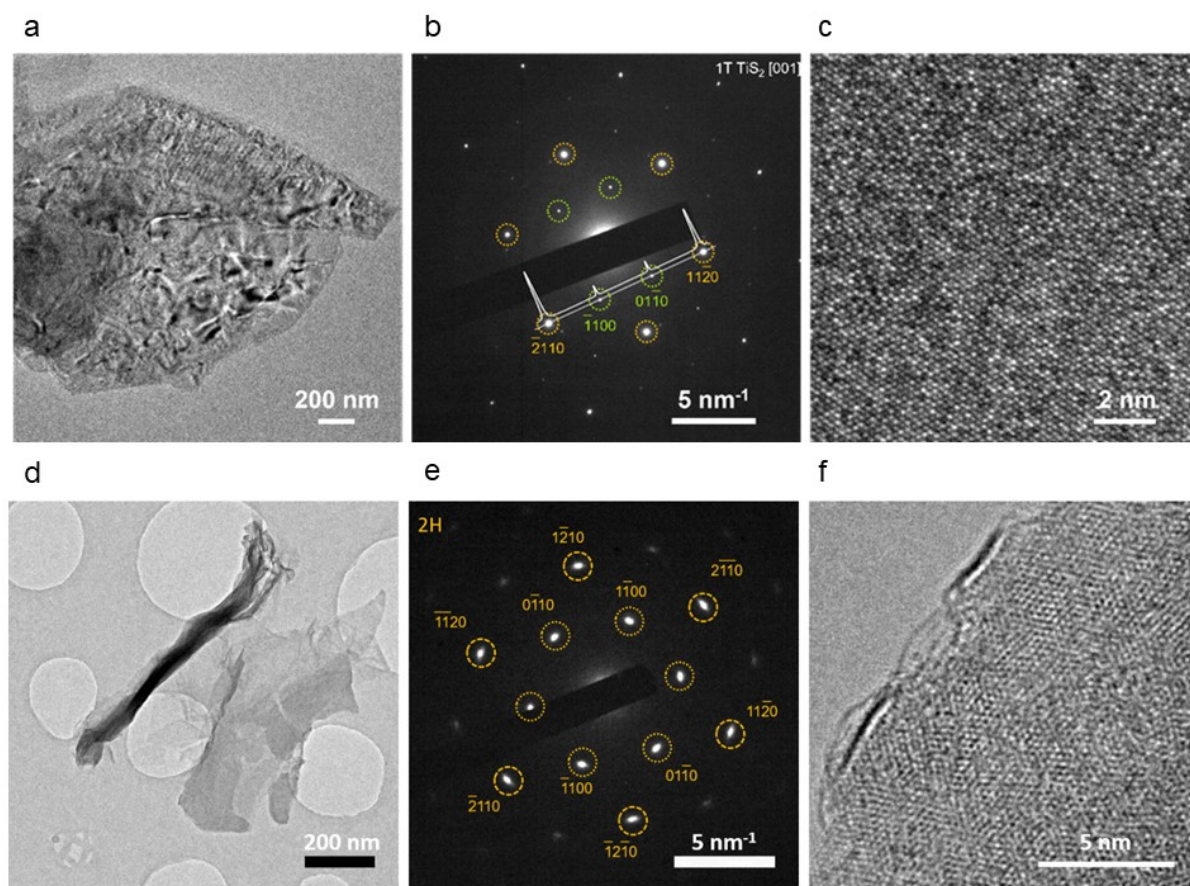


Figure 23 - Low-magnification TEM(a), SAED patterns (b) and high-resolution TEM image(c) of exfoliated TiS₂ nanosheets (top). The intensity profile in SAED pattern in panel b demonstrates the relative intensities of {100} and {110} diffraction spots characteristic to the 1T crystal phase of TiS₂. Bottom: Low-magnification TEM, SAED patterns for 2H and high-resolution TEM image of exfoliated few-layered MoS₂ nanosheets.

The zigzag chains of Mo atoms cause a period doubling along the b-axis, resulting in 2axa diffraction spots arrays in diffraction patterns of pristine 1T' phase domains. In accordance with selection rules, only the {0k0} spots, where k is odd, are allowed in the P21/m 1T' MoS₂ crystals. This leads to the systematic absences observed in panel c in diffraction patterns along the [001] ZA of pristine 1T' MoS₂, aligning well with the experimental observations (Figure 23 panel d).

Bright field TEM imaging presents atomically thin flakes of exfoliated MoS₂ and TiS₂, boasting lateral sizes over 1 micron. Close examination of these exfoliated flakes reveals the presence of single-layered flakes and few-layered flakes, hinting at the versatile composition of these

inks. Despite the stabilisation offered by Pluronic, the material layers could partially restack, as evidenced by the overlapping lattices.

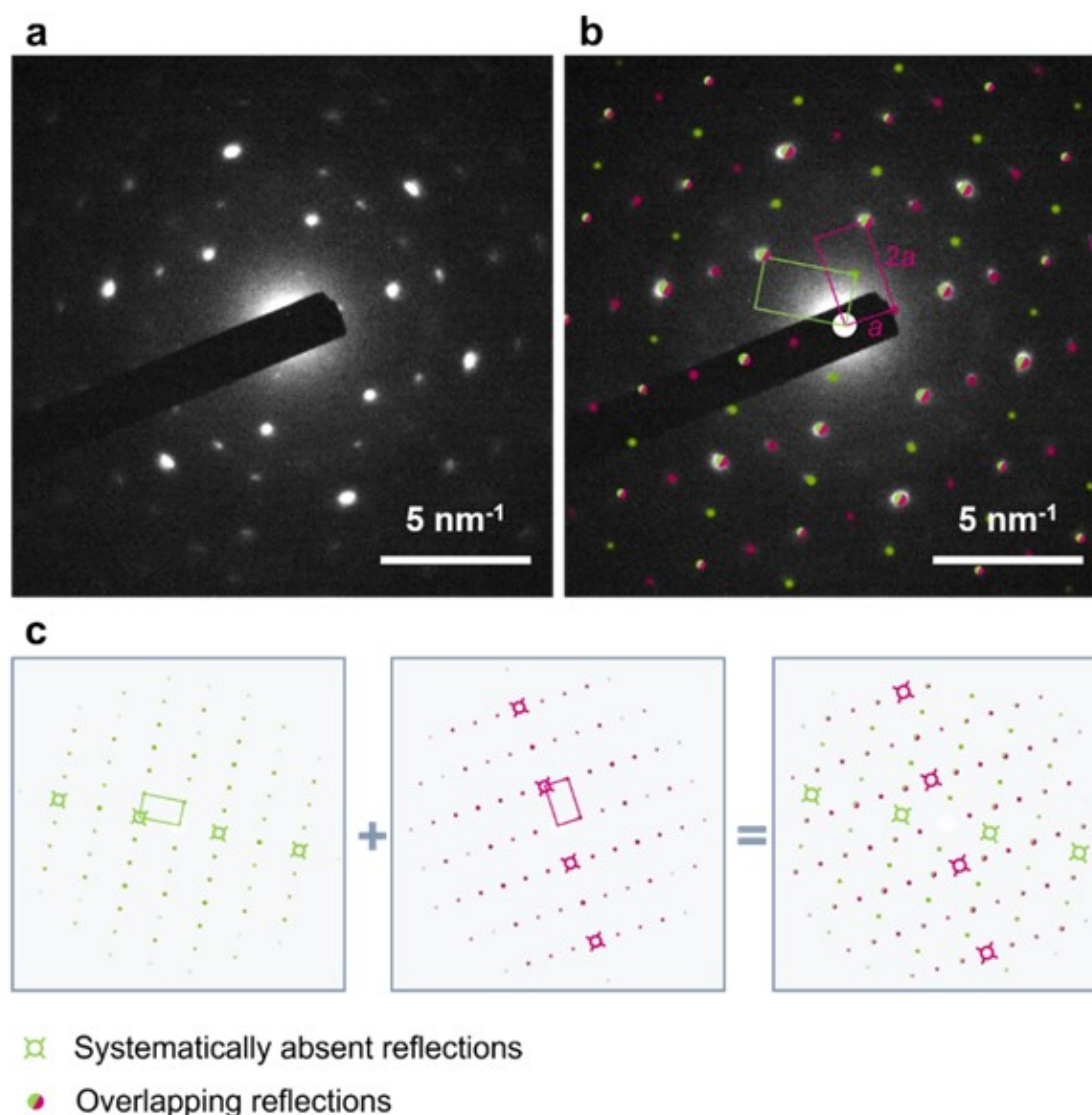


Figure 24 - A representative experimental SAED pattern (a) and the respective analysis (b) illustrating two superimposed $2a \times a$ lattices of individual $1T'$ MoS_2 domains rotated by 120° that form the superstructure seen in the diffraction patterns of exfoliated few-layer MoS_2 . The superstructure formation is shown in detail in panel c. The presence of characteristic zigzag chains of Mo atoms causes the period doubling along the b axis, that results in $2a \times a$ diffraction spots arrays in diffraction patterns of pristine $1T'$ phase domains. According to the selection rules, only the $\{0k0\}$ where k is odd are allowed in the $P21/m$ $1T'$ MoS_2 crystals. This leads to the systematic absences shown in panel c in diffraction patterns along the $[001]$ ZA of pristine $1T'$ MoS_2 and in good agreement with the experimental observations (panel a). In contrast, the ordering of entrapped Li^+ cations in either $2H$ or $1T$ MoS_2 crystals is reported to manifest as uniform $2a \times 2a$ superlattices^{169,170} that are not found in experimental SAED patterns of exfoliated MoS_2 . This supports the interpretation that the superstructure observed in the

experimental SAED of exfoliated few-layer MoS₂ originates from “twins” of 1T’ MoS₂ single layers rotated by 120°.

These patterns stem from the angular rotation of restacked single layers, providing an intriguing topographical element to the structure. Upon lithiation and exfoliation in Pluronic, TiS₂ retains the 1T crystal phase of the bulk counterpart, as confirmed by the relative intensities of the {100} and {110} diffraction spots in the respective SAED patterns.

Conversely, MoS₂ undergoes a 2H to 1T’ crystal phase conversion upon Li intercalation, and primarily the 1T’ phase is preserved in the resulting inks. The superstructures of two overlapped 2x2 lattices rotated by 120 degrees often appear in the SAED patterns of few-layered MoS₂ flakes. These 2x2 lattices arise from the zigzag distortion in the transition metal plane that is characteristic of the distorted 1T MoS₂ crystals (1T’). The observed superstructures likely originate from the “twins” of two individual 1T single crystals, rather than by the intercalated Li residues.

It is important to note that although it is likely that trapped Li cations are present in the few-layered exfoliated MoS₂ flakes, the observed superstructures in SAED shown in Figure 24 cannot be caused by the cation ordering. This assertion is evidenced by the systematic absence of a set of diffraction spots, further validating the presence of the 1T’ crystal phase of MoS₂. The conversion of the single layers of MoS₂ back into the 2H crystal phase can be caused by the loss of Li cations, aligning with previous research. Conversely, when trapped in the van der Waals (vdW) gaps of few-layered flakes, the alkali metal cations preserve the metastable 1T’ phase. Further information about these lithiated species are given below in ToF-SIMS results.

3.7 Time of Flight- Secondary Ion Mass Spectrometry of as printed and annealed extruded 3D filaments

The Time of Flight - Secondary Ion Mass Spectrometry (ToF-SIMS), a powerful and versatile technique renowned for its ultra-high sensitivity and high spatial resolution, plays a pivotal role in the analysis of as printed and annealed extruded 3D filaments.

Topographic reconstructions of $\text{MoS}_2/\text{TiS}_2/\text{LiMoS}_2/\text{LiTiS}_2$ species on the surface of extruded 3D filaments are demonstrated in Figure 25, from a top-down perspective (first four images on the left). The middle two images illustrate the depth profiling of MoS_2 (blue), Li-MoS_2 (turquoise), TiS_2 (red) and Li-TiS_2 (fuchsia) species present in as-printed and thermally annealed extruded 3D filaments. The image to the far right offers a 3D rendered species overlay topographic reconstruction of a 40x40x40 microns area in an as-printed serpentine structure, highlighting MoS_2 (blue) Li-MoS_2 (turquoise), TiS_2 (red) and Li-TiS_2 (fuchsia).

A critical observation from the ToF-SIMS data is that both as-printed and annealed electrodes feature a homogeneous distribution of both TMD variants, present in aligned patterns. Oxidation is restricted within the first hundred nanometres, with lithiation observed in the TMD lattices, forming species with a different mass than the delithiated species. A thermal annealing process results in a decrease in the percentage of Lithiated species.

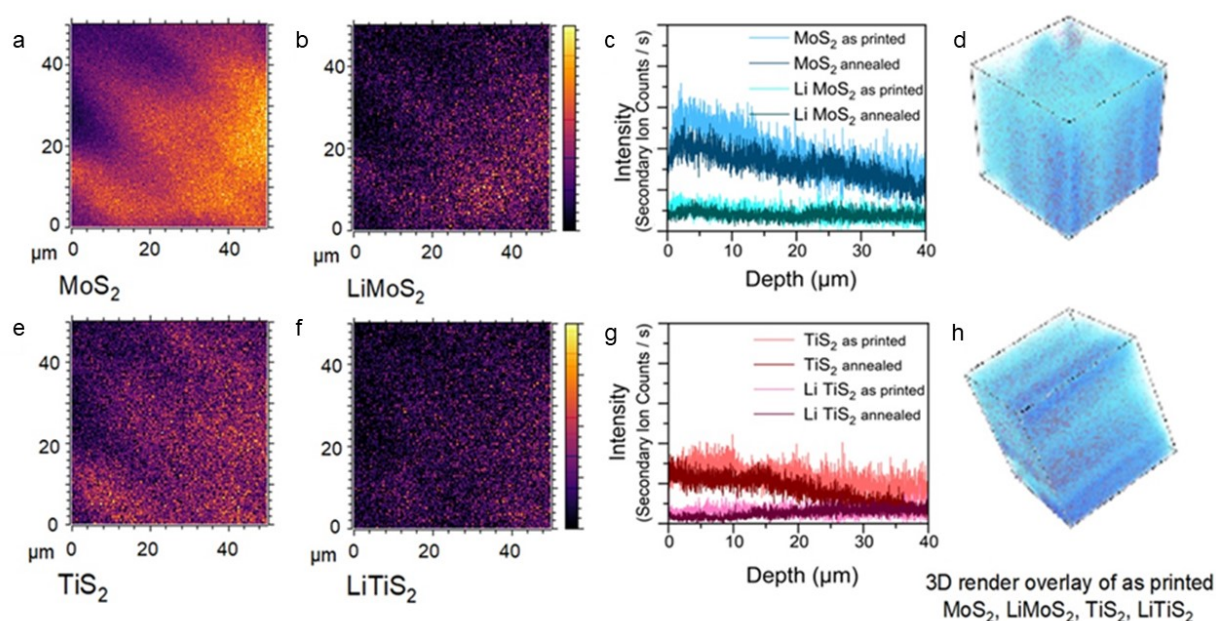


Figure 25 ToF-SIMS topographic reconstructions of $\text{MoS}_2/\text{TiS}_2/\text{LiMoS}_2/\text{LiTiS}_2$ species on the surface of extruded 3D filaments from the top (left 4). Depth profiling of MoS_2 (blue), Li-MoS_2 (turquoise), TiS_2 (red) and Li-TiS_2 (fuchsia) species present in an as printed and thermally annealed extruded 3D filaments middle 2) 40x40x40 microns 3D rendered species overlay topographic reconstruction in as printed serpentine structure. MoS_2 (blue) Li-MoS_2 (turquoise), TiS_2 (red) and Li-TiS_2 (fuchsia).

In addition, ToF-SIMS characterisation has unveiled a homogeneous distribution of MoS_2 and TiS_2 flakes within a 40x40x40 microns volume of the as-printed serpentine structure (Figure 25 g-n). Oxidation appears to be limited to the top layer of the 3D printed structures (Figure

25 i and m), equally impacting MoS₂ and TiS₂. It is interesting to note the presence of lithiated MoS₂ and TiS₂ along with their pristine counterparts, with their signals overlapping Figure 25g,h,k,l). The intercalation of Li species appears to sustain the preservation of the 1T' phase of MoS₂, crucial for achieving good electrical conductivity. This hypothesis is supported by the observed decrease in secondary ion yields after annealing, indicating a reduction in lithiated species (Figure 25i,m).

The ToF-SIMS data not only confirms the persistence of lithiated MoS₂ and TiS₂ species even after hydrolysis (Figure 25g,h,k,l) but also provides compelling evidence of Li potential role in preserving the 1T' phase of MoS₂ – a crucial determinant of good electrical conductivity.

When examining the thermal properties of the 3D printed structures, the ToF-SIMS data provides insights into how the annealing process influences the lithiation and delithiation processes (Figure 25i,m). Specifically, an observation of a decrease in lithiated species after annealing, suggesting a link between thermal annealing and phase conversion.

Interestingly, ToF-SIMS data collected from as printed versus annealed electrodes detect that a homogeneous distribution of both TMD variants are present in aligned patterns, oxidation is limited in the first hundred nanometres, there is lithiation in the TMD lattices forming species with different mass than the delithiated species, percentage of Lithiated species decrease under thermal annealing. These are very important findings, as they cement previous studies that link thermal delithiation with phase conversion¹⁶⁷.

Conclusions

This Chapter delves into the nature of the formulated inks. Rheological behaviour is paramount in ensuring smooth and precise dispensing of inks, mirroring the corresponding .cad file to achieve industrial standards and dispensing efficiency.

The rheological properties of Pluronic F127 hydrogel were thoroughly examined, focusing on different weight/volume concentrations (21-30% w/v) at varying temperatures (25°C, 35°C, and 45°C). The study highlights the hydrogel yield points and temperature sensitivity. Data showed optimal gelation and viscosity at temperatures above 25°C, facilitating continuous extrusion. A 25% w/v concentration at 25°C was found to be optimal for precision dispensing and patterning, combining the best yield point to oscillation stress ratio. Higher yield points

correlate with better shape retention post-printing, demonstrating the importance of tailored rheological properties for successful printing of mechanically stable 3D structures. DSC analysis indicated the release of water molecules at around 70°C, followed by a phase transition from 1T' to 2H in MoS₂ that fits observations from previous studies. At around 350°C, the polymer gets decomposed, reaching a maximum decomposition of 400°C. Beyond that, we observed both 2H and 1T' phases in MoS₂ inks with XPS.

TEM analysis has unveiled that both single-layered and few-layered nanosheets of MoS₂ and TiS₂ exist within the exfoliated inks, as these could restack after rearrangement. These nanosheets exhibit different phase compositions, with TiS₂ retaining the 1T phase of the bulk counterpart while MoS₂ undergoing a 2H to 1T' crystal phase conversion upon Li intercalation. The persistence of this 1T' phase in the resulting inks is likely due to the entrapment of alkali metal cations within the van der Waals (vdW) gaps of the few-layered flakes. Moreover, the appearance of superstructures within the exfoliated MoS₂ flakes' Selected Area Electron Diffraction (SAED) patterns can be attributed to "twins" of 1T' MoS₂ single layers, rather than the presence of intercalated Li residues, as the TEM samples were thoroughly washed with DI and individual flakes isolated. This observation, validated by the systematic absence of a certain set of diffraction spots, emphasises the role of TEM in identifying complex microstructural details within exfoliated two-dimensional material inks.

Complementing the TEM analysis, ToF-SIMS investigations confirm the presence of lithiated MoS₂ and TiS₂ species, even after hydrolysis, was a remarkable finding, pointing to the inherent resilience of Li within the TMD lattices. This fact, in tandem with the overlapping signals of these lithiated species with their pristine counterparts, supports the hypothesis of Li playing a potential role in preserving the 1T' phase of MoS₂, a key to achieving good electrochemical performance. The ToF-SIMS data also brought to light the effects of thermal annealing on the lithiation and delithiation processes. A decrease in lithiated species after annealing points to a link between thermal annealing, and delithiation leading to phase conversion, enriching the understanding of the complex interplay between thermal processes and structural transformations in these materials. These investigations underscore the importance of integrated analytical approaches to elucidate the complex processes underpinning Li-intercalation, phase conversion, and thermal annealing.

Chapter 4: 3D printing of TMD inks towards high performance supercapacitors

Introduction

This study focuses on 3D printing with inks derived from transition metal dichalcogenides (TMDs), particularly MoS₂ and TiS₂, highlighting experimental design, choice of architectures, and optimisation through COMSOL Multiphysics simulations. The link between the 3D architecture of printed TMDs and their performance is emphasized, with particular attention to porosity and its impact on ionic tortuosity.

The relationship between printed architecture and performance is examined in detail, demonstrating that 3D design is crucial for the functional attributes of the final product, not just aesthetics. Various architectures were designed to showcase the flexibility of 3D printing, but three specific designs were evaluated for their superior performance metrics in supercapacitors. These are the woodpile, serpentine and interdigitated electrodes.

4.1 Multiphysics modelling of the thickness effect in a serpentine electrode

In the pursuit to substantiate the observed experimental outcomes of electrochemical performance in 3D printed serpentine electrodes, particularly focusing on the role of the electrode thickness, a Multiphysics modelling exercise was undertaken. COMSOL Multiphysics, a software that enables the simulation of multiple interacting physical phenomena, was used to model the behaviour, and estimate the capacitance of a 3D serpentine electrode, precisely fabricated from copper, in a 1M H₂SO₄. The response of capacitance to variations in electrode thickness for these 3D copper electrodes is detailed in Figure 26. A close inspection of the results portrayed in Figure 26, where the calculated capacitance is plotted against the increasing thickness of the electrode layers, reveals a striking resemblance in trend with the experimental data. The similar slopes observed

validate the impact of increased thickness on the enhancement of the capacitance in the 3D printed electrodes.

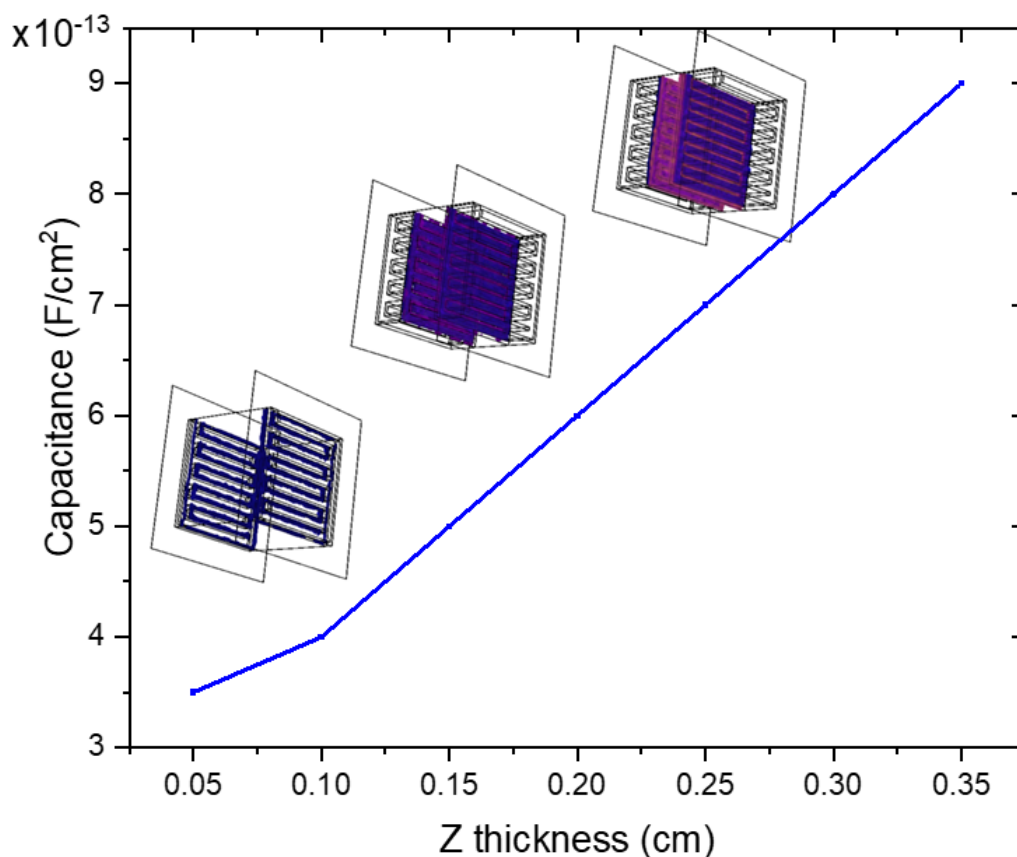


Figure 26- Capacitance in response to electrode thickness in 1x1cm 3D copper electrodes, as calculated and visualised in COMSOL® Multiphysics.

4.2 3D printing of TMD ink architectures

The general formulation strategy developed in this work, aimed to optimise the highest proportion of semimetallic nanosheets in the final electrode. The rheological characteristics of all formulations were assessed and deemed appropriate for 3D printing a variety of structures. Among these, the 50%wt MoS₂/TiS₂ blends performed optimally, enabling continuous syringe dispensing without nozzle clogging, the highest storage modulus, an excellent yield point, and impressive shape retention without buckling or sulking of the

printed structure. As a result, a diverse range of architectures was successfully printed with this ink, as illustrated in Figure 27.

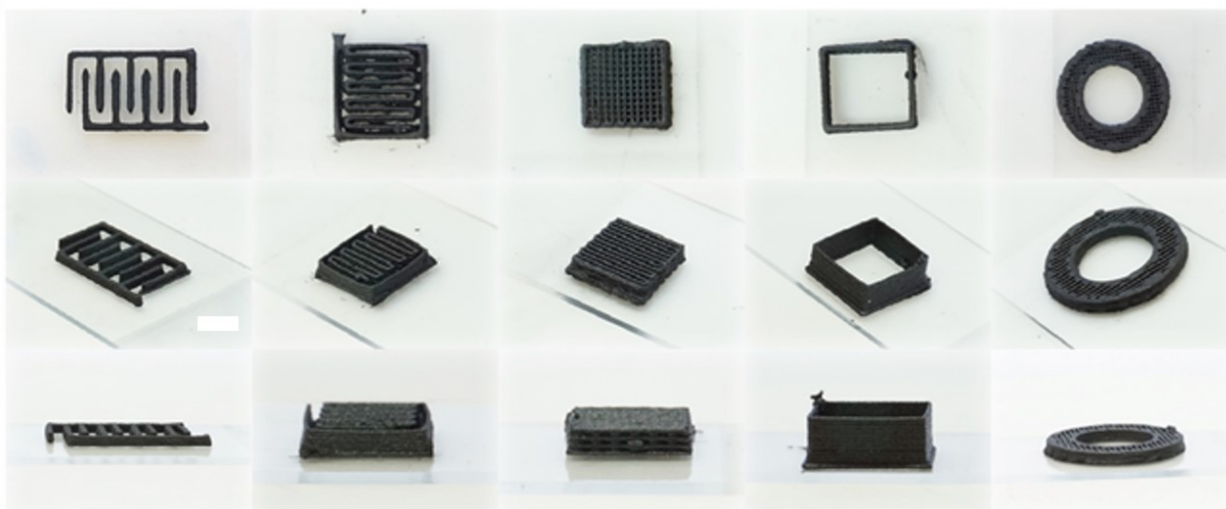


Figure 27 Various 3D printed architectures using 1T'/1T MoS₂/TiS₂ 50%wt inks printed with a 410 microns nozzle on glass slides. From left to right: interdigitated electrode(1x2cm), serpentine electrode(1x1cm), woodpile electrode(1x1cm), rectangle with unsupported high-aspect ratio walls(1x1cm), circular structure with a grid-like design(2x2cm) scale bar 0.5cm.

The architectures successfully printed were interdigitated, serpentine, woodpile, rectangular with unsupported high-aspect ratio walls and circular grid formation electrodes. Interdigitated is a planar micro-supercapacitor design which explores the addition of layers parallel to the previous layer. The structure exhibits excellent morphology and shape retention, demonstrating the efficacy of the formulated 1T'/1T MoS₂/TiS₂ inks. Serpentine electrodes were designed to maximise the surface area in contact with the current electrode. This out-of-plane supercapacitor design introduces both surface and bulk ion diffusion points. Its structure aids in maintaining a high surface area in contact with the electrolyte, despite only one side of the top layer not coming directly in contact with the electrolyte. This design also requires less ink loading compared to the Woodpile electrode, as assessed from 1x1cm 10layer electrode. Woodpile Electrodes, which are frequently 3D printed in the literature as out-of-plane supercapacitor electrodes. This architecture, with the weight of added layers distributed over many contact points, is easy to print and crucial for benchmarking accurate performance metrics. However, compared to the serpentine electrode, this design requires more ink, as assessed from a 1x1cm 10layered electrode. Rectangular Electrodes with unsupported high-aspect ratio walls, showcasing the excellent shape retention of the printed electrodes, this design attests to the high storage modulus and adequate viscosity of the

resting inks. Circular Electrodes with Grid Formation, printed to demonstrate the versatility of the ink formulation strategy, these structures combined circular and grid-like formations, reflecting high-quality printing resolution.

4.3 MoS₂/TiS₂ Inks for 3D printing high-performance supercapacitors

The MoS₂/TiS₂ 50%wt ink demonstrates exceptional performance attributes that render it suitable for 3D printing of high-performance supercapacitors. As Figure 28 illustrates, this ink, upon thorough homogenisation, exhibits an ideal consistency, as can be observed when it is scraped with a metal spatula. This rheological behaviour aligns with the optimal characteristics for 3D printable inks detailed in the introduction of this thesis.

When loaded into a syringe, fitted with a 410 microns nozzle and plunged through to extrude, the ink has a transition from a liquid-like to a solid-like behaviour, driven by surface tension forces. This property is a testament to the ink shear-thinning behaviour, an attribute that is critical in facilitating the precise extrusion and deposition of the ink during the 3D printing process.

The suitability of this ink formulation is further reinforced when used to print a 10-layer serpentine structure on a carbon foil substrate. The printed structure, as seen in the bottom right image of Figure 28, retains its shape without collapsing which is an indication that the ink has a good shape retention capacity post-extrusion.

The combination of these attributes—rheological suitability, shear-thinning behaviour, shape retention post-extrusion, and thermal stability—make the MoS₂/TiS₂ 50%wt ink an ideal candidate for 3D printing of high-performance supercapacitors. These qualities not only adhere to the theoretical framework established in this thesis but also open new avenues for further exploration and development in the field of 3D printed supercapacitors.

For the purposes of this work, two designs were chosen to assemble symmetric supercapacitor devices towards high performance metrics. These were in-plane supercapacitors and out-of-plane supercapacitors.

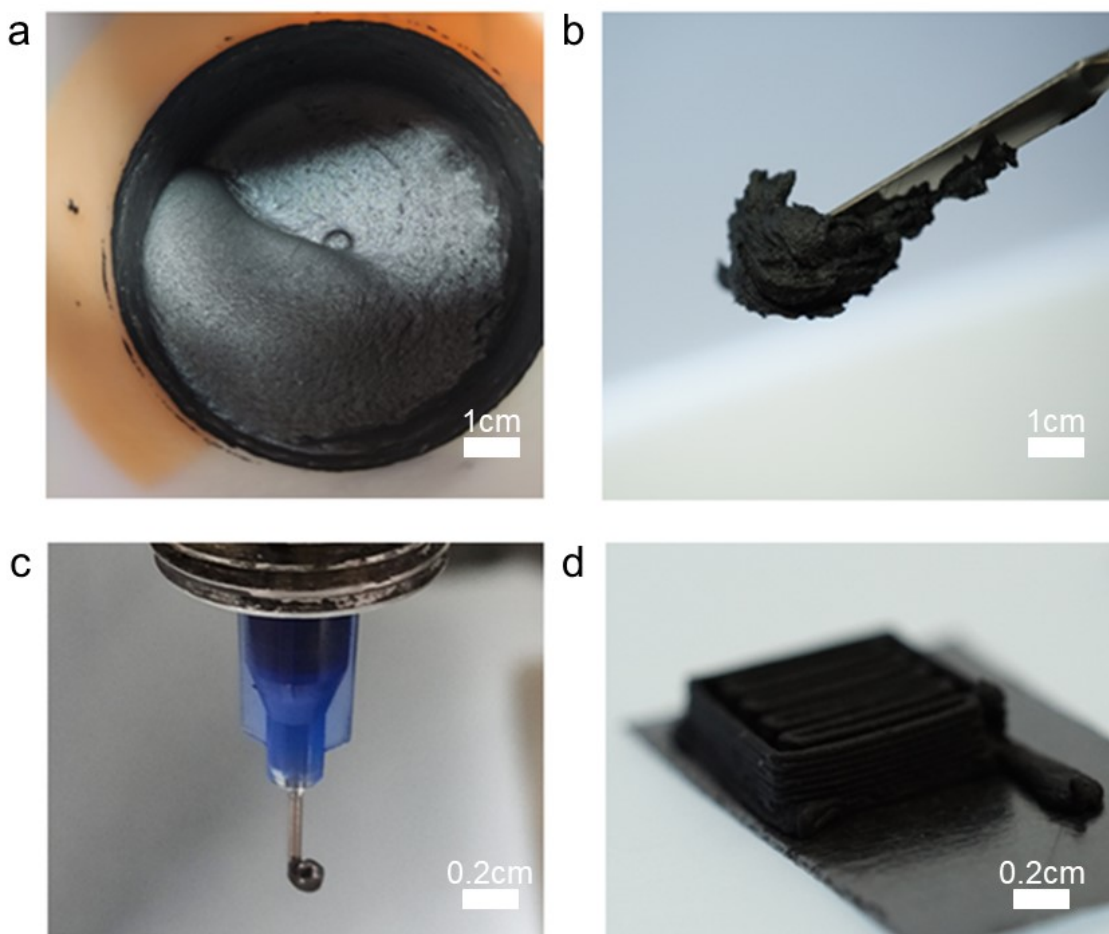


Figure 28 a) $\text{MoS}_2/\text{TiS}_2$ 50%wt ink after homogenisation b) as scraped with a metal spatula c) loaded into the syringe and ready to print with a 410 microns nozzle (- surface tension forces the ink outside while it shifts from liquid-like behaviour to solid-like behaviour) and d) 10layered serpentine structure printed on a carbon foil substrate.

4.3.1 Out-of-plane supercapacitors

For out-of-plane supercapacitors, symmetric two-electrode devices based on woodpile and serpentine electrodes were printed on carbon foil sheets and then cut into 2x1cm rectangles. 1x1 cm for a bare carbon foil to be clipped and 1x1cm of the wetted electrode area.

The average active material mass loadings and volumetric areas for electrodes electrochemically tested were experimentally measured and the averages given in the table below.

Table 4 Average active material mass loadings and volumetric areas for each electrode tested.

Layers	Serpentine Mass Loading (g)	Serpentine Volumetric Area (cm ³)	Woodpile Mass Loading (g)	Woodpile Volumetric Area (cm ³)
2	0.035	1x1x0.05	0.035	1x1x0.06
4	0.050	1x1x0.1	0.06	1x1x0.012
6	0.060	1x1x0.15	0.075	1x1x0.18
10	0.090	1x1x0.25	0.105	1x1x0.3
Thin Film	0.013 g	1x1x0.004		

4.3.2 Surface area approximation through the .stl file

Beyond the net volume area of the printed electrodes (1x1) it would be worthwhile to normalise to the approximate surface area of the wetted electrode with the electrolyte. This can be done in two ways. First is going to the .stl file and measure the surface area of the extruded filaments considering that all the filament is the actual electrode. With this method, the 10layered Serpentine .stl design measured at 158.51 cubic meters of volume with a surface area of 1548.40 square millimetres and the 10layered Woodpile .stl design measured at 184.70 cubic milli meters with a surface area of 1803.97 cubic millimetres.

4.3.3 Surface area approximation and 3D architecture morphology investigation with XCT

The second way to approximate the surface area of the 3D electrodes as opposed to the 3D design is through profiling the actual printed electrodes. One non-destructive method to do that is X-Ray Computed Tomography. With this method, 2D slices of X-ray images are collected and then reconstructed in 3D. With this technique, very accurate representations of the morphology of these slices are collected and then the light electrode areas with the dark void areas are segmented. By segmenting the image contrasts, a very accurate representation of the 3D morphology can be stripped to reveal internal features. Figure 29 demonstrates this on a 10layered serpentine electrode and a 10layered Woodpile electrode.

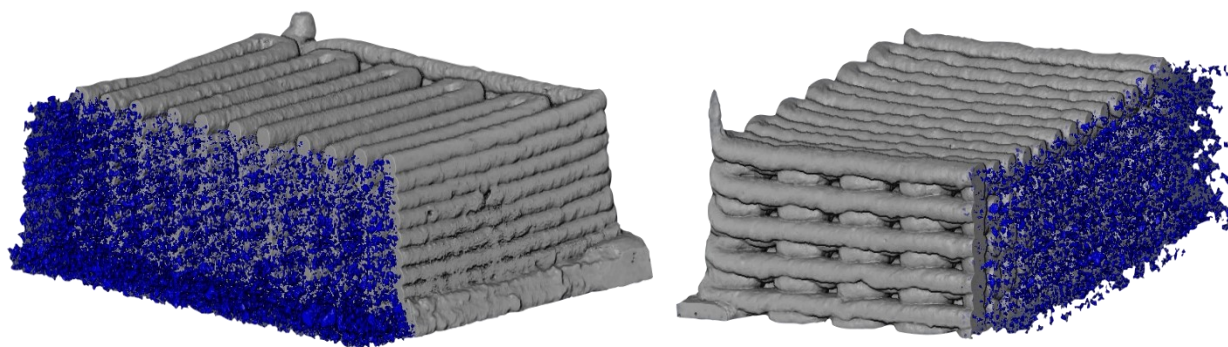


Figure 29 X-Ray Computed tomographic reconstructions and porosity estimations via image segmentation on 10x10 mm 10 layered Serpentine (left) and 10x10 mm 10 layered Woodpile structures (right).

From these reconstructions it is evident, that the regularity of the extruded filaments is retained with no significant deformations. It is also noteworthy, that while Serpentine electrode has less mass, the nature of the shape is ordering the printed layers parallel with multi-layer bulk-diffusion spots. Woodpile electrode on the other hand is ordering diffusion spots perpendicular to the printed orientation resulting in only 1-layer bulk diffusion spots.

Future operando measurements could shed light into the diffusion of the solvated ions in the structure. This phenomenon has been described in the literature as ‘layer-breathing mode’^{171,172}.

Through this work, we determined that for out-of-plane supercapacitors, namely woodpile and serpentine electrodes printed on carbon foil, has provided the most promising metrics. These structures were produced, with great flexibility in terms of architectures and printed layers. Figure 30 shows serpentine electrodes with excellent shape retention even for 10-20 layers, indicating the feasibility of such methods for mass production. Furthermore, we discovered a correlation between the increase in the number of layers and the mass loading of active material, revealing a critical factor in enhancing the performance of the supercapacitors.

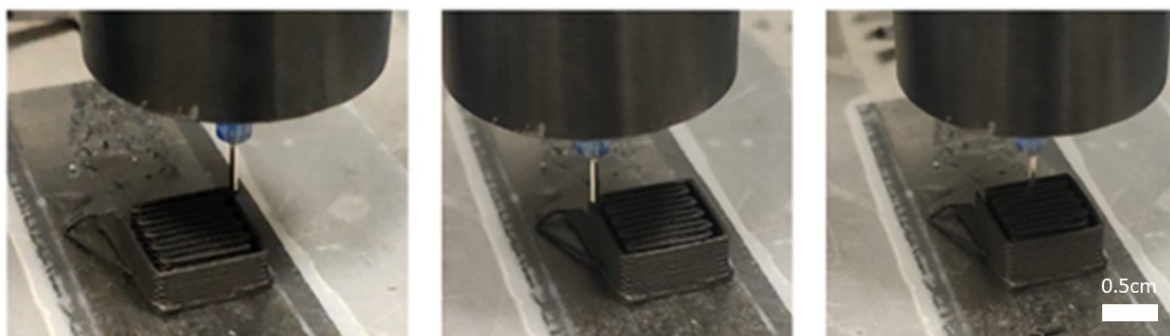


Figure 30 Layer-by-layer deposition of MoS₂/TiS₂ 50%wt ink in a serpentine architecture with a 410 microns nozzle up to 30 layers(stills from a video, taken at 30 second intervals).

Surface area approximation was another key aspect of this study, approached through two different methodologies: extraction from the .stl file and X-ray Computed Tomography (XCT). The former technique offered a preliminary approximation, while XCT provided a more sophisticated, non-destructive method to profile the printed electrodes and accurately discern the internal features of their 3D morphology. This investigative approach allowed us to observe the retention of regularity in the extruded filaments, with no significant deformations noted.

Upon comparing the serpentine and woodpile architectures, we observed that despite the lower mass, the serpentine electrode design facilitates parallel ordering of printed layers and multi-layer bulk-diffusion spots. In contrast, the woodpile electrode enables diffusion spots to align perpendicular to the printing orientation, leading to single-layer bulk diffusion spots. This difference in layer orientations and the resulting diffusion behaviours offers valuable insight into optimising 3D printed electrode designs.

4.3.4 In-plane supercapacitors

In the exploration of high-performance supercapacitors, this study also ventured into the realm of in-plane supercapacitors, with a specific emphasis on an interdigitated design. These printed structures performance was also evaluated. This evaluation process served as an

empirical assessment to understand the performance capabilities of this interdigitated design in a supercapacitor context.

4.4 Versatile resolution inks with universal formulations of 30%wt MoS₂ Inks

Here, the adaptability of the ink formulation with respect to diverse printable resolutions is explored. The focus is on a universal strategy that allows for effective 3D printing at varying resolutions. In line with this, 30%wt MoS₂ inks were experimentally found to be a beneficial formulation. The lowered material concentration in these inks offered an optimal dispensation across finer nozzles, allowing for resolution versatility. For this study, nozzles of 410, 250, and 100 microns were employed to 3D print serpentine electrodes, adjusting .stl files to correspond to the respective nozzle diameters. As illustrated in Figure 31, the 30% MoS₂ inks proved efficacious in printing serpentine structures at all examined resolutions.

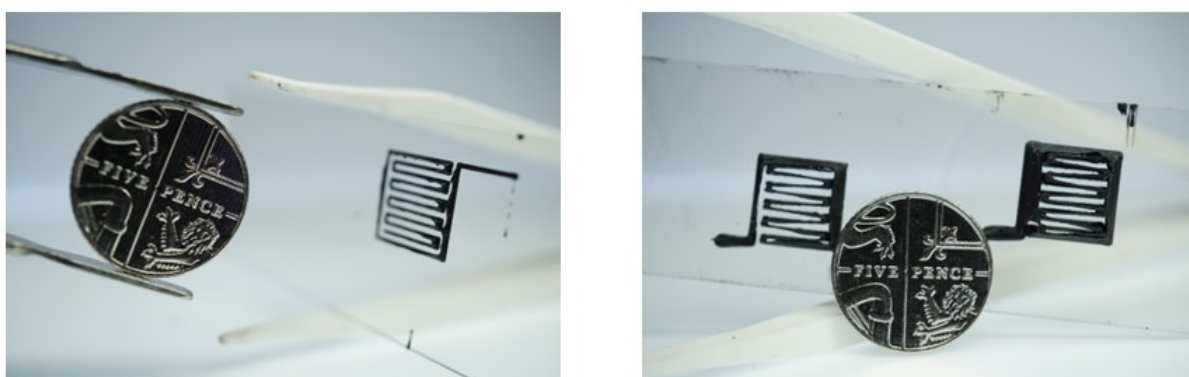


Figure 31. MoS₂ 30%wt printed serpentine structures with 100(left), 250(middle) and 410(right) microns nozzles on ITO-Glass substrates. British five pence coin for scale.

This formulation versatility carries a significant advantage for mass-producing devices, as it minimises the reconditioning times required when dealing with .stl files comprising varying resolution components.

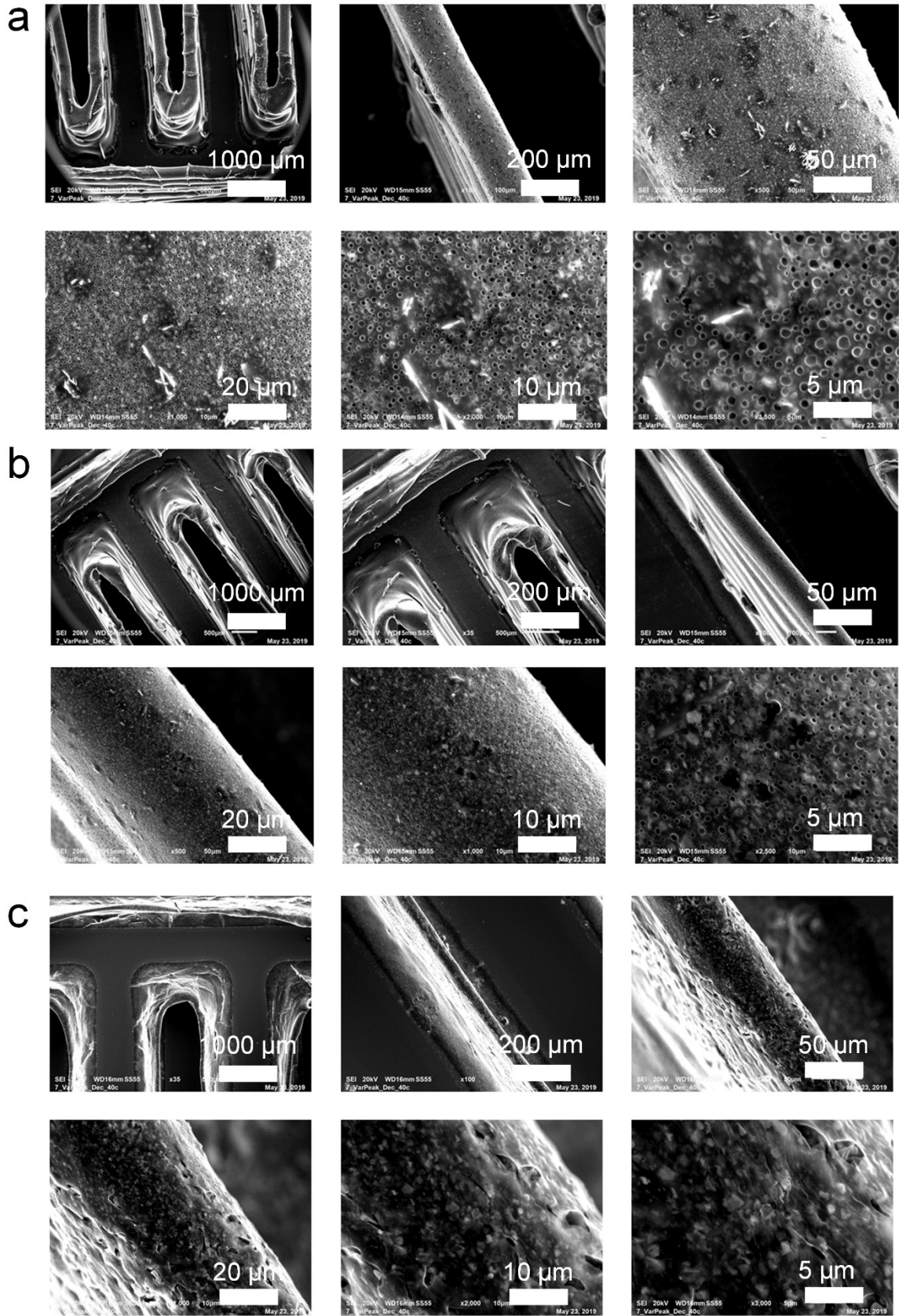


Figure 32 SEM images of MoS_2 30%wt inks using a) 410 microns nozzle (Nordson EFD blue), b) 250 microns nozzle (Nordson EFD red) and c) 100 microns nozzle (Nordson EFD yellow).

By excluding TiS_2 from the formulation, the MoS_2 ink exhibited reduced thixotropy, further facilitating the printing process across finer nozzles. However, the reduction in nozzle diameter posed certain challenges such as increased extrusion pressure and a higher likelihood of nozzle clogging due to larger agglomerates. Despite these challenges, the 30%wt MoS_2 ink effectively printed numerous electrodes including the 100 microns nozzle, without issues. SEM images, as showcased in Figure 32, confirm the high level of regularity and fidelity to the original .stl files in the printed electrodes.

One caveat was observed - when layering beyond seven, a minor slumping in the structures started to manifest, as can be seen in the photographs of the various printed structures in Figure 31. Nevertheless, the surface porosity across all three resolutions remained relatively unchanged, with pores consistently ranging between 1 to 2 microns.

In light of the rheological conditions and dispensing performance, the 30%wt MoS_2 ink can be considered as the most versatile formulation in terms of printability. However, it does compromise on active material content compared to the 50%wt ink, which might subsequently impact its performance.

In summary, the 30%wt MoS_2 ink formulation has showcased significant versatility in 3D printing across a range of resolutions. While the omission of TiS_2 from the formulation reduced thixotropy and simplified the printing process in finer nozzles, the lowered active material concentration in the 30%wt MoS_2 ink, in comparison to the 50%wt ink, signals potential performance compromise.

4.5 Ink formulation based on TiS_2

Inks based solely on TiS_2 were explored, as potential candidates for the printing of high energy density supercapacitors. Although its promise for high energy density makes TiS_2 an intriguing prospect, the inherent challenges associated with its use become evident during the experimental phase. A major issue in this strategy is that TiS_2 is prone to hydrolysis and subsequent oxidation^{141,142}, leading to complications during ink formulation and processing.

Interestingly, it was found that TiS_2 nanosheets could be stabilised in higher concentrations, up to a weight ratio of 50% for printable inks. However, this was not without its challenges.

Each processing step requiring reorientation of the nanosheets, such as homogenisation, syringe loading, and printing, was accompanied by foaming - a side effect of reactions occurring during these procedures.

The printed structures were observed to foam, and subsequent annealing under any flux of Argon gas led to their deterioration. Figure 33 provides a vivid depiction of the various processing stages and the ensuing foaming that ensued.

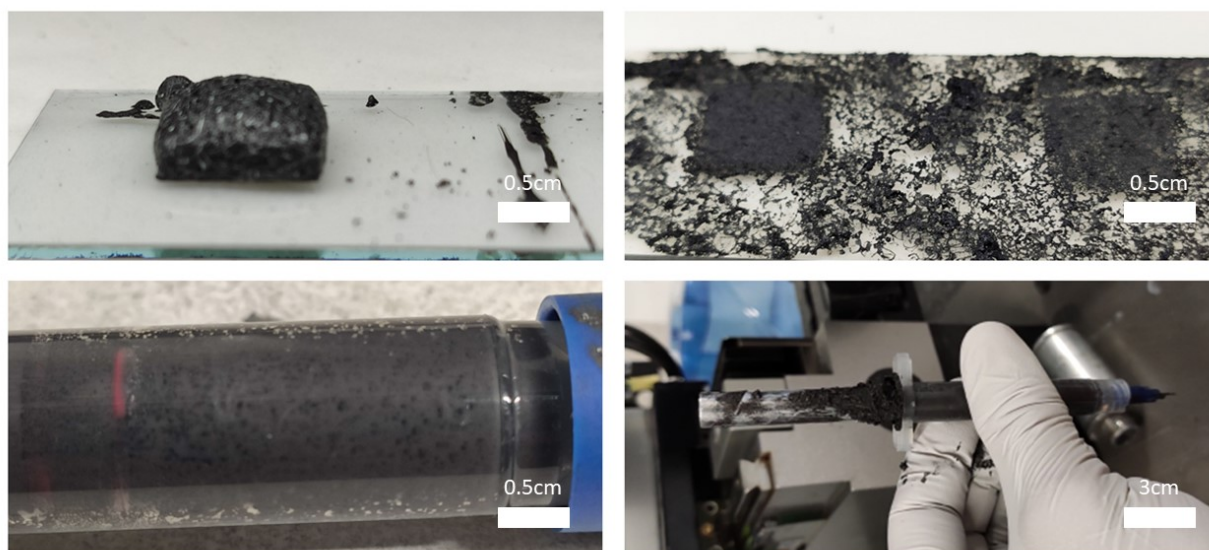


Figure 33 TiS_2 50%wt hydrolysed inks(bottom), 10layered hydrolysed serpentine structure and annealed 5layered hydrolysed serpentine structures (top left and right).

Despite these complexities, the exploration of TiS_2 -based inks presents an intriguing pathway to attaining higher energy densities in supercapacitors. Future work should aim to circumvent the issues related to hydrolysis, oxidation, and foaming, by stabilising agents or in non-aqueous chemistries altogether, to realise the full potential of these inks in the context of 3D printed supercapacitors. Additionally, 3D foams based on TiS_2 could be explored for their performance, once a stabilisation recipe in terms of material and architecture is discovered.

Conclusions

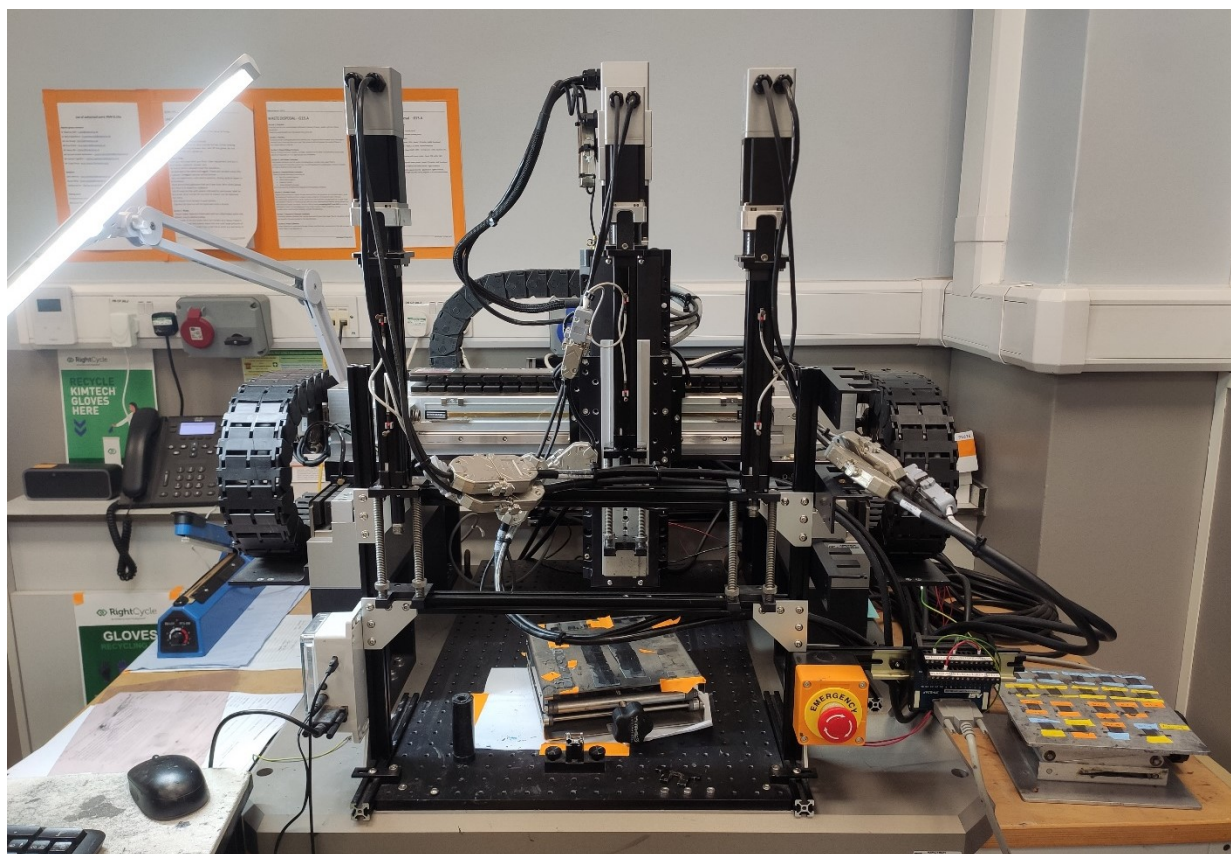


Figure 34 Photograph of Robocaster 3D printer setup used to mass produce electrodes.

This chapter delves into the utilisation of 3D printing with inks derived from transition metal dichalcogenides (TMDs), focusing particularly on MoS_2 and TiS_2 , in the pursuit of high-performance supercapacitors. Integral to this study has been the experimental design, selection of architectures, and optimisation in three dimensions through COMSOL Multiphysics simulations. By examining the impact of porosity, a discern of how different architectures affect the performance of printed structures, especially regarding their ionic tortuosity.

This underscores the critical role of deliberate design in 3D printing, emphasising that architecture transcends mere aesthetics to become a fundamental determinant of the final products functional attributes. Throughout the methodologies, a plethora of architectures for 3D printing, showcasing the versatility in design options. However, focus narrows down to three specific architectures—the woodpile, serpentine, and interdigitated electrodes—which exhibit promising outcomes in attaining higher performance metrics for supercapacitors.

Chapter 5: 3D printed microsupercapacitors of MoS₂/TiS₂ blends

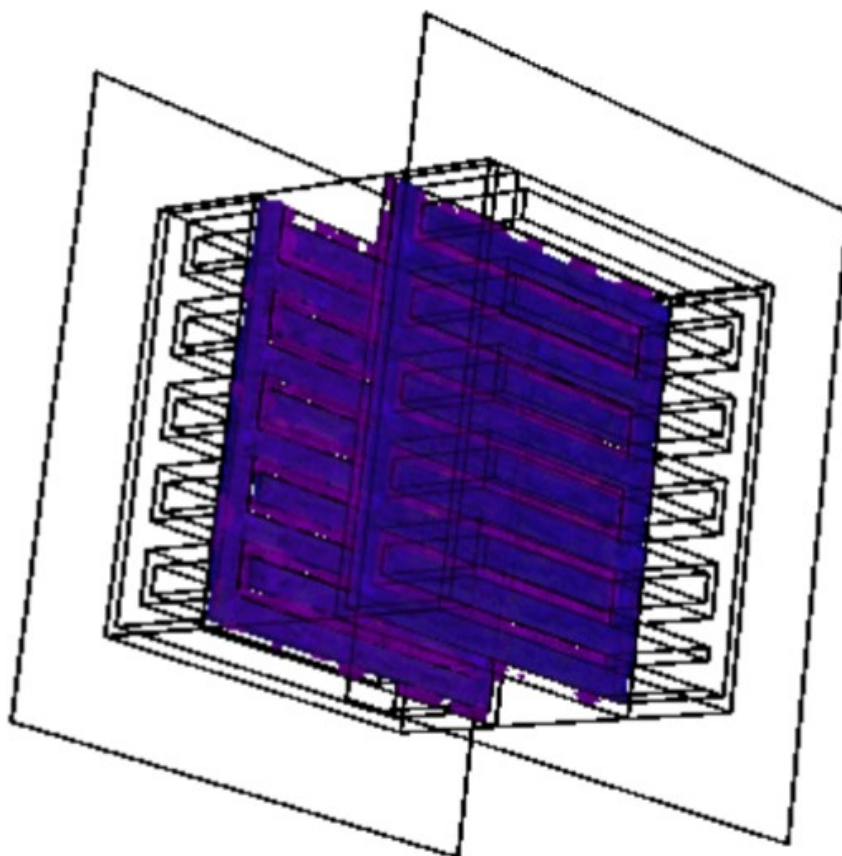


Figure 35 Multiphysics Capacitance in relation to the topography. Simulation in copper out-of-plane 10layered Serpentine electrode microsupercapacitor on 1M H₂SO₄ electrolyte, with a 1cm interelectrode distance.

In this chapter the results concerning the printing and the electrochemical characterisation of electrodes for supercapacitors. The analysis will include comprehensive electrochemical techniques such as cyclic voltammetry (CV), Cyclic Charge Discharge (CCD), Controlled Potential Coulometry (CPC) and electrochemical impedance spectroscopy (EIS), and succinct explanations for their applications will be provided.

This chapter will elucidate the concept of capacitance in the context of supercapacitors. The performance of the 3D printed structures will be evaluated from various angles – per mass

and volume – to provide a holistic view of the performance. Moreover, the methods of calculating capacitance used in this study will be compared with those prevalent in the existing literature, thereby offering a comparative understanding of the performance of these 3D printed structures.

While the foundational principles of electrochemistry will be acknowledged, the focus remains on the novelty and the unique aspects of 3D printed supercapacitors. Emphasis will be placed on the contributions of 3D printing technology to the field of energy storage and the hidden correlations between material structure and performance will be unearthed.

Finally, efforts will be made to deepen the understanding of structure-performance correlation and to delve into the fundamentals of electrochemistry, thereby establishing clear links between the 3D printed supercapacitors and the established theoretical framework. This approach aims to contribute to progress in the field, bridging the gap between traditional energy storage systems and novel 3D printed supercapacitors.

5.1 Structure architecture and effect in performance of out-of-plane 3D printed microsupercapacitors

A key focus is the exploration of the effect of varying the structure thickness, from 2 to 10 printed layers, within two distinct architectural designs: the serpentine and the woodpile designs.

The serpentine design stands out for its unique characteristic, where each extruded filament is positioned precisely over the preceding layer, ensuring an optimised mass-to-surface area coverage ratio per layer. On the other hand, the woodpile design, suggestive of its name, involves piling up extruded filaments in parallel and perpendicular directions with each added layer. This design has the benefit of being one of the easiest to print, due to the even distribution of weight across the underlying layers framework.

The woodpile design holds the distinction of having the highest mass per layer. Each layer is one extruded filament thick, and theoretically, this provides the largest electrostatically active surface area. The prevalence of the woodpile design across different applications^{160,173–178},

underscores its significance as an ideal architecture for benchmarking the performance of supercapacitor electrodes.

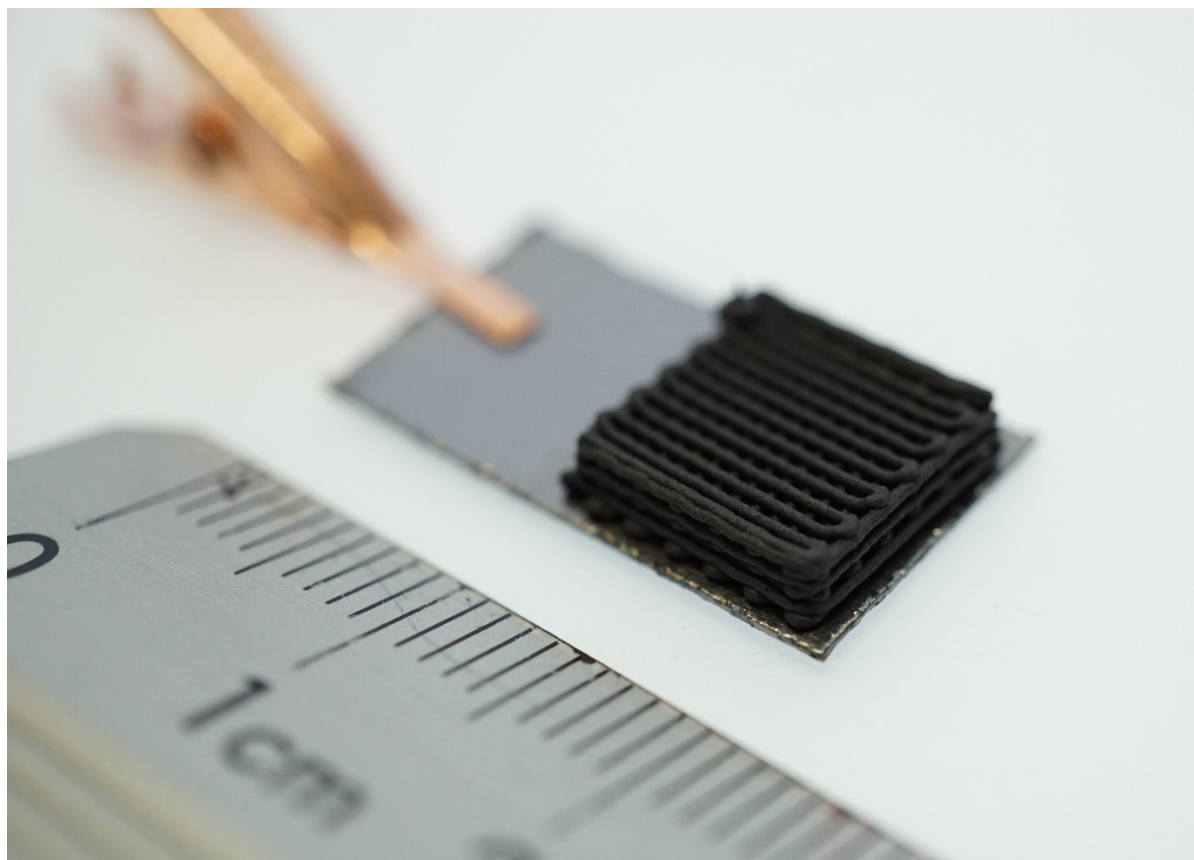


Figure 36 Out-of-plane supercapacitor 10layered 50%wt woodpile $\text{MoS}_2/\text{TiS}_2$ electrode.

According to the electrochemical scripts described in the methodologies, symmetric supercapacitors were printed and tested with an out-of-plane configuration as the general paradigm towards high-performance 3D printed supercapacitors. An example of an electrode is shown in Figure 36 .

5.1.1 Cyclic Voltammetry

Cyclic Voltammetry is an invaluable technique to investigate electrode mechanisms in a potential window and the timeframe they occur. This will reveal insights into the nature and reactions occurring in the electrode. In this case, after the potential window was established in the 0 to 0.5V range for the electrode's ability to store charges, cycling timeframe was investigated by varying the scanrates from 0.1-100,000 mV/s.

All 50%wt MoS₂/TiS₂ ink-based supercapacitors are resistive in the 1,000 to 100,000 mV/s range, indicating there only surface reactions have time to occur with no bulk adsorption phenomena at play. In the 10-1,000 mV/s, as can be seen in an example highlighted in Figure 37, a quasi-rectangular shape starts to appear, as solvated ion adsorption phenomena arise. Finally, in the slower kinetic regimes, namely in the 0.1mV/s – 10 mV/s range, mechanisms are getting more complicated. These are irreversible phenomena, predominantly water splitting due to the electrocatalytic nature of the TMDs in the high potentials.

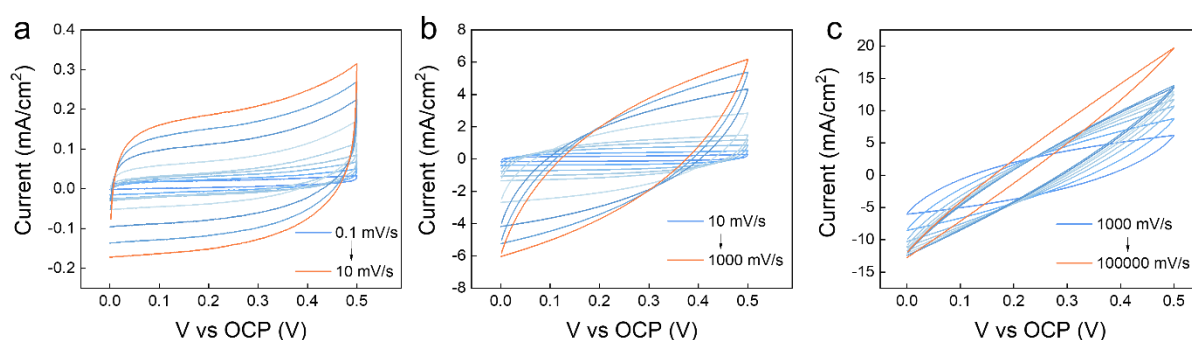


Figure 37 Cyclic Voltammograms of 50%wt MoS₂/TiS₂ 4layered Woodpile supercapacitors at different scanrates. a) 0.1-10mV/s b) 10-1,000 mV/s c) 1,000-100,000 mV/s. The 10-1,000 mV/s range combines the optimum high-energy density charge packing in response to the discharge time with the best cyclability due to the storing mechanism high reversibility.

Cyclic voltammograms in 100mV/s of substrate, thin films and 2,4 and 10 layered Serpentine and Woodpile structures are visualised in Figure 38.

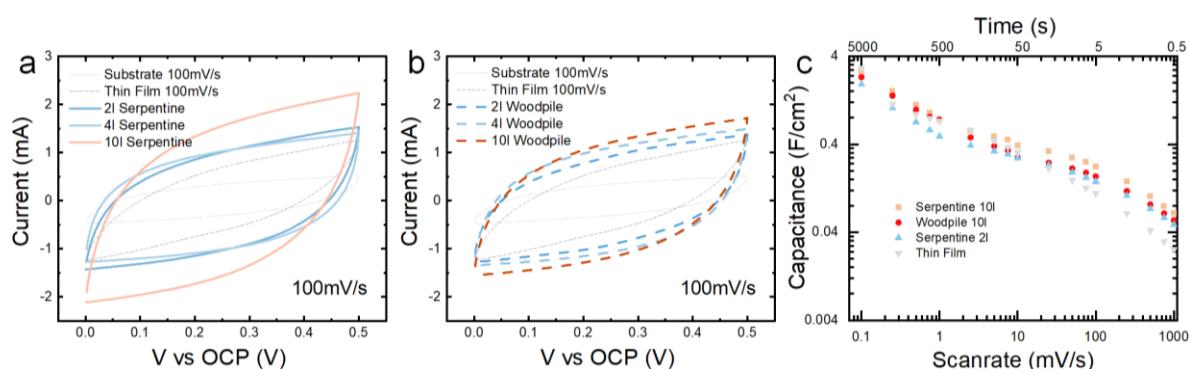


Figure 38 Cyclic Voltammograms of different architectures. a) CVs of Substrate, 50%wt MoS₂/TiS₂ Thin Films, 2layered Serpentine, 4layered and 10layered Serpentine Electrodes at 100mV/s. b) CVs of substrate, 50%wt MoS₂/TiS₂ thin film, 2layered Woodpile, 4layered Woodpile and 10layered woodpile Electrodes. c) Capacitance versus the scanrate with an indication of the timeframe for each cycle to occur. These data were extracted from Cyclic Voltammograms.

It is evident that in this scanrate, quasi-rectangular shapes are indicative of combination of surface electrostatic charges and bulk adsorption. Additionally, the addition of material between the 2,4 and 10 layers is not showing any differences in the storage mechanisms, rather than adding more charge storage spots.

Capacitance and subsequently other performance metrics can be extracted from Cyclic Voltammograms by integrating the generated current in the quasi-rectangular area, using the methodology described in Chapter 3. Capacitance versus the scanrate and therefore the timeframe that cycles occur can be seen in (Figure 38c).

5.1.2 Galvanostatic Charge Discharge

Galvanostatic Charge Discharge is another valuable technique to investigate the electrode performance. In this study, the performance of 3D printed symmetric supercapacitors based on two-dimensional semimetallic nanosheets of $\text{MoS}_2/\text{TiS}_2$ were investigated in different layers and different architectures.

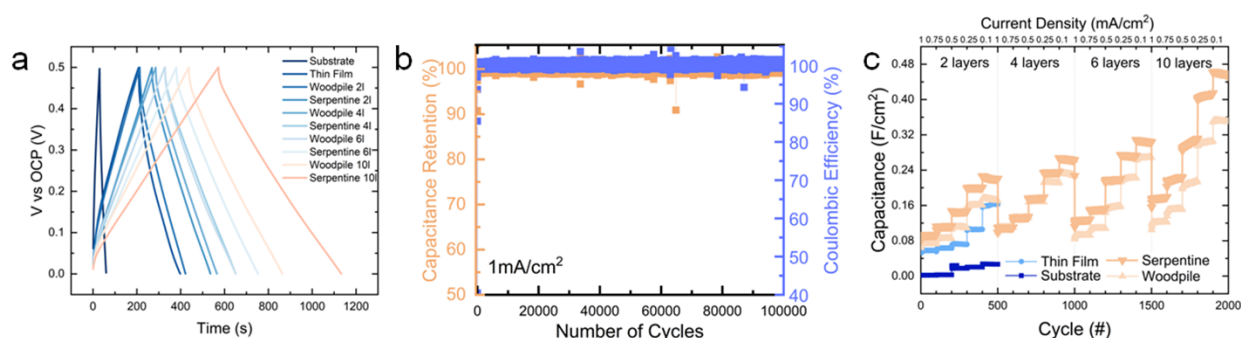


Figure 39 Cyclic Charge Discharge Profiles of 50%wt $\text{MoS}_2/\text{TiS}_2$ inks in serpentine and Woodpile architectures. a) CCD profiles at 0.1 mA/cm^2 b) Capacitance Retention and Coulombic Efficiency over 100,000 cycles, extracted from CCDs at 1 mA/cm^2 . c) Capacitance versus the Current Density and cycle number for each device comprised of 2layered, 4layered, 6layered and 10layered Woodpile and Serpentine architectures.

A direct comparison with potentiodynamic techniques such as Cyclic Voltammetry, can be made by choosing the current density that reflects the time it takes for the whole Charge / Discharge cycle, as that the one that takes the full sweep of the $0.00\text{V} - 0.50\text{V} - 0.00\text{V}$ cycle range.

Additionally, by observing the profile that the applied current is imprinting as it swipes through the operation potential, one can also gauge the underlying mechanisms. As

mentioned in the introductory chapter, a trigonal profile that is indicative of a supercapacitor, indicates highly reversible reactions such as surface electrostatic reactions as well as near surface and bulk adsorption phenomena.

In this case, the CCD profiles of various layered devices are overlaid in Figure 39. It is apparent again that the addition of layers is not introducing any more electrochemical charge storage mechanisms as the profiles are identical rather than more spots for charge storage to occur and therefore it takes longer time to swipe through the whole operating potential window when the same current is applied. Furthermore, ohmic drop is negligible and therefore the assumption that interfacial charge transfer resistance between the current collector and the electrode is very low.

All electrodes demonstrated excellent cyclability, coulombic efficiency (above 98%) and capacitance retention (~99%) up to 100,000 cycles at $1\text{mA}/\text{cm}^2$. (Figure 39) This very high cyclability is also indicative of highly reversible reactions such as electrostatic charge reactions. The amphiphilic poloxamer quasi-solid-state properties were exploited to stabilise the device and reach this level of cyclability. By having the nanosheets suspended in the same hydrogel with the electrolyte meant that the ionic tortuosity was optimised leading to excellent performance and stability.

The influence of charge storage behaviour in response to the time it takes to swipe through the potential window in different current densities can be seen in Figure 39c. The areal Capacitance of each architecture, layer along with thin films and the substrate influence can be seen in this comparison. This way it is apparent how the addition of layers influences the capacitance of these symmetric supercapacitors. However, Volumetric and Gravimetric performance is compared with the areal performance to optimise the performance metric depending on the overall device restrictions in a case-by-case scenario.

Observing Figure 40- Figure 42, the gravimetric and volumetric performance of the 2 layered structures is significantly higher than the equivalent areal performance and dropping upon increasing the layers. Interestingly, serpentine electrodes indeed having less mass and volume on each electrode is outperforming the woodpile performance in every metric consolidating the hypothesis that in this design the array of filaments is ordered far preferentially compared to the woodpile one.

Overall, from CCD experiments the industrial viability of these supercapacitors can be examined. Length of the charge/discharge cycles can be assessed, and conclusive information can be drawn on their performance in comparison with different layers and different devices. By observing these data, conclusions can be drawn on the optimum device manufacturing in relation to specific performance metrics (areal, volumetric, gravimetric) in a case-by-case scenario, as well as the device's great stability that falls under industrial specifications. Notably, devices were cycled in 100,000 cycles at 1 mA/cm², conforming to industrial requirements for supercapacitors. In this current density, each charge/discharge cycle occurred in 40s which translates to 41 days of continuous cycles.

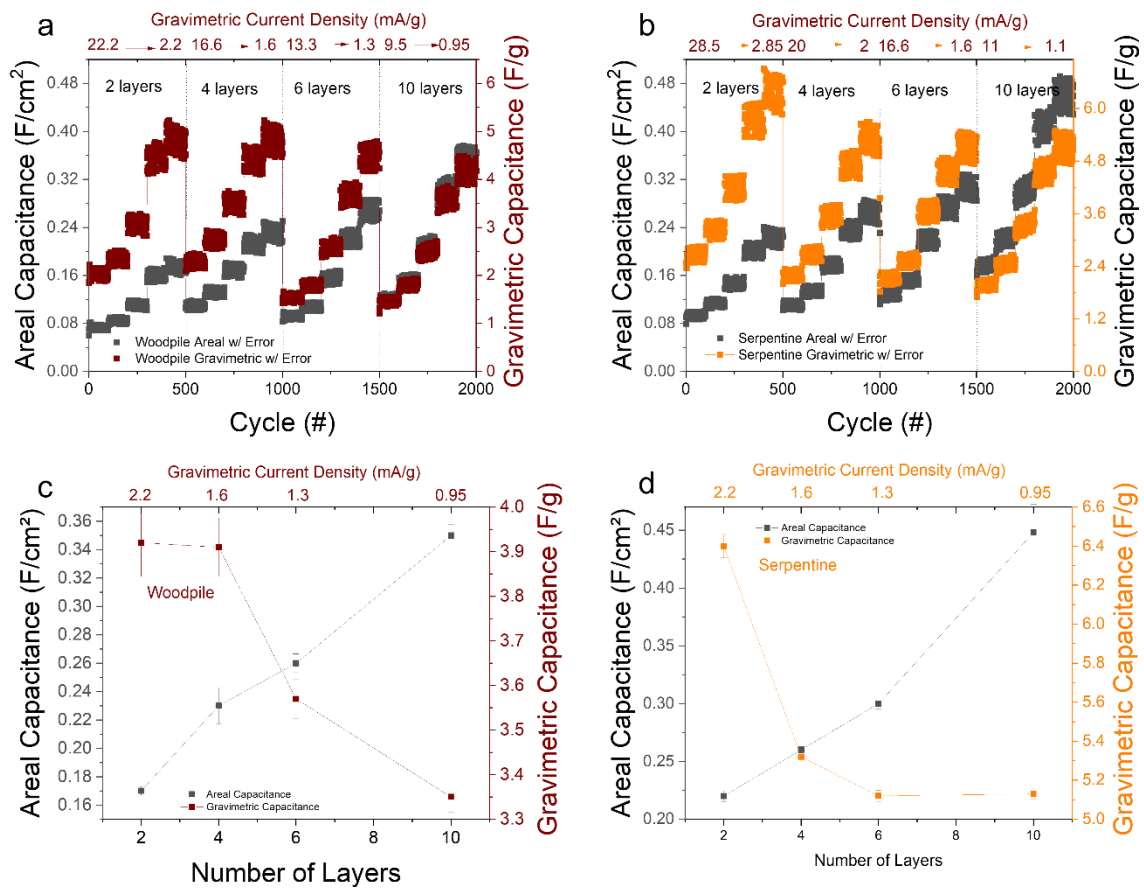


Figure 40 a) & c) areal capacitance versus gravimetric capacitance comparison during cycling charge discharge in 2-10 layered Woodpile architectures. b) & d) areal capacitance versus gravimetric capacitance comparison during cycling charge discharge in 2-10 layered serpentine architectures.

For reference, these optimised devices resulted in a two-step processing of functional inks, 3D printing of architectures with arbitrary complexity, and performance that is among the state-of-the-art with the highest record of 0.63F/cm²¹⁴⁴ in non-carbonaceous quantum sheet 2d TMD-only supercapacitors, resulting in 0.448 F/cm² areal capacitance at 90 mg/cm², 6.5

F/g, and 4.5 F/cm³ at 35 mg/cm². While areal performance was chosen as the go to method to compare device performance, volumetric and gravimetric performance in response to the added layers and current densities is also reported, as 3D electrodes also exhibited excellent cycling stability and coulombic efficiency over 100,000 cycles. This areal, gravimetric, and volumetric performance emerged from the higher conductivity of the metallic component of lithiated TMDs and their crystallographic phase engineering.

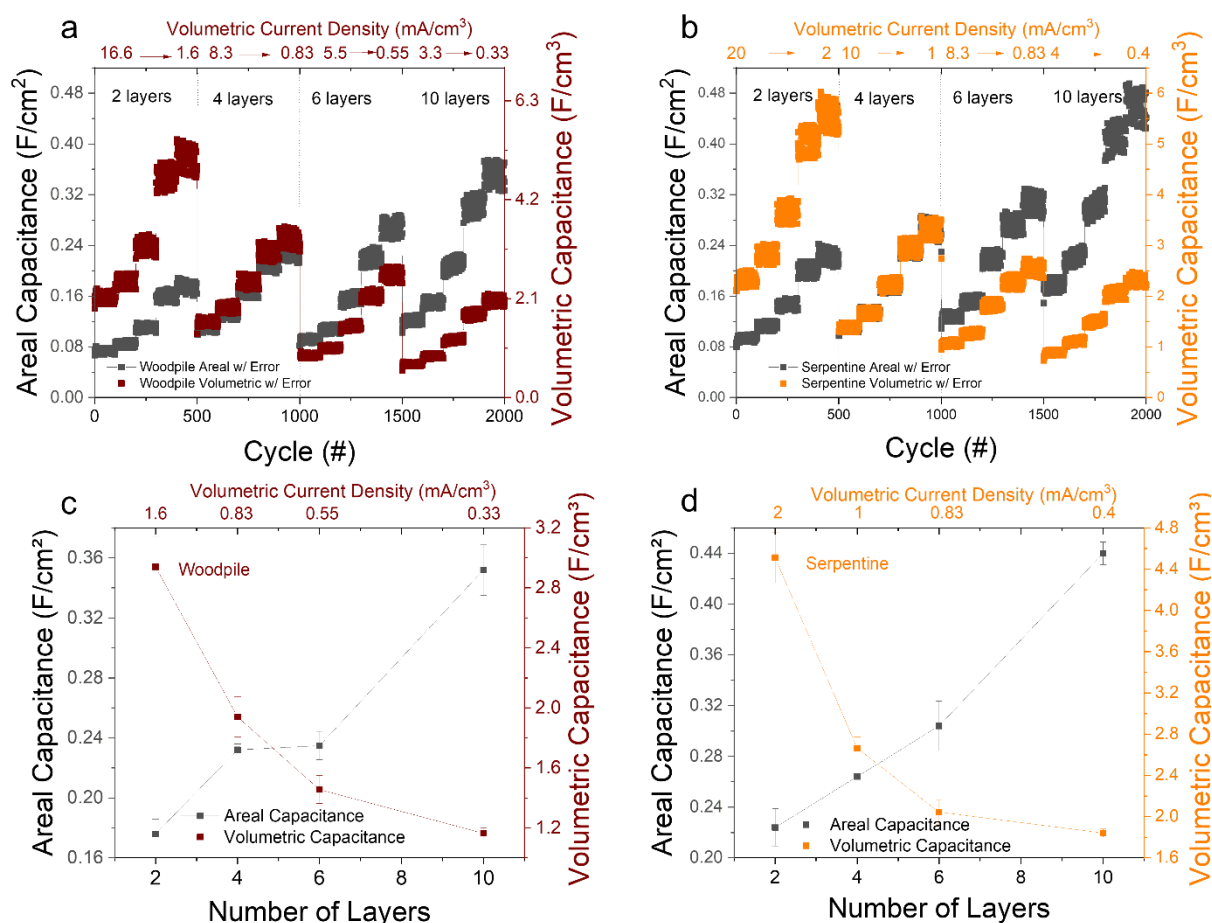


Figure 41 a) & c) Areal Capacitance versus volumetric capacitance comparison during cycling charge discharge in 2-10 layered woodpile architectures. b) & d) areal capacitance versus volumetric capacitance comparison during cycling charge discharge in 2-10 layered serpentine architectures.

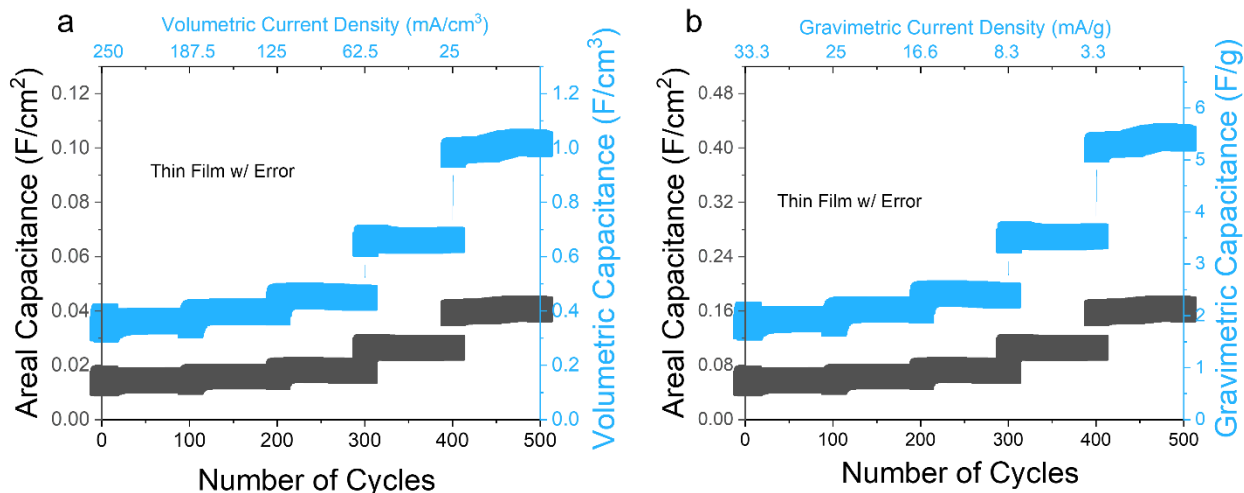


Figure 42 Areal Capacitance versus volumetric capacitance comparison during cycling charge discharge in 50%wt MoS₂/TiS₂ ink 1x1cm thin films b) areal capacitance versus gravimetric capacitance comparison during cycling charge-discharge in 50%wt MoS₂/TiS₂ ink 1x1 cm thin film.

5.1.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopies demonstrate characteristic resistive behaviour in the initial fast frequencies attributed to the interface between the substrate and the polymeric compounds of Pluronic and then capacitive behaviour once the electrode is activated. As the layers are adding up, another resistive element comes into effect, as more adsorption and diffusion processes occur from the surface to the near surface and latterly to the bulk of the electrode. This can be linked to capacitive behaviour as all electrochemical processes are reversible. This also suggests that after the first barrier in the substrate to electrode interface, the principal storing mechanisms are time-independent consolidating the fact that most of the electrochemical energy storage arises from electrostatic capacitive elements.

Additionally, the device impedance based on symmetric 2layered serpentine structures was studied when cycling through the device operating potential window with a 0.1V step size. As can be seen in Figure 43, a harmonious shift between more resistive or capacitive elements especially during high potentials, can be attributed to the ionic mobility when the device is charged or discharged.

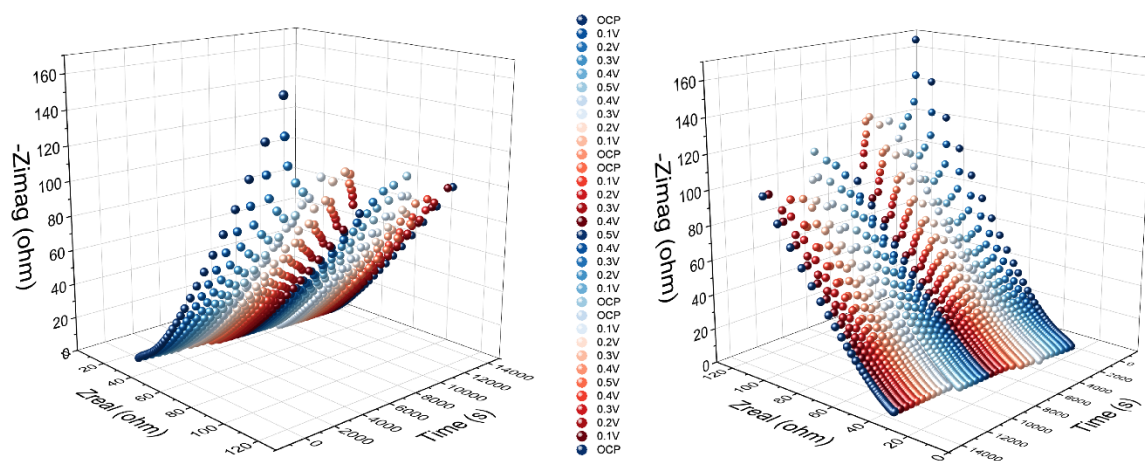


Figure 43 Stereoscopic 3D figure of the effect of electrochemical impedance in a 2layered serpentine electrode, in response to the bias applied during the device operation, with a 0.1V step size as well as the device ageing during cycling.

The symmetry between the impedance profiles under different fixed voltages suggests that the whole of the electrode is activated once the initial interfacial barrier between the substrate and the electrode is surpassed. This concludes that the TMD electrodes are readily ionically accessible throughout the operating potential window, demonstrating low charge-transfer resistance¹⁵². Furthermore, difference in resistance can be seen as the hydrogel electrolyte is aged between the initial cycles and final cycles. This could be attributed to resistive elements as the ionic mobility is impeded as the hydrogel electrolyte is transitioned into a more solid-like behaviour, due to the eventual hydrogel drying.

Overall, from this experiment the low charge transfer resistance of the substrate/electrode interface is assessed to deduct information about the device impedance throughout the operating potential window as well as with different cycles.

5.1.4 Controlled Potential Coulometry

Controlled Potential Coulometry is an electroanalytical technique used broadly in corrosion chemistry. A fixed potential is applied and held linearly over time, while the generated charges are measured. This linear fashion makes Controlled Potential Coulometry a powerful tool when measuring stored charges for supercapacitors as some devices operate at fixed potentials.

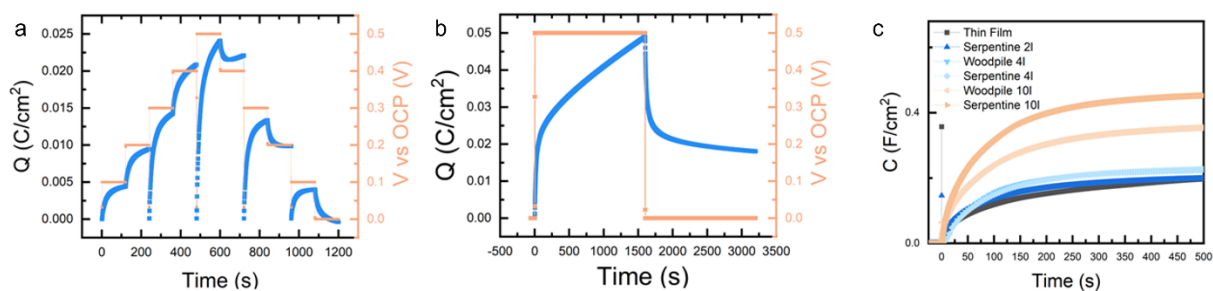


Figure 44 Controlled Potential Coulometric experiments. a) Stored charges in response to fixed potentials throughout the 4layered woodpile symmetric device operating potential window, with a 0.1V step size. b) Stored charges in a 4layered woodpile symmetric device in response to time at a biased potential of 0.5V and discharge at 0V in a 4I woodpile. c) Capacitance values as extracted from stored charges measured from Controlled Potential Coulometric profiles of different electrodes.

A study of capacitive mechanisms using Controlled Potential Coulometry is proposed for the first time in Figure 44. This way, stored charges and their mechanisms can be probed by fixing potentials reflecting the device operation window. The shape of the stored charges and the timeframe that these occur can reveal a lot about the electrochemical mechanisms at play. In Figure 44 the first initial seconds demonstrate a sharp rise of the stored charges while it eventually plateaus at a certain figure. This could be indicative of fast electrostatic capacitive elements occurring first before slower solvated ion adsorption mechanisms come into effect. Additionally, with controlled potential coulometry the effect of these mechanisms to the stored charges can be quantified with great precision and falls to the same values across the potential window even after conditioning the device every two steps. Additionally, these mechanisms can be confirmed when discharging the device at 0V. As can be seen in Figure 44b, the stored charges drop significantly to the maximum values when held at 0.5 V for the first 100s, indicating that the electrostatic surface discharge has already occurred, and the rest of the discharge can be attributed to the bulk of the electrode. Lastly, by quantifying the stored charges at fixed potentials, capacitance can also be calculated. In Figure 44c, Capacitance is directly measured in response to the time for different electrode devices.

Finally, from this experiment the charges that the electrode can store throughout the operating potential window can be quantified as well as their respective capacitive mechanisms can be qualitatively assessed with very high accuracy.

5.2 Correlative benchmarking

To benchmark device performance and investigate the electrochemical mechanisms three techniques were tried, compared, and correlated for an in-depth analysis of the effect of added layers and architecture design. The capacitance and stored charges across different devices were compared in Figure 45. This suggests that Controlled Potential Coulometry can be a powerful tool to examine electrochemical energy storage and compliments Cyclic Charge Discharge, due to their linear operation at fixed potentials and currents.

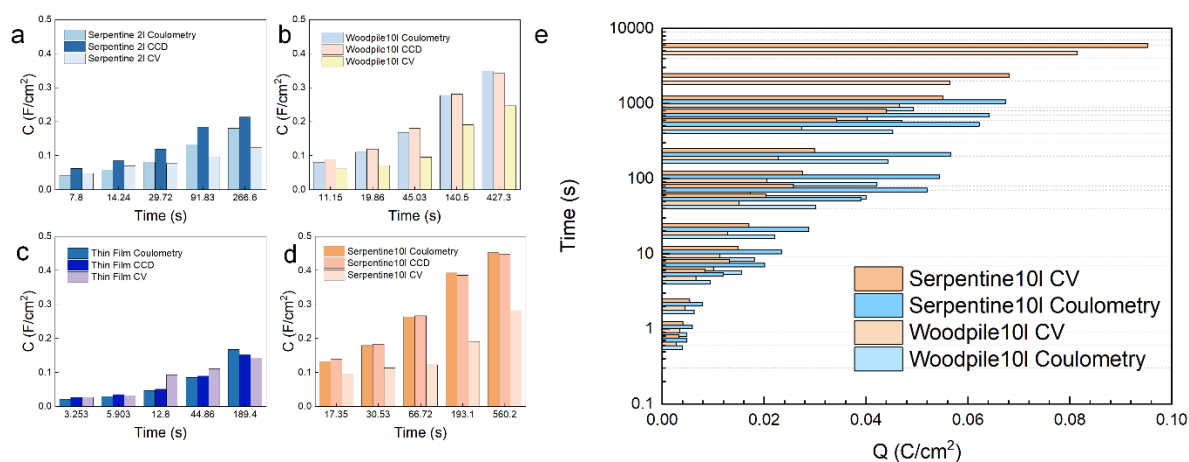


Figure 45 a)b)c)d) Benchmark of Capacitance and e) Charge Storage between different devices and electroanalytical techniques.

After comparing CV, CCD, CPC results of devices based on the same ink but different architectures and layers it can be firstly concluded that the mechanisms between different designs and layers are very similar. Secondly, the added layers have a direct impact in improving the energy storage capabilities of electrode components, as there is more active material and therefore higher accessible surface area for surface and bulk charge storage. Another remarkable experimental observation is that the serpentine architecture, even though it has less mass overall, performs the same with woodpile when in the first few layers at high current densities, when there is not much time for adsorption to occur but outperforms across slower current densities and more printed layers. A possible explanation for this could be given by the architecture itself. Woodpile bulk is only 1 layer thick each time to the perpendicular adding of extruded filaments in the Z dimension. On the other hand,

serpentine is added parallel to the previous extruded filaments in the Z dimension. This gives more layers therefore more bulk material for diffusion to occur.

5.3 State-of-the art comparison

In recent years, there has been considerable efforts to improve the performance of electrochemical energy storage devices. Lot of strategies have been planned in terms of material processing, device engineering and device operation. However, standardised methods to test and benchmark performance metrics of electrochemical energy storage devices have only been recently proposed¹⁴⁹. This leads to great ambiguity when comparing the performance with the state-of-the-art. A useful comparison can be visualised with a 'Ragone plot' where areal energy and power density can be pinned for comparison with reported values.

The most reported electrochemical characterisation technique when comparing performance metrics is Galvanostatic Charge Discharge from two-electrode cells. Although, extracted values from CV and sometimes EIS can be also found. Similarly, each technique is using a different approximation in charge integration, capacitance, energy and power density calculations. Additionally, compensations for three-electrode systems to two-electrode systems and symmetric to asymmetric cells need to be incorporated in equations¹⁴⁹. This makes accurate data reporting, as well as standardised metrics in performance comparison, a feat of paramount importance when comparing values towards new device experimentation^{179–182}.

A notable phenomenon in state-of-the-art comparison is that scientific works report Gravimetric, Volumetric or Areal performance. Additionally, in some cases the scientific methodology and used areas are not clearly defined in the experimental section. That along with the non uniformity in the equations used for each technique limits accuracy and sample breadth in comparison. In this study, as mentioned in the experimental section, 1x1cm electrode devices of 1cm fixed interelectrode distance of reported thicknesses were assembled by sealing them in the hydrogel electrolyte. Electrodes consisted of a 2x1cm carbon foil current collector with a 1x1cm electrode architecture where only the 1x1 architecture portion was covered with the electrolyte.

To this end, the data reported in Figure 46, are all extracted from reported CCD values and calculated using the same equation. Areal performance was chosen to compare upscalable strategies and fabricated microsupercapacitor devices based on Transition-Metal Dichalcogenides. From these, it is apparent that 10layered $\text{MoS}_2/\text{TiS}_2$ 50%wt supercapacitor devices outperform all TMD based supercapacitor areal reported values with the exception of one¹⁴⁴. Areal performance is increasing identified as a standardised performance metric for on-chip supercapacitors and therefore it is considered the most accurate comparison¹⁸³, especially when considering metrics over footprint area. This has profound complication in benchamarking with literature values, as thin film devices report volumetric performance⁵¹. In the context of this work, supercapacitors were also assessed for areal performance optimisation. Overall, this system exhibited overall 98% stability over 100,000 cycles and as high as 448.16mF/cm² Capacitance, energy density of 3.89 $\mu\text{Wh}/\text{cm}^2$ and a power density of 250 $\mu\text{W}/\text{cm}^2$.

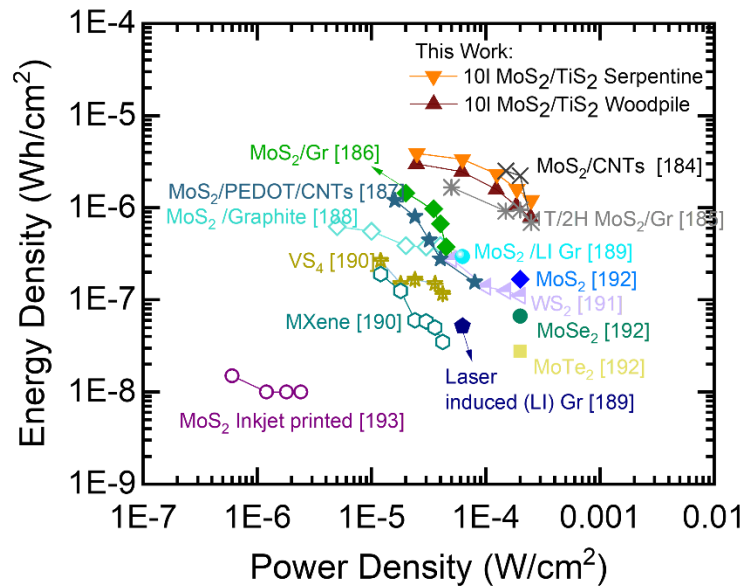


Figure 46 Ragone plot as calculated from extracted values^{184–193} of CCD in TMD based devices.

5.4 Surface analysis of as printed and electrochemically cycled electrodes

The stability of the electrodes during electrochemical cycling were investigated through Scanning Electron Microscopy and X-Ray Photoelectron Spectroscopy. As-deposited thin films of 50wt% MoS₂/TiS₂ inks were analysed both in their initial state and post electrochemical cycling in the poloxamer/ 1M H₂SO₄ electrolyte.

An SEM study (Figure 47a) and b)) revealed a clear comparison between the pristine and cycled samples. The XPS analysis, presented in Figure 47c) through h), offered a detailed surface analysis of the electrodes. The Mo 3d core level for as-deposited samples showed a doublet centred at 227.3 eV and 230.4 eV, attributed to the 1T' MoS₂ phase (Mo 4+), and another doublet at 228.2 eV and 231.2 eV, tied to the 2H MoS₂ phase (Mo 4+). An additional minor doublet associated with Mo-O bonds (Mo 6+), likely existing at the flake edges, was found at 232.32 eV and 235.37 eV.

Turning to the post-cycling samples, a similar analysis was performed. The S 2p core level for the as-printed samples displayed a doublet at 161.04 eV and 162.14 eV, which is associated with the 1T' phase of MoS₂ (S2-). However, this doublet may also encompass contributions from S2- in 1T TiS₂. Another doublet at 162.73 eV and 163.83 eV was ascribed to the 2H phase of MoS₂ (S2-). The presence of a doublet at 168.34 eV and 169.61 eV indicated sulphur in metal sulphate due to oxidation. The cycled samples showed an additional contribution from crystallised electrolyte components or by-products that surfaced after cycling.

The Ti 2p core levels of as-printed samples revealed the doublet at 456.1 eV and 462.1 eV, respectively, which are tied to the Ti⁴⁺ from TiS₂, and the doublet at 458.2 eV and 464.2 eV related to the Ti⁴⁺ from TiO₂. Post cycling, an additional purple doublet was noticed, which was assigned to the TiOx/Ti species. A complete XPS survey of as-printed and cycled samples is presented in Figure 48a) and b). Overall, these analyses provide a comprehensive understanding of the surface behaviour occurring, with no major chemical changes apart from subtle oxidation during the electrochemical cycling process.

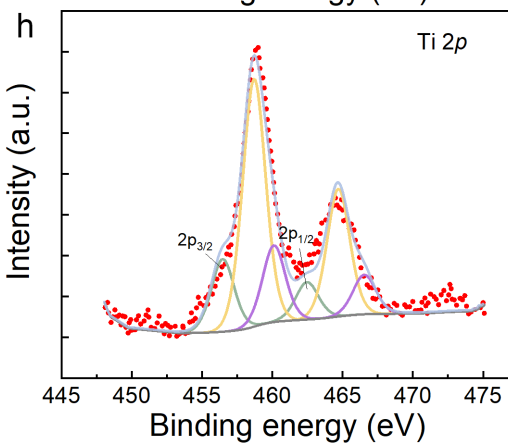
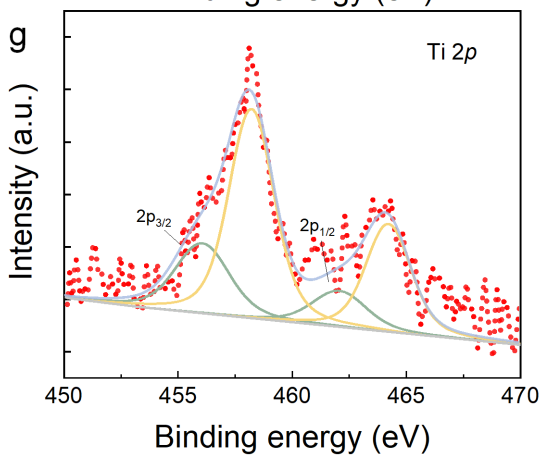
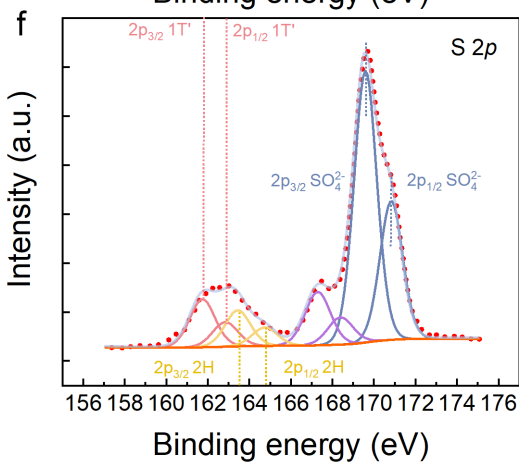
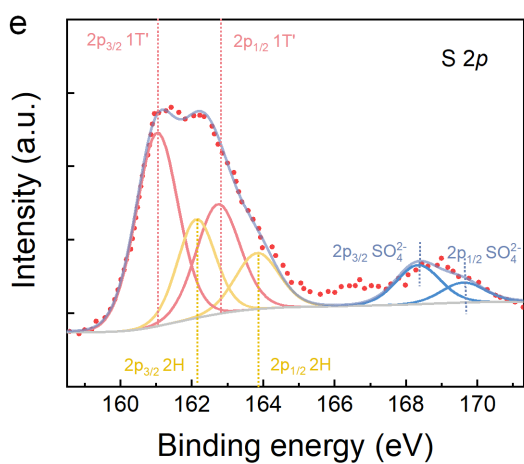
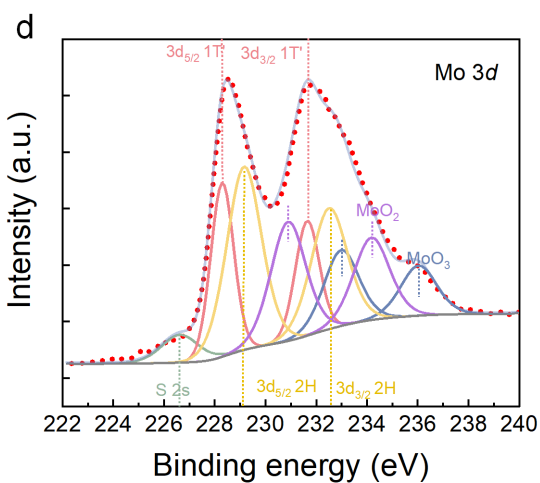
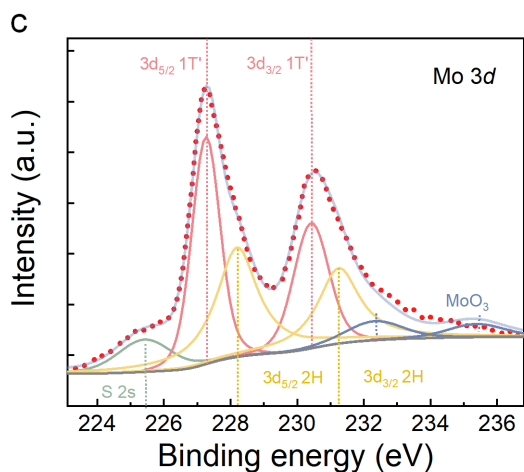
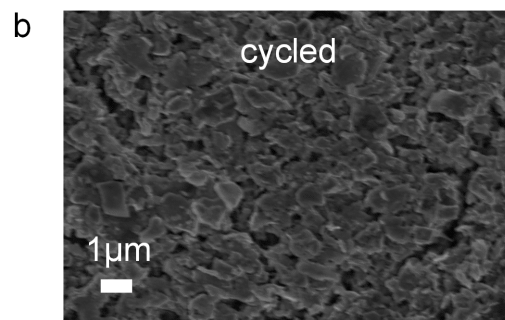
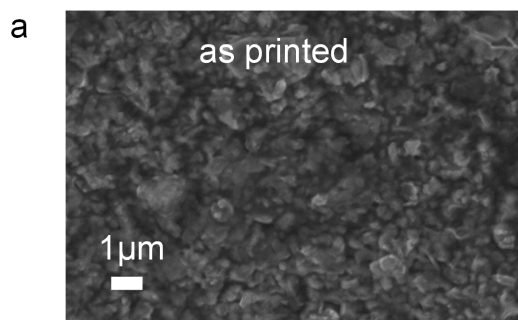


Figure 47 a) SEM Images of as printed samples and b) cycled samples in 1M H₂SO₄. c) The Mo 3d core level of as printed samples showing the doublet centred at 227.3 eV and 230.4 eV (pink line) assigned to the 1T' MoS₂ (Mo 4⁺), while the doublet at 228.2 eV and 231.2 eV (yellow line) to the 2H MoS₂ (Mo 4⁺)⁵⁰. A negligible doublet of Mo 3d 5/2 and 3/2 centred at 232.32 eV and 235.37 eV (dark blue line) is identified and is ascribable to Mo-O bonds (Mo 6⁺), which is likely to be present at the edges of the flakes^{194–196}. The peak at 225.4 eV is due to the S 2s core level (green line). A smart background was subtracted. d) The same region recorded for the sample cycled in 1M H₂SO₄. e) The S 2p core level of as printed samples showing the doublet located at 161.04 eV and 162.14 eV (pink line) assigned to the 1T' phase of MoS₂ (S²⁻), however this doublet may also have a contribution from the S²⁻ in 1T TiS₂ (this doublet appears at 160.9 and 162.1 eV and can't be resolved). The doublet centred at 162.73 eV and 163.83 eV (yellow colour line) is ascribed to 2H phase of MoS₂ (S²⁻)¹. A smart background was subtracted. The doublet at 168.34 eV and 169.61 eV can be attributed to sulphur in metal sulphate due to oxidation¹⁹⁷. f) The same region for cycled samples in 1M H₂SO₄. The purple line shows a contribution from crystallised electrolyte components or by-products that arise after cycling. g) The Ti 2p core levels of as printed samples showing the doublet of the Ti 2p_{3/2} and p_{1/2} at 456.1 eV and 462.1 eV (green line) respectively that are assigned to the Ti⁴⁺ from TiS₂, while the doublet at 458.2 eV and 464.2 eV (yellow line) to the Ti⁴⁺ from TiO₂¹⁹⁸. A smart background was subtracted. h) The same region recorded for the sample cycled in 1M H₂SO₄. The additional purple doublet is assigned to the TiO_x/Ti species.

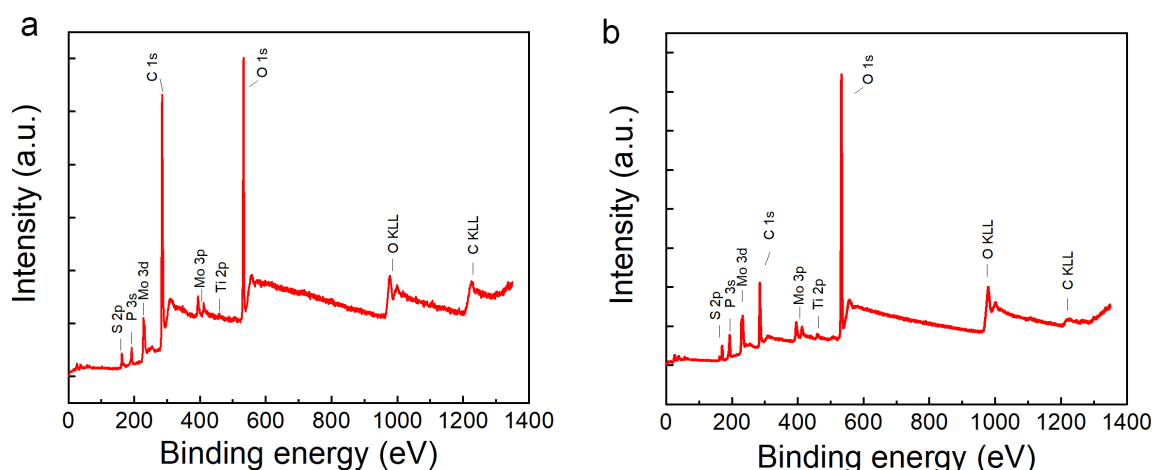


Figure 48 a) XPS survey of as printed samples and b) XPS survey of cycled samples in 1M H₂SO₄.

Finally, from the surface analysis study a definitive conclusion can be made on the nature of MoS₂/TiS₂ nanosheets. Cycled electrodes indeed have higher contributions from evolving oxide species but overall retain both the MoS₂ and TiS₂ counterparts after prolonged cycling.

5.5 Probing different solvated ion intercalation/adsorption, combining XRD and Raman

The Intercalation of various solvated ions in TMD electrodes was probed utilising both X-Ray Diffraction (XRD) and Raman spectroscopy. The investigation was carried out *ex-situ* by electrochemically cycling identical annealed MoS₂/TiS₂ 50%wt thin film 10x10mm electrodes, under the exact same conditions in different aqueous electrolyte solutions. The results from this study are presented in Figure 49.

The electrolytes tested in this study include 1M H₂SO₄, 1M Li₂SO₄, 1M Na₂SO₄, and 1M ZnSO₄, all of which have varying ionic radii and therefore different solvated ion clusters. In theory⁵¹, TMD nanosheets should be able to accommodate all these ions. However, the process of thermal annealing could potentially influence phase conversion.

According to the results from XRD and Raman analyses, as-printed MoS₂/TiS₂ films retain the 1T' phase. When subjected to annealing, there is a phase transition to 2H, characterised by a single peak at 14.2 degrees (corresponding to the 002 plane). An expansion in the interlayer distance would typically induce a shift in the 002 plane towards higher degrees. Nonetheless, under the experimental conditions applied, no signs of intercalation were observed based on static XRD and Raman outcomes.

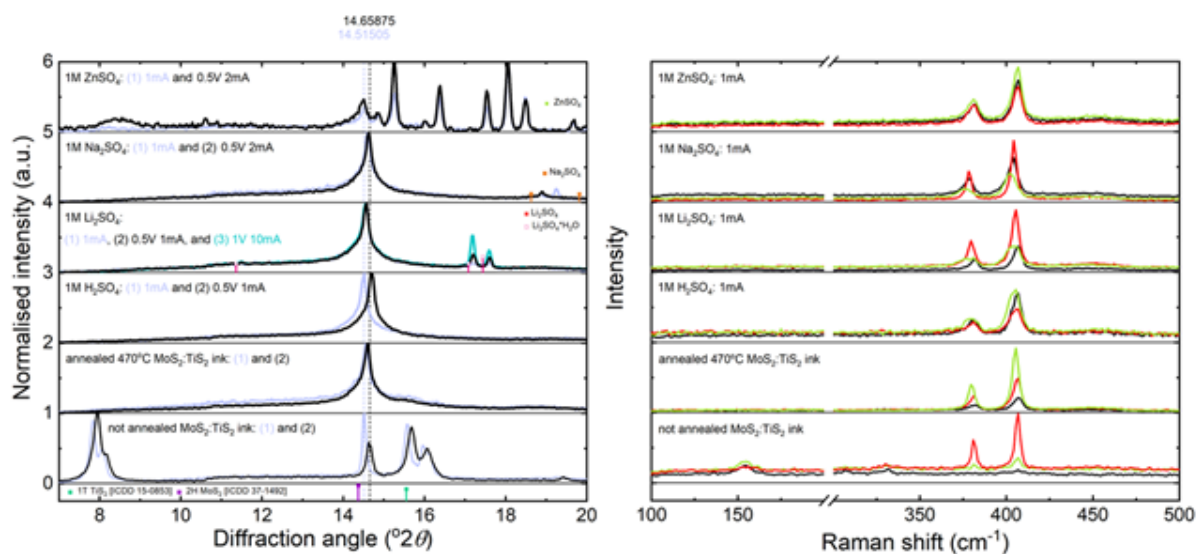


Figure 49 XRD (left) and Raman(right) measurements of 50%wt MoS₂/TiS₂ Thin Films cycled in different electrolyte solutions.

In the electrolytes Li_2SO_4 and Zn_2SO_4 , a variety of peaks became apparent. This could likely be a result of electrolyte crystal formation following drying, but in the case of Li_2SO_4 , the peaks appear to be associated with the applied current density. Going forward, it would be beneficial to observe these intercalation phenomena in-operando, as this would provide a more comprehensive understanding of the intercalation dynamics.

Overall, with this experiment the intercalation of various solvated ions in between the restacked layers was investigated *ex-situ*. However, in these conditions a definitive conclusion about the intercalation cannot be made. Time restrictions from cycling the electrode to preparing the XRD/Raman samples meant that any possible intercalation phenomena have been deintercalated by the time of the XRD measurement. There has been reports of ex-situ XRD measurements of MoS_2 electrodes in the past⁵¹, however a specific methodology was not disclosed making the replication of these experiments even more complicated.

5.6 Quantifying charges and electrode expansion with *in-operando* AFM

Probing electrochemical phenomena and correlating them with the surface topography is an emerging characterisation method to discover interfacial occurrences and volumetric changes due to underlying electrochemical phenomena. Here, the layered material expansion using in-operando Atomic Force Microscopy (AFM). This study of electrochemical phenomena, in correlation with surface topography, is crucial to unravel the intricate workings of electrochemical energy storage mechanisms.

Investigations centred around the surface topography of annealed $\text{MoS}_2/\text{TiS}_2$ 50%wt thin films. Utilising a Bruker PeakForce SECM AFM, detailed examination of these films occurred both prior to and following electrochemical cycling in a Li_2SO_4 aqueous electrolyte. A bespoke electrochemical cell was assembled, featuring annealed $\text{MoS}_2/\text{TiS}_2$ 50%wt inks deposited on Carbon Foil as the working electrode, 1M Li_2SO_4 serving as the electrolyte, and a silver wire performing the role of a pseudo-reference electrode. After immersing the probe into the electrolyte and aligning it appropriately, voltage was directly applied to the stage and thereby the working electrode.

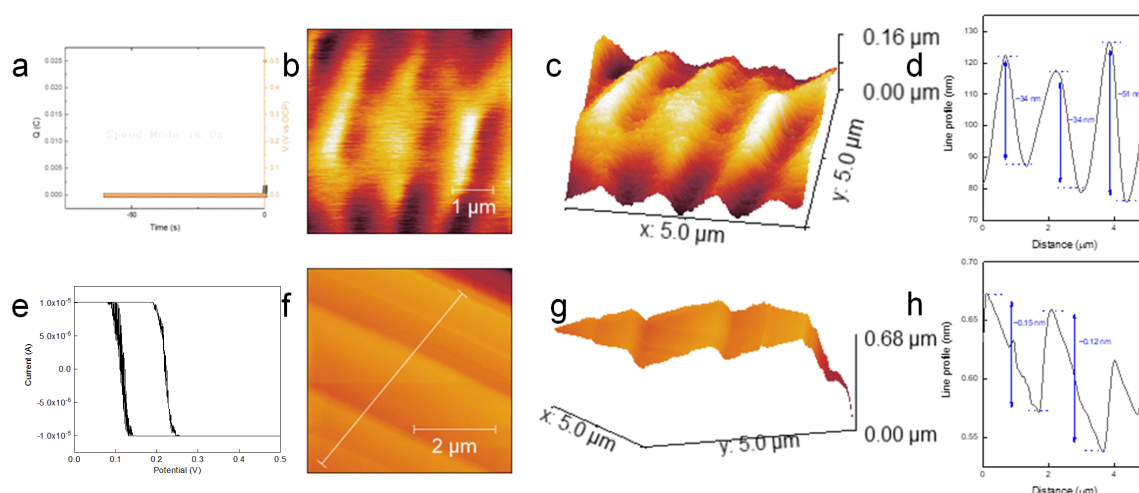


Figure 50 AFM-based Scanning Electrochemical Microscopy of MoS₂/TiS₂ 50wt thin films surface topography in a 1M Li₂SO₄ aqueous electrolyte (top row). Surface topography response to electrochemical stimulus (bottom row).

The initial stage of the process, presented in the top row of Figure 50, began at 0V with no charges stored, and the surface topography was thoroughly measured. This initial examination revealed hills and valleys in the 0.10 microns range within the morphology of the as-deposited thin films, a characteristic attributed to the doctor blading technique utilised for ink spreading.

Subsequently, as demonstrated in the bottom row of Figure 50, the working electrode was cycled within the device operating potential window. However, only in the 0.1 to 0.3V range was successful capacitive behavior recorded. After this cycling process, the surface topography was remeasured in the same mode. An expansion of 0.52 microns was observed uniformly across the MoS₂/TiS₂ working electrode surface, while the valley morphology was preserved.

This uniform expansion is attributed to the 'layer-breathing mode' in capacitive storage, as the electrode swells to accommodate solvated ions between the layers. This discovery not only sheds fresh light on electrochemical energy storage phenomena but also confirms many existing hypotheses about the underlying mechanisms of adsorption/intercalation of solvated ions resulting in the expansion of layered materials. Future studies may greatly benefit from combining Controlled Potential Coulometry with AFM. This integrated approach would provide quantifiable results regarding stored charges and volumetric expansion, enhancing accuracy and driving further advancements in understanding electrochemical energy storage.

5.7 Electrochemical comparison of Different blends and different electrolyte systems based on TMD inks

Electrochemical performance of Individual MoS_2 and TiS_2 components of the final $\text{MoS}_2/\text{TiS}_2$ devices was examined using Cyclic Voltammetry and Charge Discharge. These were examined as thin film electrodes as pure 50%wt TiS_2 inks were difficult to print due to foaming.

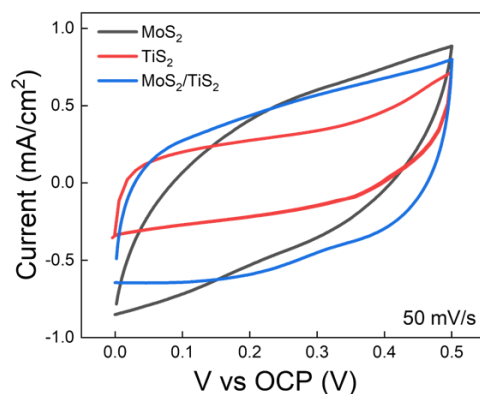


Figure 51 CVs of symmetric devices of 50%wt MoS_2 , 50%wt TiS_2 and 50%wt $\text{MoS}_2/\text{TiS}_2$ composite blends in a 50:50 molar ratio at 50mV/s scanrate. MoS_2 is more resistive in low potentials 0 – 0.2 region and TiS_2 is more capacitive in this region but demonstrates catalytic influences in high potentials at the 0.4-0.5 region. $\text{MoS}_2/\text{TiS}_2$ is more capacitive in low potentials and has lower catalytic influences.

Figure 51 shows The comparison of 1cm² thin films of MoS_2 grey, TiS_2 red and $\text{MoS}_2/\text{TiS}_2$ Blue. From this experiment it is evident that TiS_2 is more electroactive in the low potentials whereas has catalytic contribution in the high potentials for a 50mV/s scanrate. MoS_2 indicates more resistive behaviour in the low potentials but has less of a catalytic response in that scanrate. By comparing the blend, we can see that a higher electroactivity in the low potentials is present while any catalytic contribution is suppressed

Based on this evidence from Figure 51, a conclusion can be made about the electrode engineering on $\text{MoS}_2/\text{TiS}_2$ blends.

Following this, the electrochemical performance of the different MoS_2 phases was assessed using CV and CCD. In Figure 52, an electrochemical response, namely in the current generated from a 2H and a 1T'/1T electrode during a Cyclic Voltammogram in 100mV/s indicates that capacitive contribution in the 1T' phase is significantly higher than that on the 2H MoS_2 . TiS_2 contribution is not expected to change as the phase remains 1T throughout.

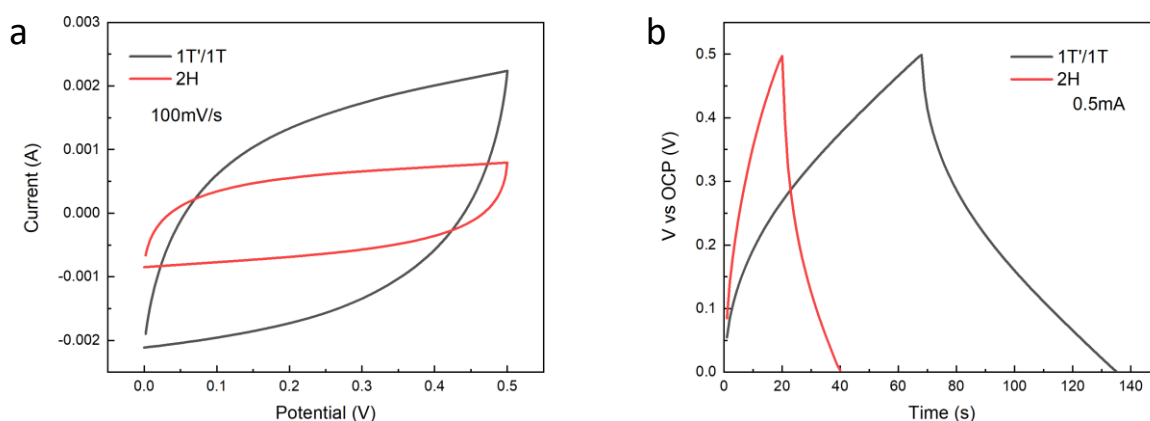


Figure 52 Comparative electrochemical properties of as printed 1T'/1T MoS₂/TiS₂ electrode and annealed (2H phase) electrodes. a) CV curves measured at a constant scan rate of 100 mV s⁻¹ and charge-discharge curves obtained at constant current of 0.5 mA cm⁻², demonstrating the higher capacitance properties for the printed 1T'/1T MoS₂/TiS₂ electrode.

By observing the CCD profiles of the same devices), this hypothesis is consolidated, as in a 0.5mA/cm² current density the 1T'/1T blend's capacitance is 3 times higher than that of the 2H/1T. With this in mind, a safe conclusion can be made that the 1T'/1T is indeed the best option for designing TMD based supercapacitors.

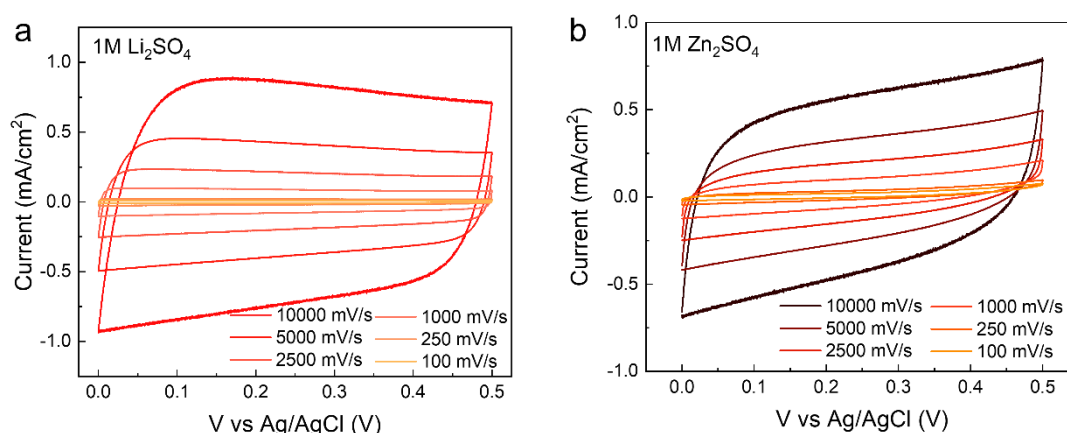


Figure 53 CVs of 2 layered 50%wt MoS₂/TiS₂ annealed Serpentine structures in a) 1M Li₂SO₄ and b) 1M Zn₂SO₄ aqueous electrolytes across different scanrates in a three-electrode system with a Ag/AgCl Reference Electrode and a carbon foil (1x1cm²) Counter Electrode.

Finally, the electrochemical performance of the effect of different electrolytes was assessed in 2layered 50%MoS₂/TiS₂ annealed serpentine structures (2H/1T) in a three-electrode configuration versus a Ag/AgCl Reference electrode. From these, it is apparent that Li₂SO₄ solvated ion adsorption in the low potentials is higher than that of ZnSO₄, resulting in higher

performance metrics overall. This can be attributed to the ionic difference, namely in terms of thickness and sphericity.

5.8 In-plane interdigitated supercapacitor devices

This chapter explores the creation and analysis of in-plane interdigitated supercapacitor devices. A previously formulated ink of $\text{MoS}_2/\text{TiS}_2$, with a 50% weight composition, was utilised to 3D print interdigitated electrodes, a commonly used design in electrochemical energy storage devices. These electrodes feature an array of interlocked 'fingers' in an in-plane assembly, a design favoured for its shorter diffusion length and smaller inter-electrode distance, eliminating the need for a separator.

However, while appealing, the interdigitated design poses challenges when scaling up the printing process, primarily due to the in-plane design necessitating pre-templating the current collector. This requirement can lead to errors when the current collector and the printed structure footprint are not correctly aligned, particularly with automated dispensing technologies currently in use.

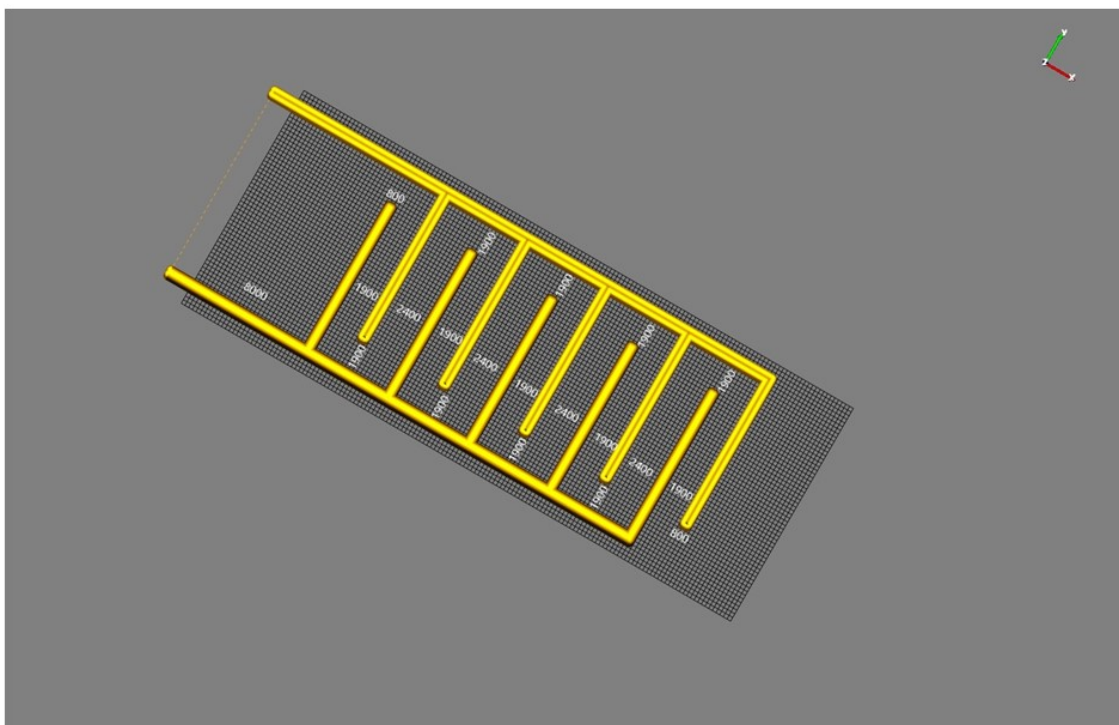


Figure 54 3D CAD design of 4layered Interdigitated structure for 410 microns nozzle (blue).

A 3D CAD design of a 4-layer interdigitated structure, designed for a 410-micron nozzle, is shown in Figure 54. To navigate the identified challenges, mass printing of 4-layer interdigitated devices was conducted as separate electrodes on carbon foil. The printed patterns were then cut to shape, accommodating the interlocking fingers of the design. Subsequently, the in-plane devices were assembled and contacted with copper clips, sealed with a 1M H_2SO_4 Pluronic 27%w/v hydrogel electrolyte. The interdigitated electrodes were brought into close proximity during this process, and the same electrochemical scripts used in prior experiments were used to test these devices.

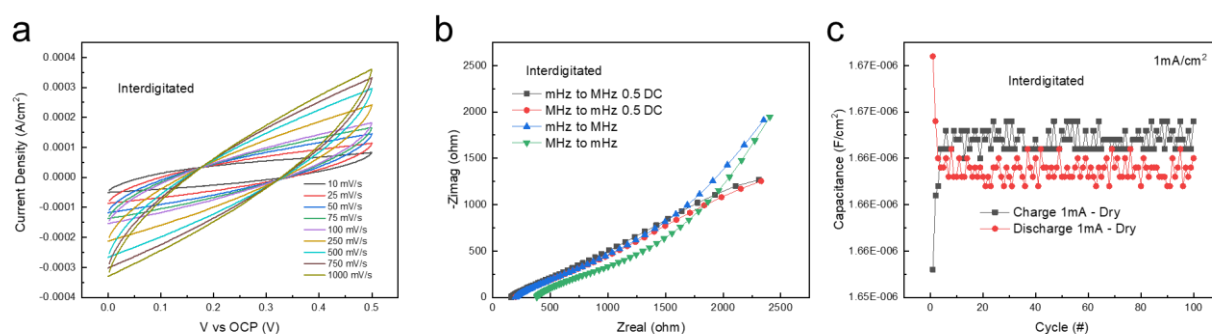


Figure 55 a) Cyclic Voltammograms, b) Electrochemical Impedance Spectroscopies and c) Cyclic Charge Discharge of Interdigitated Electrodes.

Figure 55 shows that these devices exhibited more resistive behaviour in both cyclic voltammograms and impedance spectroscopies. This observation suggests a reduction in electrostatic capacitance and hindered ionic mobility due to the design. Despite these challenges, these electrodes still have potential for use as supercapacitor electrodes, particularly when used in combination with other technologies or in device applications where increasing the z dimension presents limitations.

Finally, in the context of this experimental work this experiment was tried as a proof-of-concept to demonstrate the viability of in-plane interdigitated devices based on the same ink formulations. This configuration requires further optimisation in terms of electrolyte drying and device encasing for optimum cyclability and performance.

Conclusions

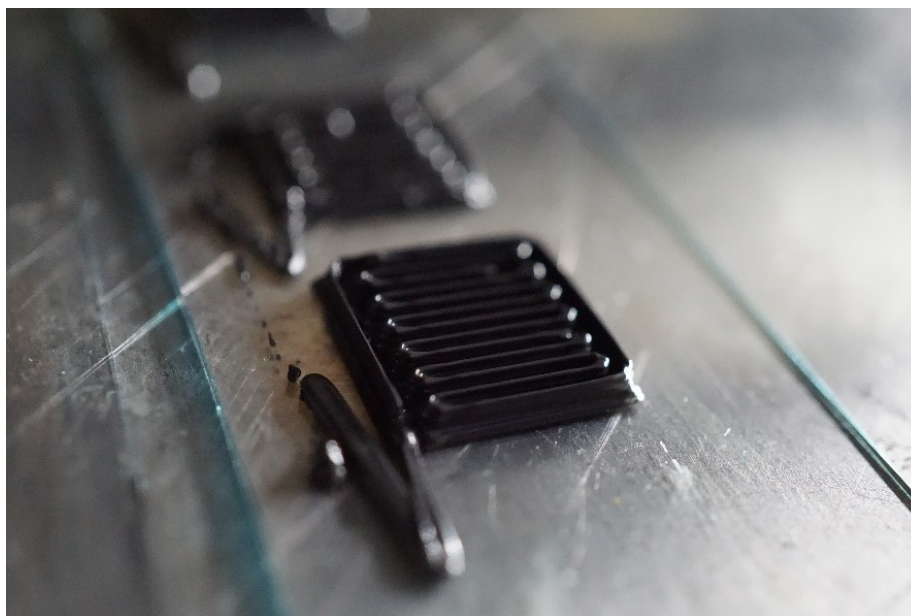
The electrochemical analyses of the various structures and designs produced in this chapter elucidated the role of the mass-to-surface area coverage ratio and the active material in the z dimension, showcasing how these factors can impact the overall performance of the supercapacitors. The comparison of serpentine and woodpile designs highlighted the unique advantages of each, with the serpentine design displaying surprisingly robust performance despite its reduced mass. The design's inherent characteristics allow for more bulk material diffusion, improving energy storage capabilities especially at slower current densities. The woodpile design, though relatively simple in construction, proved its value with a large electrostatically active surface area and showed impressive industrial viability.

Several electroanalytical techniques, including CV, CCD, CPC, and EIS, were used to measure device performance both in 3D and thin films for comparison, with the results generally indicating a positive correlation between increased active material and improved performance. The utilisation of 3D printed supercapacitors based on quasi-solid-state electrolyte hydrogels demonstrated encouraging stability and performance, with a stability of 98% over 100,000 cycles for various devices and a high capacitance of 448.16mF/cm². Moreover, these supercapacitors displayed remarkable energy density and power density, offering compelling evidence for their potential in the world of energy storage.

An in-depth analysis of the MoS₂/TiS₂ nanosheets used in the creation of these supercapacitors revealed that these materials retain their properties even after prolonged cycling up to 100,000 cycles, underscoring their durability and potential for use in long-term energy storage applications. The experiments combining XRD and Raman spectroscopy, although inconclusive due to technical constraints, provided valuable insights that will guide future investigations. Similarly, the in-operando AFM study illuminated the 'layer-breathing mode' in capacitive storage and suggests an integrated approach of Controlled Potential Coulometry with AFM for future studies.

The exploration of the effect of different electrolytes on the performance of 2-layered 50%MoS₂/TiS₂ annealed serpentine structures presented interesting findings, specifically the higher performance metrics resulting from Li₂SO₄ solvated ion adsorption in low potentials.

Chapter 6: Conclusions, outlook and perspectives



Back Cover Image – MoS₂ 30%wt inks 3D printed with a 250 microns nozzle as 5 layered serpentine architectures on ITO-Glass substrates.

6.1 Thesis Summary and Conclusions

State-of-the-art 3D printed microsupercapacitors based on two-dimensional TMDs were developed and tested using a high-loading solid-state intercalation and direct exfoliation via direct hydration in a commercial amphiphilic block-copolymer.

The current landscape of 3D printed microsupercapacitors based on two-dimensional materials was investigated and assessed. Specifically, the benefits of 3D printing in terms of scalability, speed and precision while the inherent benefits of extrusion-based additive manufacturing such as Direct Ink Writing in the performance limitations whilst adding bulk material in the z dimension resulting in low ionic tortuosity. Exfoliating two-dimensional material with high surface area and increased ionic mobility was identified as a mitigation strategy towards high-performance metrics. The intercalation of alkali metals was of paramount importance not only for successful exfoliation but also for phase conversion in semiconducting 2H MoS₂ to semimetallic 1T' MoS₂, while TiS₂ had an inherent semimetallic

1T phase. Exfoliation through Lithium Borohydride was chosen as it is the only bulk powder intercalation in solid state.

High quality and functional printed architectures were 3D printed through the careful understanding and manipulation of the rheological principles that abide them. The shear-thinning, elastic pseudoplastic behaviour of commercial Pluronic f127 tri-block copolymer hydrogels were chosen as a stability agent that provided apt rheological attributes to process TMD ink formulation in terms of storage, handling, 3D printing and testing supercapacitor devices. The concept of extrusion-based printability was mathematically expressed and fitted with the universal manufacturing strategy developed along with the careful optimisation of the mass loading, nozzle dynamics and its effect on the compaction arrangement of nanosheets for morphologically optimised architectures.

Formulation of printable inks of two-dimensional Transition Metal Dichalcogenides for 3D printing of supercapacitors involved an in-depth examination of selected ink examples in the form of Pluronic f127 rheology in different concentrations and the effect of addition of different active materials as MoS₂, TiS₂ or a blend of the two along with a brief investigation of the rheological effects of conductive additives such as Carbon Black. The nature of these inks along with the effects of phase conversion from 2H to 1T' and vice versa was investigated through a suite of material characterisation techniques. Specifically, correlative surface analysis techniques such as XPS and ToF-SIMS demonstrated the persistence of Lithiated TMD species after hydration and electrochemical cycling was of significant importance, as it highlights the multi-purpose importance of Pluronic f127 not only as a 3D printing carrier gel but as a stabilising agent for the persistence of 1T' in prolonged cycling.

Modelling and predicting of the performance of different architectures and added thickness were carried out in a commercial Multiphysics interface. Thus, 3D printing of different architectures was carried out to demonstrate the versatility of this universal strategy in terms of printing capabilities in different resolutions. However, three architecture designs were explored for the 3D printing of high-performance supercapacitors. These were in-plane interdigitated electrodes and out-of-plane woodpile architectures as per the literature convention added with a new proposition of the serpentine architecture towards higher-performance per surface area along with less material used. The surface area and effect of porosity leading to higher performance was also assessed in woodpile and serpentine designs.

Correlative performance benchmarking of 3D printed architectures within the state-of-the-art was done throughout using conventional CV, CCD, EIS as well as proposing the use of integrated chronoamperometry such as Controlled Potential Coulometry (CPC).

Beyond the persistence of lithiated species, this work demonstrates for the first time the effect of solvated ion intercalation/adsorption through the correlation of Raman, XRD and in-operando AFM. While ex-situ Raman and XRD intercalation monitoring was inconclusive due to electrolyte crystallisation effect probably hindering the observation of 002 plane expansion signifying no few-layered expansion. However, initial in-operando AFM experiments demonstrated clear expansion that is directly linked to the cycling of the electrodes.

6.2 Aims and objectives achieved

During this work, the main aim of developing a new approach and reliable protocol for systematically printing microsupercapacitors based on Transition Metal Dichalcogenides (TMDs), was successfully achieved. The challenges in upscaling processing and exfoliation of TMD inks were addressed, through a careful investigation of factors affecting printability, demonstrating printability of various architectures, and assembling and evaluating the performance of 3D-printed TMD-based microsupercapacitor devices.

The first objective focused on exfoliation and ink formulations of TMDs for extrusion-based Additive Manufacturing (AM). A consistent and reliable protocol to 3D printed microsupercapacitor devices using highly concentrated water-based inks of chemically exfoliated TMD nanosheets was successfully demonstrated. This achievement lays the foundation for scalable manufacturing methods with TMDs only suspended in a hydrogel environment for 3D printed supercapacitors.

The second objective involved investigating factors affecting the printability of TMD inks. Rheological properties, surface tension, intrinsic shear, plug flow, and adhesion to different substrates were explored and a general guideline on how to manipulate them to successfully deploy 3D printing strategies for the additive manufacturing of TMD based supercapacitors at scale. By optimising exfoliation strategies and ink formulations, challenges associated with

low-concentration suspensions were overcome, paving the way for high-quality printing of TMD-based structures utilising a universal printing strategy.

The third objective focused on demonstrating the printability of many different architectures with different resolutions using TMD inks. Through systematic experimentation, the effect of printing parameters on the quality of printed structures was evaluated. This allowed the identification of optimal printing conditions and the exploration of diverse designs of 3D-printed TMD microsupercapacitors.

The fourth objective centred on assembling and evaluating the performance of 3D-printed TMD-based microsupercapacitor devices. Key performance metrics were assessed such as capacitance, energy density, power density, and cycling stability. By characterising device nanomorphology and linking electrode and device characteristics to performance, the most promising designs were identified.

Overall, this research has contributed to advancing the field of energy storage by developing novel manufacturing methods for supercapacitors based on 2D materials. The results of this study are relevant for different technologies and in particular for the future of the Internet - of -Things where sensors can be powered by miniaturised supercapacitors.

6.3 Outlook and Future Work

Looking ahead, there are several avenues for further exploration and improvement. Firstly, continued research into optimising ink formulations and printing parameters could further enhance the performance and scalability of TMD-based microsupercapacitors. Additionally, exploring alternative electrode materials and electrolyte compositions may lead to further improvements in device performance. Specifically, exploring direct electrochemical exfoliation could increase the scalability of the inks, avoiding exothermic reactions, and reducing the thickness and size distribution and overall reducing the processing steps. Additionally, exploring tri-block-copolymers and exploit their thermoresponsive amphiphilic properties for device self-healing would add new properties to the device.

Furthermore, future work should focus on scaling up production processes to meet industrial demands and integrating TMD-based microsupercapacitors into practical applications.

Investigating the underlying mechanisms governing the electrochemical behaviour of TMD-based materials could provide valuable insights for future material design and further device optimisation. Particularly, investigation of heterojunction effects of TMDs and other carbon-based conductive additives. Additionally, exploring novel characterisation techniques *in-operando* to better understand the ion distribution, the porosity of the structures and microstructure upon degradation.

In conclusion, the research presented in this thesis lays a solid foundation for the development of miniaturised energy storage devices based on TMDs for the Internet of Things. By addressing key challenges and identifying opportunities for improvement, exciting possibilities for future research and innovation in this field have been opened up.

Bibliography

1. Simon, P. & Gogotsi, Y. Perspectives for electrochemical capacitors and related devices. *Nature Materials* 1–13 z (2020).
2. Sun, H. *et al.* Hierarchical 3D electrodes for electrochemical energy storage. *Nature Reviews Materials* 2018 4:1 4, 45–60 (2018).
3. Fleischmann, S. *et al.* Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials. *Chem Rev* **120**, 6738–6782 (2020).
4. Fleischmann, S. *et al.* Continuous transition from double-layer to Faradaic charge storage in confined electrolytes. *Nature Energy* 2022 7:3 7, 222–228 (2022).
5. Raymundo-Piñero, E., Kierzek, K., Machnikowski, J. & Béguin, F. Relationship between the nanoporous texture of activated carbons and their capacitance properties in different electrolytes. *Carbon N Y* **44**, 2498–2507 (2006).
6. Chmiola, J. *et al.* Anomalous increase in carbon at pore sizes less than 1 nanometer. *Science (1979)* **313**, 1760–1763 (2006).
7. Simon, P., Gogotsi, Y. & Dunn, B. Where do batteries end and supercapacitors begin? *Science (1979)* **343**, 1210–1211 (2014).
8. Brousse, T., Bélanger, D. & Long, J. W. To Be or Not To Be Pseudocapacitive? *J Electrochem Soc* **162**, A5185–A5189 (2015).
9. Lukatskaya, M. R., Dunn, B. & Gogotsi, Y. Multidimensional materials and device architectures for future hybrid energy storage. *Nature Communications* 2016 7:1 7, 1–13 (2016).

10. Xu, Y. *et al.* Holey graphene frameworks for highly efficient capacitive energy storage. *Nature Communications* 2014 5:1 **5**, 1–8 (2014).
11. Chen, B., Cui, T., Liu, Y. & Varahramyan, K. All-polymer RC filter circuits fabricated with inkjet printing technology. *Solid State Electron* **47**, 841–847 (2003).
12. Tagliaferri, S., Panagiotopoulos, A. & Mattevi, C. Direct ink writing of energy materials. *Mater Adv* **2**, 540–563 (2021).
13. Balani, S. B., Ghaffar, S. H., Chougan, M., Pei, E. & Şahin, E. Processes and materials used for direct writing technologies: A review. *Results in Engineering* **11**, 100257 (2021).
14. Fu, K. *et al.* Graphene Oxide-Based Electrode Inks for 3D-Printed Lithium-Ion Batteries. *Advanced Materials* **28**, 2587–2594 (2016).
15. Wei, T.-S. *et al.* 3D Printing of Customized Li-Ion Batteries with Thick Electrodes. *Advanced Materials* **30**, 1703027 (2018).
16. Ferrari, S. *et al.* Latest advances in the manufacturing of 3D rechargeable lithium microbatteries. *J Power Sources* **286**, 25–46 (2015).
17. Seol, M. L. *et al.* All-Printed In-Plane Supercapacitors by Sequential Additive Manufacturing Process. *ACS Appl Energy Mater* **3**, 4965–4973 (2020).
18. Li, W. *et al.* Printing assembly and structural regulation of graphene towards three-dimensional flexible micro-supercapacitors. *J Mater Chem A Mater* **5**, 16281–16288 (2017).
19. Shen, K., Ding, J. & Yang, S. 3D Printing Quasi-Solid-State Asymmetric Micro-Supercapacitors with Ultrahigh Areal Energy Density. *Adv Energy Mater* **8**, 1800408 (2018).
20. Li, H., Liang, J., Li, H. & Liang, J. Recent Development of Printed Micro-Supercapacitors: Printable Materials, Printing Technologies, and Perspectives. *Advanced Materials* **32**, 1805864 (2020).
21. Yan, J. *et al.* Direct-ink writing 3D printed energy storage devices: From material selectivity, design and optimization strategies to diverse applications. *Materials Today* **54**, 110–152 (2022).
22. Zhang, Q. *et al.* Direct Ink Writing of Moldable Electrochemical Energy Storage Devices: Ongoing Progress, Challenges, and Prospects. *Adv Eng Mater* **23**, 2100068 (2021).
23. Werner, J. G., Rodríguez-Calero, G. G., Abruña, H. D. & Wiesner, U. Block copolymer derived 3-D interpenetrating multifunctional gyroidal nanohybrids for electrical energy storage. *Energy Environ Sci* **11**, 1261–1270 (2018).
24. Uzel, S. G. M., Weeks, R. D., Eriksson, M., Kokkinis, D. & Lewis, J. A. Multimaterial Multinozzle Adaptive 3D Printing of Soft Materials. *Adv Mater Technol* 2101710 (2022).
25. Skylar-Scott, M. A., Mueller, J., Visser, C. W. & Lewis, J. A. Voxellated soft matter via multimaterial multinozzle 3D printing. *Nature* **575**, (2019).
26. Ke Sun, C. *et al.* 3D Printing of Interdigitated Li-Ion Microbattery Architectures. *Advanced Materials* **25**, 4539–4543 (2013).

27. Rocha, V. G. *et al.* Multimaterial 3D Printing of Graphene-Based Electrodes for Electrochemical Energy Storage Using Thermoresponsive Inks. *ACS Appl Mater Interfaces* **9**, 37136–37145 (2017).
28. Seol, M. L. *et al.* All-Printed In-Plane Supercapacitors by Sequential Additive Manufacturing Process. *ACS Appl Energy Mater* **3**, 4965–4973 (2020).
29. García-Tuñón, E. *et al.* Printing in Three Dimensions with Graphene. *Advanced Materials* **27**, 1688–1693 (2015).
30. Zhu, C. *et al.* Highly compressible 3D periodic graphene aerogel microlattices. *Nature Communications* **2015 6:1 6**, 1–8 (2015).
31. Wei, X. *et al.* 3D Printable Graphene Composite. *Scientific Reports* **2015 5:1 5**, 1–7 (2015).
32. Song, F. *et al.* Rising from the horizon: three-dimensional functional architectures assembled with MXene nanosheets. *J Mater Chem A Mater* **8**, 18538–18559 (2020).
33. Chen, X., Yang, R. & Wu, X. Printing of MXene-based materials and the applications: a state-of-the-art review. *2d Mater* **9**, 042002 (2022).
34. Cheng, M. *et al.* Direct Ink Writing of Polymer Composite Electrolytes with Enhanced Thermal Conductivities. *Adv Funct Mater* **31**, 2006683 (2021).
35. Guiney, L. M. *et al.* Three-Dimensional Printing of Cytocompatible, Thermally Conductive Hexagonal Boron Nitride Nanocomposites. *Nano Lett* **18**, 3488–3493 (2018).
36. Alinejadian, N., Kollo, L. & Odnevall, I. Progress in additive manufacturing of MoS₂-based structures for energy storage applications – A review. *Mater Sci Semicond Process* **139**, 106331 (2022).
37. Bhardwaj, S., de Souza, F. M. & Gupta, R. K. Role of 3D Printing Technology in High-Performance Supercapacitors. *Handbook of Energy Materials* 1–26 (2022).
38. Chen, K., Song, S., Liu, F. & Xue, D. Structural design of graphene for use in electrochemical energy storage devices. *Chem Soc Rev* **44**, 6230–6257 (2015).
39. Yan, J. *et al.* Template-Assisted low temperature synthesis of functionalized graphene for ultrahigh volumetric performance supercapacitors. *ACS Nano* **8**, 4720–4729 (2014).
40. Jiang, Y. *et al.* Three-dimensional printing of graphene-based materials for energy storage and conversion. *SusMat* **1**, 304–323 (2021).
41. Wu, X., Mu, F. & Lin, Z. Three-dimensional printing of graphene-based materials and the application in energy storage. *Mater Today Adv* **11**, 100157 (2021).
42. Rocha, V. G. *et al.* Multimaterial 3D Printing of Graphene-Based Electrodes for Electrochemical Energy Storage Using Thermoresponsive Inks. *ACS Appl Mater Interfaces* **9**, 37136–37145 (2017).
43. Tagliaferri, S. *et al.* Aqueous Inks of Pristine Graphene for 3D Printed Microsupercapacitors with High Capacitance. *ACS Nano* **15**, 15342–15353 (2021).
44. Zhang, C. *et al.* Additive-free MXene inks and direct printing of micro-supercapacitors. *Nat Commun* **10**, 1795 (2019).

45. Yang, W. *et al.* 3D Printing of Freestanding MXene Architectures for Current-Collector-Free Supercapacitors. *Advanced Materials* **31**, 1902725 (2019).
46. Ghidui, M., Lukatskaya, M. R., Zhao, M. Q., Gogotsi, Y. & Barsoum, M. W. Conductive two-dimensional titanium carbide 'clay' with high volumetric capacitance. *Nature* **516**, 78–81 (2015).
47. Orangi, J., Hamade, F., Davis, V. A. & Beidaghi, M. 3D Printing of Additive-Free 2D $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) Ink for Fabrication of Micro-Supercapacitors with Ultra-High Energy Densities. *ACS Nano* **14**, 1, 640-650 (2020).
48. Tetik, H. *et al.* 3D Printed MXene Aerogels with Truly 3D Macrostructure and Highly Engineered Microstructure for Enhanced Electrical and Electrochemical Performance. *Advanced Materials* **34**, 2104980 (2022).
49. Chhowalla, M. *et al.* The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chemistry* 2013 5:4 **5**, 263–275 (2013).
50. Eda, G. *et al.* Photoluminescence from chemically exfoliated MoS₂. *Nano Lett* **11**, 5111–5116 (2011).
51. Acerce, M., Voiry, D. & Chhowalla, M. Metallic 1T phase MoS₂ nanosheets as supercapacitor electrode materials. *Nature Nanotechnology* 2015 10:4 **10**, 313–318 (2015).
52. Coleman, J. N. *et al.* Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* (1979) **331**, 568–571 (2011).
53. Finn, D. J. *et al.* Inkjet deposition of liquid-exfoliated graphene and MoS₂ nanosheets for printed device applications. *J Mater Chem C Mater* **2**, 925–932 (2014).
54. Piatti, E. *et al.* Charge transport mechanisms in inkjet-printed thin-film transistors based on two-dimensional materials. *Nature Electronics* 2021 4:12 **4**, 893–905 (2021).
55. Feng, X. *et al.* A Fully Printed Flexible MoS₂ Memristive Artificial Synapse with Femtojoule Switching Energy. *Adv Electron Mater* **5**, 1900740 (2019).
56. Shao, Y. *et al.* 3D Crumpled Ultrathin 1T MoS₂ for Inkjet Printing of Mg-Ion Asymmetric Micro-supercapacitors. *ACS Nano*, **14**, 6, 7308-7318 (2020).
57. Lee, S. J. *et al.* An organic photovoltaic featuring graphene nanoribbons. *Chemical Communications* **51**, 9185–9188 (2015).
58. Balis, N., Stratakis, E. & Kymakis, E. Graphene and transition metal dichalcogenide nanosheets as charge transport layers for solution processed solar cells. *Materials Today* **19**, 580–594 (2016).
59. Jacob, S. *et al.* High-performance flexible thermoelectric modules based on high crystal quality printed TiS₂/hexylamine. *Sci Technol Adv Mater* **22**, 907–916 (2021).
60. Wang, X. *et al.* A 3D-printed scaffold with MoS₂ nanosheets for tumor therapy and tissue regeneration. *NPG Asia Materials* 2017 9:4 **9**, e376–e376 (2017).
61. Gusmão, R., Sofer, Z., Marvan, P. & Pumera, M. MoS₂ versatile spray-coating of 3D electrodes for the hydrogen evolution reaction. *Nanoscale* **11**, 9888–9895 (2019).

62. Brown, E. *et al.* 3D printing of hybrid MoS₂-graphene aerogels as highly porous electrode materials for sodium ion battery anodes. *Mater Des* **170**, 107689 (2019).
63. Zhao, Y. *et al.* 3D-Printed Topological MoS₂/MoSe₂Heterostructures for Macroscale Superlubricity. *ACS Appl Mater Interfaces* **13**, 34984–34995 (2021).
64. Yang, Z. *et al.* Core-sheath 3D printing of highly conductive and MoS₂-loaded electrode with pseudocapacitive behavior. *Chemical Engineering Journal* **423**, 130304 (2021).
65. Ghosh, K., Ng, S., Iffelsberger, C. & Pumera, M. 2D MoS₂/carbon/polylactic acid filament for 3D printing: Photo and electrochemical energy conversion and storage. *Appl Mater Today* **26**, 101301 (2022).
66. Chandrasekaran, S. *et al.* Three-Dimensional Printed MoS₂/Graphene Aerogel Electrodes for Hydrogen Evolution Reactions. *ACS Materials Au* **2**, 596–601 (2022).
67. Zhang, B. *et al.* In-Situ Assembly of MoS₂ Nanostructures on EHD-Printed Microscale PVDF Fibrous Films for Potential Energy Storage Applications. *Polymers* 2022, Vol. 14, Page 5250 **14**, 5250 (2022).
68. Yoshida, K., Kawasaki, T., Kuwabara, A., Ukyo, Y. & Ikuhara, Y. In situ electron microscopic observation of electrochemical Li-intercalation into MoS₂. *Solid State Ion* **357**, 115488 (2020).
69. Azhagurajan, M., Kajita, T., Itoh, T., Kim, Y. G. & Itaya, K. In Situ Visualization of Lithium Ion Intercalation into MoS₂ Single Crystals using Differential Optical Microscopy with Atomic Layer Resolution. *J Am Chem Soc* **138**, 3355–3361 (2016).
70. Xiong, F. *et al.* Li Intercalation in MoS₂: In Situ Observation of Its Dynamics and Tuning Optical and Electrical Properties. *Nano Lett* **15**, 6777–6784 (2015).
71. Wu, Y. *et al.* Observation of an intermediate state during lithium intercalation of twisted bilayer MoS₂. *Nature Communications* 2022 13:1 **13**, 1–8 (2022).
72. Castro Neto, A. H. Charge Density Wave, Superconductivity, and Anomalous Metallic Behavior in 2D Transition Metal Dichalcogenides. *Phys Rev Lett* **86**, 4382 (2001).
73. Py, M. A. & Haering, R. R. Structural destabilization induced by lithium intercalation in MoS₂ and related compounds, *Canadian Journal of Physics* (1983).
74. Zhang, J. *et al.* Reversible and selective ion intercalation through the top surface of few-layer MoS₂. *Nat Commun* (2018).
75. Zou, J., Li, F., Bissett, M. A., Kim, F. & Hardwick, L. J. Intercalation behaviour of Li and Na into 3-layer and multilayer MoS₂ flakes. *Electrochim Acta* **331**, 135284 (2020).
76. Wang, L., Xu, Z., Wang, W. & Bai, X. Atomic mechanism of dynamic electrochemical lithiation processes of MoS₂ nanosheets. *J Am Chem Soc* **136**, 6693–6697 (2014).
77. Mattevi, C. & Sokolikova, M. S. Direct synthesis of metastable phases of 2D transition metal dichalcogenides. *Chem Soc Rev* **49**, 3952–3980 (2020).
78. Yang, R. *et al.* Synthesis of atomically thin sheets by the intercalation-based exfoliation of layered materials. *Nature Synthesis* 2023 2:2 **2**, 101–118 (2023).

79. Voiry, D. *et al.* Enhanced catalytic activity in strained chemically exfoliated WS₂ nanosheets for hydrogen evolution. *Nature Materials* 2013 12:9 **12**, 850–855 (2013).
80. Zheng, J. *et al.* High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. *Nature Communications* 2014 5:1 **5**, 1–7 (2014).
81. Zeng, Z. *et al.* Single-Layer Semiconducting Nanosheets: High-Yield Preparation and Device Fabrication. *Angewandte Chemie International Edition* **50**, 11093–11097 (2011).
82. Zeng, Z. *et al.* An Effective Method for the Fabrication of Few-Layer-Thick Inorganic Nanosheets. *Angewandte Chemie International Edition* **51**, 9052–9056 (2012).
83. Akbari, A. *et al.* Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide. *Nature Communications* 2016 7:1 **7**, 1–12 (2016).
84. Heising, J. & Kanatzidis, M. G. Structure of restacked MoS₂ and WS₂ elucidated by electron crystallography. *J Am Chem Soc* **121**, 638–643 (1999).
85. Voiry, D. *et al.* Conducting MoS₂ nanosheets as catalysts for hydrogen evolution reaction. *Nano Lett* **13**, 6222–6227 (2013).
86. Corker, A., Ng, H. C. H., Poole, R. J. & García-Tuñón, E. 3D printing with 2D colloids: designing rheology protocols to predict ‘printability’ of soft-materials. *Soft Matter* **15**, 1444–1456 (2019).
87. Spiral: Additive manufacturing of ceramics and ceramic composites via robocasting. <https://spiral.imperial.ac.uk/handle/10044/1/55940>.
88. Karyappa, R. & Hashimoto, M. Chocolate-based Ink Three-dimensional Printing (Ci3DP). *Scientific Reports* 2019 9:1 **9**, 1–11 (2019).
89. Chen, X. B. Modeling and control of fluid dispensing processes: a state-of-the-art review. *The International Journal of Advanced Manufacturing Technology* 2008 43:3 **43**, 276–286 (2008).
90. S R Saadi, M. A. *et al.* Direct Ink Writing: A 3D Printing Technology for Diverse Materials. *Advanced Materials* **34**, 2108855 (2022).
91. Siqueira, G. *et al.* Cellulose Nanocrystal Inks for 3D Printing of Textured Cellular Architectures. *Adv Funct Mater* **27**, 1604619 (2017).
92. M’Barki, A., Bocquet, L. & Stevenson, A. Linking Rheology and Printability for Dense and Strong Ceramics by Direct Ink Writing. *Scientific Reports* 2017 7:1 **7**, 1–10 (2017).
93. Smay, J. E., Cesarano, J. & Lewis, J. A. Colloidal inks for directed assembly of 3-D periodic structures. *Langmuir* **18**, 5429–5437 (2002).
94. Hausmann, M. K. *et al.* Dynamics of Cellulose Nanocrystal Alignment during 3D Printing. *ACS Nano* **12**, 6926–6937 (2018).
95. Compton, B. G., Lewis, J. A., Compton, B. G. & Lewis, A. 3D-Printing of Lightweight Cellular Composites. *Advanced Materials* **26**, 5930–5935 (2014).
96. Feilden, E., Ferraro, C., Giuliani, F., Vandeperre, L. & Saiz, E. Progress in novel and unexpected areas. *Materials Today* **19**, 544–545 (2016).

97. Feilden, E. *et al.* 3D Printing Bioinspired Ceramic Composites. *Scientific Reports* 2017 7:1 **7**, 1–9 (2017).
98. Xu, Z., Zhang, Y., Li, P. & Gao, C. Strong, conductive, lightweight, neat graphene aerogel fibers with aligned pores. *ACS Nano* **6**, 7103–7113 (2012).
99. Allen, M. E., Hindley, J. W., Baxani, D. K., Ces, O. & Elani, Y. Hydrogels as functional components in artificial cell systems. *Nature Reviews Chemistry* 2022 6:8 **6**, 562–578 (2022).
100. Li, X., Park, E., Hyun, K., Oktavia, L. & Kwak, M. Rheological analysis of core-stabilized Pluronic F127 by semi-interpenetrating network (sIPN) in aqueous solution. *J Rheol (N Y N Y)* **62**, 107 (2017).
101. Bedrov, D., Ayyagari, C. & Smith, G. D. Multiscale modeling of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer micelles in aqueous solution. *J Chem Theory Comput* **2**, 598–606 (2006).
102. Mortensen, K. & Pedersen, J. S. Structural Study on the Micelle Formation of Poly(ethylene oxide)–Poly(propylene oxide)–Poly(ethylene oxide) Triblock Copolymer in Aqueous Solution. *Macromolecules* **26**, 805–812 (1993).
103. Wu, G., Chu, B. & Schneider, D. K. SANS study of the micellar structure of PEO/PPO/PEO aqueous solution. *Journal of physical chemistry* **99**, 5094–5101 (1995).
104. Glatter, O., Scherf, G., Schillén, K. & Brown, W. Characterization of a Poly(ethylene oxide)-Poly(propylene oxide) Triblock Copolymer (EO27-PO39-EO27) in Aqueous Solution. *Macromolecules* **27**, 6046–6054 (1994).
105. Batrakova, E. V. & Kabanov, A. V. Pluronic block copolymers: Evolution of drug delivery concept from inert nanocarriers to biological response modifiers. *Journal of Controlled Release* **130**, 98–106 (2008).
106. Constantinou, A. P. *et al.* Investigation of the Thermogelation of a Promising Biocompatible ABC Triblock Terpolymer and Its Comparison with Pluronic F127. *Macromolecules* **55**, 1783–1799 (2022).
107. Feilden, E. *et al.* 3D Printing Bioinspired Ceramic Composites. *Scientific Reports* 2017 7:1 **7**, 1–9 (2017).
108. Nommeots-Nomm, A., Lee, P. D. & Jones, J. R. Direct ink writing of highly bioactive glasses. *J Eur Ceram Soc* **38**, 837–844 (2018).
109. Diniz, I. M. A. *et al.* Pluronic F-127 hydrogel as a promising scaffold for encapsulation of dental-derived mesenchymal stem cells. *J Mater Sci Mater Med* **26**, 1–10 (2015).
110. Lewis, J. A., Smay, J. E., Stuecker, J. & Cesarano, J. Direct Ink Writing of Three-Dimensional Ceramic Structures. *Journal of the American Ceramic Society* **89**, 3599–3609 (2006).
111. Peng, L. *et al.* Two-Dimensional Holey Nanoarchitectures Created by Confined Self-Assembly of Nanoparticles via Block Copolymers: From Synthesis to Energy Storage Property. *ACS Nano* **12**, 820–828 (2018).

112. Emrooz, H. B. M., Aghdaee, A. A. & Rostami, M. R. Zinc-salt assisted synthesis of three-dimensional oxygen and nitrogen co-doped hierarchical micro-meso porous carbon foam for supercapacitors. *Scientific Reports* 2021 11:1 **11**, 1–11 (2021).
113. Penki, T. R., Shanmughasundaram, D. & Munichandraiah, N. Polymer template-assisted microemulsion synthesis of large surface area, porous Li₂MnO₃ and its characterization as a positive electrode material of Li-ion cells. *Journal of Solid State Electrochemistry* **17**, 3125–3136 (2013).
114. Lin, Y. C. *et al.* Synthesis of mesoporous carbons of high surface area and porosity by using polymer blends as template. *Journal of Solid State Electrochemistry* **12**, 895–901 (2008).
115. Sarkar, B. *et al.* Self-Assembly of Amphiphilic Block Copolymers in Ternary Solvent Mixtures: Lyotropic Liquid Crystalline Phase Behavior and Structure. *Macromol Chem Phys* **213**, 2514–2528 (2012).
116. Younus, M., Hawley, A., Boyd, B. J. & Rizwan, S. B. Bulk and dispersed aqueous behaviour of an endogenous lipid, selachyl alcohol: Effect of Tween 80 and Pluronic F127 on nanostructure. *Colloids Surf B Biointerfaces* **169**, 135–142 (2018).
117. Zhai, J. *et al.* Self-assembled Lyotropic Liquid Crystalline Phase Behavior of Monoolein-Capric Acid-Phospholipid Nanoparticulate Systems. *Langmuir* **33**, 2571–2580 (2017).
118. Chaibundit, C., Ricardo, N. M. P. S., Costa, F. D. M. L. L., Yeates, S. G. & Booth, C. Micellization and gelation of mixed copolymers P123 and F127 in aqueous solution. *Langmuir* **23**, 9229–9236 (2007).
119. da Silva, L. C. E., Borges, A. C., de Oliveira, M. G. & de Farias, M. A. Visualization of supramolecular structure of Pluronic F127 micellar hydrogels using cryo-TEM. *MethodsX* **7**, 101084 (2020).
120. Newby, G. E., Hamley, I. W., King, S. M., Martin, C. M. & Terrill, N. J. Structure, rheology and shear alignment of Pluronic block copolymer mixtures. *J Colloid Interface Sci* **329**, 54–61 (2009).
121. Simon, P. & Gogotsi, Y. Materials for electrochemical capacitors. *Nat Mater* **7**, 845–854 (2008).
122. Lukatskaya, M. R., Dunn, B. & Gogotsi, Y. Multidimensional materials and device architectures for future hybrid energy storage. *Nature Communications* vol. 7, 1–13, (2016).
123. Wu, Y., Li, D., Wu, C.-L., Hwang, H. Y. & Cui, Y. Electrostatic gating and intercalation in 2D materials. *Nature Reviews Materials* 2022 1–13 (2022).
124. Shpigel, N. *et al.* Can Anions Be Inserted into MXene? *J Am Chem Soc* **143**, 12552–12559 (2021).
125. Zhan, C. *et al.* Understanding the MXene Pseudocapacitance. *Journal of Physical Chemistry Letters* **9**, 1223–1228 (2018).
126. Shpigel, N. *et al.* In Situ Monitoring of Gravimetric and Viscoelastic Changes in 2D Intercalation Electrodes. *ACS Energy Lett* **2**, 1407–1415 (2017).

127. Wan, J. *et al.* Tuning two-dimensional nanomaterials by intercalation: Materials, properties and applications. *Chemical Society Reviews* vol. 45 6742–6765 (2016).
128. Zhou, J. *et al.* Layered Intercalation Materials. *Advanced Materials* (2021).
129. Huang, Q. *et al.* The Mechanistic Insights into the 2H-1T Phase Transition of MoS₂ upon Alkali Metal Intercalation: From the Study of Dynamic Sodiation Processes of MoS₂ Nanosheets. *Adv Mater Interfaces* **4**, 1700171 (2017).
130. Whittingham, M. S. Electrical Energy Storage and Intercalation Chemistry. *Science* (1979) **192**, 1126–1127 (1976).
131. Yoo, H. D. *et al.* Intercalation Pseudocapacitance of Exfoliated Molybdenum Disulfide for Ultrafast Energy Storage. *ChemNanoMat* **2**, 688–691 (2016).
132. Augustyn, V. *et al.* High-rate electrochemical energy storage through Li + intercalation pseudocapacitance. *Nat Mater* **12**, 518–522 (2013).
133. Wu, Y. *et al.* Observation of an intermediate state during lithium intercalation of twisted bilayer MoS₂. *Nature Communications* 2022 13:1 **13**, 1–8 (2022).
134. Park, S. *et al.* Phase Engineering of Transition Metal Dichalcogenides with Unprecedentedly High Phase Purity, Stability, and Scalability via Molten-Metal-Assisted Intercalation. *Advanced Materials* 2001889 (2020).
135. Xiong, F. *et al.* Li Intercalation in MoS₂: In Situ Observation of Its Dynamics and Tuning Optical and Electrical Properties. *Nano Lett* **15**, 6777–6784 (2015).
136. Tian, B. *et al.* Phase Transformations in TiS₂ during K Intercalation. *ACS Energy Lett* **2**, 1835–1840 (2017).
137. Suslov, E. A., Bushkova, O. V., Sherstobitova, E. A., Reznitskikh, O. G. & Titov, A. N. Lithium intercalation into TiS₂ cathode material: phase equilibria in a Li–TiS₂ system. *Ionics (Kiel)* **22**, 503–514 (2016).
138. Zhang, R., Yang, X., Xu, S., Xu, D. & Du, F. A kinetics study on intercalation pseudocapacitance of layered TiS₂ in K-ion batteries. *Physical Chemistry Chemical Physics* **21**, 25940–25944 (2019).
139. Whittingham, M. S. Chemistry of intercalation compounds: Metal guests in chalcogenide hosts. *Progress in Solid State Chemistry* **12**, 41–99 (1978).
140. Thackeray, M. M., Thomas, J. O. & Whittingham, M. S. Science and Applications of Mixed Conductors for Lithium Batteries. *MRS Bulletin* 2000 25:3 **25**, 39–46 (2000).
141. Cucinotta, C. S. *et al.* Electronic Properties and Chemical Reactivity of TiS₂ Nanoflakes. *Journal of Physical Chemistry C* **119**, 15707–15715 (2015).
142. Sherrell, P. C. *et al.* Thickness-Dependent Characterization of Chemically Exfoliated TiS₂ Nanosheets. *ACS Omega* **3**, 8655–8662 (2018).
143. Sokolikova, M. S. & Mattevi, C. Direct synthesis of metastable phases of 2D transition metal dichalcogenides. *Chem Soc Rev* (2020).

144. Chen, W. *et al.* Two-dimensional quantum-sheet films with sub-1.2 nm channels for ultrahigh-rate electrochemical capacitance. *Nature Nanotechnology* 2021 17:2 **17**, 153–158 (2021).
145. Panagiotopoulos, A. *et al.* 3D printed inks of two-dimensional semimetallic MoS₂/TiS₂ nanosheets for conductive-additive-free symmetric supercapacitors. *J Mater Chem A Mater* **11**, 16190–16200 (2023).
146. Heising, J. & Kanatzidis, M. G. Structure of restacked MoS₂ and WS₂ elucidated by electron crystallography. *J Am Chem Soc* **121**, 638–643 (1999).
147. Hagenmuller, P. Intercalation chemistry and chemical bonding. *Journal of Physics and Chemistry of Solids* **59**, 503–506 (1998).
148. Heising, J. & Kanatzidis, M. G. Exfoliated and restacked MoS₂ and WS₂: Ionic or neutral species? Encapsulation and ordering of hard electropositive cations. *J Am Chem Soc* **121**, 11720–11732 (1999).
149. Stoller, M. D. & Ruoff, R. S. Best practice methods for determining an electrode material's performance for ultracapacitors. *Energy and Environmental Science* vol. 3 1294–1301 (2010).
150. Shao, H., Lin, Z., Xu, K., Taberna, P. L. & Simon, P. Electrochemical study of pseudocapacitive behavior of Ti₃C₂T_x MXene material in aqueous electrolytes. *Energy Storage Mater* **18**, 456–461 (2019).
151. Zhang, S., Pan, N., Zhang, S. & Pan, N. Supercapacitors Performance Evaluation. *Adv Energy Mater* **5**, 1401401 (2015).
152. Mathis, T. S. *et al.* Energy Storage Data Reporting in Perspective—Guidelines for Interpreting the Performance of Electrochemical Energy Storage Systems. *Adv Energy Mater* **9**, 1902007 (2019).
153. Simon, P. & Gogotsi, Y. Perspectives for electrochemical capacitors and related devices. *Nature Materials* 2020 19:11 **19**, 1151–1163 (2020).
154. Rueschhoff, L., Costakis, W., Michie, M., Youngblood, J. & Trice, R. Additive Manufacturing of Dense Ceramic Parts via Direct Ink Writing of Aqueous Alumina Suspensions. *Int J Appl Ceram Technol* **13**, 821–830 (2016).
155. Costakis, W. J., Rueschhoff, L. M., Diaz-Cano, A. I., Youngblood, J. P. & Trice, R. W. Additive manufacturing of boron carbide via continuous filament direct ink writing of aqueous ceramic suspensions. *J Eur Ceram Soc* **36**, 3249–3256 (2016).
156. Fu, Z. *et al.* Micro- and macroscopic design of alumina ceramics by robocasting. *J Eur Ceram Soc* **37**, 3115–3124 (2017).
157. Feilden, E. *et al.* 3D Printing Bioinspired Ceramic Composites. *Scientific Reports* 2017 7:1 **7**, 1–9 (2017).
158. Glymond, D. & Vandeperre, L. J. Robocasting of MgO-doped alumina using alginic acid slurries. *Journal of the American Ceramic Society* **101**, 3309–3316 (2018).
159. Tang, X. *et al.* Generalized 3D Printing of Graphene-Based Mixed-Dimensional Hybrid Aerogels. *ACS Nano* **12**, 3502–3511 (2018).

160. Jiang, Y. *et al.* Direct 3D Printing of Ultralight Graphene Oxide Aerogel Microlattices. *Adv Funct Mater* **28**, 1707024 (2018).
161. Ke Sun, C. *et al.* 3D Printing of Interdigitated Li-Ion Microbattery Architectures. *Advanced Materials* **25**, 4539–4543 (2013).
162. Valentine, A. D. *et al.* Hybrid 3D Printing of Soft Electronics. *Advanced Materials* **29**, 1703817 (2017).
163. Lacey, S. D. *et al.* Extrusion-Based 3D Printing of Hierarchically Porous Advanced Battery Electrodes. *Advanced Materials* **30**, 1705651 (2018).
164. Feilden, E., Blanca, E. G. T., Giuliani, F., Saiz, E. & Vandeperre, L. Robocasting of structural ceramic parts with hydrogel inks. *J Eur Ceram Soc* **36**, 2525–2533 (2016).
165. Wypych, F. & Schöllhorn, R. 1T-MoS₂, a new metallic modification of molybdenum disulfide. *J Chem Soc Chem Commun* 1386–1388 (1992).
166. Zhuang, H. L., Johannes, M. D., Singh, A. K. & Hennig, R. G. Doping-controlled phase transitions in single-layer MoS₂. *Phys Rev B* **96**, 165305 (2017).
167. Dungey, K. E., Curtis, M. D. & Penner-Hahn, J. E. Structural Characterization and Thermal Stability of MoS₂ Intercalation Compounds. *Chemistry of Materials* **10**, 2152–2161 (1998).
168. Dou, Q., Karim, A. A. & Loh, X. J. Modification of Thermal and Mechanical Properties of PEG-PPG-PEG Copolymer (F127) with MA-POSS. *Polymers* 2016, Vol. 8, Page 341 **8**, 341 (2016).
169. Huang, Q. *et al.* The Mechanistic Insights into the 2H-1T Phase Transition of MoS₂ upon Alkali Metal Intercalation: From the Study of Dynamic Sodiation Processes of MoS₂ Nanosheets. *Adv Mater Interfaces* **4**, 1700171 (2017).
170. Heising, J. & Kanatzidis, M. G. Exfoliated and restacked MoS₂ and WS₂: Ionic or neutral species? Encapsulation and ordering of hard electropositive cations. *J Am Chem Soc* **121**, 11720–11732 (1999).
171. Lin, M. L., Wu, J. Bin, Liu, X. L. & Tan, P. H. Probing the shear and layer breathing modes in multilayer graphene by Raman spectroscopy. *Journal of Raman Spectroscopy* **49**, 19–30 (2018).
172. Zhao, Y. *et al.* Interlayer breathing and shear modes in few-trilayer MoS₂ and WSe₂. *Nano Lett* **13**, 1007–1015 (2013).
173. Yao, B. *et al.* Printing Porous Carbon Aerogels for Low Temperature Supercapacitors. *Nano Lett* (2021).
174. Chang, P., Mei, H., Zhou, S., Dassios, K. G. & Cheng, L. 3D printed electrochemical energy storage devices. *J Mater Chem A Mater* **7**, 4230–4258 (2019).
175. Brown, E. *et al.* 3D printing of hybrid MoS₂-graphene aerogels as highly porous electrode materials for sodium ion battery anodes. *Mater Des* **170**, 107689 (2019).
176. Song, Y. *et al.* Three-dimensional carbon architectures for electrochemical capacitors. *J Colloid Interface Sci* **509**, 529–545 (2018).

177. Lewis, J. A. Direct Ink Writing of 3D Functional Materials. *Adv Funct Mater* **16**, 2193–2204 (2006).
178. Yao, B. *et al.* Efficient 3D Printed Pseudocapacitive Electrodes with Ultrahigh MnO₂ Loading. *Joule* **3**, 459–470 (2019).
179. Gogotsi, Y. & Simon, P. True performance metrics in electrochemical energy storage. *Science* (1979) **334**, 917–918 (2011).
180. Kaner, R. *et al.* Towards establishing standard performance metrics for batteries, supercapacitors and beyond. *Chem Soc Rev* **48**, 1272–1341 (2019).
181. Cao, Y., Li, M., Lu, J., Liu, J. & Amine, K. Bridging the academic and industrial metrics for next-generation practical batteries. *Nature Nanotechnology* | **14**, (2019).
182. Baptista, J. M., Sagu, J. S., KG, U. W. & Lobato, K. State-of-the-art materials for high power and high energy supercapacitors: Performance metrics and obstacles for the transition from lab to industrial scale – A critical approach. *Chemical Engineering Journal* **374**, 1153–1179 (2019).
183. Kyeremateng, N. A., Brousse, T. & Pech, D. Microsupercapacitors as miniaturized energy-storage components for on-chip electronics. *Nature Nanotechnology* 2016 12:1 **12**, 7–15 (2016).
184. Tiwari, P., Jaiswal, J. & Chandra, R. Hierarchical growth of MoS₂@CNT heterostructure for all solid state symmetric supercapacitor: Insights into the surface science and storage mechanism. *Electrochim Acta* **324**, 134767 (2019).
185. Zhang, C. *et al.* Hybridized 1T/2H-MoS₂/graphene fishnet tube for high-performance on-chip integrated micro-systems comprising supercapacitors and gas sensors. *Nano Research* 2020 14:1 **14**, 114–121 (2020).
186. Zhao, J., Gao, L., Wang, Z., Wang, S. & Xu, R. Boosting the performance of flexible in-plane micro-supercapacitors by engineering MoS₂ nanoparticles embedded in laser-induced graphene. *J Alloys Compd* **887**, 161514 (2021).
187. Wang, Q., Liang, X., Zhang, D. & Miao, M. A multifunctional supercapacitor based on 2D nanosheets on a flexible carbon nanotube film. *Dalton Transactions* **49**, 9312–9321 (2020).
188. Mohammed, M. M. M. & Chun, D. M. All-Solid-State Supercapacitor Based on MoS₂–Graphite Composite Prepared by the Vacuum Kinetic Spray Method. *Journal of Thermal Spray Technology* **28**, 963–973 (2019).
189. Clerici, F. *et al.* In situ MoS₂ Decoration of Laser-Induced Graphene as Flexible Supercapacitor Electrodes. *ACS Appl Mater Interfaces* **8**, 10459–10465 (2016).
190. Sharma, A. *et al.* All-solid-state asymmetric supercapacitors based on VS₄ nano-bundles and MXene nanosheets. *J Mater Sci* **56**, 20008–20025 (2021).
191. Choudhary, N. *et al.* High-Performance One-Body Core/Shell Nanowire Supercapacitor Enabled by Conformal Growth of Capacitive 2D WS₂ Layers. *ACS Nano* **10**, 10726–10735 (2016).

192. Mukherjee, S. *et al.* Exfoliated transition metal dichalcogenide nanosheets for supercapacitor and sodium ion battery applications. *R Soc Open Sci* **6**, (2019).
193. Han, Z. *et al.* A Study of All-solid-state Planar Micro-supercapacitors Using Printable MoS₂ Inks. **50**, 452–455 (2020).
194. Cattelan, M. *et al.* New Strategy for the Growth of Complex Heterostructures Based on Different 2D Materials. *Chemistry of Materials* **27**, 4105–4113 (2015).
195. Martinez, H. *et al.* Influence of the cation nature of high sulfur content oxysulfide thin films MOySz (M=W, Ti) studied by XPS. *Appl Surf Sci* **236**, 377–386 (2004).
196. Dupin, J. C., Gonbeau, D., Benqlilou-Moudden, H., Vinatier, P. & Levasseur, A. XPS analysis of new lithium cobalt oxide thin-films before and after lithium deintercalation. *Thin Solid Films* **384**, 23–32 (2001).
197. Moulder, J. F., Chastain, Jill. & King, R. C. Handbook of x-ray photoelectron spectroscopy : a reference book of standard spectra for identification and interpretation of XPS data. 261 (1995).
198. Huckaba, A. J. *et al.* Low-Cost TiS₂ as Hole-Transport Material for Perovskite Solar Cells. *Small Methods* **1**, 1700250 (2017).
199. Liu, F. *et al.* Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential. *Carbon Energy* **1**, 173–199 (2019).
200. Yang, S. *et al.* Fluoride-Free Synthesis of Two-Dimensional Titanium Carbide (MXene) Using A Binary Aqueous System. *Angewandte Chemie* **130**, 15717–15721 (2018).
201. Zeng, Z. *et al.* Single-Layer Semiconducting Nanosheets: High-Yield Preparation and Device Fabrication. *Angewandte Chemie International Edition* **50**, 11093–11097 (2011).
202. Li, J. *et al.* Printable two-dimensional superconducting monolayers. *Nat Mater* 1–7 (2020).
203. Yang, Y. *et al.* Electrochemical exfoliation of graphene-like two-dimensional nanomaterials. *Nanoscale* **11**, 16 (2018).

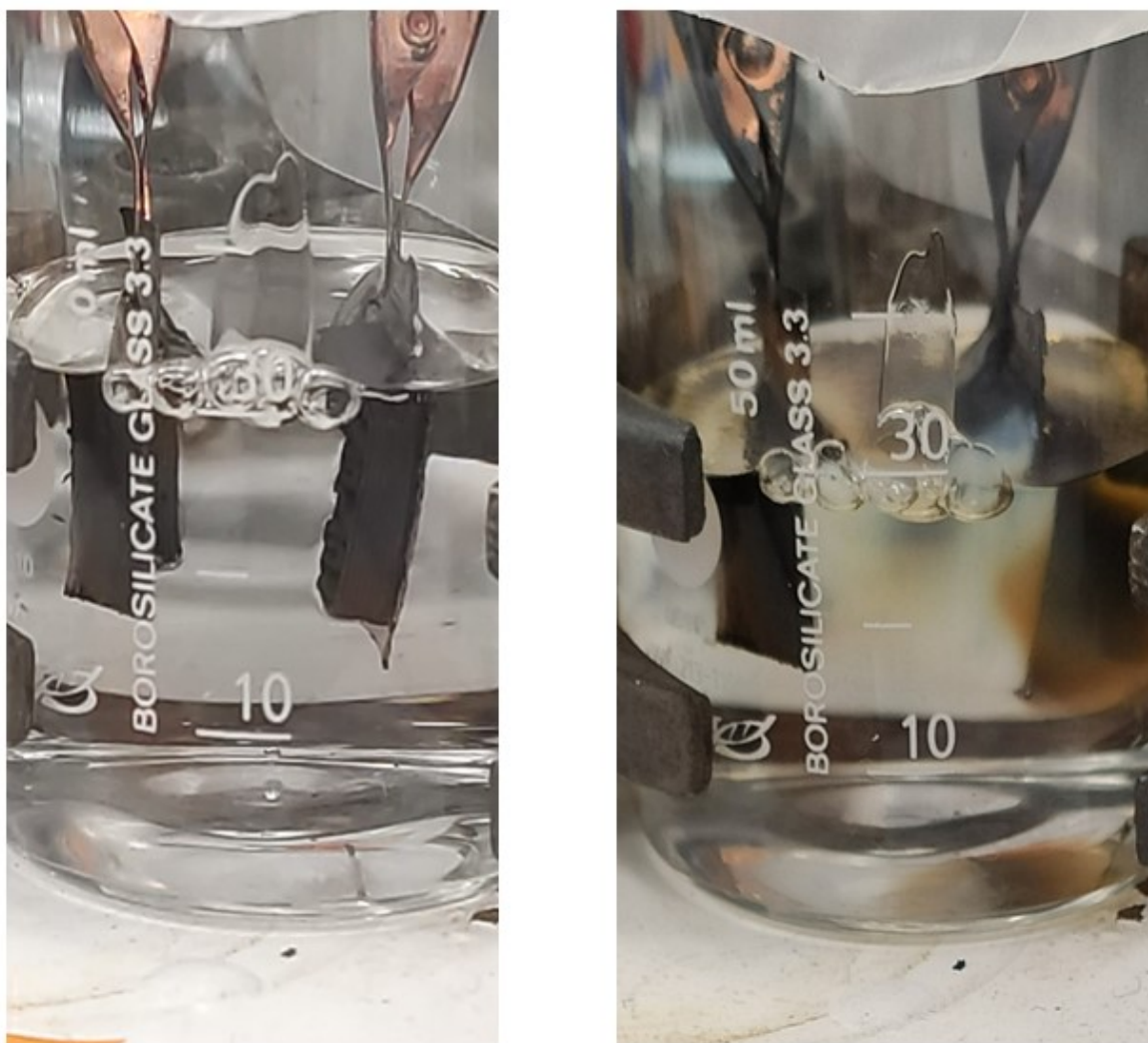


Figure 56 - Electrochemical Cell Assembly. Two 10layered $\text{MoS}_2/\text{TiS}_2$ 50%wt serpentine electrodes fixed in position with copper clamps in 50ml borosilicate glass cells with 30ml initial volume of $1\text{M H}_2\text{SO}_4$ Pluronic 27%w/v hydrogel electrolyte, sealed with parafilm. Fresh device (left). Cycled Device after 50,000 cycles (right). This cell was a failed example. The active electrode area in the hydrogel electrode is $1\text{x}1\text{cm}$ but the tip of the substrate is less than 1cm . Gradual wetting of the substrate in contact with copper clips resulted in contamination of the cell.

Appendices

A1 Electrochemical exfoliation of MoS_2

Electrochemical exfoliation is a very attractive technique with high upscaling potential. If crystals or films created from bulk powders can be exfoliated, they can be readily scaled up to fit demand in already established industrial manufacturing. A lot of successful studies have been carried out in a variety of Layered bulk materials but usually use Pt or volatile metals as counter electrodes, making the process expensive and dangerous^{199–203}. To that, an initial

study on the exfoliation potential of bulk MoS₂ crystals with abundant Zn foil as the counter electrode in 1M Na₂SO₄ aqueous electrolyte.

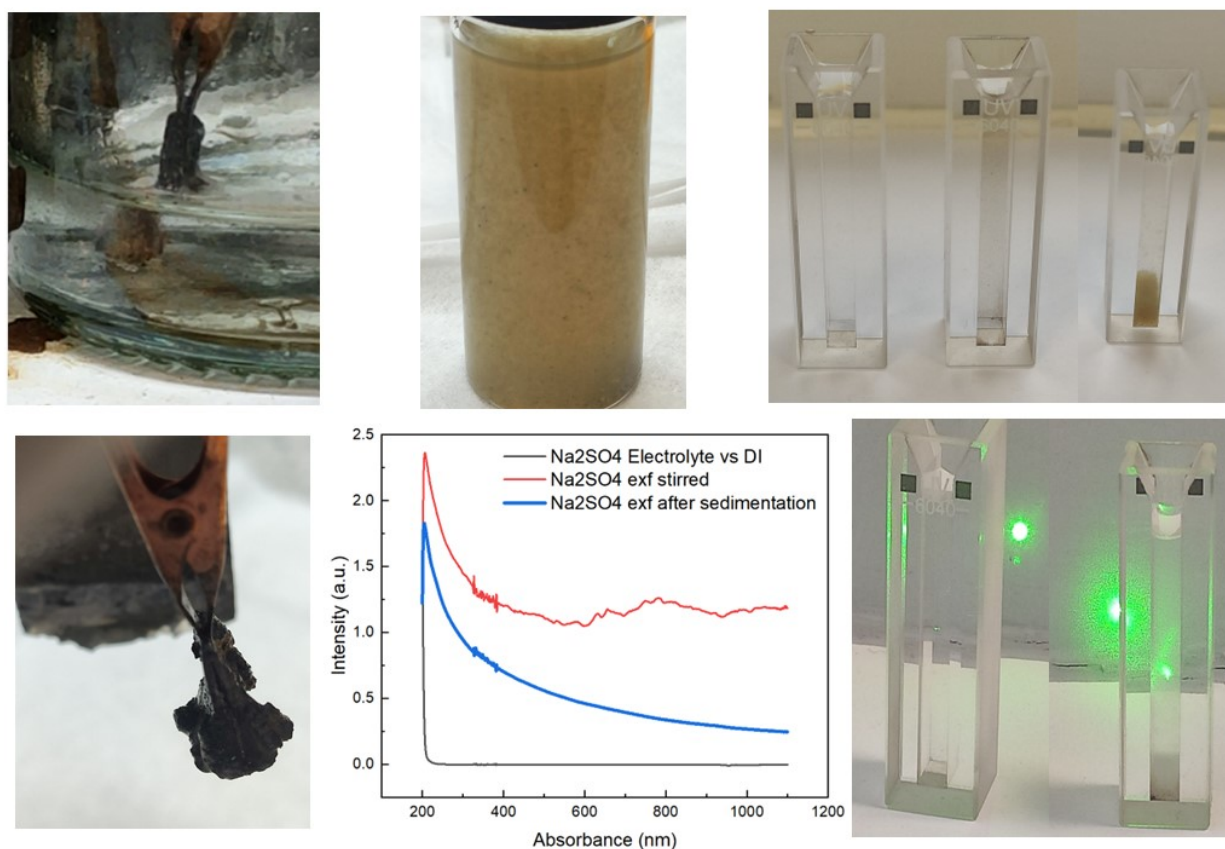


Figure 56 MoS₂ Crystal exfoliation versus Zn foil in 1M Na₂SO₄ electrolyte. Exfoliation yield assessment through UV-Vis Spectroscopy.

Exfoliation was carried out in an electrochemical cell, by applying steadily ramped voltage on each of the two-electrode. Starting from 2V for 120s for each electrode and gradually reaching 8V with a 2V step size. The MoS₂ yield after the exfoliation can be seen in Figure 56.

There was a clear distinction between the exfoliated particles and the otherwise colourless Na₂SO₄. However, exfoliated particles were large enough to sediment on the bottom after several hours.

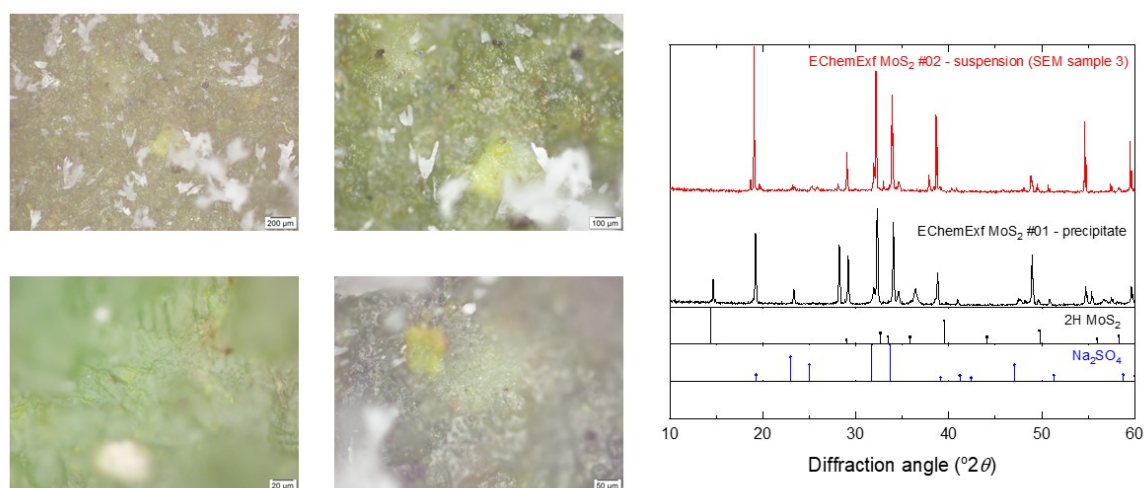


Figure 57 Drop casted MoS₂ exfoliation yield on glass substrates. Images and Crystallographic results.

Furthermore, sedimented exfoliations were drop casted onto glass substrates and optical microscopy images can be seen in Figure 57. As is evident, crystallised particles of Na₂SO₄ can be seen on the surface along with a characteristic green hue of MoS₂. The crystallographic nature of the exfoliated yields was investigated with XRD. As can be seen in Figure 57, both MoS₂ and Na₂SO₄ are present in exfoliated yields and further processing steps need to be taken in order to isolate pure MoS₂ flakes and study them.

A2 Thermal Annealing effect in electrochemistry of 3D printed out-of-plane microsupercapacitors

Thermal annealing effect in electrochemical performance was investigated in a study testing 10layered structures as printed and after thermal annealing held at 470°C for 1', under Ar flux. Annealing was carried out to Pluronic from the structures and expose the conductive nanosheets in direct contact with the hydrogel electrolyte. Electrochemical testing of two-electrode symmetric devices was carried out, using Cyclic Voltammetry, Impedance Spectroscopy and Cyclic Charge Discharge.

A2 Cyclic Voltammetry

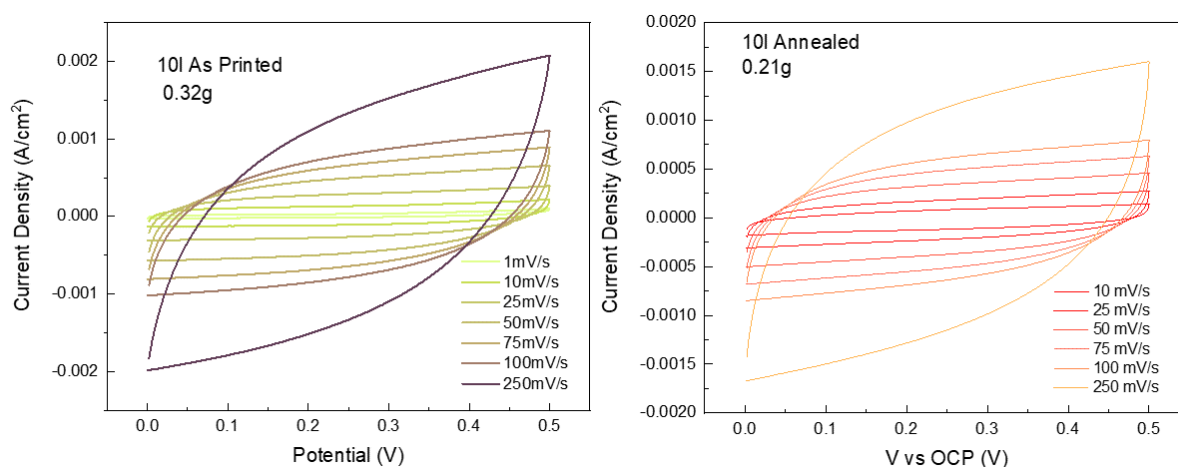


Figure 58 Cyclic Voltammograms at different scanrates for 10layered serpentine as printed structures (left) and 10layered serpentine structures after thermal annealing (right).

Cyclic Voltammograms at different scanrates for as printed versus annealed 10layered serpentine structures can be seen in Figure 58. These show quasi-rectangular behaviour due to electrostatic double-layer capacitance and solvated ion adsorption in the surface to near-surface of MoS₂/TiS₂ conductive nanosheets, with no crystallographic phase change. Both examples demonstrate identical mechanisms, indicating there is no electrochemical contribution of the polymeric compounds, as was expected. Whereas as printed structures generate more current density in the device's operating potential window and therefore has higher capacitance. This could be attributed to the loss of lithiated species in the active material and the conversion of semimetallic 1T' MoS₂ to semiconducting 2H.

A2 Electrochemical Impedance Spectroscopy

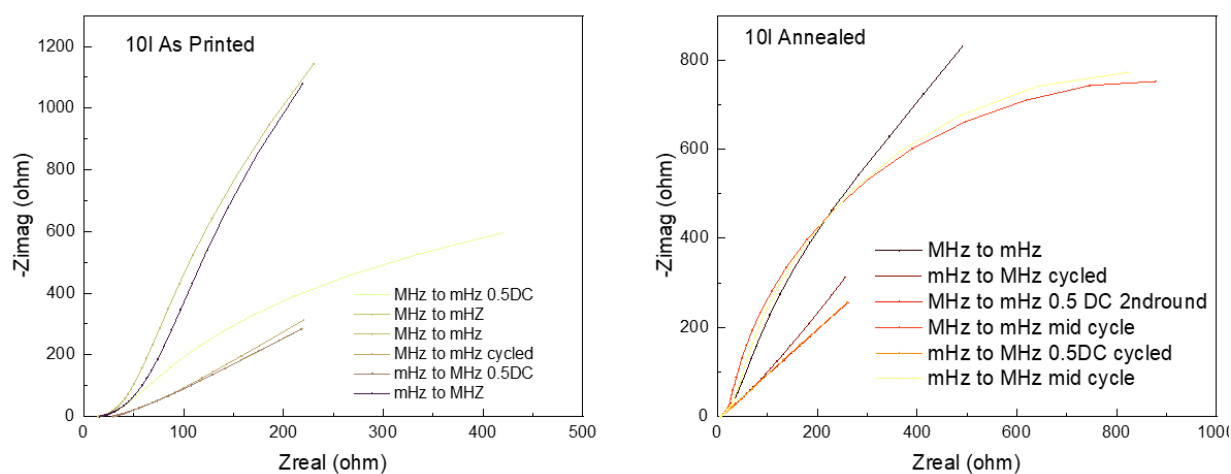


Figure 59 Electrochemical Impedance Spectroscopies of 10layered serpentine structure on carbon foil as printed (left) and after thermal annealing (right).

Electrochemical Impedance results demonstrate the same energy storage mechanisms as CV. As is demonstrated on Figure 59, energy storage arises predominantly from electrostatic double-layer capacitance. An initial semicircle acts as the resistive element in the interface between the substrate and the as printed electrode, due to the polymeric barrier which is followed by a capacitive slope once the electrode is electrochemically activated. The sloping final region falls to the resistive behaviour of solvated ion absorption once a slower regime is dominating the system. Annealed examples lacked the initial semicircle, possibly due to more surface area of the active material coming in direct contact with the substrate and again showcasing resistive elements due to solvated ion adsorption in the surface to near-surface of the active material. When a direct bias of 0.5V is applied to devices, resistive elements acting in the capacitive elements of the electrode as an ionic direction flow is established. Annealed examples demonstrated less impedance overall as opposed to the as printed examples. This behaviour is expected from a larger abundance of non-active polymeric compounds.

A2 Cyclic Charge Discharge

The final confirmation of mechanisms and electrochemical results comes with cyclic charge discharge experiments. Symmetric triangular cyclic profiles are indicative of the electrostatic

capacitive behaviour with negligible ohmic losses and an imperceptible curvature of the sloping regions, again indicative of the adsorption procedure, which becomes more pronounced during longer cycles.

A2 Conclusions

Based on these results and in this hydrogel system, as printed structures outperformed annealed examples at all ranges. The only reason that an energy demanding post-printing step such as thermal annealing could be justified is contact optimisation. Otherwise, the mass/ volume that is lost in the hydrogel removing process is gained by more electrolyte volume of the same carrier hydrogel. Therefore, as printed electrode examples were only electrochemically tested henceforth.

A3 MoS₂/TiS₂/Graphene Blends

Based on the MoS₂/TiS₂50%wt ink formulation paradigm, another study is demonstrated. Graphene in 5%wt is added to MoS₂50%wt and MoS₂/TiS₂50%wt inks to further increase the conductivity. Graphene is an upscalable abundant material and has already been demonstrated in printed electrochemical energy storage devices based on the conductivity and ability to intercalate solvated ions in between the sheets. Therefore, it was deemed a prime candidate to further increase the performance of all-printed electrochemical energy storage devices.

A3 Printed Supercapacitors

For this study, thin films of all formulated inks were spread on carbon foil thin films in 1x1cm of working electrode surface area. These were assembled in electrochemical cells with 1cm of interelectrode area and sealed with 1MH₂SO₄ Pluronic 27%w/v hydrogel electrolyte. The same electrochemical scripts were used to probe the underlying energy storage mechanisms.

A3 Cyclic Voltammetry

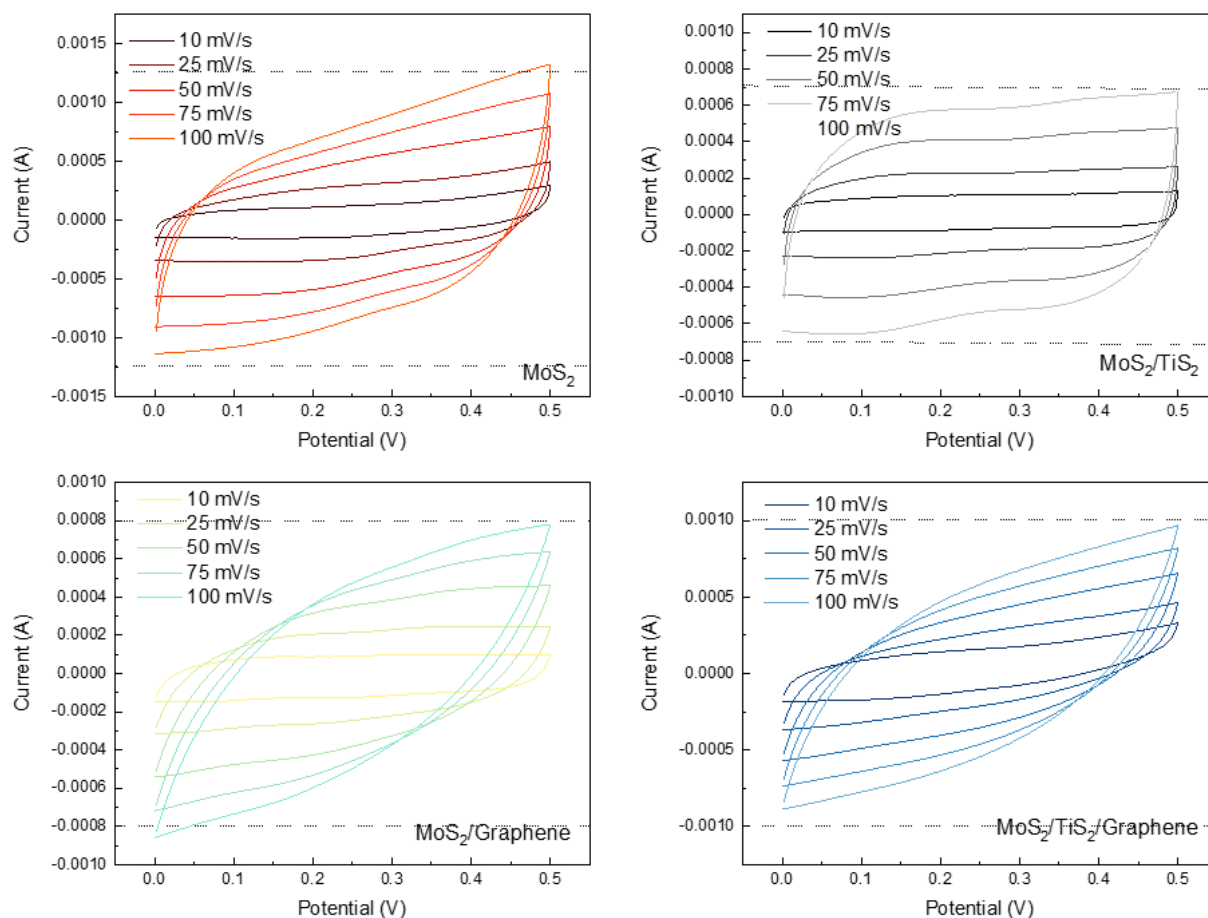


Figure 60 Cyclic Voltammograms of 50%wt MoS₂ (top left), MoS₂/TiS₂(top right), MoS₂/Graphene (bottom left) and MoS₂/TiS₂/Graphene (bottom right) thin film electrodes, in 1M H₂SO₄ Pluronic 27%w/v hydrogel electrolyte across 10-100 mV/s.

From Cyclic Voltammograms shown on Figure 60, MoS₂ inks showcase quasi-rectangular Voltammograms indicative of electrostatic energy storage with a sharp rise at high potentials due to catalytic reactions. This influences the generated current but is a non-reversible reaction and could hinder devices cyclability. MoS₂/TiS₂ electrodes demonstrate rectangular cyclic voltammograms with capacitive electrostatic, adsorption and reversible intercalation mechanisms with no crystallographic phase change. This intercalation mechanism can be observed from four barely noticeable reduction/oxidation peaks around 0.4V and 0.1V. Clearly defined redox peaks is a sign of crystallographic phase change. However, it has been observed that MoS₂ undergoes an intermediate state during lithium intercalation of twisted

bilayers⁷¹. Therefore, these slight redox peaks could be an indication of this meta-stable phenomenon.

Overall, MoS₂/Graphene has better contacting, increased current generation and quasi-rectangular cyclic voltammograms. This phenomenon could arise from suppression of catalytic reactions or because the capacitive elements are dominant over catalytic ones. MoS₂/TiS₂/Graphene Cyclic Voltammograms exhibit higher current generation and more rectangular shapes. One hypothesis is that TiS₂ sheets are increasing adsorption and intercalation phenomena present in the electrodes and has the best conductivity that arises from reversible reactions.

A3 Galvanostatic Charge Discharge

Capacitance and cyclability were measured with Cyclic Charge Discharge at the 1-0.1 mA/cm² range. Charge/Discharge profiles exhibit capacitive behaviour in triangular symmetric shape. In line with Cyclic Voltammetry data, MoS₂ barely outperforms MoS₂/TiS₂ electrodes, especially in slower charge/discharge times when lower current density is used. However, based on Cyclic Voltammograms, this arises from irreversible catalytic reaction which becomes more prominent after 100 cycles and will limit the device's cyclability. All other devices demonstrate reversible reactions with enhanced performance when 5%wt Graphene is added respectively.

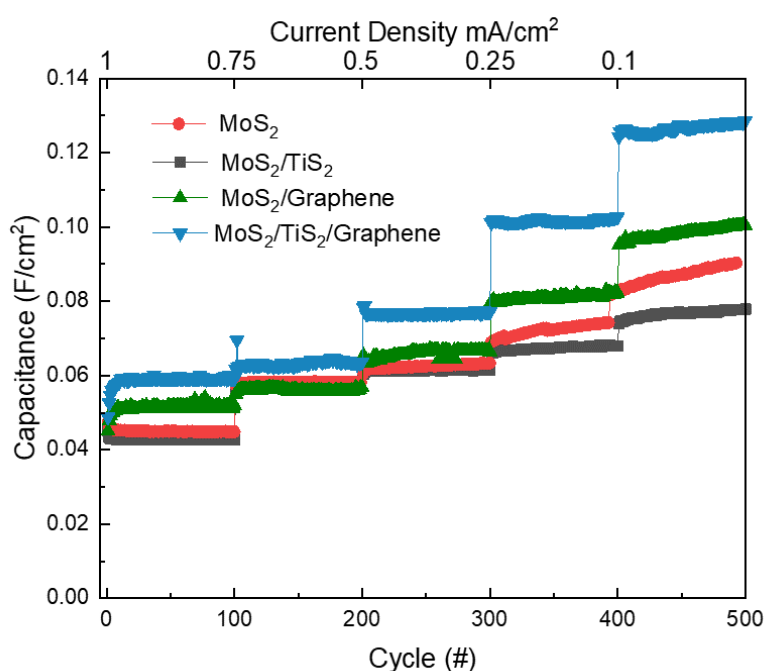


Figure 61 Capacitance versus cycle number as extracted from Charge/Discharge profiles of symmetric devices based on MoS₂, MoS₂/TiS₂, MoS₂/Graphene and MoS₂/TiS₂/Graphene electrodes at current densities from 1-0.1mA/cm².

A3 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopies of MoS_2 , $\text{MoS}_2/\text{TiS}_2$, $\text{MoS}_2/\text{Graphene}$ and $\text{MoS}_2/\text{TiS}_2/\text{Graphene}$ can be seen in Figure 61. MoS_2 appears to be more capacitive to $\text{MoS}_2/\text{TiS}_2$ but has higher impedance overall. This could be due to less diffusion mechanisms in the MoS_2 examples. 5%wt Graphene addition limits the overall impedance but doesn't change the mechanisms significantly.

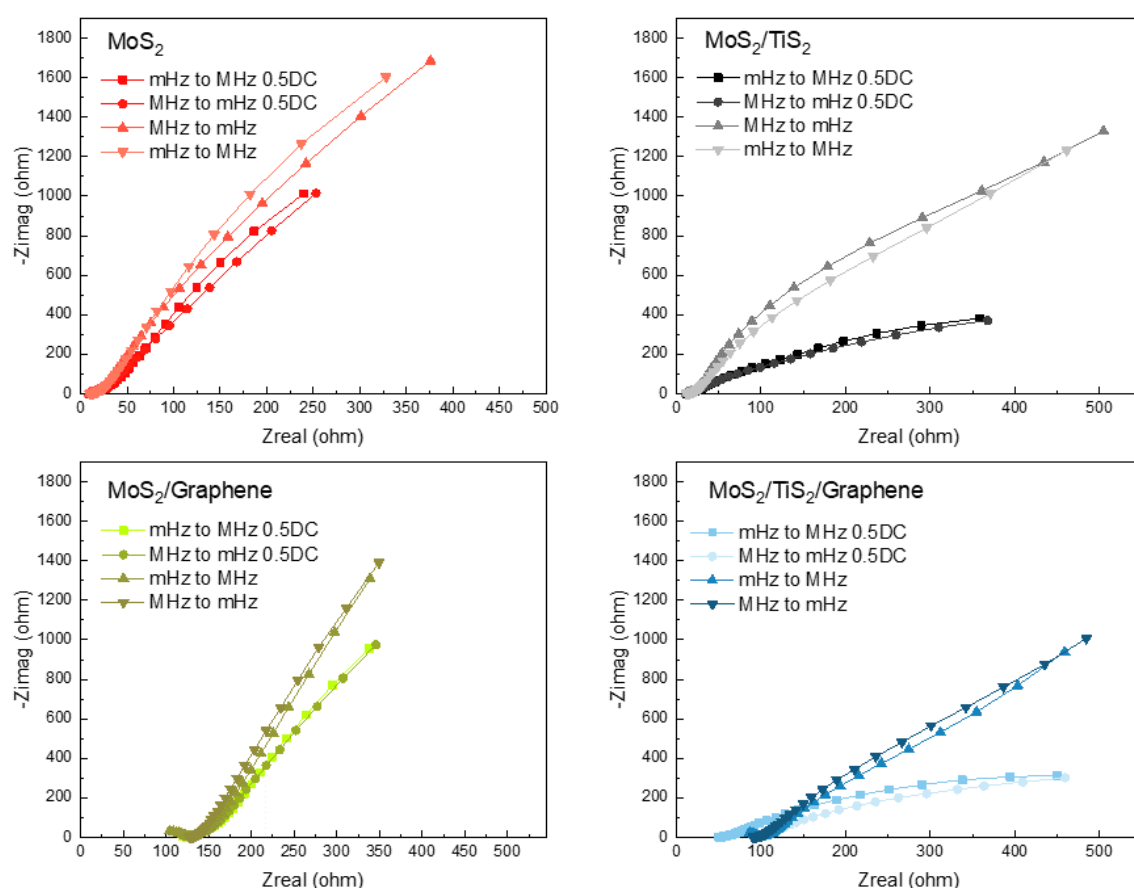


Figure 62 Electrochemical Impedance Spectroscopies of symmetric devices based on MoS_2 , $\text{MoS}_2/\text{TiS}_2$, $\text{MoS}_2/\text{Graphene}$ and $\text{MoS}_2/\text{TiS}_2/\text{Graphene}$ electrodes at different frequencies and different potentials.

A3 Conclusions

Overall, Graphene is demonstrated as a potential additive for enhancing the conductivity and electrochemical energy storage capabilities of electrodes based on TMDs. However, these mechanisms are always straightforward, and conductivity could initiate different electrochemical reactions. Therefore, detailed studies need to be carried out to assess the capabilities of additives.

Dissemination

Publications from work or parts of work present in this thesis

Panagiotopoulos A., Nagaraju G., Tagliaferri S., Grotta C., Sherrell P. C., Sokolikova M., Cheng G., Iacoviello F., Sharda K., Mattevi C. '3D printed inks of two-dimensional semimetallic MoS₂/TiS₂ nanosheets for conductive-additive-free symmetric supercapacitors. (Advance Article) *J. Mater. Chem. A.*, 2023, DOI: 10.1039/D3TA02508J

Goli N., Tagliaferri S., **Panagiotopoulos A.**, Och M., Quintin-Baxendale R., Mattevi C. 'Durable Zn-ion hybrid capacitors using 3D printed carbon composites' (Paper) *J. Mater. Chem. A*, 2022, 10, 15665-15676, DOI: 10.1039/D2TA03488C

Tagliaferri S., Goli N., **Panagiotopoulos A.**, Och M., Cheng G., Iacoviello F., Mattevi C., 'Aqueous Inks of Pristine Graphene for 3D Printed Microsupercapacitors with High Capacitance' (Paper) *ACS Nano* 2021, 15, 9, 15342–15353, DOI: 10.1021/acsnano.1c06535

Tagliaferri S., **Panagiotopoulos A.**, Mattevi C. 'Direct Ink Writing of Energy Materials' (Review Article) *Mater. Adv.*, 2021, 2, 540-563. DOI: 10.1039/D0MA00753F

Other Publications

Xu L, Ramadan S., Gil Rosa B., Zhang Y., Yin T., Torres E., Shaforost E., **Panagiotopoulos A.**, Li B., Kerherve G., Kim D. K., Mattevi C., Jiao L.R., Petrov P.K., Klein N., ' On-chip integrated graphene aptasensor with portable readout for fast and label-free COVID-19 detection in virus transport medium' (Paper) *Sens. Diagn.*, 2022, 1, 719-730, DOI: 10.1039/D2SD00076H

Ioannidis L. A., Nikolaou P., **Panagiotopoulos A.**, Vassi A., Topoglidis E., 'Microperoxidase-11 modified mesoporous SnO₂ film electrodes for the detection of antimalarial drug artemisinin' (Paper) *Anal. Methods*, 2019, 11, 3117-3125, DOI: 10.1039/C9AY00764D

Panagiotopoulos A., Gkouma A., Vassi A., Johnson C.J., Cass A.E.G., Topoglidis E., 'Hemin modified SnO₂ Films on ITO-PET with Enhanced Activity for Electrochemical Sensing' (Paper) *Electroanalysis*, 2018, 30,9,1956-1964, DOI: 10.1002/elan.201800188

Sagasti, A., Bouropoulos N., Kouzoudis D., **Panagiotopoulos A.**, Topoglidis E., Gutierrez Jon, 'Nanostructured ZnO in a Metglas/ZnO/Hemoglobin Modified Electrode to Detect the

Oxidation of Hemoglobin Simultaneously by Cyclic Voltammetry and Magnetoelastic Resonance' (Paper) Materials, 2017, 10,8,849, DOI: 10.3390/ma10080849

Presentations

This work has been presented numerous times in internal and external international conferences.

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Author: Michael K. Hausmann, Patrick A. Rühls, Gilberto Siqueira, et al

Publication: ACS Nano

Publisher: American Chemical Society

Date: Jul 1, 2018

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Hydrogels as functional components in artificial cell systems

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Publication: Nature Reviews Chemistry

Publisher: Springer Nature

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Figure 63 - Exothermic reaction of TMD exfoliation via direct hydration of Li intercalated TMD bulk powders.