

IMPERIAL

**Ultrafast Spectroscopic Studies of Two-
Dimensional Materials and Devices**

Tong Wang

Department of Chemistry
Imperial College London

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This thesis is dedicated to my parents and my wife and in memory of my grandmother.

Declaration of Originality

I hereby declare that the contents of this thesis were originated from and written entirely by me, except where specific reference is made to the contribution of work by others. This work has not been submitted, either in whole or in part, for any other degree or diploma at this or any other university.

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Tong Wang

September 2024

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Abstract

2D materials have garnered significant interest over the past two decades due to their extraordinary properties, including strong quantum confinement, high carrier mobility, and unique light-matter interactions. These attributes make them highly promising for applications in electronics and optoelectronics. Despite substantial progress in large-scale fabrication methods and device optimization, fundamental understanding of carrier dynamics and excitonic behaviour remains limited. Such insights are critical for advancing 2D materials and their integration into next-generation technologies.

This thesis investigates the photophysics of excited states—particularly free carriers and excitons—in 2D materials using steady-state and ultrafast spectroscopic techniques. The first two chapters introduce the structural and photophysical principles of widely studied transition metal dichalcogenides (TMDs) and MXenes. Chapter 3 details the spectroscopic methods employed in this research.

Chapter 4 investigates hot carrier relaxation in SL TMDs using pump-probe photoluminescence spectroscopy. It reveals the roles of carrier density and excess energy in cooling dynamics and identifies evidence of hot carrier trapping at high energy levels.

Chapter 5 focuses on carrier and lattice cooling in metallic MXene thin films, showing that while carrier relaxation occurs within picoseconds, lattice cooling requires hundreds of nanoseconds due to inefficient inter-flake thermal transport.

In Chapter 6, steady-state and ultrafast photocurrent spectroscopy are applied to multilayer MoS₂ photodetectors, demonstrating band-like photoexcited free carrier transport, and providing evidence of an exciton-to-dark-state transition.

Overall, this thesis provides valuable insights into the interactions among free carriers, phonons, and excitons in 2D materials following photoexcitation. The findings contribute to the fundamental understanding of 2D material photophysics and support their development for future technological applications.

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List of Publications

1. **Tong Wang**, Chengning Yao, Ruoyu Gao, Martin Holicky, Beier Hu, Sihui Liu, Shuwei Wu, Hyunho Kim, Haoqing Ning, Felice Torrisi, Artem A. Bakulin, Ultrafast Carrier and Lattice Cooling in Ti_2CT_x MXene Thin Films (accepted by *Nano Letters*, DOI: 10.1021/acs.nanolett.4c04583).
2. Haoqing Ning, Marios Maimaris, Jiewen Wei, Emilie G rouville, Evangelos Moutoulas, Zhu Meng, Clement Ferchaud, Dmitry Maslennikov, Navendu Mondal, **Tong Wang**, Colin Chow, Aleksandar P Ivanov, Joshua B. Edel, Saif A. Haque, Misha Ivanov, Jon P. Marangos, Dimitra G. Georgiadou, Artem A. Bakulin, Ultrafast Broadband Strong-Field Tunnelling in Asymmetric Nanogaps for Time-Resolved Nanoscopy, *arXiv:2405.12851*, (under review).
3. Sander J.W. Vonk, P. Tim Prins, **Tong Wang**, Jan Matthys, Luca Giordano, Pieter Schiettecatte, Navendu Mondal, Jessi E.S. van der Hoeven, Thomas R. Hopper, Zeger Hens, Pieter Geiregat, Artem A. Bakulin, Freddy T. Rabouw, Hot-Carrier Trapping Preserves High Quantum Yields but Limits Optical Gain in InP-Based Quantum Dots (under review).
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6. Ben P. Carwithen, Thomas R Hopper, Ziyuan Ge, Navendu Mondal, **Tong Wang**, Rozana Mazlumian, Xijia Zheng, Franziska Krieg, Federico Montanarella, Georgian Nedelcu, Martin Kroll, Miguel Albaladejo Siguan, Jarvist M Frost, Karl Leo, Yana Vaynzof, Maryna I Bodnarchuk, Maksym V Kovalenko, Artem A. Bakulin, Confinement and Exciton Binding Energy Effects on Hot Carrier Cooling in Lead Halide Perovskite Nanomaterials. *ACS Nano* 2023, 17, 6638.
7. **Tong Wang**, Thomas R Hopper, Navendu Mondal, Sihui Liu, Chengning Yao, Xijia Zheng, Felice Torrisi, Artem A. Bakulin, Hot Carrier Cooling and Trapping in Atomically Thin WS₂ Probed by Three-Pulse Femtosecond Spectroscopy, *ACS Nano* 2023, 17, 6330.

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Nomenclature

Physical Constants

$\hbar$	Reduced Plank's constant	$1.05 \times 10^{-34} \text{ J s}$
e	Elementary charge	$1.60 \times 10^{-19} \text{ C}$
ε_0	Permittivity of vacuum	$8.85 \times 10^{-12} \text{ F m}^{-1}$
g	Standard Gravity	9.8 m s^{-2}
k_B	Boltzmann constant	$1.38 \times 10^{-23} \text{ J K}^{-1}$

Chemical and Material Names

BBO	Beta barium borate
BP	Black phosphorus
DMF	Dimethylformamide
EtOH	Ethanol
h-BN	Hexagonal boron nitride
IPA	Isopropanol
ITO	Indium tin oxide
MeCN	Acetonitrile
NMP	N-Methylpyrrolidone

PVP	Polyvinylpyrrolidone
THAB	Tetrabutylammonium bromide
YAG	Yttrium aluminium garnet

Abbreviations

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic force microscopy
CB	Conduction band
CCD	Charge-coupled device
CVD	Chemical vapor deposition
ES	Excited state
FC	Free carrier
FET	Field-effect transistor
GS	Ground state
IR	Infrared

LPF	Long-pass filter
NIR	Near-infrared
PL	Photoluminescence
PP	Pump-probe
PPP	Pump-push-probe
PPPe	Pump-push-photocurrent
SL	Single layer
SPF	Short-pass filter
TA	Transient absorption
THz	Terahertz
UV	Ultraviolet
VB	Valance band
vis	Visible

“路漫漫其修远兮，吾将上下而求索。”

——《离骚》屈原

Chapter 1 Introduction

1.1 Development of 2D materials and motivation

The exploration of 2D materials represents one of the most significant advancements in the field of materials science over the past two decades. Initiated by the successful isolation of graphene by mechanical exfoliation in 2004,¹ the field has expanded to explore a wide range of materials with unique and promising properties. Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, has demonstrated exceptional mechanical, thermal, and electrical properties, which earned the Nobel Prize in Physics in 2010 for its discoverers, Geim and Novoselov.¹ This seminal discovery has paved the way for the synthesis and study of other 2D materials. The development of 2D materials and devices is confronted with challenges such as scalable production techniques, stability under operational conditions, and seamless integration into existing manufacturing processes. These challenges are at the forefront of current research efforts, aiming to harness the full potential of these materials in practical applications.² Fig 1.1 summarises a timeline of some key steps in the development of widely studied 2D materials in the past two decades. The development of 2D materials and devices is confronted with challenges such as scalable production techniques, stability under operational conditions, and seamless integration into existing manufacturing processes.

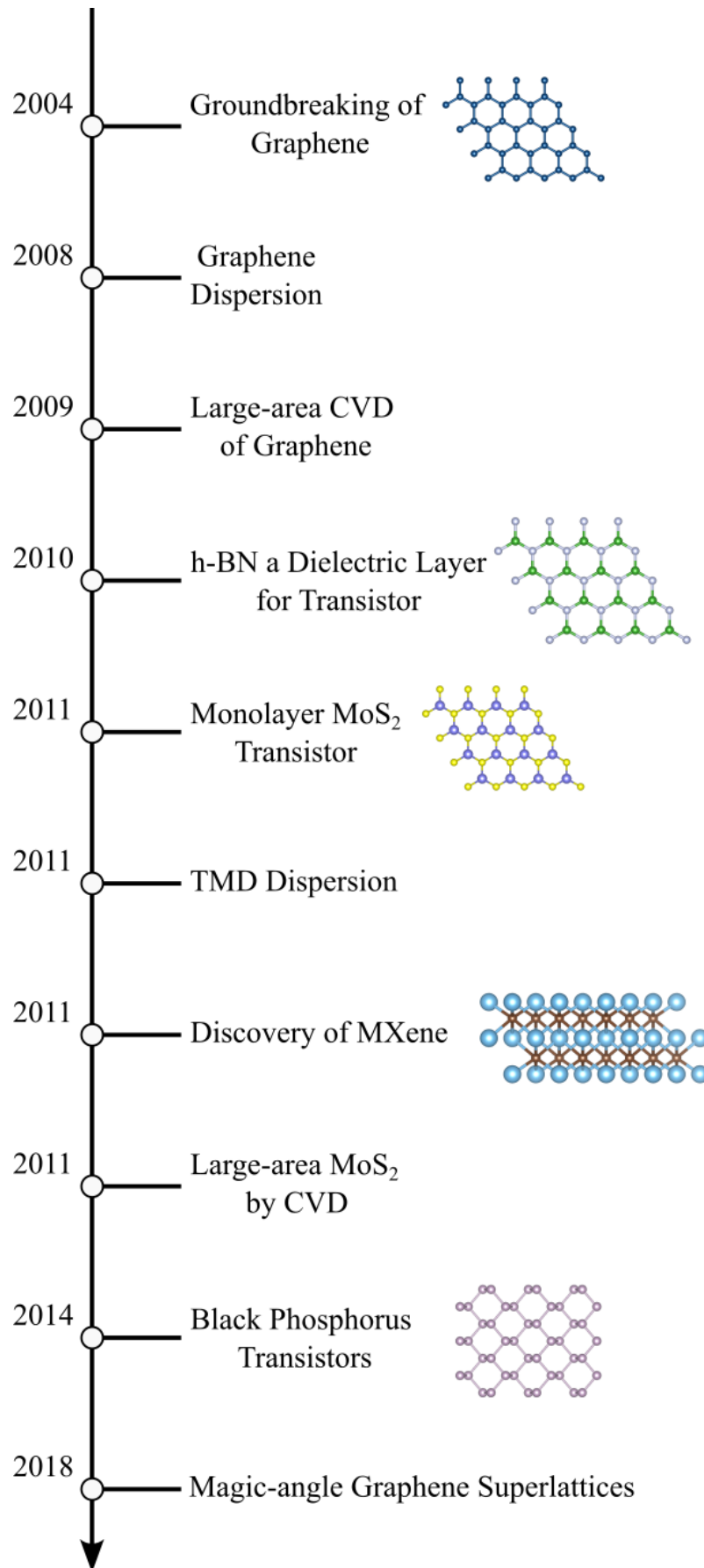


Figure 1.1 Key breakthroughs in the development of 2D materials.^{1,3-11}

The 2D material family encompasses a wide range of compositions which cover most elements of the periodic table. Consequently, the electronic and optical properties of these materials vary widely, including superconductors, metals, semimetals, insulators, and semiconductors with direct and indirect bandgaps spanning from the UV to the IR spectrum, as shown in Fig 1.1.^{12–15} This diversity endows 2D materials with promising potential for applications in nanoscale, integrated, and flexible electronics, and optoelectronics. Graphene, a semi-metallic material, exhibits low optical absorption in the visible region, making it an ideal candidate for use as transparent electrodes in semi-transparent optoelectronic devices.^{16,17} Additionally, its exceptionally high electron mobility positions graphene as a promising material for a wide range of electronic applications. However, its intrinsic lack of a bandgap presents a critical limitation for transistor technology. This bandgapless nature hinders the ability of graphene-based transistors to achieve a fully switched-off state, resulting in high leakage currents. Consequently, this drawback significantly impacts their applicability in digital electronics, where a well-defined on/off switching behaviour is essential for reliable and efficient operation. h-BN is an insulator with the bandgap around 6 eV, which is commonly used as the dielectric layer in FETs, an encapsulation layer of other 2D materials, and single-photon emitters.^{10,18} TMDs are semiconductors in 2H phase with the bandgap around 0.65 to 2 eV depending on the composition and number of layers.^{19,20} Therefore, TMDs have been utilized in FETs as the channel materials due to the high carrier mobility and on/off ratio.⁴ Additionally, SL TMDs demonstrate great potentials in photodetectors and LEDs.^{21–23} BP is another semiconducting material, whose bandgap can be tuned from 0.3 to 2 eV by controlling the number of layers.²⁴ This tunability makes BP suitable for integration into optoelectronic devices operating in the IR region.^{24,25} MXenes are group of 2D materials including semiconductors (such

as $\text{Nb}_4\text{C}_3\text{T}_x$) and metals (such as $\text{Ti}_3\text{C}_2\text{T}_x$).²⁶ The metallic MXenes are widely used in batteries, supercapacitors, electromagnetic interference (EMI) shielding layers, and photothermal therapies.^{27–29}

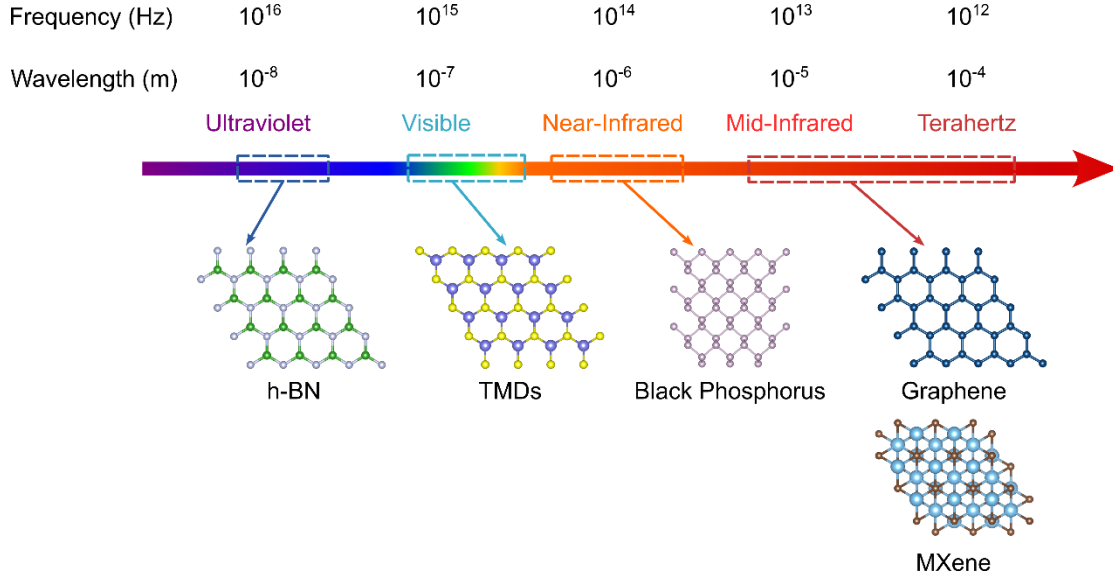


Figure 1.2 Bandgaps of widely studied 2D materials.

To fabricate 2D materials on large scales, various methods have been developed, with CVD and liquid phase exfoliation (including electrochemical exfoliation) being the most commonly used techniques. Despite their widespread use, these methods often produce 2D material flakes and films with defects and disorders, which can affect charge carrier behaviour and ultimately limit device performance.^{30,31} Understanding and mitigating these issues is crucial for advancing the practical applications of 2D materials. This thesis aims to investigate the dynamics of charge carriers in 2D materials prepared by large-scale fabrication approaches, focusing specifically on TMDs and MXenes. By exploring these materials, we hope to gain deeper insights into their fundamental properties and provide guidance on designing improvements to enhance the performance of 2D material-based devices.

1.2 Transition metal dichalcogenides

Among various 2D materials, TMDs with a formula as MX_2 (M refers to metal atom and X refers to chalcogen atom), are one of the most widely studied categories due to the semiconducting behaviour, which shows great potential in (opto-)electronics and photosynthesis.^{32,33} The structure of TMD was first determined by Linus Pauling in 1923.³⁴ In 1963, Robert Frindt first reported the optical properties of ultrathin MoS_2 produced by adhesive tapes.³⁵ About two decades later, in 1986, SL MoS_2 suspension was first produced after intercalation with lithium.³⁶ After the discovery of graphene in 2004, the study of TMDs has been boosted particularly focusing on SL TMDs.

1.2.1 Crystal structure of TMDs

Although TMDs show several polytypes, of which 2H, 3R, and 1T have been studied most extensively,³⁷ the 2H polytype is the most thermodynamically stable phase with a hexagonal unit cell. The structures of 2H, 3R, and 1T polytypes are schemed in Fig 1.3. Only the group-VI TMDs (M=Mo, W; X=S, Se, and Te) in 2H phase is discussed in this thesis, which are semiconductors. The other polytypes and TMDs are not in the scope of this thesis.

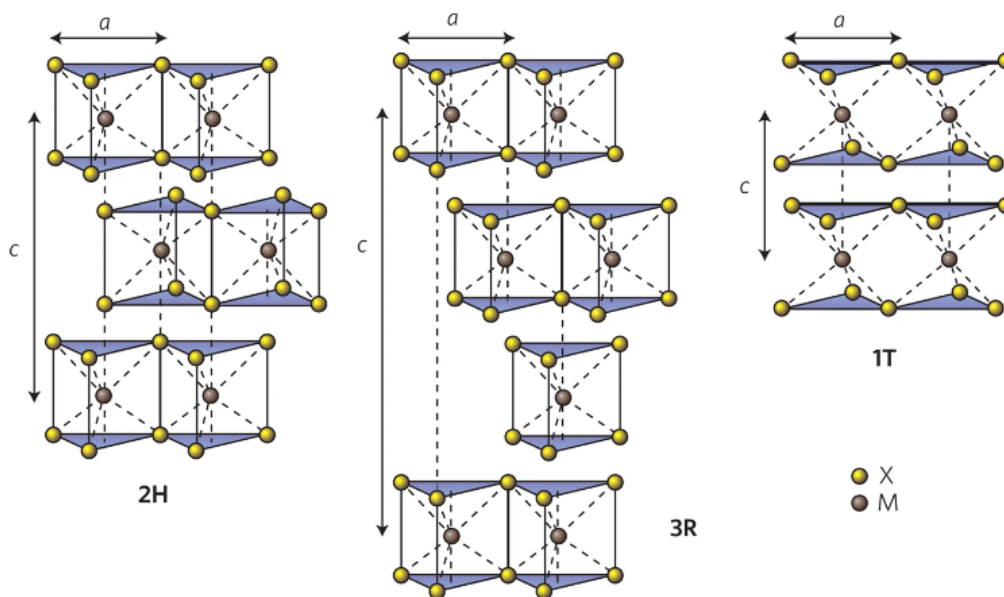


Figure 1.3 Scheme of structures of 2H, 3R, and 1T polytypes. The chalcogen atoms (X) are yellow and the metal atoms (M) are grey.³³ Reproduced with permission from ref 33. Copyright 2017 John Wiley and Sons.

1.2.2 Preparation of TMD layers

The preparation of SL and multilayer TMDs can be divided into two main categories: bottom-up and top-down methods. The most used bottom-up method is CVD. Typically, chemical reactions of the precursors happen on the substrate leading to the formation and growth of the TMDs. For example, the conventional method to grow MoS_2 is using solid-state MoO_3 or Mo to react with H_2S vapour.³⁸ More recently, metal-organic CVD (MOCVD) is developed using organometallic compounds as precursors, such as Mo(CO)_6 and W(CO)_6 .³⁹ The TMDs grown by CVD can be controlled as fully-covered polycrystalline films or discrete single crystals.³⁹ However, the deposition process typically requires high temperatures, which are energy-intensive, and the growth mechanism is highly sensitive to the substrate, which is usually sapphire, Si/SiO₂, or metal foils.⁴⁰ Despite the development of various transfer techniques, maintaining the cleanliness of the grown layers remains challenging.⁴¹

Due to the van der Waals force between the layers of TMDs, additional energy is required to delaminate the bulk material into single- or multilayer flakes. Mechanical exfoliation and liquid phase exfoliation are the two main top-down methods.^{4,42} Single- or multilayer TMD flakes can be peeled off using sticky tapes which is similar to the first exfoliation of graphene in 2004.¹ TMD flakes prepared by this method are of the highest quality, which are commonly used to study the pristine properties and ultimate device performances. In addition, the mechanically exfoliated flakes can be encapsulated by h-BN to avoid contamination and degradation.⁴³ However, this method is inefficient for large scale production. To obtain large amounts of single- or multilayer TMDs nanosheets, liquid phase exfoliation is a scalable and cost-effective approach which is able to produce large volumes of TMDs nanosheets suspensions.⁴⁴ The suspensions can be printed to patterns by inkjet printing or deposited by spray coating and spin coating.⁴⁴ Liquid phase exfoliation starts with bulk TMD crystal or powder which is exfoliated in a solution by sonication.

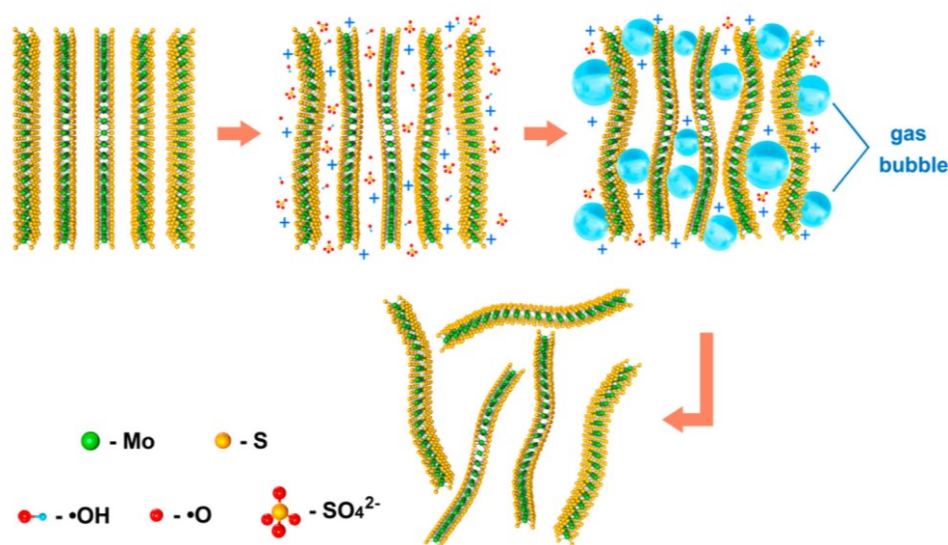


Figure 1.4 Schematic illustration of steps in electrochemical exfoliation.⁴⁵ Reproduced with permission from ref 45. Copyright 2014 American Chemical Society.

To improve the exfoliation efficiency, the bulk TMD can be intercalated

electrochemically by organic molecules, transition metal halides, and lithium ions before sonication.^{38,46} This method is commonly called as *electrochemical exfoliation*.

The essential steps of electrochemical exfoliation are illustrated in Fig 1.4. Normally NMP or PVP is added to the suspension as a stabiliser.^{5,45}

1.3 MXenes

MXenes are an advancing and growing category of the 2D metal carbides and nitrides with a formula $M_{n+1}X_nT_x$, where M is an early transition metal, X is carbon and/or nitrogen, $n = 1-4$, and T represents surface functional groups (such as -OH, =O, -Cl, and -F).^{28,29} Currently, a diverse range of MXenes (Ti_2CT_x , $Ti_3C_2T_x$, Nb_2CT_x , Mo_2CT_x and some others) has been successfully synthesized and used in different applications.⁴⁷ Although there are semiconducting MXenes have been developed, only metallic MXenes are discussed in this thesis unless specified otherwise.

$Ti_3C_2T_x$ MXene is the most extensively studied MXene with metallic behaviour,¹⁴ which has been used in batteries, supercapacitors, photodetectors, and photovoltaics.^{28,29} Different from graphene and TMDs whose bulk precursors are 2D layers stacked by van der Waals forces, MXenes are typically synthesized from the MAX phase by selectively etching the A element layers by HF, shown in Fig 1.5.^{28,48} To avoid the hazardous nature of HF, alternative etching solutions such as a mixture of HCl and LiF have been developed. This method generates HF in situ, leading to safer and more controllable etching conditions.⁴⁸ During the etching process, surface terminal groups can be formed, such as hydroxyl (-OH), oxygen (-O), and fluorine (-F) groups. These hydrophilic groups enable the formation of stable dispersions of MXene flakes in water avoiding using toxic volatile solvents and additive stabilisers.

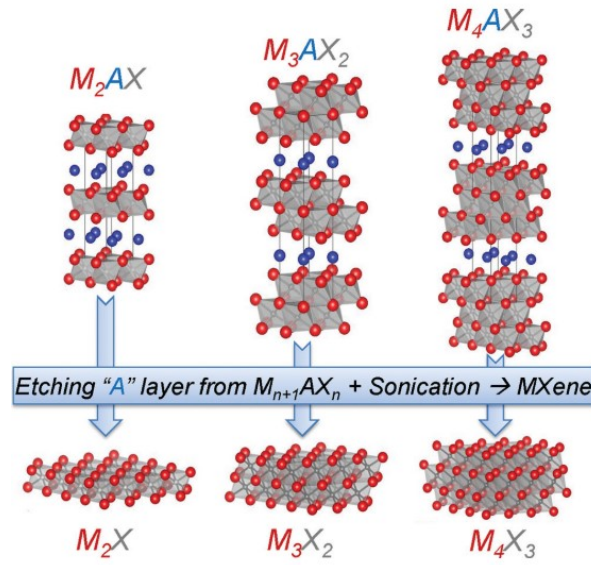


Figure 1.5 Exfoliation from MAX phase to MXenes.²⁸ Reproduced with permission from ref 28. Copyright 2014 John Wiley and Sons.

Due to the high free electron density, MXenes show strong coupling of incident photons of free-carrier plasma oscillations (plasmons). The plasmonic resonances range from visible to NIR with different compositions.⁴⁷ The plasmonic behaviour endows MXenes great potential for photothermal, sensing, and photonic applications, such as photothermal therapy, broadband photodetector and plasmonic waveguides.^{49–51}

Chapter 2 Photophysics of 2D Materials

2D materials are widely used in optoelectronics and photonics. It is essential to understand the fundamental mechanisms to explain the photo-response and guide the design of higher-performance devices and explore new applications.

2.1 Photophysics of TMDs

2.1.1 Band structure of TMDs

A broad range of electronic properties is observed, not only the band structure character (metallic or insulating) and correlated and topological phases, due to the diverse chemical compositions and structural phases of TMDs.¹⁹ MoS₂ is one of the most widely studied TMDs, which is selected as a representative of most other TMDs. In the thermodynamically stable 2H phase, MoS₂ and other group-VI TMDs are semiconductors.

The evolution of band structures of bulk and SL MoS₂ are calculated from the first principles with density function theory shown in Fig 2.1 (a) and (b). In the bulk MoS₂, the valence band maximum (VBM) locates at the Γ point, and the conduction band

minimum (CBM) is at the midpoint between the K and Γ points in the Brillouin zone.⁵² The major contribution of the electronic states at the K point in CB is d_{z^2} and in VB is $d_{xy} + d_{x^2-y^2}$ orbitals of the transition metals.^{53,54} While the electronic state at the Γ point has the contribution of the p_z orbitals of the chalcogen atom and the d_{z^2} orbitals of the transition metal.^{53,54}

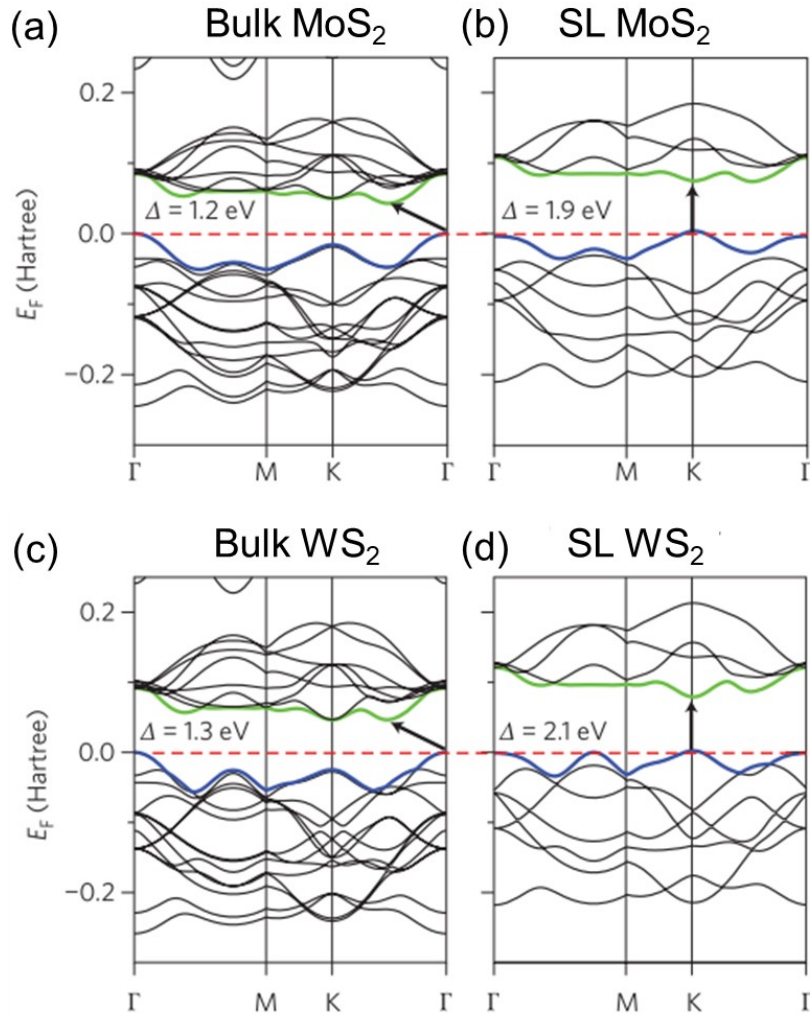


Figure 2.1 Calculated band structure of MoS₂ and WS₂ for bulk to SL using first-principles density function theory.⁵² Reproduced with permission from ref 52. Copyright 2011 American Physical Society.

The band structure of MoS₂ changes with the number of layers. Since the direct energy gap is primarily determined by the Mo atoms within a single layer, the direct energy

gap at the K points is not significantly affected by a reduction in the number of layers. However, the strong spatial overlap between the orbitals of chalcogen atoms in adjacent MX₂ layers leads to an increase in the energy gap at the Γ point and the midpoint between the K and Γ points as the number of layers decreases—from bulk to multilayer and ultimately to SLs.^{53–55} Consequently, in the bulk or multilayer form, MoS₂ exhibits an indirect bandgap of approximately 1.2 eV. In contrast, in the single-layer form, the bandgap transitions to a direct bandgap and increases to approximately 1.8 eV. Similar to graphene, in SL TMDs, the VBM and CBM are both located at the K point in the Brillouin zone, shown in Fig 2.1 (b).^{52,56} Fig 2.1 (c) and (d) show similar changes of band structure in bulk and SL WS₂. Due to the abundant energy local minima within the band structures of TMDs, excitons can be formed with the electron and hole locate at different points in the Brillouin zone. These excitons cannot be excited directly by photons, forbidden by the momentum conservation, which are so called *momentum forbidden dark excitons*.⁵⁴

2.1.2 Excitonic effects in TMDs

As a semiconductor, after absorption of a photon with above-gap energy, an electron is promoted to the CB, leaving behind a hole in the VB. The electron and hole are attracted to each other by the Coulomb force forming a bound state called *exciton*.

In SL TMDs, the exciton can be described as a hydrogenic model. The exciton binding energy, E_b , is given by Eq. 2.1:

$$E_b = \frac{\mu e^4}{2(4\pi\epsilon_0\epsilon_r)^2\hbar^2} \quad \text{Eq. 2.1}$$

where ϵ_r is the dielectric constant of the material, and μ is the effective mass of the exciton, which is given by

$$\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*} \quad \text{Eq. 2.2}$$

where m_e^* and m_h^* are effective mass for electron and hole, respectively.

The *exciton Bohr radius*, a_B , is a characteristic distance that describes the size of the exciton, or the average spatial separation between the electron and hole in a bound state. It is analogous to the Bohr radius in a hydrogen atom but modified to account for the material-specific properties of a semiconductor. The formula for the exciton Bohr radius is:

$$a_B = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{\mu e^2} \quad \text{Eq. 2.3}$$

Therefore, E_b is inversely proportional to the square of a_B .

In SL TMDs, the electrons and holes are tightly bounded to form excitons with typical E_b on the order of hundreds meV, due to the weak dielectric screening and strong quantum confinement, which is different from traditional inorganic semiconductors and organic semiconductors.^{54,57} In traditional inorganic semiconductors, due to the high dielectric constant (~ 12 in Si for example), the excitons have low E_b and can delocalise beyond the lattice constant, which are called *Wannier-Mott* excitons. In organic semiconductors, the dielectric constant is small ($\sim 2-4$ for most organic semiconductors).⁵⁸ This leads to the formation of tightly bound and localised excitons called *Frenkel* excitons. Fig 2.2 illustrates the comparison of Wannier-Mott exciton and

Frenkel exciton in a semiconductor lattice. Although the exciton radii are small and E_b are large, the excitons in TMDs can still be described by Wannier-Mott excitons which show analogies to the electronic structure of the hydrogen atom.⁵⁴ This excitonic behaviour of TMDs makes these materials different from traditional inorganic and organic semiconductors.

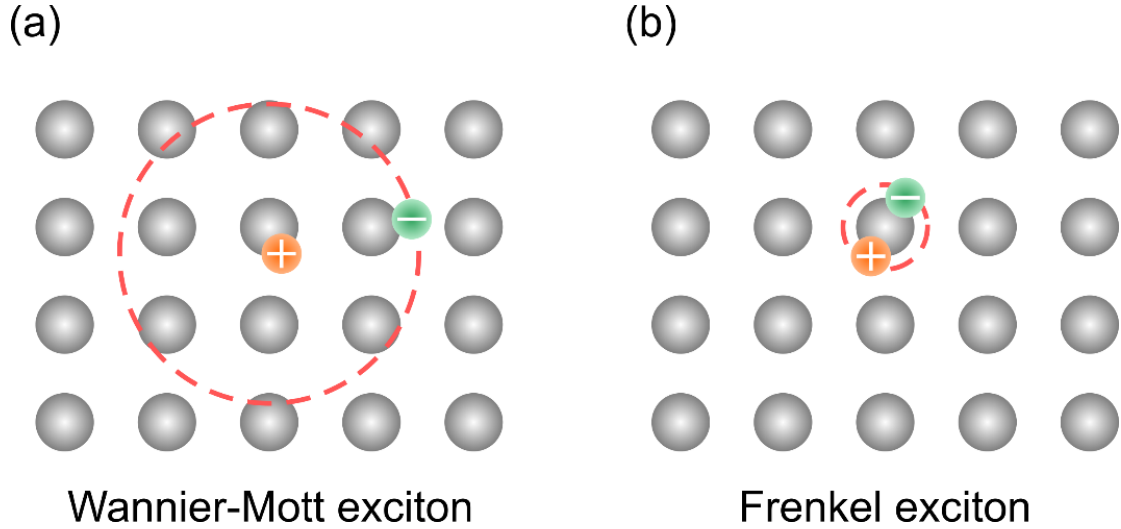


Figure 2.2 Real-space illustration of excitons in a semiconductor lattice.

The E_b of excitons in TMDs induces renormalised quasiparticle bandgap which locates at lower energy than the free-carrier bandgap with the energy difference equal to the binding energy. Fig 2.3 shows a scheme of optical absorption of an exciton in a 2D semiconductor.^{54,57}

The quantum number n represents the atom-like energy levels of the higher-order excitonic states. The excitonic ground state is denoted as $n = 1$ with the energy of E_b below the free-carrier bandgap (i.e., $n = \infty$). Within the excitonic regime, the transition energies are discrete, and resonant transitions can be observed optically.⁵⁹ Above the E_b , carriers are free from the Coulombic forces without forming excitons and locate in continuum showing broadband optical absorption.

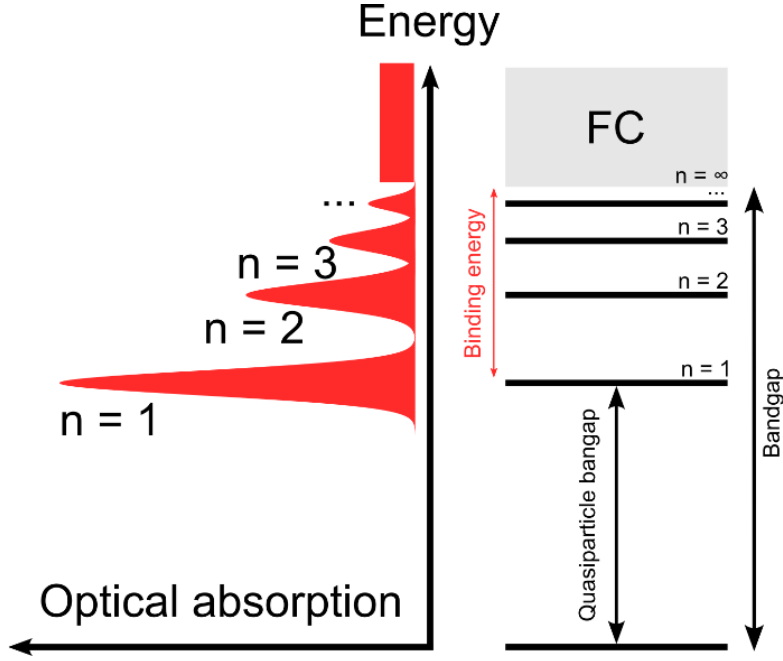


Figure 2.3 Scheme of the optical absorption of an ideal 2D semiconductor including the series of excitonic transitions.

In a 3D system, the Columbic interaction is governed by:

$$V(r) = \frac{e^2}{4\pi\epsilon_0\epsilon_r r} \quad \text{Eq. 2.4}$$

where r is the distance between the electron and the hole.

Due to the reduced dimensionality and non-uniform screening, in a 2D system, the Columbic interaction between an electron and a hole can be described by the Rytova-Keldysh model:

$$V(r) = \frac{e^2}{4\pi\epsilon_0 r} \left[H_0\left(\frac{r}{r_0}\right) - Y_0\left(\frac{r}{r_0}\right) \right] \quad \text{Eq. 2.5}$$

where r_0 is the screening length, $H_0(x)$ is Struve function, and Y_0 is Neumann function.

r_0 is given by

$$r_0 = \frac{2\pi\chi}{\epsilon_{eff}} \quad \text{Eq. 2.6}$$

where χ is the polarizability of the material, and ϵ_{eff} is the effective dielectric constant, representing the combined screening effect of the 2D material and its surrounding environment. Therefore, the Coulombic interaction strength scales with the inverse of ϵ_{eff} . Consequently, E_b is inversely proportional to the square of ϵ_{eff} .

At higher order excitonic states ($n>1$), the spatial extent of the exciton wavefunction is increased, resulting in an increased exciton radius, and thus decreased Coulombic interaction. Following the hydrogenic model, the E_b is inversely proportional to the square of n .

Therefore, E_b can be modified as:

$$E_b \propto \frac{1}{n^2} \frac{1}{\epsilon_{eff}^2} \quad \text{Eq. 2.7}$$

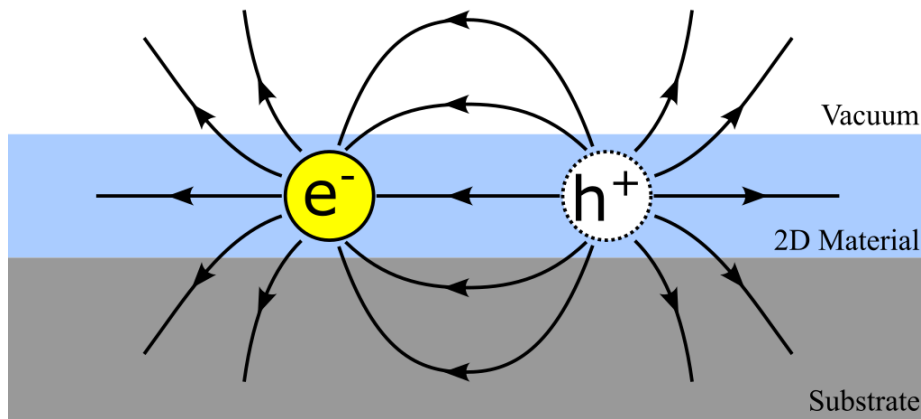


Figure 2.4 Illustration of the reduced dielectric screening of 2D materials.

Due to the reduced dimensionality of 2D materials, ϵ_{eff} is determined by the surrounding environment and the material itself. For example, Fig 2.4 illustrates

reduced dielectric screening of a 2D material placed onto a substrate in vacuum. Therefore, dielectric screening for a 2D material is reduced, and thus, E_b can be as high as hundreds of meV.^{57,60,61}

Apart from the neutral excitons, the strong Coulomb interaction in TMDs facilitates the formation of complex excitonic species by binding neutral excitons with other quasiparticles. This interaction leads to the formation of biexcitons, trions (charged excitons), and exciton-trion complexes with E_b of tens meV, as depicted in Fig 2.5.⁶¹ The formation of these excitonic complexes can be modulated by carrier density and temperature.^{61–63} These excitonic complexes can be utilized for engineering new excitonic states, ranging from valley-polarized excitonic complexes with an increased lifetime in monolayer TMDs to correlated excitons in material heterojunction or even moiré superlattices.⁶⁴

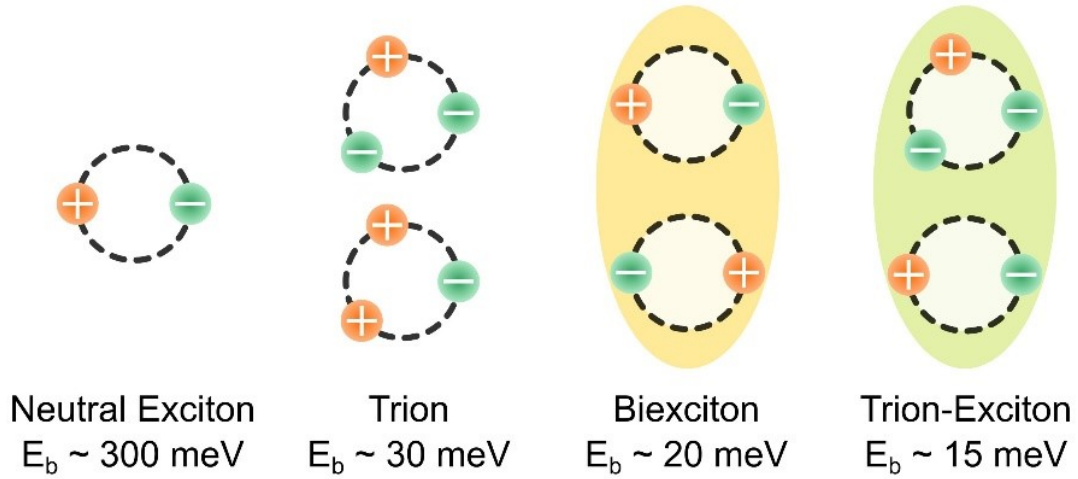


Figure 2.5 Scheme of the excitonic complexes in TMDs and binding energies.

Due to the heavy metal in TMDs and the involvement of the transition metal d orbitals, the *spin-orbital interaction* is very strong in TMDs. In SL TMDs, the spin splitting at the K point in VB is around 0.2 eV in MoX_2 and 0.4 eV in WX_2 .^{20,55} This coupling results in two valence sub-bands, accordingly to two types of excitons, A and B. While

the energy splitting at the K point in CB is 1-2 orders of magnitude lower ($\sim 1-30$ meV).^{55,65} Interestingly, depending on the metal atom (Mo or W), the spin splitting in CB has a different sign comparing to in VB, as indicated in Fig 2.6.

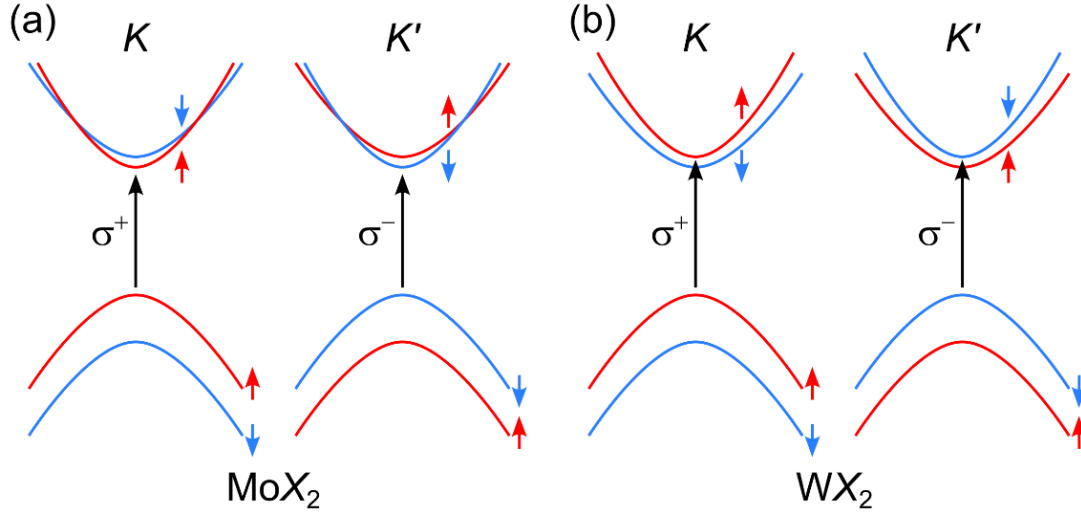


Figure 2.6 Valley and spin dependent optical transition selection rules in SL MoX_2 and WX_2 .

According to the spin-orbital coupling induced optical selection rules, the excitons can be categorised as “*bright*” (i.e., optically active) and “*dark*” (i.e., optically inactive) excitons depending on whether the spin is allowed or forbidden in the optical transition. These dark excitons are so called *spin forbidden* dark excitons.

While the A and B excitons are well-studied, corresponding to direct transitions at the K and K' points in the Brillouin zone, TMDs also show higher energy excitonic states known as C and D excitons which are typically associated with transitions involving higher conduction bands and other points in the Brillouin zone. The resonant energy of C excitons is significantly higher than that of A and B excitons, often found in the ultraviolet region of the spectrum. The C exciton is understood to arise from the band nesting region where the valence and conduction bands are parallel over an extended region between the Γ point and midpoint between the K and Γ points (also denoted as

Λ point). For example, in monolayer MoS_2 , the C exciton is observed at around 2.9 eV.²⁰ Similar to C excitons, D excitons reside at higher energies, typically observed at even higher energies than C excitons. D exciton is thought to reside close to the Γ point outside the band nesting region.⁶⁶ Experimentally, Fig 2.7 demonstrates the steady-state differential reflectance and emission spectra of SL TMDs with the excitonic resonances. Typically, the PL peak locates around the energy of A exciton.

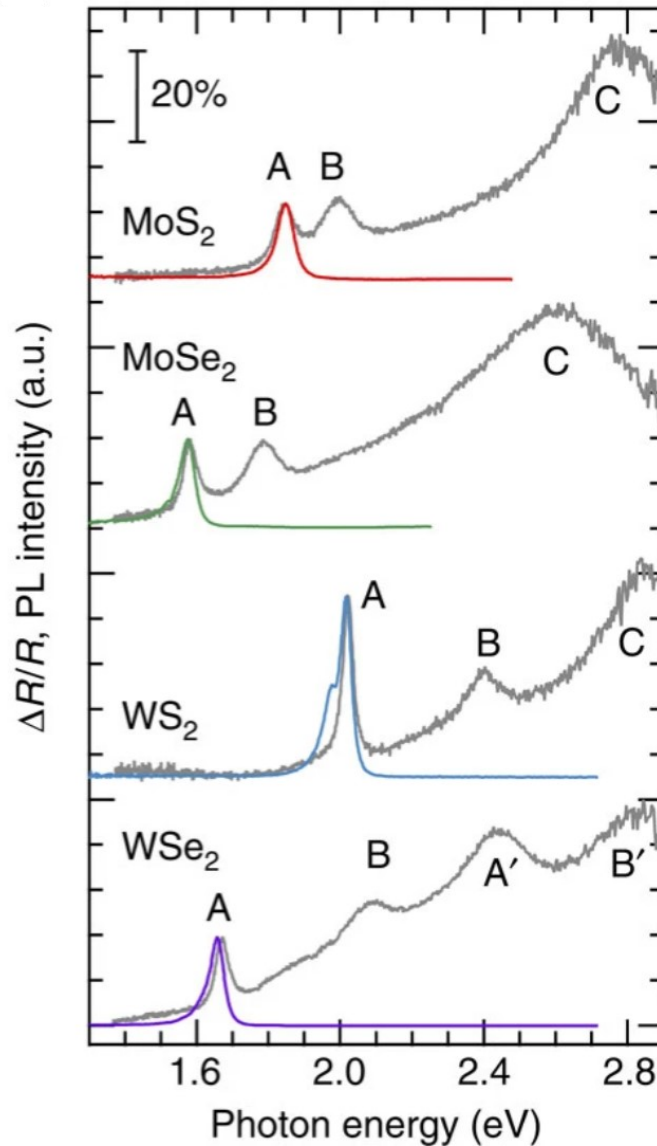


Figure 2.7 Differential reflectance and emission spectra of SL TMDs.⁶⁷ Reproduced with permission from ref 66. Copyright 2014 Springer Nature.

2.1.3 Dynamics of excited states in TMDs

Previous sections have introduced the origins of ESs in TMDs from the energetic aspect without any dynamic descriptions. The formation of these ESs and interplays between them and with other quasiparticles need to be investigated in real time. The major interactions of quasiparticles in TMDs are similar to other semiconductors.

2.1.3.1 Electron-phonon coupling

After generation of carriers by photoexcitation, the material lattice is displaced from the equilibrium positions to minimise the overall energy of the system. The distortion of the material lattice can be described by quantised vibrations, called *phonons*. The interaction of carriers and phonon can increase the effective mass and reduce the mobility of the carrier when the carrier is moving through the lattice. The *electron-phonon* (e-ph) *coupling* can be described by Fröhlich interaction in which the relevant phonons in polar materials (including TMDs) are *longitudinal optical* (LO) phonons. E-ph coupling is critical for understanding phenomena such as electrical and thermal conductivity, superconductivity, and carrier relaxation dynamics.

The strength of the e-ph coupling can be expressed by a Fröhlich constant, α_F ²⁶:

$$\alpha_F = \frac{e^2}{4\pi\hbar\epsilon_0} \left(\frac{1}{\epsilon_{optic}} - \frac{1}{\epsilon_{static}} \right) \sqrt{\frac{m^*}{2\hbar\omega_{LO}}} \quad \text{Eq. 2.8}$$

where ϵ_{optic} and ϵ_{static} are optical and static dielectric constants respectively, m^* is the carrier effective mass, and ω_{LO} is the angular frequency of the dominant LO phonon. When the α_F is very low, the rigid material lattice does not couple to the carriers

efficiently. When α_F is greater than 1, e-ph interaction is significant, resulting in a quasiparticle called *polaron*. In conjugated organic semiconductors, the polarons are considered as *small polarons* which exhibit thermal assisted hopping transport. If the polaron size is greater than the lattice constant, i.e., *large polaron*, band-like transport is dominant.

2.1.3.2 Hot carrier cooling

In most optoelectronic applications and spectroscopic measurements, the excitation photon energy is larger than the exciton ground-state energy. Therefore, the exciton formation dynamics and energy relaxation mechanisms are essential for a quantum confined system. In an excitonic material, such as TMDs and nanocrystals, exciton formation refers to the formation of band-edge bound excitons (cold excitons) from high-energy (weakly bound) electron-hole pairs or plasma (hot excitons).^{68–70} Generally speaking, the hot exciton relaxation process is a kind of hot carrier cooling process, which normally refers to free carriers in bulk inorganic semiconductors.

The study of exciton formation in quantum confined 2D system can date back a few decades when people studied GaAs quantum wells. In GaAs quantum wells, people observed geminate and bimolecular exciton formation processes.^{71,72} In geminate process, the photoexcited electron-hole pair (i.e., hot exciton) relaxes to the cold exciton with the emission of phonons.⁷¹ The geminate exciton formation rate is proportional to the photoexcited electron-hole pair density (i.e., excitation density). The bimolecular exciton formation rate is proportional to the probability that the hot electrons and holes interact each other and is therefore proportional to the product of electron and hole densities.⁷¹ Different from III-VI and II-VI quantum wells, TMDs only exhibit geminate exciton formation process which is similar to the classical hot “free” carrier

cooling process in bulk materials.⁵⁴ Fig 2.8 (a) illustrates the temporal evolution of carrier distribution in a semiconductor with above bandgap excitation by a laser pulse. For simplicity, the density of states of CB and VB is assumed as the same.

After above-gap laser excitation, the carriers are at high-energy non-equilibrium states. These carriers redistribute the energy to the electron gas in fs timescale, which is called *thermalisation* and the thermalised carriers are called *hot carriers*. These hot carriers will then dissipate their excess energy to the material lattice by emitting LO phonons, as shown in Fig 2.8 (b). This cooling process normally happens in sub-ps to ps timescale in inorganic semiconductors. After carrier cooling, the heat in the material lattice will be dissipated via phonon-phonon interactions.

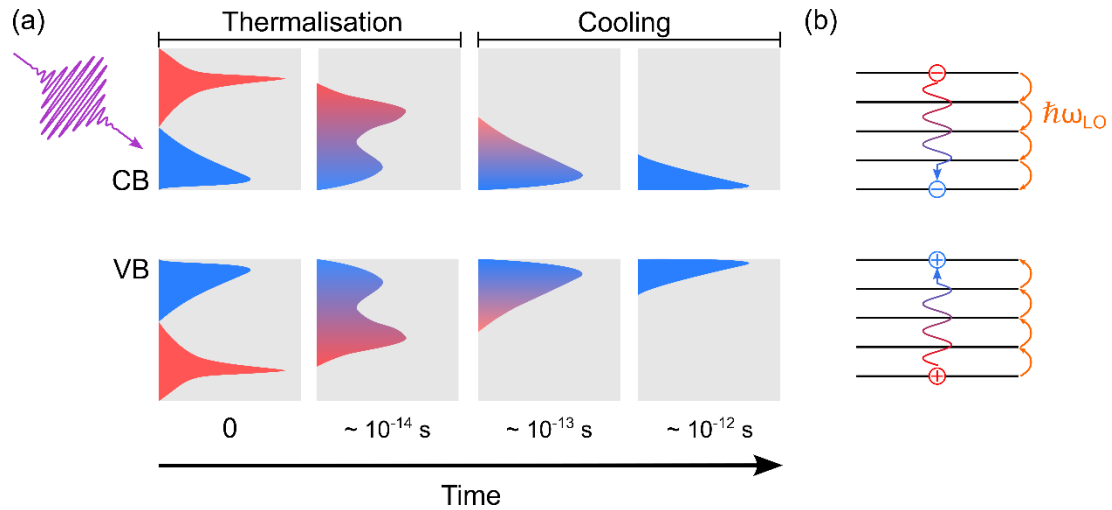


Figure 2.8 Hot carrier relaxation in semiconductors. (a) Temporal evolution of the distribution of electrons and holes after laser excitation. (b) Hot carrier cooling via scattering with LO phonons with the energy $\hbar\omega_{LO}$.

The hot carrier cooling time can be prolonged when the semiconductor is highly excited due to the *hot-phonon bottleneck* (HPB) effect. The excess energy dissipated from the hot carriers prevents the equilibrium of the LO phonons and the entire lattice because the LO phonons continuously reabsorb the energy released from the hot carriers, keeping the electron gas and phonons hot.⁷³

In a system with strong quantum confinement, the energy levels are more separated comparing to the bulk material, as shown in Fig 2.9. It has been predicted that the hot carrier relaxation in a quantised system is slower than the bulk system,⁷⁴ because the energy difference between the electronic levels is higher than the energy of LO phonon. The hot carrier cooling mechanism in SL TMD is discussed in Chapter 4.

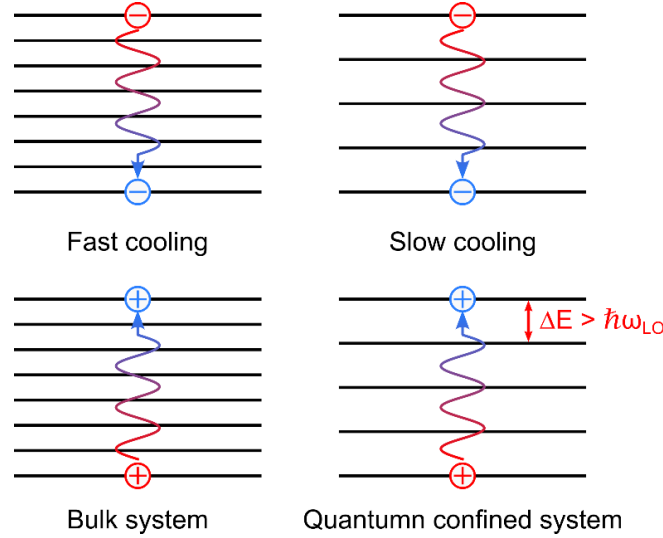


Figure 2.9 Slow hot carrier cooling in quantum confined system.

2.1.3.3 Recombination of excited states

Previous section has outlined the generation of excitons (or free carriers) in a semiconductor with photoexcitation. The equilibrium between these quasiparticles depends on the material properties and the experimental conditions such as excitation density, temperature, and electromagnetic field.

When the exciton density is low, the recombination mechanism is a first order (i.e., monomolecular) process. In this process electron and hole produced by the same excitation recombine directly with photon emission (i.e. radiatively) or with phonon emission (i.e., non-radiatively). The population of excitons, n , can be written as:

$$\frac{\delta n}{\delta t} = -k_1 n \quad \text{Eq. 2.9}$$

where k_1 is the monomolecular recombination rate.

When the exciton density is high, one exciton can annihilate with another exciton, which refers to second order (i.e., bimolecular) recombination, also called *exciton-exciton annihilation* (EEA). The population of excitons as the function of time can be written as:

$$\frac{\delta n}{\delta t} = -k_2 n^2 \quad \text{Eq. 2.10}$$

where k_2 is the bimolecular recombination rate (or annihilation rate). EEA can also be used as a tool to investigate the diffusion length (or mobility) of the excitons.⁷⁵

The recombination mechanisms of separated charge carriers (i.e., electrons and holes) also depend on the excitation densities. In a disordered material, when one of the carriers is trapped (i.e., localised) by a defect such as elemental vacancies, substitutions or interstitials, the recombination mechanism follows monomolecular dynamics, shown as Eq. 2.9, since one of the carriers is not mobile.⁷⁶ This trap-assisted recombination is also called *Shockley-Read-Hall* (SRH) recombination.⁷⁶ When both charge carriers are mobile, the electrons and holes recombine follow bimolecular dynamics, since the population of one species depends on the density of its own and its recombining partner. When the excitation density is even higher, normally with pulsed laser excitation with high photon flux, many-body process happens for free carriers (rather than excitons), called *Auger recombination*. Here, the energy released from electron-hole interband recombination of is transfer to another electron or hole. Therefore, the population

dynamics follows a third-order process:

$$\frac{\delta n}{\delta t} = -k_3 n^3 \quad \text{Eq. 2.11}$$

where k_3 is the Auger recombination rate.

2.2 Photophysics of MXenes

2.2.1 Surface plasmon

The metallic MXenes, such as $\text{Ti}_3\text{C}_2\text{T}_x$, have substantial density of free carriers in equilibrium state, on the order of 10^{22} cm^{-3} .⁴⁷ As a 2D material, the reduced dimensionality enables strong light confinement on the surface, making them excellent platforms for plasmonic studies.⁴⁹

Plasmon is a quantum of plasma oscillation. Usually in a 3D system, the plasmon frequency, ω_p , can be described by

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}} \quad \text{Eq. 2.12}$$

where N is the density of free carriers per volume, and m^* is the effective mass of free carriers. In a 2D system, N is the density of free carriers per area. Therefore, Eq. 2.6 can be modified as following:

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 l m^*}} \quad \text{Eq. 2.13}$$

where l refers to the effective thickness of the electron layer.

Surface plasmons (SPs) are the plasmons that are confined to the surfaces, normally at the interface between metal-dielectric interface.⁷⁷ SPs can be either localised or propagating. The propagating SPs are also called *surface plasmon polaritons* (SPPs).⁷⁷

The bulk plasmon energy of $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits a thickness independence due to the weak interlayer coupling, whereas SP frequency shows dependence on thickness and functional groups.⁴⁹ The plasmonic resonance of MXenes changes with the elemental compositions, which spans a broadband spectrum from visible to IR.⁴⁷ For example, Ti_2CT_x shows the plasmonic resonance around 500 nm, and $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits plasmonic resonance around 780 nm.⁴⁷ Fig 2.10 demonstrates the steady-state transmittance spectra of MXenes.

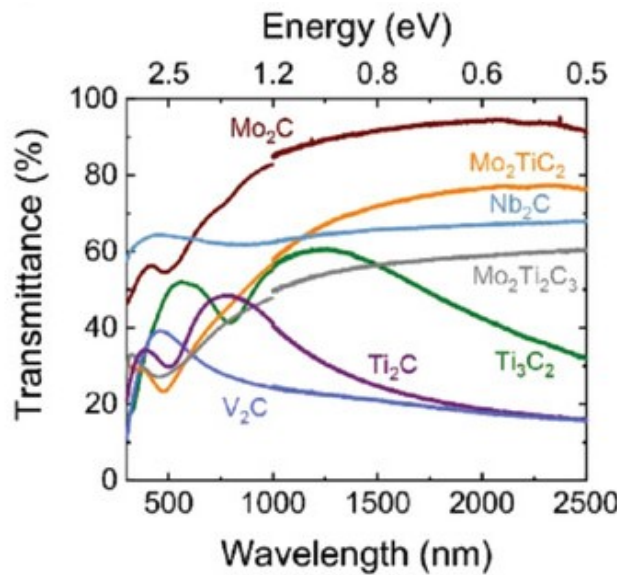


Figure 2.10 UV-vis-NIR transmittance spectra of MXene thin films.⁴⁷ Reproduced with permission from ref 47. Copyright 2020 John Wiley and Sons.

2.2.2 Electron-phonon interactions in MXenes

Previous sections have shown that e-ph interaction is essential for energy dissipation in semiconductors after photoexcitation. Intuitively, the energy dissipation in metallic MXenes should be similar to the plasmonic metal nanoparticles. In noble metal nanostructures, photoexcited SPs relax to nonthermal (cold) electrons after Landau damping.⁷⁸ Then the cold electrons become hot through electron-electron (e-e) scattering within hundreds of fs. Eventually, the hot electrons dissipate the energy to the material lattice via e-ph coupling in a few ps. The thermal equilibrium between hot carriers and material lattice can be described by a semiclassical two-temperature model.^{79,80} The timescale is determined by the e-ph coupling strength, free carrier heat capacity and conductivity, and lattice heat capacity.^{79,80} Fig 2.11 schematically illustrates the thermal equilibrium between the hot carriers and lattice.

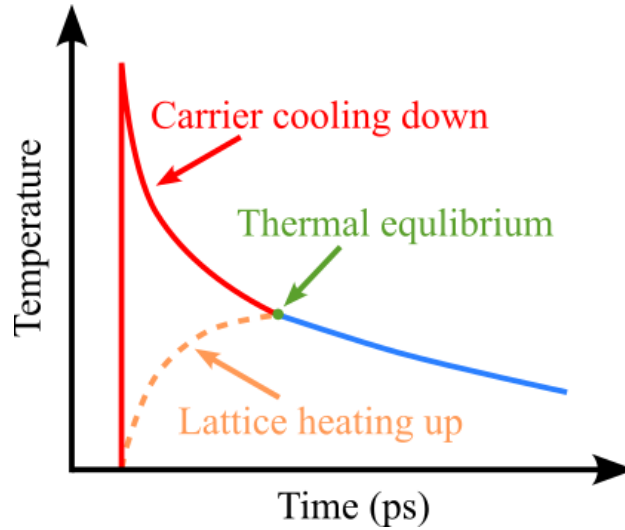


Figure 2.11 Evolution of carrier temperature and lattice temperature by the two-temperature model.

2.3 Advances in ultrafast dynamics of TMDs and MXenes

Ultrafast laser spectroscopy has been widely employed to observe the real-time behaviour of excited states. This section provides a brief overview of recent advances in spectroscopic studies focusing on e-ph interactions and excitonic dynamics in TMDs and MXenes.

2.3.1 Electron-phonon coupling in TMDs

In steady state, the out-of-plane A_{1g} , in-plane E_{2g}^1 , and interlayer breathing, and shear vibrational modes are observed in TMDs by Raman scattering with continuous-wave excitation. The Raman spectra of MoS_2 with different number of layers is shown in Fig 2.12 as an example.

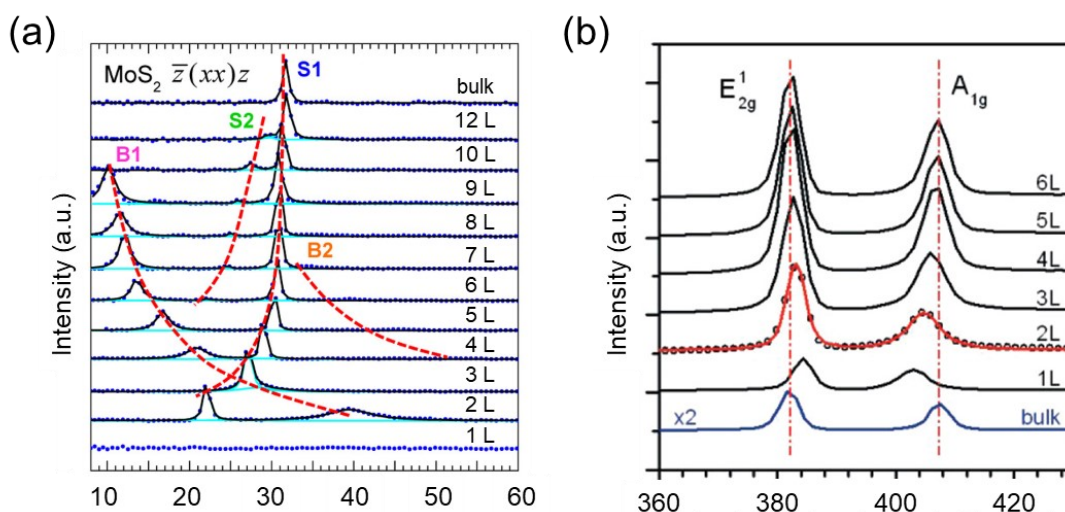


Figure 2.12 Steady-state Raman spectra of MoS_2 at different layers.^{81,82} Reproduced with permission from ref 81 and 82. Copyright 2013 American Chemical Society and Copyright 2010 American Chemical Society.

Although Chow et al. claimed that deformation potential coupling is more dominating than Fröhlich interactions in SL MoSe₂, indicated by the PL peak splitting at 5 K,⁸³ in most studies of ultrafast dynamics of SL TMDs, the Fröhlich e-ph coupling is believed very strong. This is evidenced by the coherent e-ph coupling, manifested as oscillations observed in PP dynamics,^{84–87} and the frequencies of such oscillations agree well with the out-of-plane vibration modes (i.e., A_{1g} mode and breathing mode) in Raman spectrum. The disagreement on the e-ph coupling mechanisms can be caused temperature of the measurements. In most of PP studies, the measurements were performed above 80 K, in which LO phonon is more prevalent than acoustic phonons.

E-ph coupling plays a significant role in the hot carrier cooling process in TMDs. Achieving bandgap excitation is challenging, not only due to the varying bandgaps across different TMDs but also because of the complexities associated with generating specific laser wavelengths (as discussed in Chapter 3). Above-gap excitation is often unavoidable, both in fundamental research and in the optical control of optoelectronic devices. Consequently, understanding the cooling timescales and mechanisms is not only crucial for elucidating the nature of e-ph coupling in these materials but also for optimizing the design and performance of TMD-based optoelectronic devices, such as photovoltaics, photodetectors, spintronics, and valleytronics. For instance, the rapid relaxation rate of hot carriers poses a significant challenge in transferring hot carriers from one material to another. This thermal loss is a major factor limiting the efficiency of photovoltaic devices.⁸⁸ Different from traditional bulk photovoltaic materials, such as silicon and hybrid perovskites, by forming heterojunction with other materials, hot carrier transfer from TMDs to the adjacent materials has already been observed by many studies.^{89–91} Notably, Austin et al. reported that placing SL MoS₂ onto a photoelectrode enables the utilization of hot carriers to drive photoelectrochemical

reactions.⁹⁰ This study underscores the promising potential of TMDs for future applications in photovoltaics and solar fuel technologies. The ease of hot carrier transfer from TMDs can be caused by the atomically thickness and long hot carrier cooling time.

To investigate and manipulate the hot carrier cooling time in TMDs, people have focused on the early dynamics following photoexcitation by the pump pulse in PP measurements. Notably, in the study conducted by Nie et al., LO phonons were found to be coherently coupled with carriers during the cooling process.⁹² This study further confirmed that Fröhlich e-ph coupling is dominant during the cooling process in TMDs. However, the LO phonon frequency is an intrinsic property of the material and cannot be easily adjusted. Consequently, alternative strategies are needed to effectively control the hot carrier cooling rate. As discussed in section 2.1.3.2, HPB effect provides a promising approach to retard the carrier cooling process in photoactive devices. Typically, a rising signal is observed in the dynamics after above-gap excitation, which indicates the gradual buildup of the “cold” state population at the band edge.^{70,93–95} It has been observed that the cooling time increases linearly with both the excitation photon energy and the excitation density, which can be explained by the HPB effect.^{70,92,95,96} Furthermore, using ultrafast absorption microscopy, Liu et al. observed that the diffusivity of hot carriers in SL WS₂ is approximately 9 times greater than that of “cold” band-edge bound excitons.⁶⁸ This study highlights the “free carrier” nature of the hot states in SL TMDs.

2.3.2 Exciton dynamics in TMDs

In addition to e-ph interactions, excitonic interactions play a crucial role in TMDs and related devices. Due to the direct bandgap nature of SL TMDs, the exciton dynamics

can be effectively studied using time-resolved PL spectroscopy. The radiative lifetime of excitons in SL TMDs has been observed to be approximately 1 nanosecond.^{75,97,98} However, the high mobility of excitons in SL TMDs leads to exciton-exciton annihilation, as described by Eq. 2.10, which occurs within tens of picoseconds.^{75,98–101} This rapid annihilation limits their potential applications in lasers and LEDs.

In contrast, in multilayer TMDs, the PL efficiency is significantly reduced due to the indirect bandgap, which requires phonon assistance during recombination. As a result, PL spectroscopy is less applicable for studying exciton dynamics in multilayer TMDs. Instead, conventional pump-probe (PP) spectroscopy methods have been widely employed. Studies have revealed that the indirect bandgap nature of multilayer TMDs results in much longer exciton (or free carrier) lifetimes, often exceeding a few nanoseconds.^{97,102} Additionally, the exciton annihilation rate is suppressed in multilayer TMDs, likely due to reduced exciton diffusivity.⁷⁵

Trap states also critically impact exciton dynamics. When the exciton density is lower than the density of trap states, geminate recombination occurs, as described in Eq. 2.9.¹⁰³ Conversely, when the exciton density exceeds the trap state density, non-geminate recombination dominates.¹⁰³

Due to the complex band structures of TMDs, the existence of dark excitons has been experimentally observed in time-resolved spectroscopy studies. As outlined by the selection rules in Fig. 2.6, circularly polarized PP studies have demonstrated the generation of spin-forbidden dark states in SL TMDs.^{104,105} Additionally, thermally activated dark states in SL TMDs have been inferred from reduced PL efficiency at low temperatures, along with faster exciton decay dynamics.^{106–108} However, the origin of these thermally activated dark states remains unclear. Moreover, strain and defects in

SL TMDs can further facilitate the formation of dark excitons by altering the band structure.^{109,110} This highlights the need for further investigations into the mechanisms governing dark exciton formation and their interactions with external perturbations.

2.3.3 Energy dissipation in MXenes

E-ph coupling in MXenes is crucial for heat dissipation from hot carriers to material lattice and material lattice to the environment,^{111,112} and the mechanisms have been widely studied using different time-resolved spectroscopic methods. In 2021, Volkov et al. reported lattice structural changes after photoexcitation within 230 fs evidenced by ultrafast electron diffraction measurements.¹¹³ However, the strength of the coupling between electrons and phonons remains unclear. In 2022, Zheng et al. reported relatively weak e-ph coupling in both metallic and semiconducting MXenes with the e-ph coupling strength around 1 by time-resolved THz spectroscopies.²⁶ The weak e-ph coupling enables the formation of large Fröhlich polarons, and thus, band-like transport dominates short-range intra-flake carrier conduction.²⁶ In the same year, Zhang et al. observed coherent phonons with <40 fs pulsed laser excitation, indicating strong e-ph coupling.⁷⁸ Their study has demonstrated a new energy dissipation pathway in $\text{Ti}_3\text{C}_2\text{T}_x$: cold carriers can directly damp the energy from photoexcited SPs to lattice via strong coupling with A_{1g} mode and weak with E_g mode without undergoing the e-e scattering.⁷⁸

It is widely observed that the carrier cooling time in MXenes does not show any HPB effects, even though the elemental compositions are different. After photoexcitation, the MXene lattice can easily be heated up due to the strong e-ph interaction.^{112–114} However, the heat dissipation from MXene to the environment is slow. Zhang et al.

reported that the TA spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at 40 picosecond after optical excitation can be described as the heat-induced absorption change. Different from traditional noble metal nanostructures, this thermal effect can take more than a few nanoseconds, suggesting low thermal conductivity in MXenes.^{111,112}

In practical applications, e-ph and phonon-phonon (ph-ph) interactions are fundamental for photothermal conversion. MXenes, with their unique properties, show great potential in photothermal therapies.⁵¹ To shine a light on the reason of small thermal conductivity observed in the 2D metallic MXenes, Huang et al. have demonstrated that in Nb_2C e-ph scattering has great impact on ph-ph scattering which is essential for thermal conductivity with Ab initio calculations, although they believe e-ph coupling in Nb_2C is weak.¹¹² Their results show that ph-ph scattering is extremely dominant at high temperature (>800 K) in which e-ph scattering is negligible, however, at below 300 K, e-ph scattering becomes as strong as ph-ph scattering.¹¹² Therefore, the thermal conductivity is low in 2D metallic materials, since strong e-ph scattering rate, $\frac{1}{\tau_{e-ph}}$, can decrease the total phonon scattering time, τ_{total} , to Mattiessen's rule as shown in Eq. 2.14:^{115,116}

$$\frac{1}{\tau_{total}} = \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_{ph-ph}} \quad \text{Eq. 2.14}$$

where τ_{ph-ph} is the ph-ph scattering time.

2.3.4 Scientific questions to be addressed

2.3.4.1 Hot carrier cooling in TMDs

As discussed in section 2.3.1, the rising signal in pump-probe (PP) dynamics is widely recognized as a signature of hot carrier cooling. However, the dynamics become more complex when the excitation density is high enough for higher-order recombination processes to occur within the same time window. The spectral and temporal overlap of multiple photophysical processes complicates the isolation of cooling dynamics, making it challenging to quantitatively analyse the impact on the density of cold carrier which can dissipate the excess energy from hot carriers via carrier-carrier interactions.^{117,118}

Additionally, conventional PP methods are limited in their ability to visualize other behaviours of hot carriers, such as trapping. As a result, a new approach is required to disentangle cooling dynamics from other concurrent processes, providing a more comprehensive understanding of the cooling mechanisms in TMDs.

In Chapter 4, PPP spectroscopy has been applied to isolate the cooling dynamics using a third NIR laser pulse. This approach enables the quantitative investigation of the impacts of both cold carrier and hot carrier densities on the cooling dynamics. Additionally, evidence of hot carrier trapping is observed when the excess energy of the carriers is sufficiently high.

2.3.4.2 Hot carrier and lattice cooling in MXenes

As discussed in section 2.3.3, the heat dissipation from the MXene lattice to the surrounding environment is relatively slow, reflecting its low thermal conductivity.

However, the limited detection time range of ultrafast PP measurements, typically restricted to less than a few nanoseconds, prevents a complete characterization of the heat distribution dynamics across the MXene film. To address this limitation and provide a detailed analysis of energy dissipation in MXene films—from carrier relaxation to lattice cooling—PP measurements spanning timescales from sub-picoseconds to microseconds were employed in Chapter 5. This comprehensive study offers a quantitative and thorough understanding of the energy dissipation dynamics in MXene films.

2.3.4.3 Exciton dynamics in multilayer MoS₂

As discussed in Section 2.3.2, exciton dynamics in TMDs are critical for the performance of TMD-based optoelectronic devices. However, the indirect bandgap of multilayer TMDs makes it challenging to study exciton dynamics using PL-based spectroscopy methods. While PP measurements have been employed to address this challenge, isolating exciton dynamics from other processes, such as free carrier contributions, remains complex. To specifically investigate exciton dynamics in multilayer MoS₂, PPPc spectroscopy has been utilized in the multilayer MoS₂ photodetectors, as detailed in Chapter 6. The PPPc method naturally enables the sensitive detection of bound states in the studied devices. The details of PPPc approach are discussed in section 3.2.5.

Chapter 3 Spectroscopic

Methods

Spectroscopy is a field of study about the interaction between light and matter. The spectroscopic methods can be divided into two main categories. *Linear* spectroscopies commonly refer to light-matter interaction with the weak incident radiation field while the system keeps in equilibrium. In *non-linear* spectroscopies, intense light field is applied to excite the material to ESs to bring the system to non-equilibrium. The dynamics of the system to recover to equilibrium can be recorded using pulsed laser excitations, which is also called as *time-resolved spectroscopy*. This chapter aims to describe the operating principles and general conditions of the main steady-state and time-resolved spectroscopic methods used in the thesis.

3.1 Steady-state optical spectroscopy

3.1.1 UV-vis absorption spectroscopy

Due to the existence of optical bandgap in the semiconductors, the photons with the energy higher than the bandgap can be absorbed by the semiconductors. UV-vis absorption spectroscopy is used to record the absorption of light by a semiconductor as the function of wavelength. Fig 3.1 shows a scheme of a UV-vis absorption spectrophotometer, including a light source, monochromator, and a detector. The white light provided by the lamp is dispersed by the monochromator with a grating or prism to allow a “single” colour light coming out of the slit. The light intensities at different wavelength with, $I_T(\lambda)$, and without, $I_0(\lambda)$, the sample are recorded by the detector. Therefore, *transmittance*, $T(\lambda)$, and *absorbance*, $A(\lambda)$, of the sample can be calculated by Eq. 3.1. All UV-vis absorption measurements in this thesis were performed using a commercial spectrophotometer (Cary 60, Agilent). A blank background was taken with an empty substrate for an individual sample and was subtracted automatically in the software.

$$A(\lambda) = -\log T(\lambda) = -\log \left(\frac{I_T(\lambda)}{I_0(\lambda)} \right) \quad \text{Eq. 3.1}$$

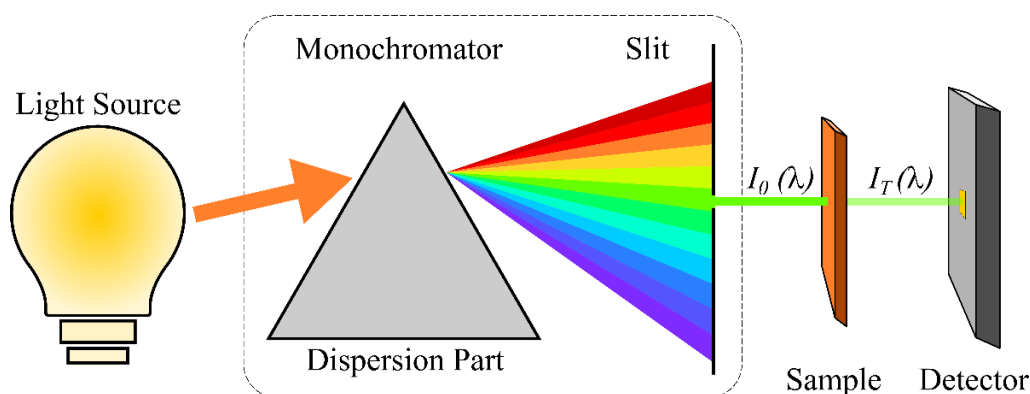


Figure 3.1 Scheme of the absorption spectrometer.

3.1.2 Raman spectroscopy

Raman spectroscopy measures the energy of vibrational modes of a sample based on Raman scattering, which can provide the fingerprint of chemical and structural information of the material. When light shines on a molecule, the molecule can be excited to a high-energy state which is considered as a very short-lived virtual state. There are three fates of the scattered photons. The majority of the incident photon is scattered elastically without changing photon energy, called *Rayleigh scattering*. However, a very small number of photons are scattered inelastically (i.e., the energy of scattered photon is changed), which is called *Raman scattering*. If the molecule is excited to higher vibrational state by the incident light, the scattered photon loses energy, called *Stokes Raman scattering*. In contrast, if the molecule relaxes to lower vibrational state after excitation by the incident light, the scattered photon gains energy, called *Anti-Stokes Raman scattering*. The origin of Stokes and Anti-Stokes Raman scattering is shown in Fig 3.2. According to the Boltzmann distribution, the molecule has much higher probability to locate on the ground vibrational state. Therefore, Stokes Raman scattering is always more intense than the Anti-Stokes Raman scattering, and Stokes Raman scattering is measured in most Raman spectroscopy.

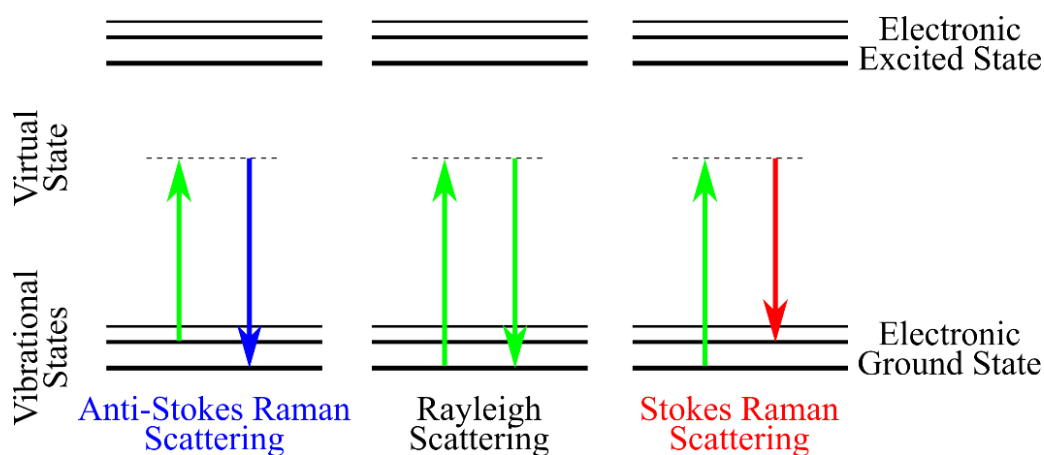


Figure 3.2 The origin of Raman scattering.

3.1.3 Photocurrent spectroscopy

When the semiconductor is excited above the bandgap, FCs can be generated either from direct excitation or other quasiparticles. The FCs can be extracted to the external circuit to generate photocurrent with proper applied electrical field. Photocurrent spectroscopy records the photocurrent as a function of excitation wavelength.

3.1.3.1 General experimental details

The photocurrent spectroscopy measurements were carried out in a home-built system, schemed in Fig 3.3, including a lamp (SLS401, Thorlabs) and a monochromator to generate “single” colour excitation light to the device. The incident light was modulated by a chopper (MC1F10HP, Thorlabs), which was synchronised to a lock-in amplifier (MFLI, Zurich Instrument) to record the photocurrent at the modulation frequency by a MATLAB code. The voltage was applied by the “Aux Output” from the lock-in amplifier. The setup was built by Dmitry Maslennikov (Imperial College London), and the MATLAB code was written by Dmitry Maslennikov, Ivy Wang (Imperial College London), and Longren Li (Imperial College London).

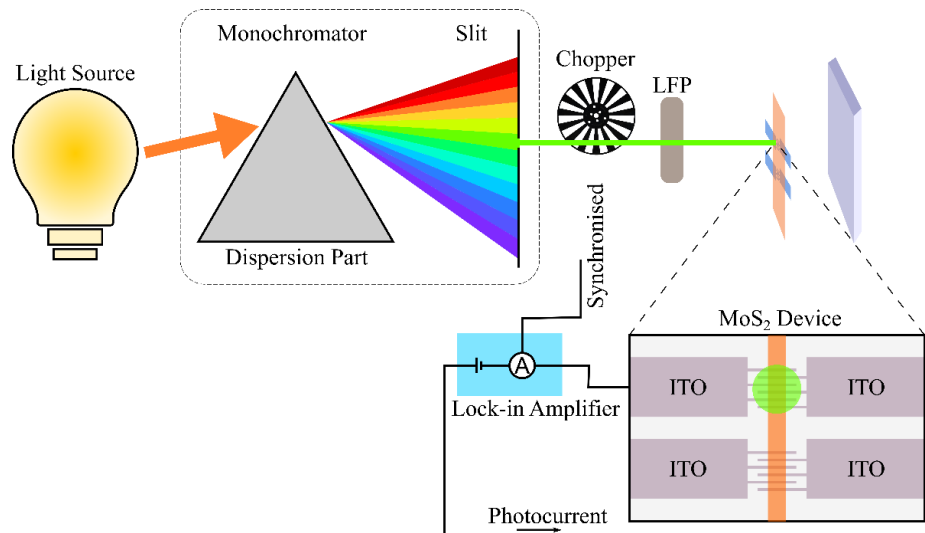


Figure 3.3 Scheme of the photocurrent response spectroscopy.

A LPF (FGL420M, Thorlabs) was placed between the monochromator and the sample to remove the high order diffraction from the grating inside the monochromator. The white light can be diffracted by a grating to different angles following Eq. 3.2:

$$m\lambda = d(\sin\theta_i + \sin\theta_m) \quad \text{Eq. 3.2}$$

where m is the order of diffraction, λ is the wavelength of the diffracted light, θ_i is the angle between the diffracted light and the grating normal, and θ_m is the angle between the incident light and the grating normal. Apart from 0 order (direct reflection), the first order diffraction has the highest intensity, which is desired in monochromator. However, the light from second order diffraction can overlap with the light from first order diffraction on some angles, as shown in Fig 3.4. For example, the diffracted 800 nm light from the first order diffraction may have the same θ_m as the diffracted 400 nm light from the first order diffraction. Therefore, a LPF is required to cut off the high order diffraction. The detection wavelength range was also controlled less than twice of the wavelength of the LPF to avoid contamination from the second order diffraction.

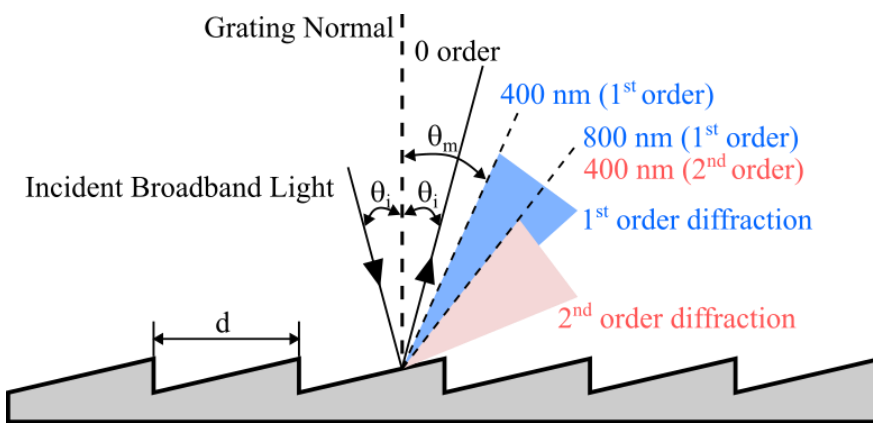


Figure 3.4 Illustration of first and second order diffraction from a grating.

3.1.3.2 Data interpretation

The photocurrent of the sample, $I_{sample}(\lambda)$, needs to be calibrated because the light intensity from the lamp changes with wavelength. A Si photodetector (PDA10A2, Thorlabs) was used to replace the sample to record the photocurrent as a function of wavelength, $I_{Si}(\lambda)$. The responsivity of the Si photodetector, $R_{Si}(\lambda)$, is obtained from Thorlabs with the unit of A/W, shown in Fig 3.5.

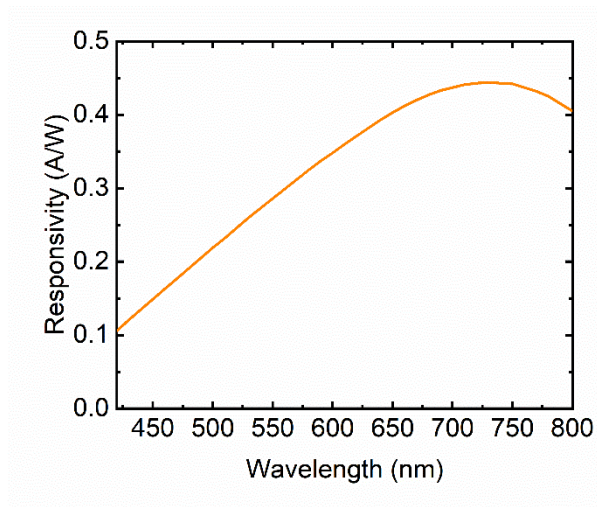


Figure 3.5 Responsivity of Si photodetection.

The calibrated photocurrent from the sample, $I_{sample}^{cal}(\lambda)$, is given by Eq. 3.3.

$$I_{sample}^{cal}(\lambda) = I_{sample}(\lambda) \frac{I_{Si}(\lambda)}{R_{Si}(\lambda)} \quad \text{Eq. 3.3}$$

In the thesis, except for further notification, all the photocurrent spectroscopy results refer to calibrated photocurrent, $I_{sample}^{cal}(\lambda)$, rather than raw data, $I_{sample}(\lambda)$.

3.2 Time-resolved spectroscopy

As mentioned in the introduction, the electrons in the GS of a material can be excited to the ESs with a laser pulse to investigate the dynamics of ESs. Commercially available diode lasers are with a pulse duration down to tens of ps with switchable repetition rate (normally tens of MHz). However, many ultrafast nonlinear processes happen within tens of ps, as mentioned in the introduction. Therefore, in most ultrafast spectroscopy measurements, an intense laser pulse with fs pulse duration is needed to obtain the ultrafast carrier dynamics from fs to tens of ps.

3.2.1 Laser pulse generation

3.2.1.1 Resonator cavity

The fundamental part of a laser is the *resonator cavity*, which contains of a pair of mirrors surrounding a lasing medium, known as *gain medium*. Fig 3.6 shows the basic construction of resonator cavity. Mirror 1 (M1) is an entirely non-transparent mirror, and mirror 2 (M2) is partially transparent mirror, also called *output coupler*, which allows the generated radiation to leave the cavity.

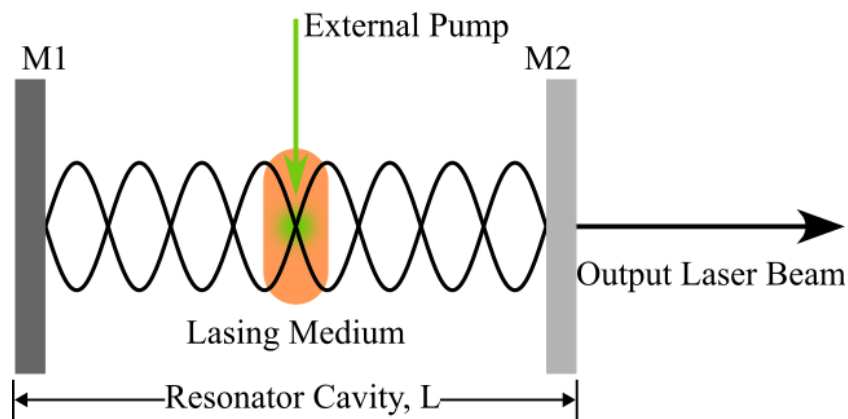


Figure 3.6 Basic structure of laser.¹¹⁹

The gain medium can be excited by an external source either electronically or optically, which is called as *pump*. Note that this *pump* term is different from the pump laser to excite the samples. Initially, when the population of ES is low, the main decay pathway of the ES is *spontaneous emission*. As the accumulation of population of ES, stimulated emission becomes the major decay pathway. In stimulated emission, an incident photon interacts with the ES without being absorbed, and results in a second photon which is identical to the incident photon, including energy, phase, and direction. In other word, two identical photons are produced via stimulated emission by a single incident photon, which is also called *amplification*. This is the fundamental working principle of the gain medium. Eventually, the population of the ES is accumulated enough that the population in the GS becomes lower than the population of the ES, which is known as *population inversion*. When the population inversion is achieved, the emission is stronger than absorption.

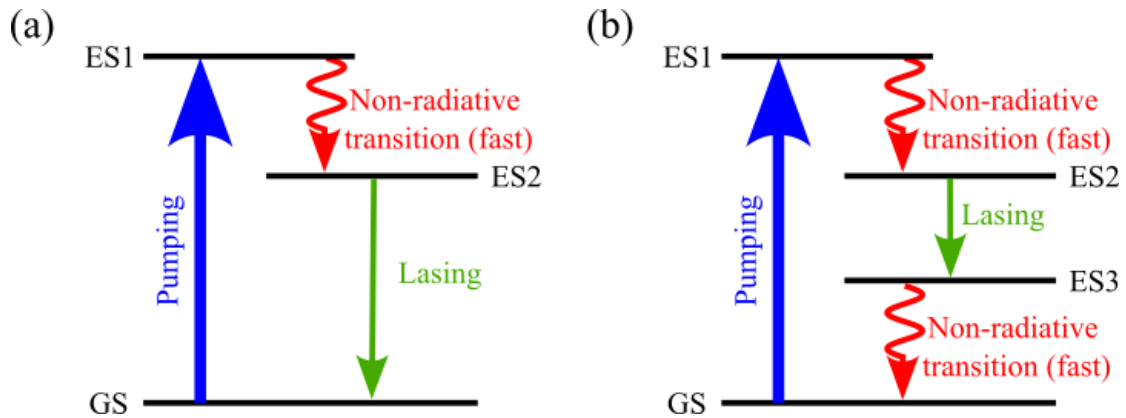


Figure 3.7 Energy diagram of gain medium. Three-level system (a) and four-level system (b) to reach population inversion.¹¹⁹

To obtain the population inversion, the gain medium cannot be a two-level system, because the emitted photon can be reabsorbed by the medium itself. Therefore, a three-level system is required, shown in Fig 3.7 (a). After excitation by the external *pump*, the carriers on ES1 have two relaxation pathways: (1) decaying radiatively or non-

radiatively to GS, and (2) decaying non-radiatively to the lower level, ES2. In the realistic gain medium, the transition from ES1 to ES2 is much faster than the decay from ES1 to GS, and the lifetime in the state ES2 is much longer than that in the state ES1. Therefore, population inversion can be reached between ES2 and GS in the three-level system. Eventually, the emission intensity in the resonator cavity becomes higher than the absorption and stimulated radiation generates the output laser beam.

To reach population inversion, one can either increase the population in the high energy state (i.e., ES) or reduce the population in the low energy state (i.e., GS). However, in the three-level system, only increasing population of ESs is available because stimulated emission happens between ES2 and GS. To reach higher efficiency of population inversion, four-level system is typically used, as shown in Fig 3.7 (b). In four-level system, stimulated emission happens between ES2 and ES3 and the non-radiative transition from ES3 to GS is fast to deplete the population of ES3. Therefore, the four-level system has high efficiency of population inversion without delivering additional pumping energy.

3.2.1.2 Active Q-switching laser

Base on the resonator cavity shown in Fig 3.6, the intracavity energy can be increased with the light oscillates within the cavity. The quality factor Q of the resonator is the ratio of the energy stored in the cavity to the energy loss per cycle. To modulate the Q -factor of the resonator cavity, a fast-response electro-optic shutter, called *Pockels cell*, can be put on the optical axis inside the cavity, schemed in Fig 3.8. The Pockels cell acts as a waveplate whose polarisation is controlled by the applied voltage. When there is no voltage applied on the Pockels cell, the polarisation of the light, Pockels cell and the polariser is parallel, so the light is allowed to pass the polariser and oscillate within

the cavity to gain energy. The light is reflected out of the resonator cavity by the polariser when the polarisation of the Pockels cell is rotated 90 degrees after adding voltage. Therefore, the Q-factor of the resonator cavity is modulated by the Pockels cell. Due to the external electric control, this Q-switching is called *active Q-switching*.

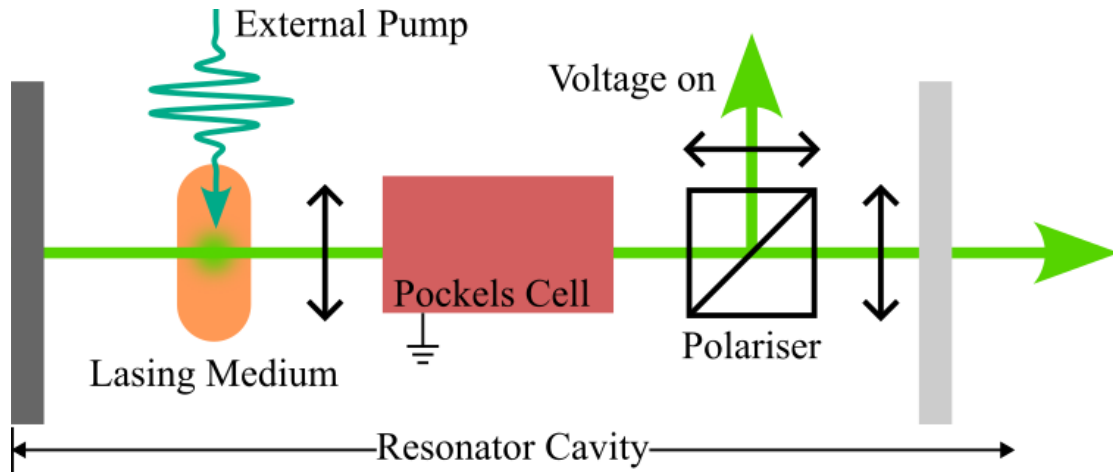


Figure 3.8 Scheme of Q-switching laser with a Pockels cell.

3.2.1.3 Passive Q-switching laser

In active Q-switching laser, the generated pulse duration is normally in ns level due to the limitations of the external controlling electronics and pulse build-up time.¹²⁰ To reach shorter pulse duration, the external controlling electronic part can be replaced by an “optically” controlled component. A saturable absorber can be placed inside the resonator cavity to control the Q-factor to replace the Pockels cell and the polariser. The transmittance of light by the saturable absorber decreases with increasing light intensity, and the transmittance keeps constant when the light intensity is sufficiently high. Therefore, when the intracavity energy is building up, the Q-factor is increased because the transmittance of the saturable absorber is reduced. When saturable absorber reaches the threshold, the laser pulse is released out of the cavity and the Q-factor is reduced. After generating a laser pulse, the saturable absorber recovers to the low Q-factor state again. The saturable absorption is a nonlinear optical process without using

any electronic control, and thus, passive Q-switching method can generate laser pulses with short pulse duration.

3.2.1.4 Mode locking

To generate ultrashort pulse with the duration in fs level, mode locking is used in the laser system. In the resonator cavity, only standing waves can survive in the resonator cavity, whose wavelength can match Eq. 3.4.

$$\lambda = \frac{2L}{m} \quad \text{Eq. 3.4}$$

where λ is the wavelength of the light, L is the length of the resonator cavity, and m is the number of the mode, which is integer. These standing waves are called *longitudinal modes*. In mode locking, several longitudinal modes at the same phase are required. By taking the superposition of these longitudinal modes, an intense mode-locked mode can be obtained.¹²⁰ Mode locking generates a train of pulses with a repetition period which is equal to the round-trip time in the resonator cavity, and the pulse duration equals to the round-trip time divided by the number of modes.

In active mode locking, the voltage on Pockels cell is applied periodically to coincide with the round-trip time of the resonator cavity.¹²⁰ Although the pulse duration cannot reach ultrashort due to the external control, the voltage pulse can be synchronised to an external reference.¹²¹

To obtain ultrashort pulse duration with mode locking, passive mode locking is used. Among all the passive mode locking methods, in a realistic mode locking ultrafast solid-state laser, *Kerr-lens mode locking* is the most common approach. *Optical Kerr*

effect describes a continuous change in the refractive index of a material in response to the incident light intensity.¹²⁰ Among all the available modes in the resonator cavity, some modes share the same phase which are mode-locked to form high intensity pulses, while the other modes with random phase cannot be mode-locked and the intensity is weak. When the light passes through the Kerr medium, the refractive index is higher for the mode-locked pulses. Therefore, the high-intensity mode-locked pulses can be focused to small size to pass the aperture, while the low intensity beam is not focused enough which is blocked by the aperture, shown in Fig 3.9. This structure preferentially filters out the low energy beam at the edge which is normally a continuous wave. Due to the instantaneous response of Kerr effect, Kerr-lens mode locking can generate laser pulse with duration down to fs level.¹²²

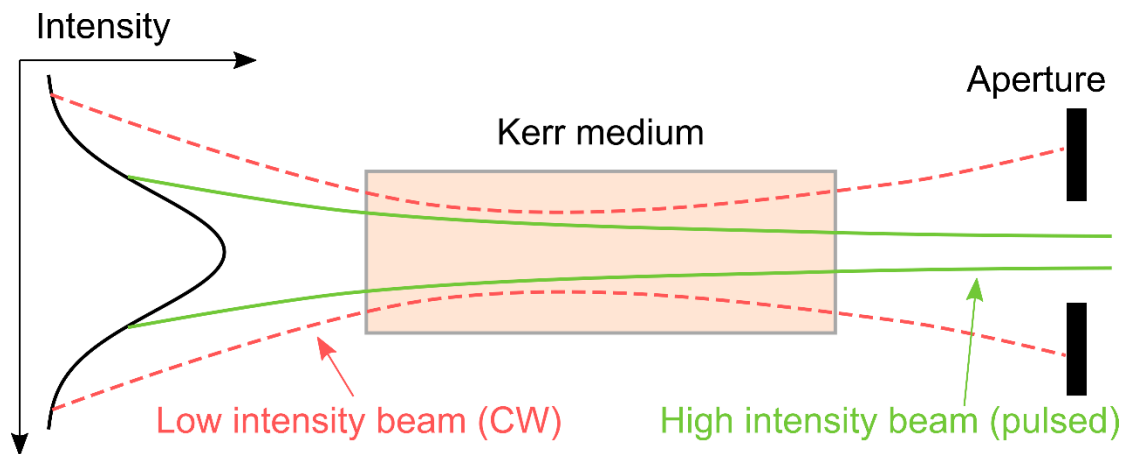


Figure 3.9 Structure of Kerr-lens mode locking.

Ti: Sapphire crystal is widely used in the commercial ultrafast lasers as a four-level gain medium, with a broad spectral range 670-1070 nm.¹²³ Meanwhile, $\text{Ti:Al}_2\text{O}_3$ (Ti:Sapphire) crystal can also work as the Kerr medium for self-mode locking.¹²³

Due to the broad spectral range of femtosecond laser pulses, a prism pair is typically incorporated into the laser cavity to compensate for dispersion, ensuring that the ultrashort pulse duration is preserved.

3.2.1.5 Amplification of ultrashort pulses

After generating the ultrashort pulses, the intensity of these pulses needs to be amplified. One of the most widely utilised method is called *chirped pulse amplification* (CPA), which won the Nobel Prize in 2018. The principle of CPA is shown in Fig 3.10. The ultrashort pulses generated from the resonator cavity are amplified using a gain medium (normally Ti:Sapphire crystal) in the regenerative amplifier. However, the damaging threshold of the gain medium is normally smaller than the intensity of the ultrashort pulses. Therefore, the input ultrashort pulses are stretch to several hundreds of ps using a pair of gratings, called *stretcher*, so that the intensity of the laser pulse does not arrive at the gain medium at the same time and space to avoid damage. After re-amplification through the regenerative amplifier, the stretched laser pulse is compressed to back to the fs level by another pair of gratings, called *compressor*.

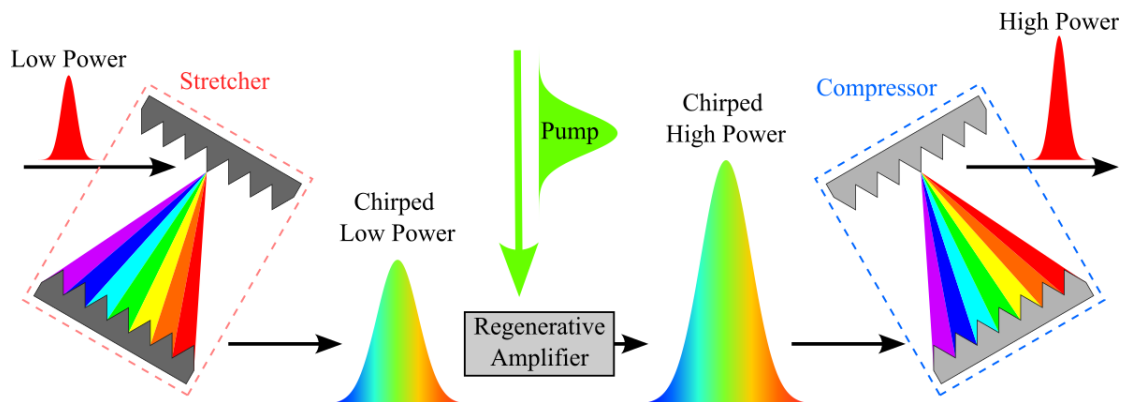


Figure 3.10 Scheme of chirped pulse amplification.

3.2.2 Wavelength tuning of the ultrashort pulses

The wavelength range of the laser pulse from the output through CPA is very limited. To use the ultrashort pulses for spectroscopic measurement, the laser pulses need to be tuneable in a wide range. The most common way of manipulating the wavelength of the ultrashort pulses is by an *optical parametric amplifier* (OPA). Coherent optical signals are generated in OPA in a nonlinear process, called *parametric amplification*, within second-order nonlinear crystals. The energy from the incident pump beam is transferred to two beams with lower frequency following the energy conservation, as shown in Eq. 3.5.

$$\omega_p = \omega_s + \omega_i \quad \text{Eq. 3.5}$$

where ω_p , ω_s , and ω_i are the frequencies of pump, signal, and idler beams, respectively. To achieve high conversion efficiency, the three beams must satisfy the *phase-matching* condition.

In most commercial Ti:Sapphire lasers, the fundamental output is around 800 nm (1.55 eV) and the default wavelengths of the signal and idler beams are around 1300 nm (0.95 eV) and 2000 nm (0.6 eV) from the OPA. The UV-vis beam used in the thesis were generated by *second harmonic generation* (SHG) and *sum-frequency generation* (SFG) by the NIR beams with nonlinear crystals. In SFG, two photons at different low frequencies are converted into one photon at high frequency, and in SHG, two incident photons have the same frequency.

Apart from generating beams with different colours from the fundamental laser beam, broadband beam, called *supercontinuum*, can also be generated by the fundamental

beam. The broadband beam is generated by *self-phase modulation* effect, which is a third-order nonlinear process. When the fundamental laser beam is focused on some crystals, such as sapphire and YAG, the refractive index is increased for rising edge of the Gaussian pulse, while the refractive index is reduced for the dropping edge of the Gaussian pulse. Therefore, the frequency is reduced on the rising edge (i.e., red-shifted), but the frequency increased for the dropping edge (i.e., blue shifted). In this thesis, the generated broadband beams in visible and NIR region are shown in Fig 3.11 with proper filters. The visible spectrum was generated by a sapphire crystal and the NIR spectrum was generated by a YAG crystal. Both broadband spectra were generated with a fundamental laser beam at 800 nm. The broadband beam was used to investigate the ES dynamics in the sections 3.2.3 and 3.2.4.

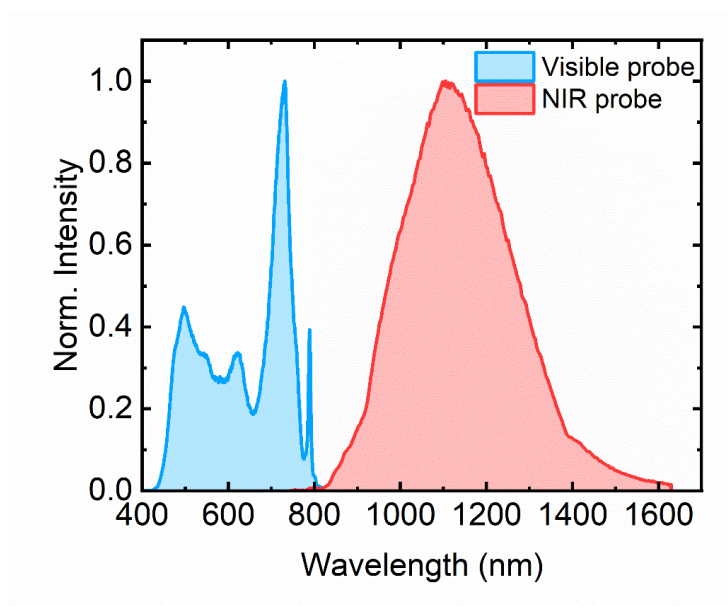


Figure 3.11 Spectra of broadband laser beam in visible and NIR region.

3.2.3 Transient absorption spectroscopy

3.2.3.1 Basic principles

To investigate the ES dynamics in a material, PP spectroscopy is commonly used. The material is excited by the *pump* pulse to promote electrons from GS to Ess. And then a weaker *probe* pulse is used to detect the transmittance change, ΔT , of the material with and without the pump pulse using a chopper. The chopper is synchronised to the laser to block every other pump pulse. The obtained ΔT is normalised to the transmittance, T , when the pump is blocked by the optical chopper, shown in Eq. 3.6.

$$\frac{\Delta T}{T} = \frac{T_{on} - T_{off}}{T_{off}} \quad \text{Eq. 3.6}$$

The transmittance signal can be converted to the absorption signal following the Eq.

3.1. The absorption change induced by the pump pulse is shown in Eq. 3.7:

$$\begin{aligned} \Delta A &= A_{on} - A_{off} = -\log(T_{on}) - [-\log(T_{off})] = -\log\left(\frac{T_{on}}{T_{off}}\right) \\ &= -\log\left(\frac{T_{on} - T_{off}}{T_{off}} + 1\right) \\ &= -\log\left(\frac{\Delta T}{T} + 1\right) \\ &= -\frac{1}{2.3} \ln\left(\frac{\Delta T}{T} + 1\right) \end{aligned} \quad \text{Eq. 3.7}$$

The value of $\frac{\Delta T}{T}$ is in the level of 10^{-3} , and thus, Eq. 3.7 can be rearranged to Eq.3.8:

$$\Delta A \approx -\frac{1}{2.3} \times \frac{\Delta T}{T} \quad \text{Eq. 3.8}$$

To obtain the dynamics, ΔA is recorded as a function of delay time between the pump and probe pulses. The time delay can be generated by a mechanical delay stage (DS), which can achieve delay time from tens of fs to a few ns.

The PP spectroscopy is also called TA spectroscopy when the supercontinuum white light probe is used. However, it is noted that TA spectroscopy is named as PP spectroscopy in section 3.2.4 and Chapter 4 for a clear comparison between the pump-probe and the pump-push-probe spectroscopy. Otherwise, in this thesis, the PP-named spectroscopy describes the two-colour scheme.

3.2.3.2 General experimental details

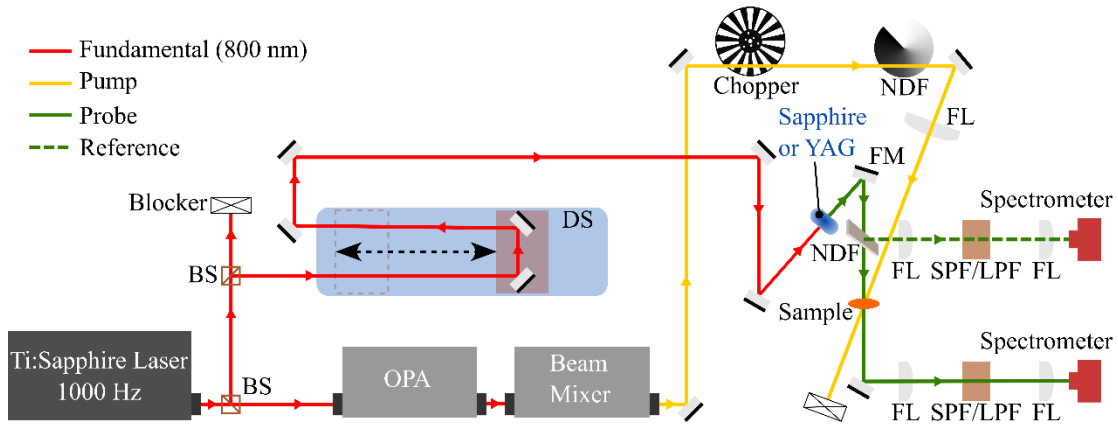


Figure 3.12 Scheme of the setup of transient absorption spectroscopy. BS: beam splitter; DS: delay stage; NDF: neutral density filter; FM: focusing mirror; FL: focusing lens; SPF: short-pass filter; LPF: long-pass filter.

In this thesis, all TA experiments were carried out using a commercial setup in “ ΔA ” mode (HELIOS, Ultrafast Systems). The layout of the TA setup is schemed in Fig 3.12. The fundamental 800 nm (1 kHz, <100 fs pulse duration) laser pulses were generated by a Ti:Sapphire regenerative amplifier (Solstice, Spectra Physics, Newport

Corporation). The fundamental beam was split into three portions, but only two portions were used in TA measurements. The third portion was used in PPP measurements in section 3.2.4. One portion was sent into an OPA (TOPAS Prime, Light Conversion) and a frequency mixer (Niruviz, Light Conversion) to generate visible pulses as the pump. The other portion was delayed by the DS and focused on sapphire or YAG crystal to generate visible and NIR broadband beam as the probe. The spectra of the broadband probes have been shown in Fig 3.11. The pump and broadband probe were focused on the same point of the sample with a spot size $\sim 0.5 \text{ mm}^2$. The transmitted probe beam was coupled to an optical fibre and collected by a CCD spectrometer. To mitigate shot-to-shot noise, another spectrometer was used to measure fluctuations in a reference beam that was split off from the probe before shining the sample by a neutral density filter.

3.2.3.3 Chirp correction

Due to the broad spectrum of the probe pulse, as shown in Fig. 3.11, optical dispersion causes photons at different wavelengths to arrive at the sample at different times, typically within a time window of 1 ps. This temporal misalignment necessitates chirp correction to compensate for dispersion and ensure that photons at all wavelengths arrive at the sample simultaneously.

Fig. 3.13 presents the original TA spectrum of SL WS₂ at around the temporal overlap between the pump and probe pulses prior to chirp correction. The data clearly show that shorter-wavelength (blue) light arrives earlier than longer-wavelength (red) light, highlighting the impact of optical dispersion.

In this thesis, chirp corrections were performed using the *Surface Xplorer* software. The

half-rise time of the kinetics was chosen as the criteria of time zero (i.e., the temporal overlap between the pump and probe pulse). By selecting at least four points at different wavelengths, the software automatically fits the dispersion to a polynomial function, ensuring accurate chirp correction across the spectrum.

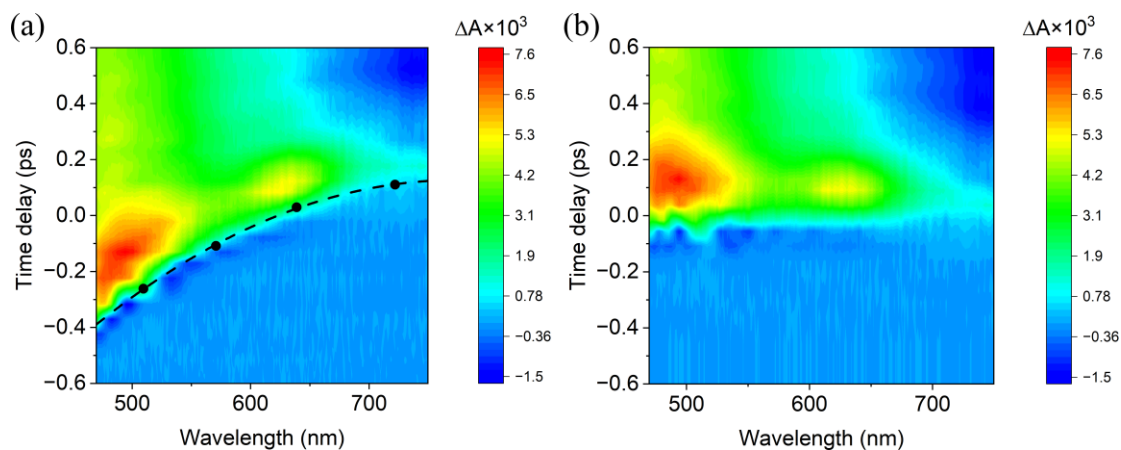


Figure 3.13 TA spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene before (a) and after (b) chirp correction. The four points are selected to be fitted by a polynomial function, and the dashed curve is the fit.

3.2.3.4 Data interpretation

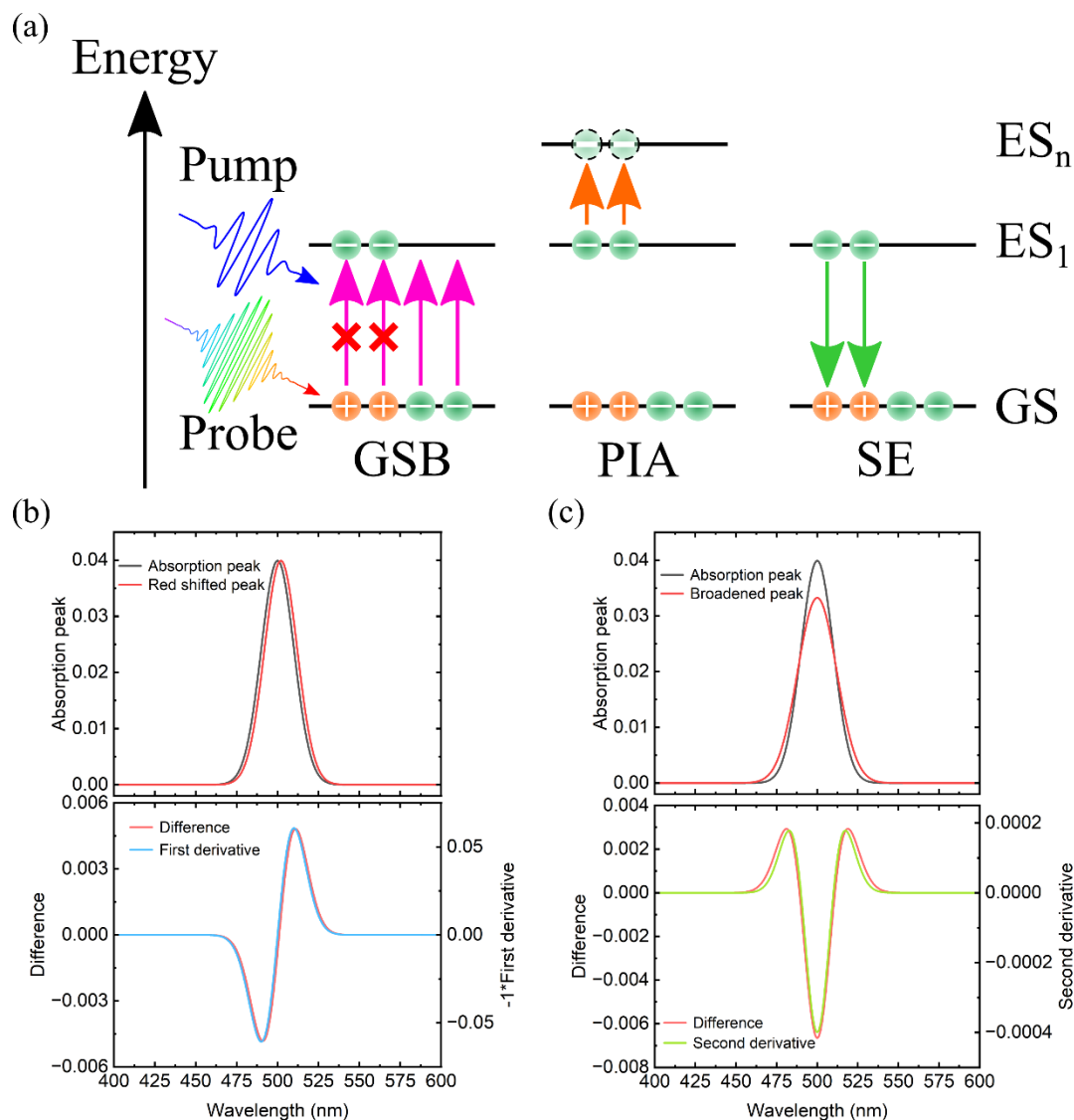


Figure 3.14 Typical signals observed in TA measurements. (a) Pathways of electronic transitions. (b) Peak shifting induced spectral change. (c) Peak broadening induced spectral change.

The typical signals of TA measurements are shown in Fig 3.14 (a), including *ground state bleach* (GSB), *photoinduced absorption* (PIA), and *stimulated emission* (SE). These transitions are caused by transitions between the electronic states caused by the laser pulse excitation.

- The GSB shows negative signal measured in ΔA due to the depletion of GS

population by filling the ESs by the pump. The peak positions always follow the steady-state absorption spectrum.

- The PIA shows positive signal measured in ΔA due to the transition from an ES to higher ESs, due to the increased population in ES excited by the pump.
- The SE shows negative signal measured in ΔA due to the emission from the ES.

Spectral changes can arise from various effects, including the optical Stark effect (discussed in Chapter 4) and the thermochromic effect (discussed in Chapter 5). These effects can induce shifts and/or broadening of the steady-state optical absorption peak. The top panels of Fig. 3.14 (b) and (c) illustrate simulations of red-shifting and broadening of the absorption peak, respectively, with all peaks modelled as Gaussian distributions. The bottom panels show the corresponding difference spectra, calculated as the modified peak subtracted from the original peak.

As depicted in the bottom panel of Fig. 3.14 (b), the difference spectrum resulting from red shifting can be accurately modelled by the inverse of the first derivative of the original absorption spectrum. Conversely, the bottom panel of Fig. 3.14 (c) demonstrates that the difference spectrum arising from broadening is well described by the second derivative of the original absorption spectrum.

These results highlight the importance of carefully attributing the origins of the TA spectrum, as spectral changes may not solely result from electronic transitions but could also be influenced by these additional effects.

3.2.4 Pump-push-probe spectroscopy

3.2.4.1 Basic principles

The PPP spectroscopy is designed to investigate the relaxation process from a high energy level ES to a low energy level ES. A portion of carriers on the low ES is re-excited to the high ESs by an intense NIR push pulse at some time delay after pump pulse resulting in quenched signal in PP. By subtracting the PP signal (i.e., without push) from the PPP signal (i.e., with push), $\delta(\Delta A)$ is obtained, shown in Eq. 3.9.

$$\delta(\Delta A) = \Delta A_{PPP} - \Delta A_{PP} \quad \text{Eq. 3.9}$$

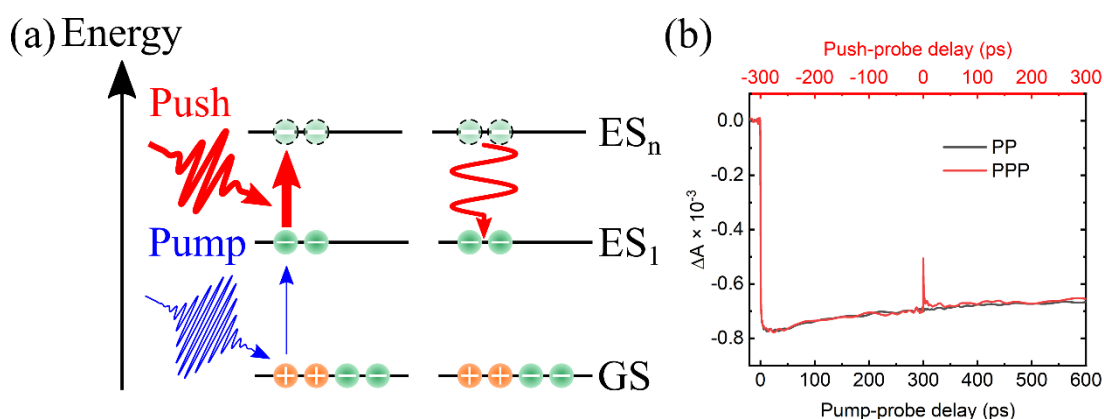


Figure 3.15 Principles of PPP spectroscopy. (a) Relevant photophysical processes with NIR push in PPP measurements. (b) Comparison between PPP and PP of the GSB signal of InP quantum dot colloidal.

Fig 3.15 (a) shows the scheme of the energy transition of ESs with NIR push in PPP measurement. Fig 3.15 (b) shows an example of a comparison between PPP and PP signal obtained from the GSB signal of an InP quantum dot colloidal sample.

3.2.4.2 Benefits of PPP spectroscopy

As shown in the basic principle, PPP spectroscopy is particularly useful to investigate the hot carrier cooling process in the semiconductor, although PP spectroscopy has been widely used. In PP method, there are two typical ways to investigate the hot carrier cooling process.

1. The rising signal at GSB or PIA is observed as the feature of hot carrier cooling and the cooling time is defined as time constant of the rising signal. An example of this method is shown in Fig 3.16 (a).
2. The carrier temperature is extracted by fitting the TA spectral shape in a time window with Maxwell-Boltzmann distribution, an example shown as shown in Fig 3.16 (b). The carrier temperature as a function of delay time is then fitted to obtain the cooling time, shown in Fig 3.16 (c).

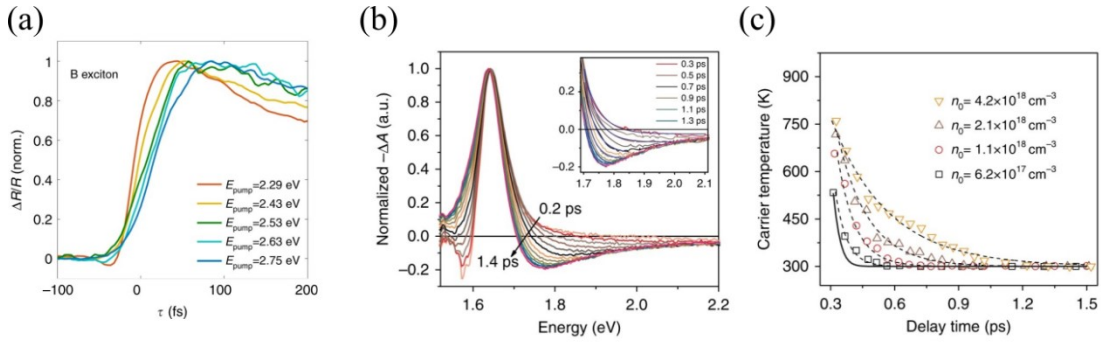


Figure 3.16 Methods of investigation of hot carrier cooling by PP spectroscopy. (a) Early time GSB signal of B exciton GSB in MoS₂ with above-gap excitation.⁷⁰ Reproduced with permission from ref 70. Copyright 2020 Springer Nature. (b) Early time TA spectra fitted by Maxwell-Boltzmann distribution.¹²⁴ (c) Extracted carrier temperature from (b) as a function of time.¹²⁴ Reproduced with permission from ref 124. Copyright 2017 Springer Nature.

However, there are many limitations of using conventional PP method to study hot carrier dynamics. In the first method, the pump fluence needs to be kept low to avoid

the many-body interactions which can merge the hot carrier cooling process. In the second method, the Maxwell-Boltzmann distribution is used to fit the PP spectral shape in a certain spectral window. The estimation of carrier temperature depends on the selection of the fitted spectral range.¹²⁵ Therefore, PPP spectroscopy can be used to investigate hot carrier cooling process to overcome the problems mentioned above with two main benefits.

1. The pump-push delay time is controlled until the complicated photophysical processes diminish in a tens of ps (or longer). This control allows using a simple two-state model which just contains a hot state and a cold state to describe the cooling process, which can be used in a wide range of semiconductors.
2. Due to the controlled pump-push delay time, the push can be delivered to the sample after the many-body interactions after pump excitation. Therefore, PPP spectroscopy can be used to investigate the impact of cold carrier density on the hot carrier cooling process by simply manipulating the pump fluence. This offers a new dimension to study the hot carrier cooling process, which cannot be done in normally PP spectroscopy because of the overlapping between hot carrier cooling and other ultrafast photophysical processes in the time domain.

Investigation of hot carrier cooling with PPP spectroscopy was first reported by Guyot-Sionnest et al. in 1999 on colloidal CdSe quantum dots.¹²⁶ This method was then carried forward by Bakulin and coworkers.^{127–129}

3.2.4.3 General experimental details

The PPP setup, shown in Fig 3.17, is modified by Shawn (Xijia) Zheng (Imperial College London) and Thomas R. Hopper (Imperial College London) from the TA setup

3.2.5 Pump-push-photocurrent spectroscopy

3.2.5.1 Basic principles

The sample with PPP spectroscopy is measured at open circuit condition to understand the relaxation process. In PPPc measurement, the ESs in the sample are modulated by the NIR push pulse in short circuit condition (i.e., in a photocurrent-generating device). Photocurrent, J , can be extracted from the FC s obtained when the active layer is generated by the pump:¹³⁰

$$J(T) \propto N_{free}(T) \times \eta_{extract}(T) \quad \text{Eq. 3.9}$$

where N_{free} is the population of free charges and $\eta_{extract}$ is the extraction efficiency of the free charges from the device. Apart from the free charges, *bound states*, such as excitons and trapped carriers, can also be formed after pump excitation. The NIR push is then sent to the sample to re-excite a portion of population in the bound states to the free charges. Therefore, with NIR push, additional photocurrent as the function of pump-push delay time, $\Delta J(t)$, can be extracted:¹³⁰

$$\Delta J(t, T) \propto N_{bound}(t, T) \times \varphi_{activation}(T) \times \eta_{extract}(T) \quad \text{Eq. 3.10}$$

where $N_{bound}(t)$ is the population of bound state as the function of pump-push delay time and $\varphi_{activation}$ is the possibility of re-excitation of the bound states to free charges by the NIR push. Assuming that the transport and extraction processes are the same for pump- and push-induced free charges, the PPPc transient can be given as:

$$\frac{\Delta J(t, T)}{J(T)} \propto \frac{N_{bound}(t, T)}{N_{free}(T)} \propto \frac{1}{e^{-\frac{E_a}{k_B T}}} \quad \text{Eq. 3.11}$$

where E_a is the activation energy to dissociate the bound states to the free states.

The energy transition of ESs with NIR push in PPPc measurement is schemed in Fig 3.18.

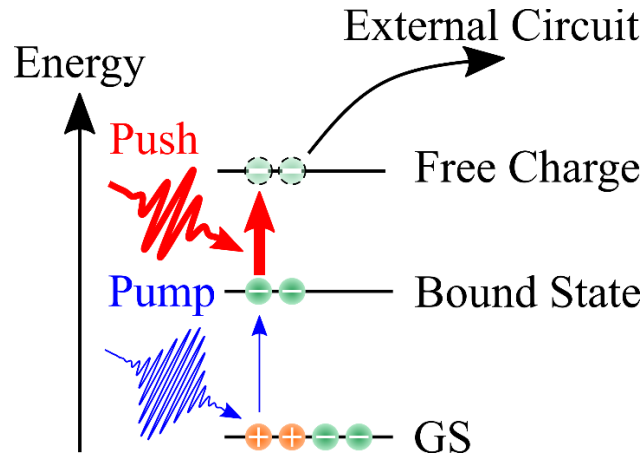


Figure 3.18 Relevant photophysical processes in PPPc measurements.

3.2.5.2 General experimental details

A layout of the PPPc spectroscopy setup is shown in Fig 3.19. The fundamental 800 nm (4 kHz, 35 fs pulse duration) laser pulses were generated by a Ti:Sapphire regenerative amplifier (Astrella, Coherent). The fundamental laser beam was split into three portions and two portions were sent to OPAs (TOPAS Prime, Coherent). The visible pump pulses were generated by SHG or SFG of the NIR signal pulses from the OPA-I using a BBO crystal. The residual NIR light was filter out by the SPF. The 2000 nm push pulses were obtained from the idler beam from the OPA-II. A Si filter was used to remove the residual visible light. The pump beam was delayed using a mechanical DS to generate pump-push time delay. A dichromic mirror was used to align the pump and push beams colinearly. The colinear beam was focused onto the

sample by a FM. The pump beam was not modulated (4 kHz) and the push beam was modulated at half of the frequency of the pump beam (2 kHz) by a chopper. A lock-in amplifier (MFLI, Zurich Instruments) was used to measure J at the pump frequency, 4 kHz, and ΔJ at the push frequency, 2 kHz. The bias was applied by the “Aux Output” from the lock-in amplifier. The integration time is 0.2 s for both frequency channels. The current signal output from the lock-in amplifier was read by a LabView code.

The setup was built by Thomas R. Hopper and Ben P. Carwithen (Imperial College London). The LabView code was written by Shawn (Xijia) Zheng.

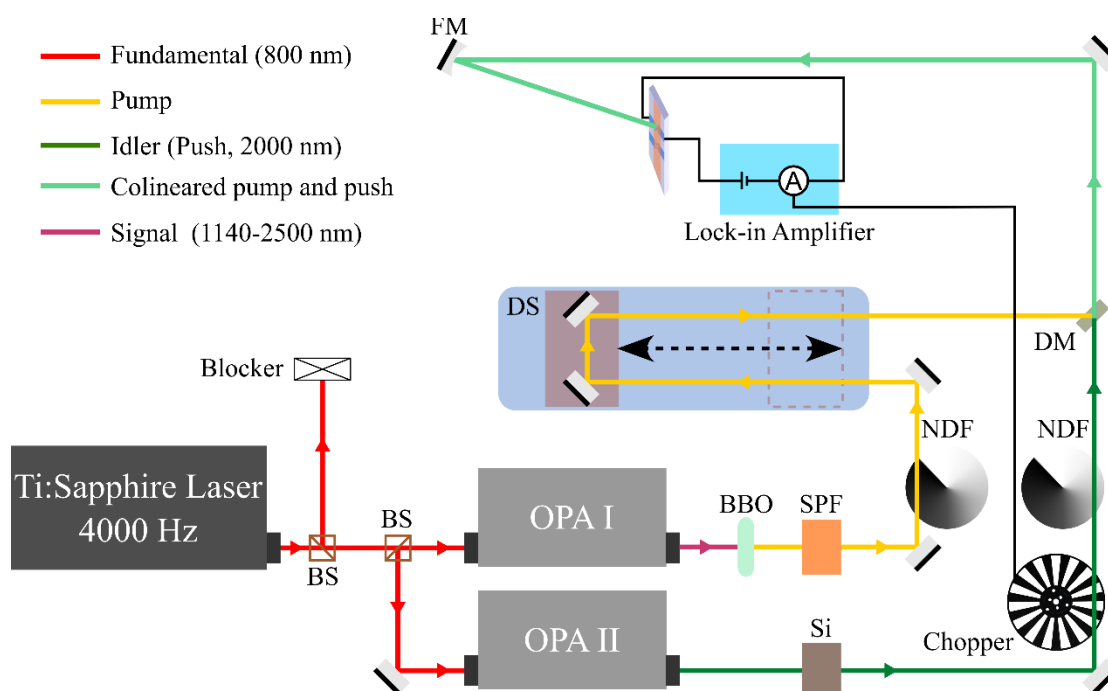


Figure 3.19 Scheme of the setup of pump-NIR push-photocurrent spectroscopy.

3.2.6 Nanosecond-pump-probe spectroscopy

The time-resolved spectroscopic methods mentioned in the previous sections are all within a few ns. To investigate the PP kinetics at even longer timescale, the time delay between the pump and probe needs to be generated electrically, rather than mechanically.

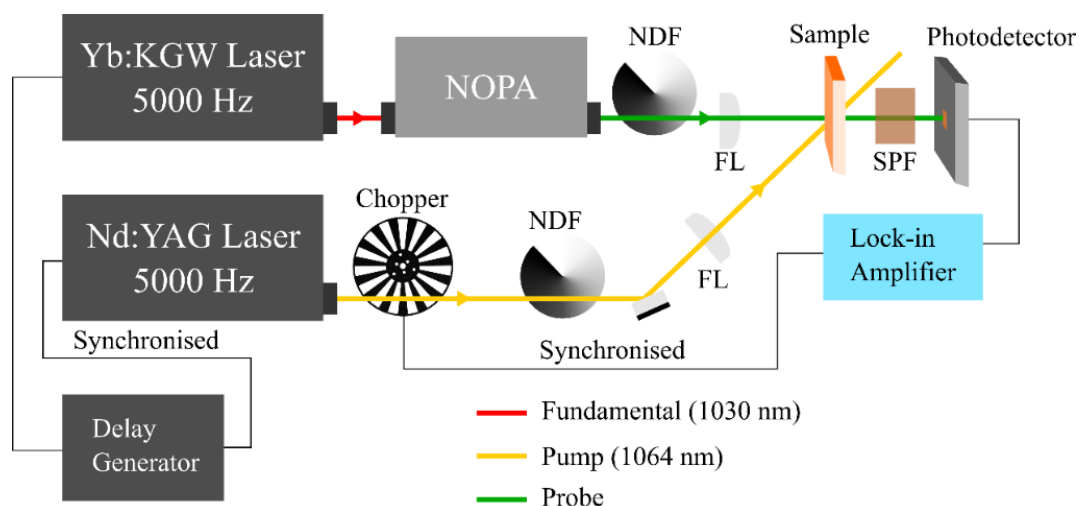


Figure 3.20 Scheme of the setup of nanosecond-pump-probe spectroscopy.

Fig 3.20 shows the scheme of a nanosecond-PP (ns-PP) setup used in this thesis, in which a Q-switch Nd:YAG laser (Innolas) was synchronised to a Yb:KGW laser (Pharos, 1030 nm, Light Conversion) at 5 kHz. When the delay generator (DG645, Stanford Research Systems) received the electric pulse from the Yb:KGW laser when the laser pulse was generated, the delay generator sent a delayed electric pulse after some user-defined time delay to trigger the Pockels cell in the Q-switch Nd:YAG laser to release a ns pulse. The Yb:KGW laser was used as pump at 1064 nm, and probe pulses with different wavelengths were generated by a nonlinear optical parametric amplifier (NOPA, ORPHEUS-N, Light Conversion). The pump beam was modulated at 2.5 kHz by a chopper.

A silicon photodiode (PDA36A2, ThorLabs) was used to measure the transmitted probe

intensity, with a lock-in amplifier (MFLI, Zurich Instruments) operating at an integration time of 0.2 seconds. The probe beam intensity was carefully maintained within the linear response range of the photodiode, ensuring that the voltage output from the photodiode was directly proportional to the transmitted probe beam intensity.

The voltage signal at 5 kHz corresponds to the intensity of the transmitted probe beam without optical excitation by the pump pulse, T , while the voltage at 2.5 kHz represents the intensity change of the transmitted probe beam following optical excitation, ΔT . These voltage signals were acquired using a LabView code interfaced with the lock-in amplifier. The $\frac{\Delta T}{T}$ signal was recorded as a function of delay time.

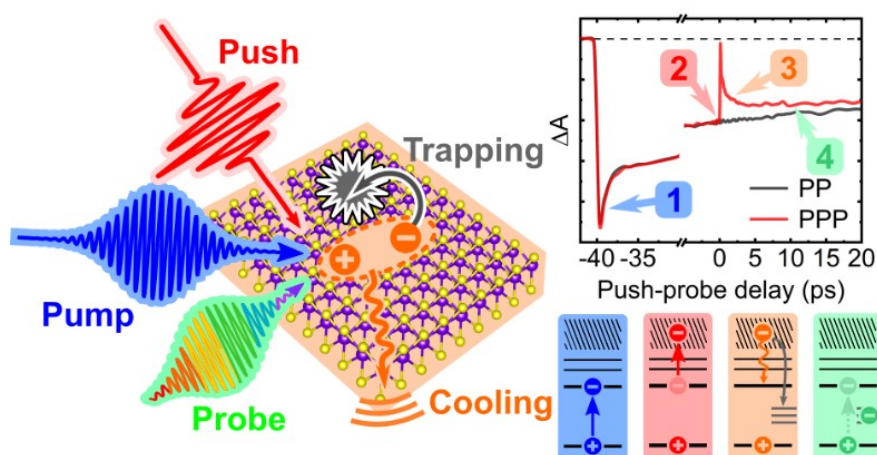
A short-pass filter (SPF, FESH0800, ThorLabs) was employed to block scattered pump light from reaching the photodetector, ensuring accurate measurements of the probe signal.

The setup was built by Tong Wang (the author) and Beier Hu (Imperial College London), and the LabView code was written by Ziming Chen (Imperial College London).

Chapter 4 Hot Carrier Cooling and Trapping in SL WS₂

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This chapter describes an ultrafast spectroscopic study of the hot carrier cooling process in the SL WS₂ using PPP spectroscopy, which aims to give a comprehensive picture of the hot carrier cooling process in the SL WS₂ with quantitative descriptions of the HPB effect.



4.1 Introduction and motivation

2D TMDs are widely considered as promising candidate materials for the next generation ultrathin and flexible optoelectronic devices. Different from the bulk and multilayer counterparts, SL TMDs have been widely investigated and integrated into devices in various optoelectronic applications, such as light emitting diode, photovoltaics, spintronics, and valleytronics.^{23,131–134} SL TMDs show direct bandgap,^{135,136} strong spin-orbital coupling,^{137,138} high exciton binding energy,^{57,60,139} and intriguing spin-valley physics.^{140,141} These properties are intimately linked to the relaxation of charge carriers, and more broadly to the interactions between charge carriers, the lattice, and the defects therein.

As in other semiconductors, ‘hot’ electrons (or holes) with initial kinetic energy above the CB (or VB) edges can be generated in SL TMDs by above-gap optical excitation or electrical injection of charges, or high-order Auger-type recombination processes. In 2D TMDs, free hot carriers with a high transient electronic temperature of thousands of Kelvin can be generated by above-gap optical excitation.^{93,142} As discussed in Chapter 2, the excess energy of the free hot carriers is dissipated to the lattice via the coupling to LO phonons, and results in a slightly elevated lattice temperature and ‘cold’ bound excitons at the band edge.^{68,69} The cooling process occurs mostly on the sub-ps timescale but can be further slowed down due to the HPB effect.⁶⁸ The slowed cooling enables direct extraction of the hot carriers to material heterojunctions,^{143–145} or participate in carrier multiplication,^{146,147} which are both desirable for efficient photon-to-electron conversion.

To simplify the terminology, in this chapter, the term “hot carrier cooling process”

refers to the formation of cold excitons at the band edge from free hot carriers. Therefore, “hot carrier” refers to free hot carriers, and “cold carrier” refers to band-edge excitons.

To understand the dynamics of the hot carriers and HPB effect in semiconducting nanomaterials (not only SL TMDs), many ultrafast spectroscopic methods have been used including PP spectroscopy,^{70,96,124,148} time-resolved PL spectroscopy,^{149,150} and some other sophisticated methods.^{93,151} PP spectroscopy is the most widely used method to investigate the carrier relaxation process by tracking the rising signal in kinetics or changes of the spectral shape for either GSB or PIA.^{70,96,152} As discussed in section 3.2.4.2, the pump fluence in the PP method needs to be kept weak so that the signal of carrier cooling is not contaminated by the photophysical processes which happen in the similar timescale, such as Auger-type exciton-exciton annihilation,^{75,99,100} exciton formation and dissociation,^{153,154} state filling,^{70,92,155} ultrafast trapping,^{156,157} and band gap renormalization.^{158,159} For instance, it has been reported that with increasing pump intensity, the HPB and Auger heating effect can contribute simultaneously to prolong carrier relaxation process in SL MoS₂.⁹⁵ Therefore, the conventional PP spectroscopy cannot always isolate the hot carrier dynamics in TMDs from the other phenomena occurring in the ultrafast time domain by simply controlling the pump parameters. The hot carrier cooling dynamics in SL TMDs needs to be understood more comprehensively using other ultrafast spectroscopic method.

This chapter presents the work of the first implementation of PPP on SL TMDs. By carefully controlling the pump fluence, the hot carrier cooling time is observed to scale linearly with the hot carrier density in the SL WS₂, which can be explained by the HPB effect. The intrinsic cooling time (i.e., in the absence of HPB) is found to be 18 ± 2.7

eV/ps. However, the HPB effect can be weakened by increasing the cold carrier density (i.e., pump fluence). By comparing two NIR push wavelengths (1300 nm, 0.95 eV and 2000 nm, 0.62 eV), HPB effectiveness is found to be linearly increasing with the excess energy of the hot carrier. In addition, hot carrier trapping is also observed when the excess energy of the hot carrier is high enough (with 1300 nm push). Apart from the hot carrier cooling dynamics, significant optical Stark effect is observed at the arrival of the intense NIR push pulse. This work gives a comprehensive picture of the hot carrier cooling process in the SL WS₂ with quantitative descriptions of the HPB effect.

4.2 Experimental details

4.2.1 Sample details

A fully covered polycrystalline SL WS₂ on quartz substrate (1 cm × 1 cm) produced via low-pressure chemical vapor deposition was commercially procured (CVD-TSF-WS₂-QZ, 2D Semiconductors, United States) and measured without further modification.

4.2.2 Sample characterization

4.2.2.1 UV-vis absorption spectroscopy

The steady-state UV-vis absorption spectrum was measured with a Cary 60 UV-vis spectrophotometer (Agilent).

4.2.2.2 Raman and PL spectroscopy

Raman spectroscopy was performed by Sihui Liu (Imperial College London).

Raman and PL spectra were both collected by a Renishaw lab Raman with the 50× objective lens and 532 nm laser excitation in an incident power of 0.16 mW at the same spot.

4.2.2.3 AFM

The AFM measurement was done by Chengning Yao (Imperial College London).

The AFM measurements were performed at the centre of the fully covered SL WS₂ film. The fully covered SL WS₂ film was scratched by a sharp needle in the central part, leaving the exposed quartz substrate as a baseline for the AFM measurement. The AFM measurement was performed after all optical measurements.

4.2.3 Ultrafast spectroscopy

PPP spectroscopy was carried out using the setup described in section 3.2.4. The push pulse was delivered to the sample at 40 ps after pump excitation. PP spectroscopy was carried out using the same configuration as PPP spectroscopy with the push beam being blocked. In all the measurements, the probe spectra when the pump is on and off were averaged for 1 second at each delay time. The SL WS₂ was measured in N₂ atmosphere sealed in a quartz cuvette at room temperature. All the data was analysed after chirp correction.

4.3 Results and discussion

4.3.1 Steady-state characterisation

Before performing ultrafast spectroscopy measurements, the SL WS₂ was characterised by the steady-state UV-vis absorption, PL, and Raman spectroscopy, shown in Fig 4.1.

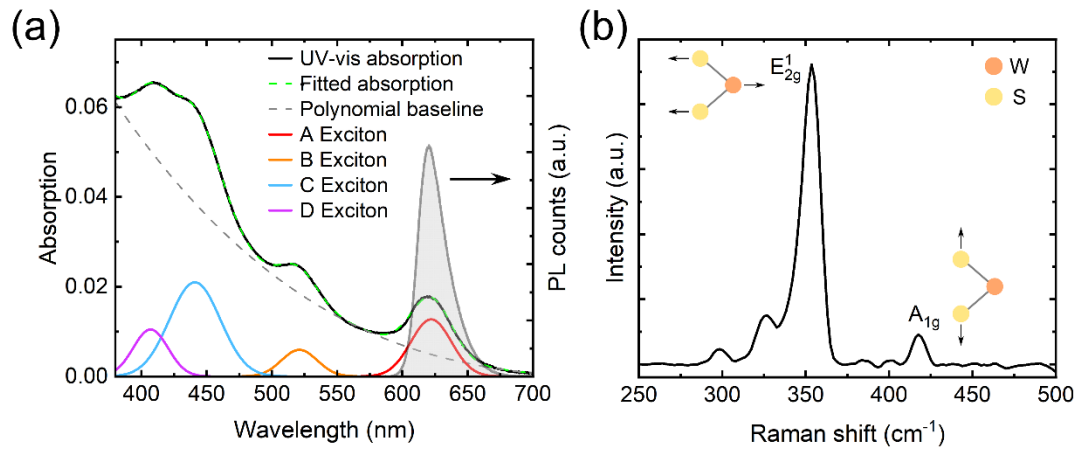


Figure 4.1 Steady-state characterization of SL WS₂. (a) UV-vis absorption (solid dark curve) and PL spectra (grey shaded region). (b) Raman spectrum of SL WS₂ with depictions of the in-plane and out-of-plane vibrational modes.

In Fig 4.1 (a), the UV-vis absorption spectrum can be reproduced by four Gaussian peaks and a second-order polynomial baseline (dashed grey curve). Based on our fitting, the A, B, C and D excitonic resonances are situated at 620, 520, 440, and 407 nm, shown in red, orange, blue and magenta respectively, which agree well with the literature.^{66,160}

The PL spectrum from the SL WS₂ in Fig 4.1 (a) contains a single peak at around 620 nm, which originates from the radiative recombination of the lowest-lying A exciton. The asymmetry of the spectrum has been ascribed to the presence of defects in

polycrystalline films.¹⁶¹

Fig 4.1 (b) shows the Raman spectrum of the SL WS₂ upon excitation at 532 nm. The difference ($\Delta\omega$) between the E_{2g}¹ mode (~ 355 cm⁻¹, in-plane vibration) and A_{1g} mode (~ 417 cm⁻¹, out-of-plane vibration) is approximately 62 cm⁻¹. These values are consistent with previous Raman spectroscopy characterizations of SL WS₂.¹⁶²

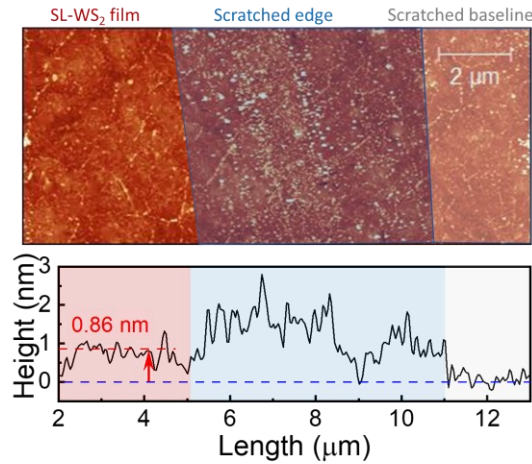


Figure 4.2 AFM image of SL WS₂. The AFM tip height profile demonstrates the thickness of the SL WS₂ as a function of length from the scratched edge.

AFM was used to further characterize the SL nature and ~ 0.86 nm thickness of the WS₂ sample, presented in Fig 4.2.^{163,164} Due to the scratch by the needle, the blank substrate area can be seen at the right of the top panel of Fig 4.2, with the scratched edge in the middle region, and the SL WS₂ film in the left region. The scratched edge region is ignored for the determination of the sample thickness. The real thickness of SL WS₂ is determined by the average height of left region (dashed red line), relative to the baseline in the right region (dashed blue line). The 0.86 nm thickness further confirms the SL character of the sample in the measurement.^{163,164}

4.3.2 Pump-probe spectroscopy

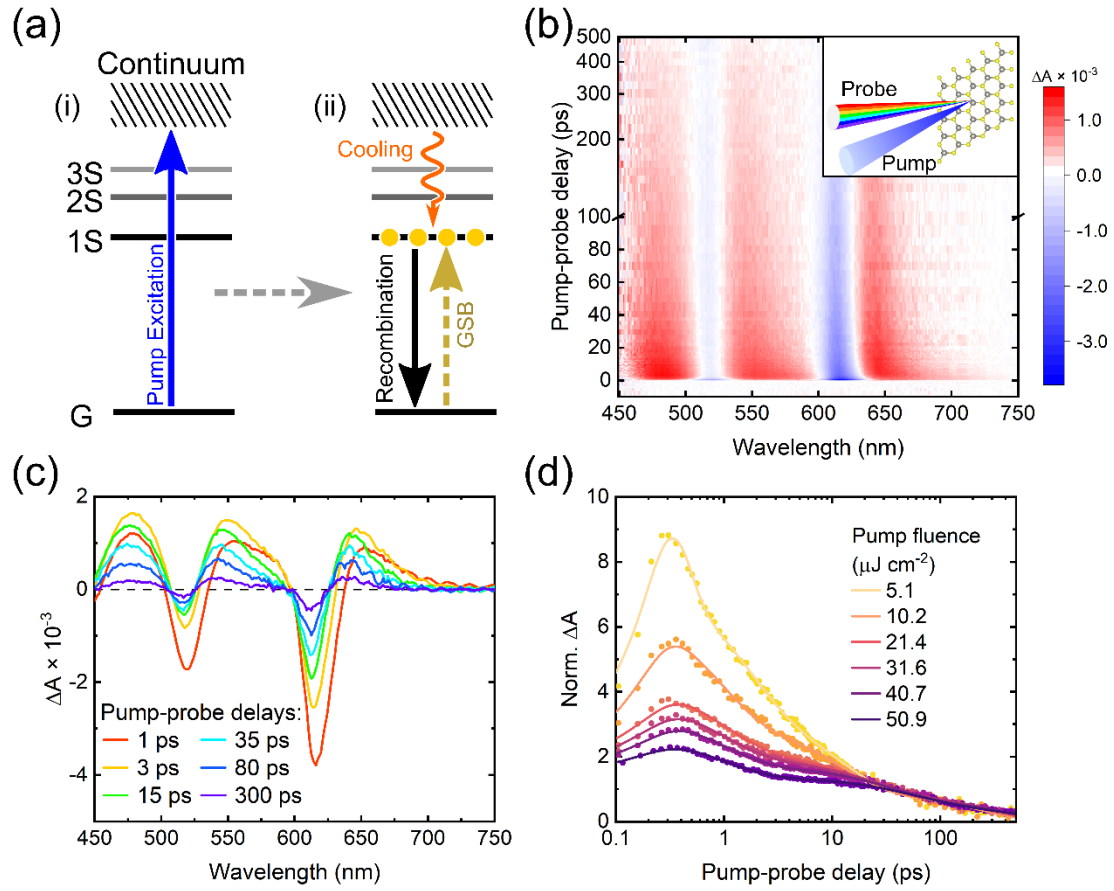


Figure 4.3 Pump-probe spectroscopy of SL WS₂. (a) State diagram depicting the action of the pulses in the PP spectroscopy. (b) and (c) heatmap and corresponding spectra at time slices for SL-WS₂ excited by a 400 nm pump. (d) Kinetics of the A exciton GSB at different pump fluences, normalised by the signal amplitudes at 40 ps. The solid lines are fits by a Gaussian convoluted multiexponential decay.

Before investigating hot carrier dynamics with PPP spectroscopy, pump fluence dependent PP spectroscopy was carried out to assess the dynamics of SL WS₂ at the excitonic resonances. In the PP measurements, a 400 nm pump was used to excite electron-hole pairs across the bandgap, and a broadband probe spanning the visible region was used to probe the resultant charge dynamics. The action of the pulses is depicted steps (i) and (ii) of Fig 4.3 (a), alongside the TA surface and corresponding

time-resolved spectral slices in Fig 4.3 (b) and (c). As discussed in section 3.2.3, the reduced absorption (negative signal, shown in blue) produces a GSB signal. The high-contrast features with negative amplitude at around 620 and 520 nm are assigned to the GSB of the A and B exciton resonances identified in the linear absorption spectra, shown in Fig 4.1 (a).^{139,153}

The three positive ΔA regions in Fig 4.3 (b) (shown in red) at ~670, 570, and 470 nm are assigned as PIA signal from the A, B and C excitons, respectively. Within 10 ps, a time-dependent blue shifts of the PIA signal peaks for both the A and B exciton in the ΔA spectrum was observed, which have previously been attributed to the relaxation of hot carriers generated by the above-gap pump,⁹⁵ band-gap renormalisation,^{66,153} and other excited-state transitions.^{153,165} As the origin of these PIA features still remain disputed, the GSB peaks was focused as a marker for the charge dynamics in this work. Although it should be noted that GSB peaks can represent a mixture of different phenomena, such as Stark effect and bandgap renormalisation, the nature of the excited-state transition in GSB peaks is easier to interpret. GSB comes from depopulation of the ground state and, therefore, all the excitons (A, B, and C) contribute to it in the same way.

To study the excited state population dynamics further, pump fluence dependent measurements were carried out. The normalized transients of the A exciton GSB are shown in Fig 4.3 (d). The later-time dynamics (> 40 ps) are independent of the excitation density. This behaviour was assigned to the monomolecular recombination of the A-exciton, ostensibly due to radiative recombination.¹⁶⁶ It is noted that this long-lived GSB signal should not be attributed to the result of thermal effect of the lattice following photoexcitation, which can induce similar spectral features like the interband

electronic transitions, as shown in Fig 3.14 (b) and (c). The detailed explanation will be discussed in section 4.3.3. Meanwhile, the early-time dynamics (< 40 ps) are dependent on the excitation density. Based on the transients alone, it is difficult to conclude this behaviour with a single mechanism. Previous studies have invoked trapping effects and many-body interactions such as Auger recombination, exciton-exciton annihilation, or bandgap renormalization and formation of exciton complexes.^{100,101,158,167,168} This fluence dependence at the early time demonstrates that it is often complicated to extract the hot carrier cooling dynamics from the early time dynamics in two-pulse experiments.

4.3.3 Pump-push-probe spectroscopy

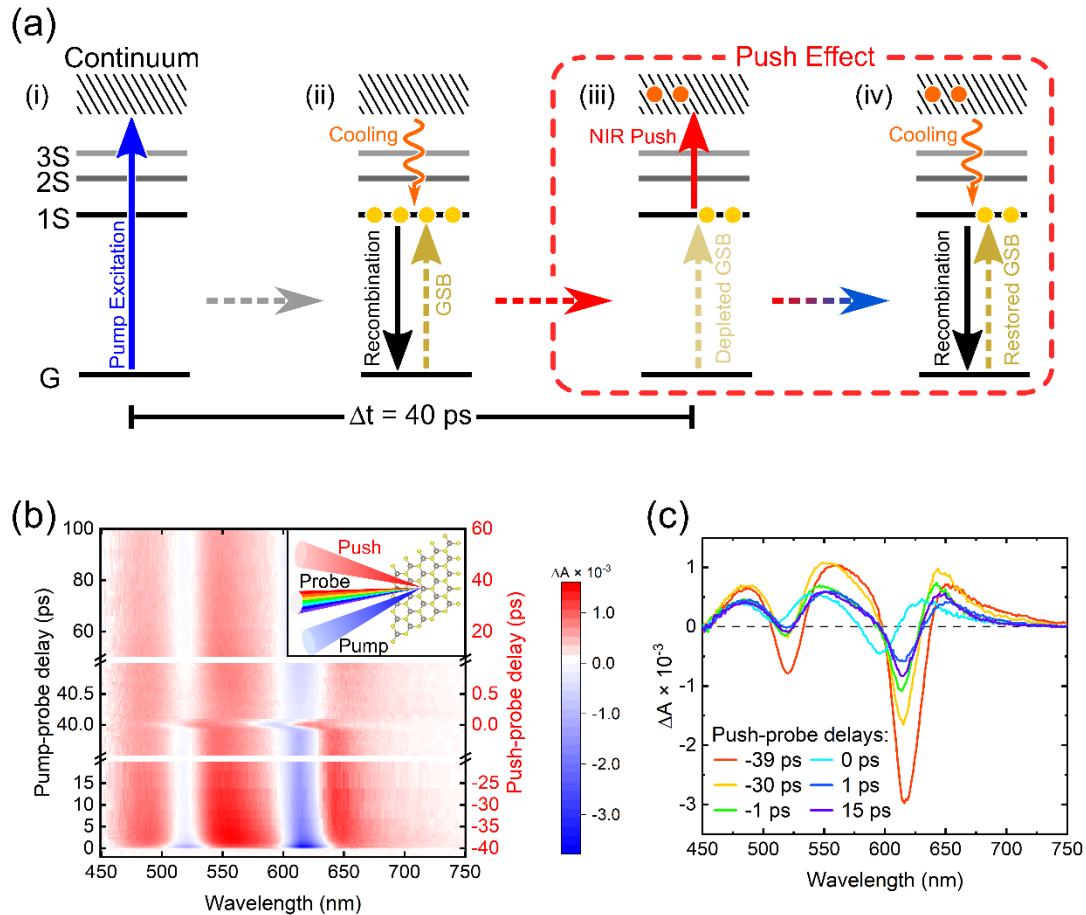


Figure 4.4 Pump-push-probe spectroscopy of SL WS₂. (a) State diagram depicting the action of the pulses in the PPP spectroscopy. (b) and (c) heatmap and corresponding

spectra at time slices with 400 nm pump and 1300 nm push.

To avoid the ambiguity in PP measurements, PPP spectroscopy was used to investigate the hot carrier cooling dynamics of SL WS₂, which can be used to extract not only the cooling timescale, but also critical information about the interactions of hot carriers with cold carriers and defects in a way that conventional PP experiments cannot.

As shown in Fig 4.3 (d), the A exciton dynamics becomes pump fluence independent after 40 ps. Therefore, the NIR push pulse was controlled to delay 40 ps after pump to avoid the sophisticated photophysical processes at very early time delay. Fig 4.4 (a) depicts the action of the pulses in the PPP scheme in the SL WS₂. (i) and (ii) represent the carrier transitions which are observed in PP technique. In (iii), a time delayed NIR push pulse (40 ps after the pump) is introduced to optically heat up the cold states to hot carriers, resulting in reduced GSB peak amplitude. As the carriers cool down to the band edge, the reduced GSB peak amplitude recovers to the stronger PP amplitude without push, shown in (iv).

Given that the highest 400 nm pump fluences used in this work was 21.7 $\mu\text{J cm}^{-2}$, the initial carrier density after interband excitation, n_0^{total} , can be calculated by Eq. 4.1:

$$n_0^{total} = A_{400} \frac{F}{3.1 \text{ eV}} \quad \text{Eq. 4.1}$$

where A_{400} is the absorbance of SL WS₂ at 400 nm which obtained from the UV-vis absorption spectrum in Fig 4.1 (a), and F is the incident 400 nm pump fluence with unit of eV cm^{-2} . The n_0^{total} in the studied SL WS₂ film is estimated to be $\sim 10^{12} \text{ cm}^{-2}$. This carrier density is two orders of magnitude lower than the reported Mott density of SL WS₂ ($1.1 \times 10^{14} \text{ cm}^{-2}$) where excitons transition to an electron-hole plasma.¹³⁹ Therefore,

the cold excited states re-excited by the NIR push can be treated as excitons rather than free carriers. Based on the Rydberg model for excitons in TMDs, the cold excitons are promoted to the continuum by the NIR push (1300 and 2000 nm, 0.95 eV and 0.62 eV), whose photon energy is greater than the exciton binding energy (~ 0.3 eV).^{57,169} Within this picture, carrier cooling process in the SL WS₂ refers to the relaxation of hot carriers in the continuum to the cold bound excitons where the constituent charges reside at the band edges.

Fig 4.4 (b) and (c) plot the spectral response as a function of the push-probe delay time. The spectral features are the same as the PP experiment in Fig 4.3 (b) and (c), except for a blue shift of the GSB peaks at the exciton resonances which is ascribed to the optical Stark effect (OSE). Fig 4.4 (d) compares the dynamics of A exciton GSB signal in PPP and PP measurements. When the NIR push pulse arrives, the GSB signal is quenched due to the depleting of band-edge cold carriers. In a few ps after push pulse, the GSB gradually recovers back to the PP signal when the hot carriers cool down to the band edge.

Fig 4.5 (a) compares the A exciton GSB signal in PP and PPP measurements where the push wavelength is 1300 nm. Due to the overlap of ΔA dynamics in the first 40 ps, the SL WS₂ sample was not degraded by the laser irradiation before and after PPP measurements. To analyse the push induced hot carrier cooling dynamics, the difference between PPP and PP signals was calculated, for two different push wavelengths of 1300 and 2000 nm, shown in Eq. 4.2.

$$\delta(\Delta A) = \Delta A_{PPP} - \Delta A_{PP} \quad \text{Eq. 4.2}$$

The resulting $\delta(\Delta A)$ kinetics in Fig 4.5 (b) to (d) are comprised of three components

intuitively: (1) a very fast ~ 100 fs component, (2) a few-ps component dominating the recovery, and (3) a long-lived component with >10 ps decay time for 1300 nm push, but not for the 2000 nm push. Therefore, the $\delta(\Delta A)$ kinetics with 1300 nm and 2000 nm push at different push fluences is fitted by Eq. 4.3:

$$(\Delta A)(t) = G(t) \otimes \left[A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_{cool}}\right) + H \right] \quad \text{Eq. 4.3}$$

where $G(t)$ is Gaussian response function (~ 100 fs), A_1 , τ_1 and A_2 , τ_{cool} represent the amplitudes and decay times of the fast and slow decay components, and H is a constant value to represent the long-lived component (fixed as 0 for 2000 nm push). The fitting results are shown in Fig 4.5 (b) to (d).

The decay time of the fast component, τ_1 , is fixed to 0.01 ps to numerically represent the instant OSE, the cooling time τ_{cool} is a free parameter for fitting, and the amplitude of H reflects the density of trapped hot carriers. The three components will be discussed in detail in the following sections. As shown in Fig 4.5 (d), the lifetime of the $\delta(\Delta A)$ dynamics with 2000 nm push is less than 2 ps, photoinduced thermal effect is negligible at the long-lived (> 40 ps) GSB signal observed in Fig 4.3 (d).

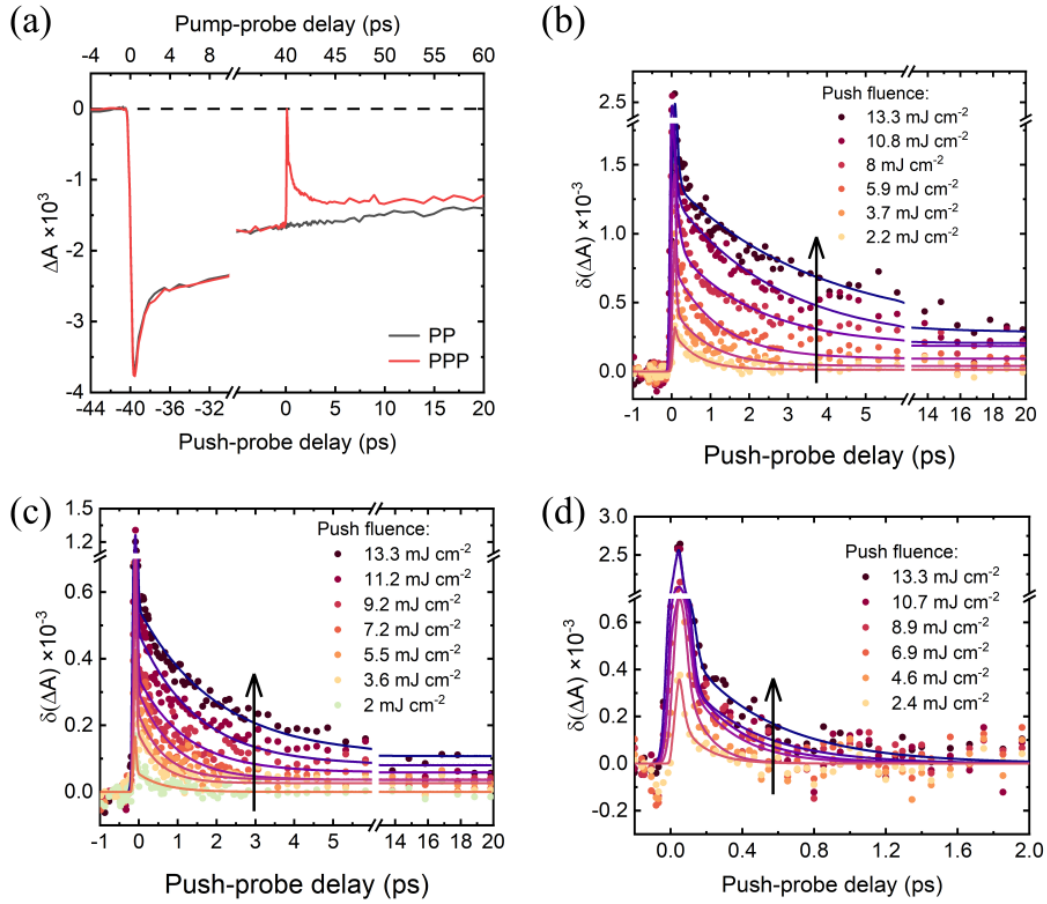


Figure 4.5 Hot carrier cooling dynamics in SL WS₂ measured by PPP. (a) Kinetics of the A exciton GSB with the 1300 nm push off (PP, black) and on (PPP, red). (b) and (c) $\delta(\Delta A)$ dynamics with 1300 nm push at the pump fluences of 21.7 and 8.66 $\mu\text{J cm}^{-2}$ respectively. (d) $\delta(\Delta A)$ dynamics with 2000 nm push at the pump fluence of 21.7 $\mu\text{J cm}^{-2}$.

4.3.3.1 Optical Stark effect

The kinetics of the first fast component, τ_1 , around 0 ps follow the instrument response function of our setup around 100 fs. This indicates that this component originates from a coherent interaction between the push pulse and SL WS₂.^{170–172} Therefore, other incoherent process like bandgap renormalisation, thermal effect, and photodoping can be excluded as the origin of the spectral shift at the arrival of the intense NIR push pulse. Fig 4.6 (a) compares PPP spectra of SL-WS₂ before, during, and after the push arrival. Upon the push pulse arrival (at 0 ps, red curve), the spectrum shows blueshifts by ~ 20

nm, producing a spectral shape that follows the first derivative of the UV-vis absorption spectrum, displayed in Fig 4.6 (b). This suggests that the initial (~ 100 fs) dynamics stem from the OSE generated by the electric field of the push pulse.

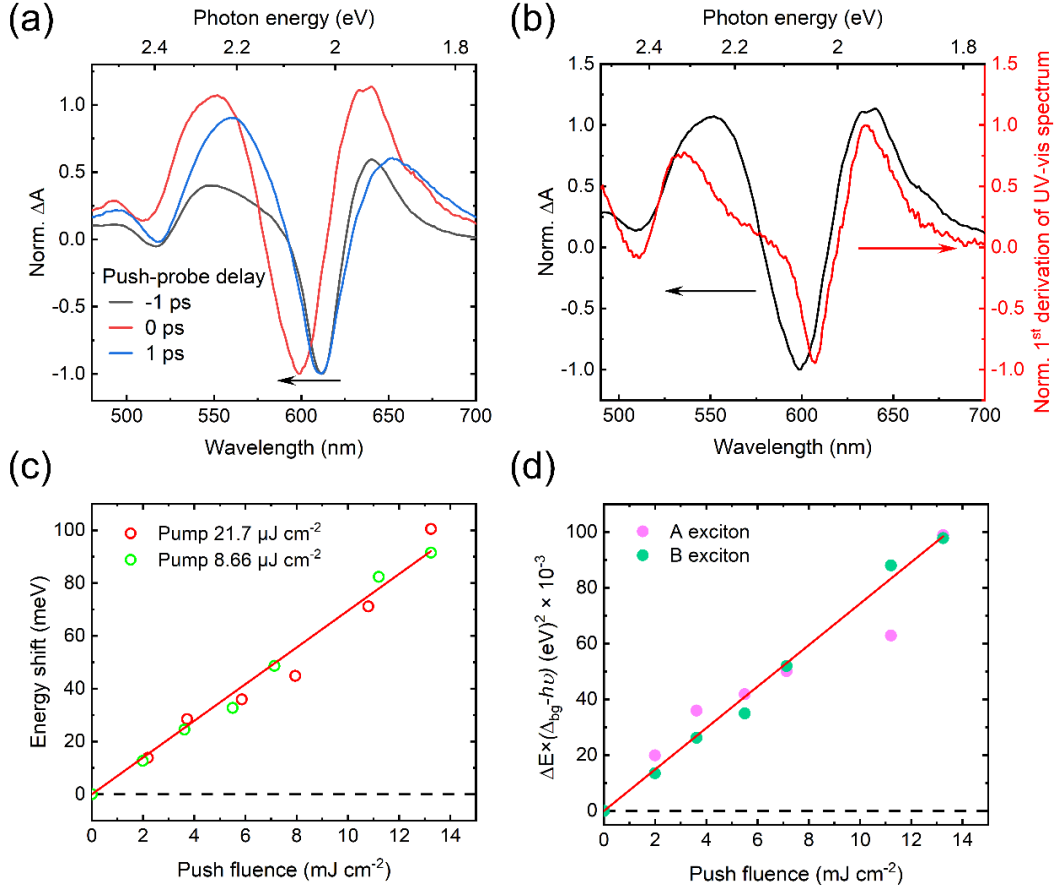


Figure 4.6 Optical Stark effect upon the arrival of 1300 nm push pulse in SL WS₂. (a) Normalized PPP spectra at -1 ps, 0 ps, and at 1 ps. (b) PPP spectrum at 0 ps and the first derivation of UV-vis absorption spectrum. (c) The maximum Stark shifting for the A exciton GSB at different pump and push fluences. (d) $\Delta E(\Delta_{bg} - hv)$ for A exciton and B exciton with a linear fit at the same pump fluence.

The energy shift (ΔE) by OSE in a two-level system can be quantified as:

$$\Delta E = 2 \frac{M^2 \varepsilon^2}{\Delta - \hbar \nu} \quad \text{Eq. 4.4}$$

where ε is the applied electric field strength, M is the polarization matrix element

between the initial and final states, Δ is the energy difference between these states, and $h\nu$ is the incident photon energy.^{170,171} In this work, the initial and final states are defined as the ground state and the first excited state of the A and B excitons of WS₂. Therefore, the energy shift, ΔE , is linearly increased to ε^2 , which is proportional to the push fluence.

Fig 4.6 (c) demonstrates that the results fit Eq. 4.4 well. The maximum shift scales only linearly with the push fluence but is independent on the pump fluence. Note that the experimental ΔE is calculated from the shift in the GSB peak position incurred by the application of the push by comparing the transient spectra at -1 and 0 ps push-probe delay.

Fig 4.6 (d) compares the OSE on the A and B excitonic resonances in SL WS₂ by presenting their respective $\Delta E(\Delta - h\nu)$ (by rearranging Eq. 4.4) dependences as a function of the push fluence. Based on the shift of the GSB peak wavelengths, the energy difference, Δ , between the ground state and the first excited state is 2.02 and 2.39 eV for the A and B excitons, respectively. In Fig 4.6 (d), the scaling of $\Delta E(\Delta - h\nu)$ with the push fluence does not show much difference for the A and B excitons and obeys the linear fitting well. This implies that the values of M^2 for the A and B excitons are almost identical, which agrees with previous studies of SL-MoS₂ that indicate that the oscillator strengths of the A and B excitons are similar because they both originate at around the K (or K') valley.¹⁷³

4.3.3.2 Hot carrier cooling

The second time constant, τ_{cool} , is used to fit the hot carrier cooling time in the SL WS₂ from Eq. 4.3. The fitted τ_{cool} is plotted against initial hot carrier density, $\langle n_0^{hot} \rangle$, in Fig

4.7 with 1300 nm push at two different pump fluences. The estimation of $\langle n_0^{hot} \rangle$ is shown below.

The cold carrier density just before the push pulse, n_0^{cold} , can be described by Eq. 4.1. $GSB_{39.8\text{ ps}}$ is the amplitude of the A exciton GSB signal at 39.8 ps pump-probe delay, and GSB_{max} is the maximum of the GSB signal. We assume that the A exciton GSB signal at 40 ps is the same as the GSB signal at 39.8 ps.

$$n_0^{cold} = n_0^{total} \frac{GSB_{39.8\text{ ps}}}{GSB_{max}} \quad \text{Eq. 4.5}$$

As shown in Fig 4.6, the OSE shows up in the A exciton GSB signal at the arrival of the push pulse. Therefore, to avoid the interference by the optical Stark effect, we used the amplitude difference between the A exciton GSB signal at 40.2 ps (hot) and at 39.8 ps (cold) to represent the initial hot carrier density, $\langle n_0^{hot} \rangle$. By using Eq. 4.6 and substituting n_0^{cold} from Eq. 4.5, the approximate value of $\langle n_0^{hot} \rangle$ with different push fluences can be obtained. The estimated $\langle n_0^{hot} \rangle$ as the function of push fluence is shown in Fig 4.7. The linear relationship between $\langle n_0^{hot} \rangle$ and push fluence indicate the absence of high order interactions between the carriers and the intense NIR push pulse.

$$\begin{aligned} \langle n_0^{hot} \rangle &= n_0^{cold} \frac{GSB_{40.2\text{ ps}} - GSB_{39.8\text{ ps}}}{GSB_{39.8\text{ ps}}} \\ &= n_0^{total} \frac{GSB_{40.2\text{ ps}} - GSB_{39.8\text{ ps}}}{GSB_{max}} \end{aligned} \quad \text{Eq. 4.6}$$

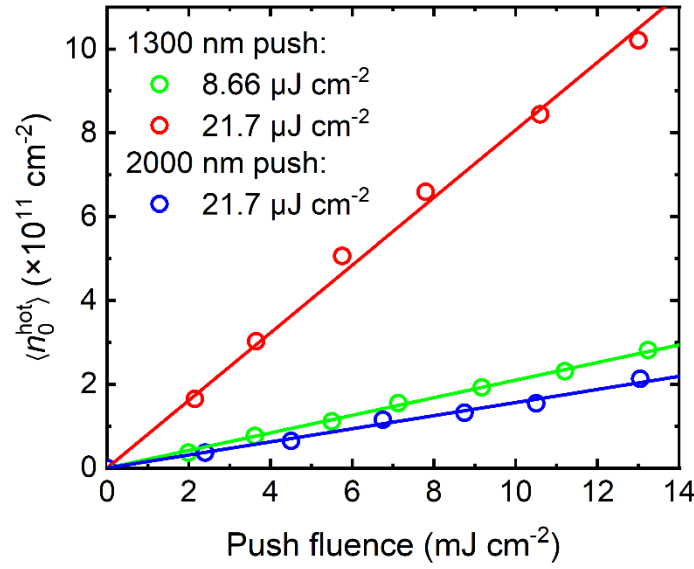


Figure 4.7 Effect of push on hot carrier density. Linear relationship of initial hot carrier density with push fluence. The solid lines are linear fits.

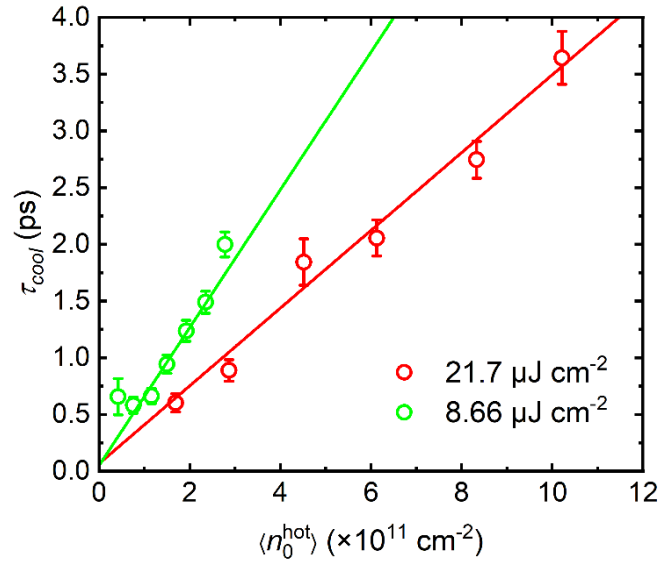


Figure 4.8 Cooling time as a function of hot carrier density plotted for two different push fluences with 1300 nm push.

As shown in Fig 4.8, τ_{cool} is increased linearly with the increase of $\langle n_0^{hot} \rangle$. The linear dependence of the τ_{cool} with the hot carrier density has been observed in previous studies on TMDs and other polar semiconductors by PP spectroscopy, which is assigned to the HPB effect.^{92,94,174–176} As discussed in Chapter 2, the HPB effect occurs when the

cooling hot carriers dissipate the excess energy into a limited pool of LO phonons. When the hot carrier's density becomes too high, the excess energy cannot be efficiently dissipated efficiently via accessible phonons into the cold lattice, resulting in prolonged cooling process. Furthermore, the linearity of the plot rules out many-body processes, such as Auger-type heating. Since photons do not carry momentum information, the cold carriers interact with the NIR laser pulse are not expected to be scattered to other valleys from K (or K') valley (detailed discussion is shown in section 4.3.3.3). Therefore, the interaction with zone-edge acoustic phonons which have similar energy as LO phonons but dominate in intervalley scattering can be excluded from the hot carrier cooling process.^{177,178}

The linear fits of τ_{cool} as a function of $\langle n_0^{hot} \rangle$ in Fig 4.8 provides a y-intercept value at $\langle n_0^{hot} \rangle = 0$, corresponding to the 'intrinsic' hot carrier cooling time when HPB effect is absent. The two different pump fluences with the 1300 nm (0.95 eV, equal to the excess energy of the hot carrier) push give the similar intercepts from the linear fits, which corresponds to an intrinsic cooling rate of $\sim 18 \pm 2.7$ eV/ps. Comparing with previous studies on other materials, the cooling rate of SL WS₂ is much faster than halide perovskites (~ 1 to 3 eV/ps), CdSe quantum dots (sub-meV/ps), and graphene (a few eV/ps).^{128,179,180} Therefore, the cooling rate of SL WS₂ is very fast, however, the HPB effect can prolong the cooling time efficiently to a few picoseconds by simply increasing the hot carrier density.

Compared to conventional PP spectroscopy, as discussed in section 3.2.4.2, PPP spectroscopy provides an additional dimensionality to investigate the impact of cold carrier density to the hot carrier cooling dynamics. Fig 4.8 compares the HPB effect in SL WS₂ at two pump fluences, 8.66 and 21.7 $\mu\text{J cm}^{-2}$. In the previous studies by Hopper

et al., the slope in the linear fit of the plot of τ_{cool} against $\langle n_0^{hot} \rangle$ represents the sensitivity of the cooling dynamics to the HPB effect.^{117,118,128} Therefore, the flatter slope obtained by the linear fit at the higher pump fluence shows that the HPB effect in the SL WS₂ can be weakened as the increase of cold carrier density. This observation signifies that the HPB effect is weakened by additional energy dissipation channels produced by interaction between the hot and cold states. Similar acceleration of the cooling dynamics by cold carriers has been observed in halide perovskites and nanocrystals by Hopper et al.¹¹⁸

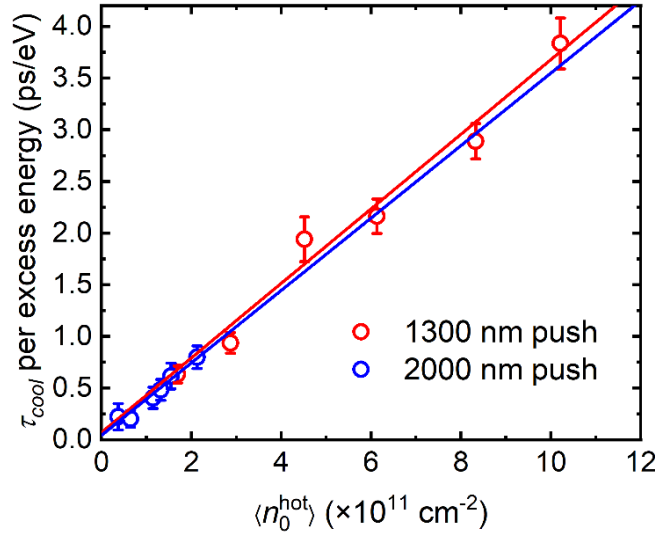


Figure 4.9 Cooling time per excess energy as a function of hot carrier density for 1300 and 2000 nm push, at the same pump fluence.

In PPP spectroscopy, different push wavelengths provide different excess energies to the cold state. In this work, apart from push at 1300 nm (0.95 eV), push at 2000 nm was also used to provide the excess energy of the hot carriers around 0.62 eV. Fig 4.9 shows the plot of τ_{cool} normalised by the hot carrier excess energy (i.e., push photon energy) as the function of $\langle n_0^{hot} \rangle$ at the same pump fluence, 21.7 $\mu\text{J cm}^{-2}$. The linear fits of these two datasets can be interpolated to the same intercept, which indicates that the intrinsic

cooling rate is independent of hot carrier excess energy. The identical slopes of the two linear fits in Fig 4.9 suggests that the effectiveness of the HPB effect in the SL WS₂ is linearly dependent on the excess energy of the hot carriers at the same cold carrier density.

The slope in the linear fits in Figs 4.8 and 4.9 can be used to quantify the effectiveness of HPB effect.^{118,128,181,182} To compare the HPB effect in SL WS₂ with other materials in literatures, it is logically correct to compare the slope at the same cold carrier density and the excess energy of the hot carriers. However, it is difficult to control the cold carrier density in different studies. Therefore, the comparison in the following discussion is limited to the same excess energy of hot carriers.

By taking the thickness of SL WS₂ as ~0.86 nm from AFM (Fig 4.2), the slope of the linear fit with 2000 nm (0.62 eV) push is $\sim 0.17 \pm 0.017$ ps per 10^{18} cm^{-3} , which is up to four times lower than 3D perovskites, which are not excitonic, (from ~ 0.25 to 1 ps per 10^{18} cm^{-3}) measured with the same excess energy.¹²⁸ This indicates that the HPB effect in the SL WS₂ is much weaker than in bulk hybrid halide perovskite materials. The reduced HPB effect has also been observed in perovskite nanoplatelets and 2D perovskites, which might be caused by the pronounced excitonic nature of the excited states and their extreme quantum confinement in the atomically-thin TMD layer.^{182–184} However, different from SL WS₂, in 2D hybrid perovskites, HPB effect is negligible (i.e., the slope is close to 0). This distinction likely arises from the coupling between the organic cations and the inorganic octahedral framework within the 2D hybrid perovskite structure.^{185,186} Such coupling may influence the energy dissipation process by introducing the effects of high-energy phonons associated with the organic cations.

4.3.3.3 Hot carrier trapping

In the $\delta(\Delta A)$ kinetics with 1300 nm push, a long-lived component was observed at different pump and push fluences, which is represented by a constant H in Eq. 4.3. This long-lived signal shows that after 1300 nm push a portion of hot carriers does not relax down back to the band edge to contribute to the GSB signal. This hot carrier loss in SL WS₂ can be potentially caused by many reasons, such as, exciton dissociation, intervalley scattering, bimolecular recombination, and hot carrier trapping. These potential mechanisms are discussed as following.

Firstly, the hot carrier loss with 1300 nm (0.95 eV) push should not be explained by exciton dissociation related issue. The photon energy of 2000 nm (0.62 eV) push is still higher than the exciton binding energy in SL WS₂, but no loss was observed in Fig 4.5.

Secondly, the energy of 1300 nm (0.95 eV) photon is larger than the energy gap (~ 0.88 eV) between the K valley (A exciton) to the band nesting region (C exciton), however, the massless push photons cannot provide any momentum to the carriers to be scattered between valleys in the Brillouin Zone. Even if the intervalley scattering were to occur, it is expected that carriers scattered to other valleys should eventually flow back to the band edge of the K (or K') valley as A excitons within a few hundred femtoseconds rather than tens of picoseconds.^{67,92} Therefore, the carrier-zone-edge-phonon interactions can be excluded in this study.

Finally, the 1300 nm push may excite carriers from VB or interband trap states to CB which can annihilate the pump excited carriers to reduce the GSB signals. However, Fig 4.10 shows that the value of H exhibits a linear dependence with push fluence. Therefore, the exciton dissociation, intervalley scattering, and many-body interactions

can be ruled out from the reasons.

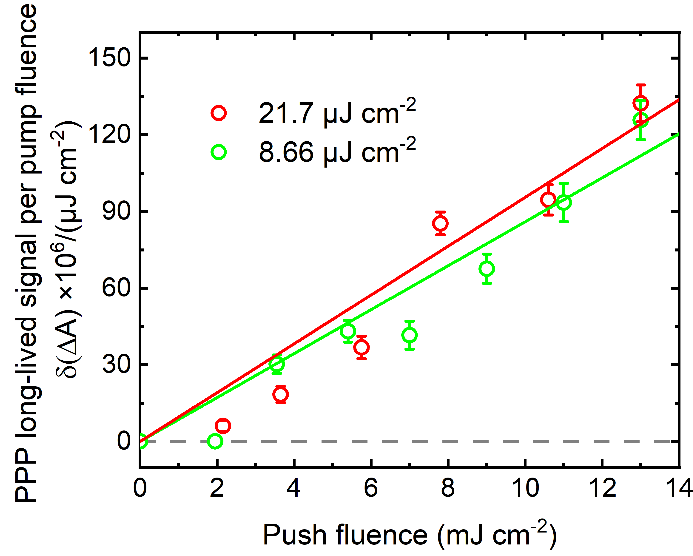


Figure 4.10 Amplitude of the long-lived $\delta(\Delta A)$ kinetics, H , per pump fluence, F_{pump} , for A exciton GSB as a function of push fluence.

As shown in Fig 4.10, after normalizing the value of H by the pump fluence, F_{pump} , the two different pump fluences give similar values at the range of push fluences, which strongly indicates that the long-lived component in the $\delta(\Delta A)$ kinetics with 1300 nm push is dominated by hot carriers rather than cold carriers. Taking all the evidence above, the loss of the GSB signal upon pushing at 1300 nm is proposed to be the result of hot carrier trapping. The trap states can originate from defects due to the polycrystalline nature of the SL WS₂ deposited by CVD. S vacancies, nucleation centers and grain boundaries are known to create additional energy levels that act as charge trapping sites within the bandgap.^{23,161,187}

Furthermore, the absence of long-lived signal in the $\delta(\Delta A)$ kinetics was not observed with 2000 nm push, shown in Fig 4.5 (d). This suggests that the hot carrier excess energy needs to be high enough to overcome some energy barriers to be scattered to the trap states. The energy dependent hot carrier trapping behaviour was also found in

perovskites and quantum dots with PPP spectroscopy, which has been used to rationalize the low PL efficiencies of these materials after high-energy excitation comparing with band-edge excitation.^{126,188} The weaker PL efficiencies with above-gap excitation have been reported in SL TMDs, but have been ascribed to charge separation in the Brillouin Zone in the band nesting region.⁶⁷ Because defects in these materials are invariably especially the ones produced by CVD, this work suggests that hot carrier trapping can also contribute to the reduced PL efficiency in TMDs after high energy photoexcitation.

4.4. Conclusions

This chapter showcases PPP spectroscopy as a novel approach to systematically investigate the dynamics and fate of hot carrier in SL TMDs, summarized in Fig 4.11. The HPB in SL WS₂ manifests as a slowing of the carrier cooling with increasing hot carrier density by controlling the push fluences. The intrinsic cooling rate of an isolated hot carrier in SL WS₂ is substantially faster than other semiconductors. However, the efficient HPB effect can dramatically prolong the hot carrier cooling time to a few picoseconds. In contrast to previous studies of TMDs, an additional hot carrier energy dissipation pathway was observed via carrier-carrier interactions, which is evidenced by a suppression of the HPB at higher cold carrier density. The PPP approach also unveils that hot carriers can be trapped during cooling when the excess energy is high enough. Overall, this work reveals carrier-phonon and carrier-carrier interactions and their interplay in SL TMDs. This work offers new insights into the dynamics and manipulability of hot carrier relaxation within TMD-based optoelectronics, with potential implications extending to diverse domains including high-speed switching, spintronics, and quantum technologies.

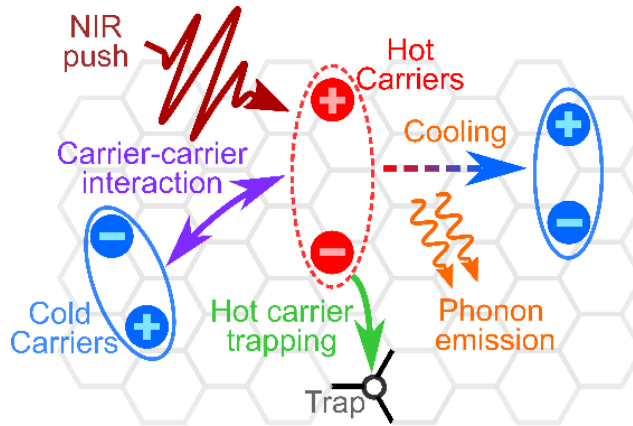
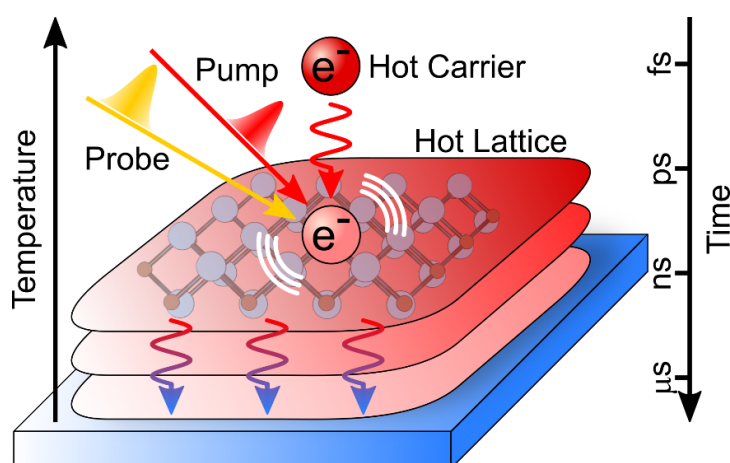


Figure 4.11 Fates and energy pathways of hot carrier cooling in SL WS₂.

Chapter 5 Ultrafast Carrier and Slow Lattice Cooling in MXenes

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Chapter 4 demonstrated the carrier relaxation dynamics in semiconducting 2D materials, specifically in SL WS_2 . The complex TA spectra observed in SL WS_2 highlighted the need for more advanced techniques, such as PPP measurements, to disentangle overlapping photophysical processes. In contrast, as discussed in Section 2.2.2, metallic MXenes are expected to exhibit simpler TA spectra and dynamics, dominated primarily by thermal effects. Consequently, this chapter focuses on TA measurements alone, covering timescales from sub-picoseconds to microseconds to quantitatively investigate the cooling dynamics of hot carriers and lattice.



5.1 Introduction and motivation

As introduced in previous chapters, MXenes are an advancing and growing category of the 2D materials with a formula $M_{n+1}X_nT_x$, where M is an early transition metal, X is carbon and/or nitrogen, $n = 1-4$, and T represents surface functional groups (such as -OH, =O, -Cl, and -F).^{28,29} $Ti_3C_2T_x$ MXene is one of the most studied MXenes, including theoretical explanation, material characterization, and applications in energy storage and (opto-)electronics.^{28,29,189-191} However, the other Ti based MXene, Ti_2CT_x , has not been systematically studied nowadays.

Ti_2CT_x MXene has the lowest formula weight among the MXene family with high DC conductivity,^{47,192} which is believed to be one of the most promising candidates to significantly improve the energy density of supercapacitor and batteries.¹⁹³⁻¹⁹⁵ While Ti_2CT_x MXene is shown to be an excellent candidate in the development of the next-generation energy storage devices, it has also exhibited great potentials in photonic, photothermic, and optoelectronic applications. Zhang et al. demonstrated third-order nonlinear response of the Ti_2CT_x MXene using Z-scan experiments.¹⁹⁶ Due to the optical nonlinearity of Ti_2CT_x MXene, many studies have shown that Ti_2CT_x MXene can be used as the saturable absorbers for Q-switching mode-locked fiber laser for near-Infrared (NIR, 1000-2000 nm) laser pulse generation.¹⁹⁶⁻²⁰⁰ Apart from the optical nonlinearity, Szuplewska et al. showed that the effective photothermic effects of Ti_2CT_x MXene which can be used to photothermal therapy treatment of different types of tumor.²⁰¹ Moreover, in photovoltaic applications, the stability and efficiency of hybrid perovskite solar cell can be improved by adding Ti_2CT_x MXene quantum dots.²⁰² The research on Ti_2C MXene has so far focused on the preparation and applications, the

fundamentally the energy dissipation mechanisms of electrons and lattice of Ti_2CT_x MXene are still unclear.

Different from the semiconducting TMDs discussed in Chapter 4 which has a finite bandgap, Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes show metallic properties.^{14,203} To investigate the hot carrier cooling dynamics in such a system, PPP spectroscopy is not applicable since the push pulse can easily excite the carriers on the ground state in the material rather than carriers on the excited states. Therefore, PP spectroscopy is normally chosen to study metallic materials. Similar to the dynamics in metal films and metal nanoparticles, the relaxation kinetics of MXenes can be divided into three timescales.^{26,79,80,204–207} (1) After pulsed laser irradiation, photoexcited electrons acquire an excess energy of few eV, which is ~ 100 times higher than thermal energy. Electron-electron (e-e) scattering in the femtosecond timescale leads to increase in the effective temperature of electron gas above thousands K.^{79,80,111,204,205} (2) During the hot electron gas cooling process, the excess energy of the hot electrons is dissipated to the lattice via e-ph coupling on a picosecond timescale.^{111,204,205} (3) After the electrons and lattice reaching quasi-thermal equilibrium above the environmental temperature, the hot lattice dissipates the thermal energy to the environment within hundreds of picoseconds or longer.^{208–210} In the metallic MXene films, long-lived signal reflecting this process has been observed in the PP measurements,^{111,211} however the time window of the experiments ($< 5\text{-}6$ ns) was not sufficient to completely track the lattice cooling dynamics.²⁰⁵

The hot carrier dynamics including the specific cooling timescales and their interplay are not known for Ti_2CT_x MXene. The plasmonic (e.g., resonant frequency) and mechanical (e.g., density) properties of this material are distinctly different from other MXene types, suggesting potential differences in photoexcitation dynamics and heat

dissipation. These differences are critical, for instance, in photovoltaics, photothermal therapy and other prospective applications of MXene materials.

Therefore, this work focuses on the hot carrier cooling dynamics in the Ti_2CT_x MXene and the lattice cooling dynamics of both Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. This work aims to make an integral picture of the energy dissipation kinetics of MXenes, which is helpful for the development of MXene based devices and photothermal management.

5.2 Experimental details

5.2.1 Sample preparation

All samples were prepared by Chengning Yao and Ruoyu Gao (Imperial College London).

5.2.1.1 Synthesis of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes

HCl (12 M, 14.0 mL for $\text{Ti}_3\text{C}_2\text{T}_x$ and 11.2 mL for Ti_2CT_x) was added into deionized water (6.0 mL for $\text{Ti}_3\text{C}_2\text{T}_x$ and 4.8 mL for Ti_2CT_x) in a vented polyethylene (HDPE) container, followed by adding LiF (1.5 g for $\text{Ti}_3\text{C}_2\text{T}_x$ and 1.0 g for Ti_2CT_x) powder into the solution.²¹² The mixture was stirred for 5 mins using a magnetic polytetrafluoroethylene (PTFE) bar to fully dissolve the salt. MAX (1.0 g for $\text{Ti}_3\text{C}_2\text{T}_x$ and 0.9 g for Ti_2CT_x) powder was then carefully added to the solution over the course of 10 mins to avoid initial overheating by aggressive exothermal reactions. The container was then immersed in a silicon oil bath (at 45 °C for 24 hours for $\text{Ti}_3\text{C}_2\text{T}_x$ and at 25 °C for 15 hours for Ti_2CT_x) to allow a fully selective Aluminium etching. After the etching process, the mixture was washed for 3-4 cycles via centrifugation (GT2R

centrifuge, Fisher, TX-400 rotor) until the pH of the supernatant reached approximately 6. In each washing cycle, the solution was added with deionized water and centrifuged at 800 ~ 3000 rcf for 5 mins, after which the supernatant was discarded, and the sediment was redispersed in deionized water. The fully washed mixture was manually shaken (minimally intensive layer delamination, MILD method) to allow delamination of MXene flakes and centrifuged at 800 rcf for 10 mins. The obtained supernatant was collected as the MXene suspension for further characterization and thin-film deposition.²¹³

5.2.1.2 Preparation of MXene films

The MXene films were deposited by spray coating. The MXene suspension was diluted to 1.0 mg mL⁻¹ and was sprayed onto a pre-cleaned glass using an airbrush (Everything, AB-130, 0.25-mm nozzle, 1.5 bar N₂ flow). The nozzle-glass distance was kept at 15 cm and the thickness of the film was dependent on the amount of suspension used for spray.

5.2.2 Sample characterisation

5.2.2.1 UV-vis absorption spectroscopy

The steady-state UV-vis absorption spectrum was measured with an Agilent Cary 60 UV-vis spectrophotometer.

In the temperature-dependent measurements, the background was taken when a pre-cleaned glass substrate was placed inside the cryostat. The background spectrum was subsequently subtracted in each measurement automatically by the software.

5.2.2.2 Raman spectroscopy

Raman spectroscopy was performed by Chengning Yao.

Raman spectra were acquired by a Renishaw inVia micro-Raman spectrometer (WiRe 4.1) using a 532 nm laser with a $\times 50$ objective lens. An incident power of ≤ 1 mW was used to avoid thermal damage. Samples for Raman spectroscopy was deposited as thin films on pre-cleaned (iso-propanol/acetone) Si/SiO₂ substrates (Si-Mat).

5.2.2.3 AFM

The AFM measurement was done by Chengning Yao.

AFM was performed using the Keysight 5500 SPM AFM (Keysight Technologies). Measurements were collected over a $20\ \mu\text{m} \times 20\ \mu\text{m}$ area at a scanning rate of 0.40 Hz using a point probe (Silicon-SPM-Sensor, PPP-NCLR-50, Nano-sensors) operating in a tapping mode. The ink was diluted at a factor of 1000 and then drop-casted onto a pre-cleaned Si/SiO₂ substrate.

5.2.3 Time-resolved spectroscopy

TA measurements were carried out using the setup described in section 3.2.3. In all the measurements, the probe spectra when the pump is on and off were averaged for 1 second at each delay time. All the data was analysed after chirp correction. The samples were measured within the cryostat under high vacuum.

The ns-PP was performed using the setup schemed in section 3.2.6. In the ns-PP experiment, both MXenes films are excited at 1064 nm, and the Ti₂CT_x MXene film and the Ti₃C₂T_x MXene film are probed at ~ 630 nm and ~ 500 nm, respectively. The

samples were measured in N₂ atmosphere sealed in a quartz cuvette at room temperature.

5.2.4 Temperature control

In temperature dependent UV-vis absorption spectrum and TA measurements, the samples were measured within the cryostat (OptistatDN-V, Oxford Instruments) under high vacuum. The temperature was controlled by the temperature controller (MercuryiTC).

5.3 Results and discussion

5.3.1 Steady-state characterisation

5.3.1.1 Characterisation at room temperature

The UV-vis absorption spectra of Ti₂CT_x and Ti₃C₂T_x MXenes are shown in Fig 5.1 (a) measured at room temperature. The characteristic plasmonic resonant peaks around 500 nm and 780 nm are observed for Ti₂CT_x and Ti₃C₂T_x MXenes, respectively.^{47,214} In addition, an increase in absorption with an onset from 850 nm is observed in Ti₂CT_x MXene, which agrees with the previous literature.⁴⁷

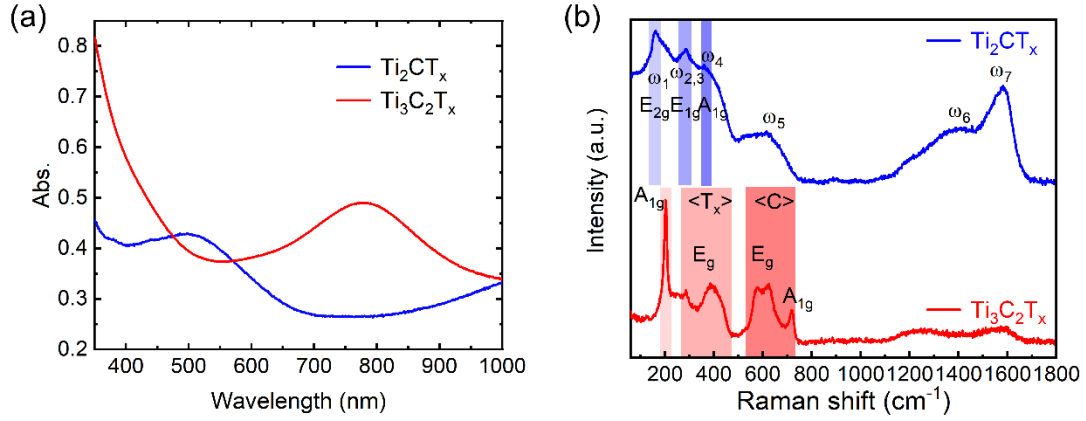


Figure 5.1 Steady-state characterisation of MXene films at room temperature. (a) Steady-state absorption spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films. (b) Raman spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films.

The Raman spectra of Ti_2CT_x (blue curve) and $\text{Ti}_3\text{C}_2\text{T}_x$ (red curve) MXenes are shown in Fig 5.1 (b). $\text{Ti}_3\text{C}_2\text{T}_x$ shows two broad resonant regions (T_x between ~ 223 and $\sim 480 \text{ cm}^{-1}$, and C between ~ 503 and $\sim 750 \text{ cm}^{-1}$), which originate from the E_g in-plane vibrations of T_x functional surface groups, and in-plane E_g vibrations plus A_{1g} out-of-plane vibrations of the C atoms, respectively. An additional peak at $\sim 205 \text{ cm}^{-1}$ originates from an A_{1g} out-of-plane vibrational mode of Ti atoms and T_x ($-\text{OH}$, $-\text{O}$, and $-\text{F}$).^{14,215} The Raman peaks (ω_1 , $\omega_{2,3}$ and ω_4) of Ti_2CT_x correlate to the active E_{2g} , E_{1g} , and A_{1g} modes, respectively,²¹⁶ which originate from the shear and longitudinal vibrations of the Ti and the Al atoms.²¹⁷ The slightly weak broad peak (ω_5) at $\sim 616 \text{ cm}^{-1}$ may be attributed to non-stoichiometric TiC_x .²¹⁷ Two peaks (ω_6 and ω_7) observed at 1398 cm^{-1} and 1578 cm^{-1} originate from the D and G bands of amorphous carbon, respectively, which indicates the existence of carbon in the disordered Ti_2CT_x .²¹⁸

AFM statistics in Fig 5.2 (a) and (d) is used to estimate the thickness ($\langle t \rangle$) and lateral size ($\langle S \rangle$) distribution of the delaminated Ti_2CT_x MXene flakes ($\langle t_{\text{Ti}_2\text{CT}_x} \rangle$ and $\langle S_{\text{Ti}_2\text{CT}_x} \rangle$) and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes ($\langle t_{\text{Ti}_3\text{C}_2\text{T}_x} \rangle$ and $\langle S_{\text{Ti}_3\text{C}_2\text{T}_x} \rangle$). AFM statistics were

collected separately from 89 $\text{Ti}_3\text{C}_2\text{T}_x$ flakes and 38 Ti_2CT_x flakes, respectively. The $\langle S \rangle$ is obtained via $\langle S \rangle = xy^{0.5}$, where x and y refer to the length and width of a particular flake. Log-normal distributions are applied to fit the AFM statistics, with the peak values as the mean $\langle t \rangle$ and $\langle S \rangle$.

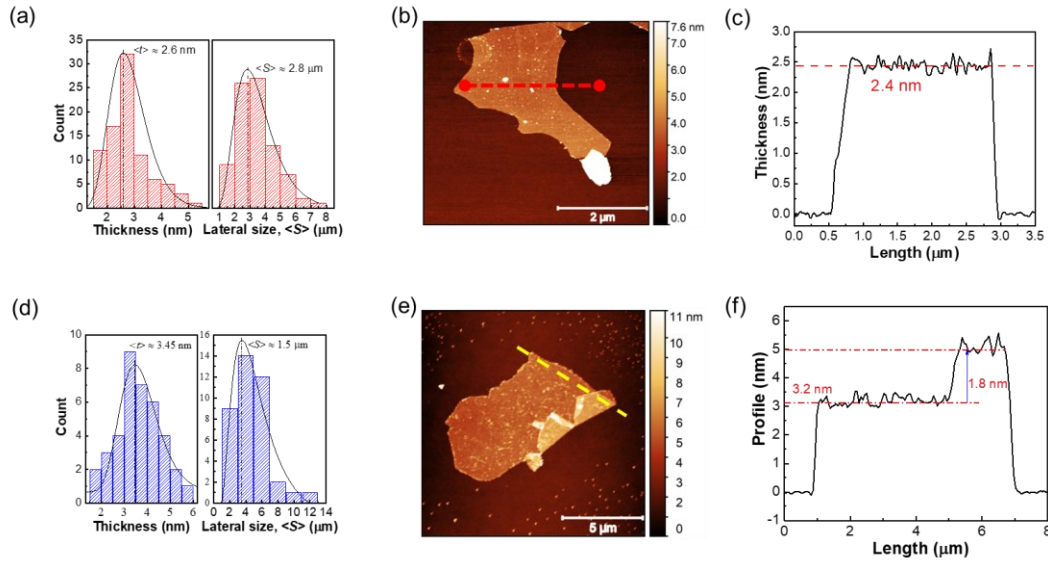


Figure 5.2 AFM measurements of MXene flakes. (a) AFM statistics on the thickness and lateral size over 89 $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, (b) a typical monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake and (c) its height profile over the lateral length; (d) AFM statistics on the thickness and lateral size over 38 Ti_2CT_x flakes, (e) a typical monolayer Ti_2CT_x flake and (f) its height profile over the lateral length.

Fig 5.2 (a) shows that the distribution of $\langle t_{\text{Ti}_3\text{C}_2\text{T}_x} \rangle$ and $\langle S_{\text{Ti}_3\text{C}_2\text{T}_x} \rangle$ both follow a log-normal distribution peaked at 2.6 nm and 2.8 μm , respectively. The results indicate the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$ solutions consists of $\sim 70\%$ monolayer and bilayer flakes, considering a monolayer thickness of 1.6 nm and additional thickness attributed to the 1-nm water molecules trapped between the flake and the substrate.^{213,219} Fig 5.2 (b) and (c) present a high-resolution AFM image for a monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ flake with a $\langle t_{\text{Ti}_3\text{C}_2\text{T}_x} \rangle$ of 2.4 nm and a $\langle S_{\text{Ti}_3\text{C}_2\text{T}_x} \rangle$ of 2.5 μm .

Fig 5.2 (d) shows that the distribution of $\langle t_{\text{Ti}_2\text{CT}_x} \rangle$ and $\langle S_{\text{Ti}_2\text{CT}_x} \rangle$ also follow a log-normal distribution peaked at 3.5 nm and 3.5 μm , respectively. Fig 5.2 (e) and (f) present a high-resolution AFM image for a folded Ti_2CT_x flake with a $\langle t_{\text{Ti}_2\text{CT}_x} \rangle$ of 3.2 nm and a $\langle S_{\text{Ti}_2\text{CT}_x} \rangle$ of 6.6 μm . The thickness of the folded edge of the flake is 1.8 nm, which indicates it is a monolayer. An additional thickness of 1.4 nm can be attributed to the water molecular trapped between the flake and the substrate.

Due to the highly anisotropic thickness and lateral size of the MXene flakes, the preferred orientation of the MXene flakes is parallel to the substrate.¹⁴

5.3.1.2 Low temperature UV-vis absorption spectroscopy

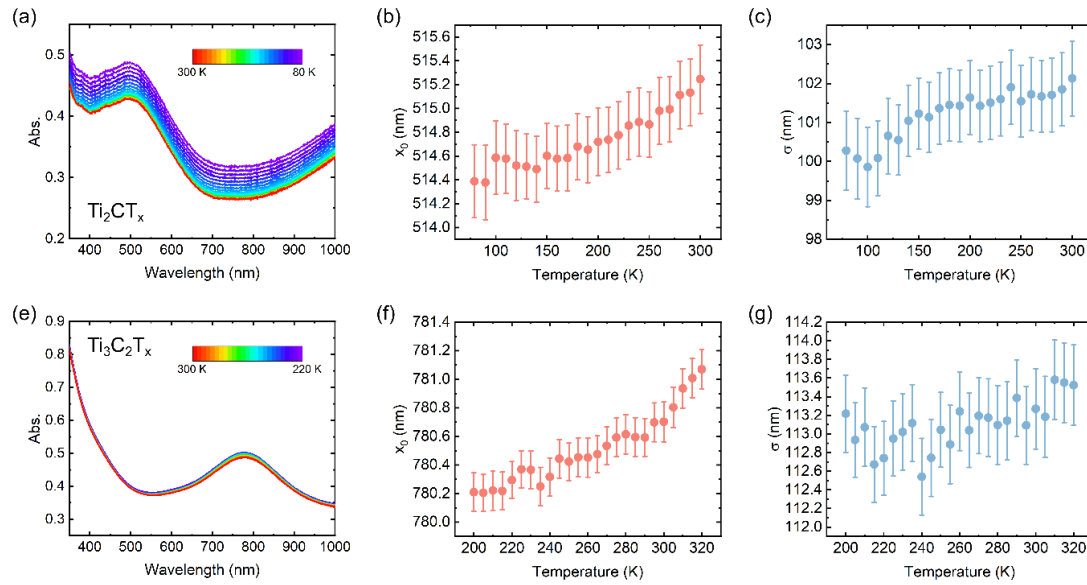


Figure 5.3 Low temperature UV-vis absorption spectra of MXenes. (a) and (e) UV-vis absorption spectra for Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films at different temperatures. (b-c) and (f-g) Peak position and width of plasmonic resonant at different temperatures for Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films.

The UV-vis absorption spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films were measured as a function of temperature. The plasmonic resonant peaks are fitted by a Lorentzian

function with a linear baseline, shown in Eq. 5.1.

$$y = H \frac{\sigma}{(x - x_0)^2 + \sigma^2} + ax + b \quad \text{Eq. 5.1}$$

where H is the peak height, σ is the peak width, x_0 is the peak center position, and a and b are parameters for the linear baseline. The extracted x_0 and σ for both MXenes films as a function of temperature is shown in Fig 5.3 (b-c) and (d-e) respectively. As shown in Fig 5.3 (b) and (c), the plasmonic resonant peak for Ti_2CT_x MXene film is red-shifted and broadened. In the contrast, in Fig 5.3 (e) and (f), the plasmonic resonant peak for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film is red shifted, but the peak width at different temperatures keeps almost constant. The spectral shifts indicate thermochromic effect of the MXenes, which will be discussed in more details in the following sections.

5.3.2 Hot carrier cooling

5.3.2.1 TA spectral analysis

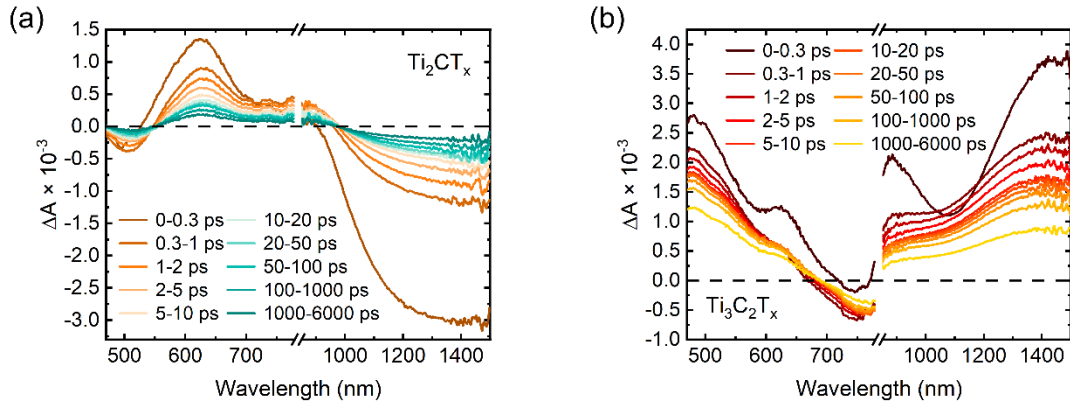


Figure 5.4 Vis-NIR TA spectra of Ti_2CT_x (a) and $\text{Ti}_3\text{C}_2\text{T}_x$ (b) MXene films under 450 nm excitation with the fluence of $200 \mu\text{J cm}^{-2}$.

Fig 5.4 (a) and (b) compare the TA spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes measured

using 450 nm excitation. In both MXenes, a negative photobleaching (PB) signal is observed in the visible region (470-780 nm), which coincides with the location plasmonic resonances in Ti_2CT_x MXene (~ 500 nm) and in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (~ 780 nm). Similar PB spectral features have been observed in previous studies on MXenes.^{78,111} Apart from the negative PB features, PIA spectral features can be observed on the either side of the PB signal for both MXenes. In the NIR region (850-1500 nm), another PB signal with higher intensity (compared with the PB signal around 500 nm) is observed in Ti_2CT_x MXene from 1000 nm to more than 1500 nm, however, only PIA signal is observed in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. The PB signal for Ti_2CT_x MXene in NIR region can be assigned as the resonance of a high concentration of plasma in Ti_2CT_x MXene, according to the study by Maleski et al.⁴⁷ Although PB feature is not observed in the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in the NIR region, the positive PIA spectral feature shows a decreasing trend around 1500 nm. Similar spectral shape for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in the NIR region is also observed by Rawat et al.²¹¹ It is believed that there is a PB feature in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at higher wavelength around 2000 nm, as shown in Fig 2.10, which falls outside the bandwidth of the spectrum of the probe.⁴⁷

In both MXenes, within the first ~ 300 fs after photoexcitation, the shapes of TA spectra deviate significantly from the spectra at later times (shown in Fig 5.5). The photophysical process within this time range is commonly attributed to e-e scattering.^{111,204,205} Due to the limit of the pulse duration in the setup (~ 100 fs), the details of e-e scattering cannot be resolved in our study. Within the next 5 ps, the TA spectra of both MXenes keep evolving, showing slight differences compared with later times, as shown in Fig 5.5.

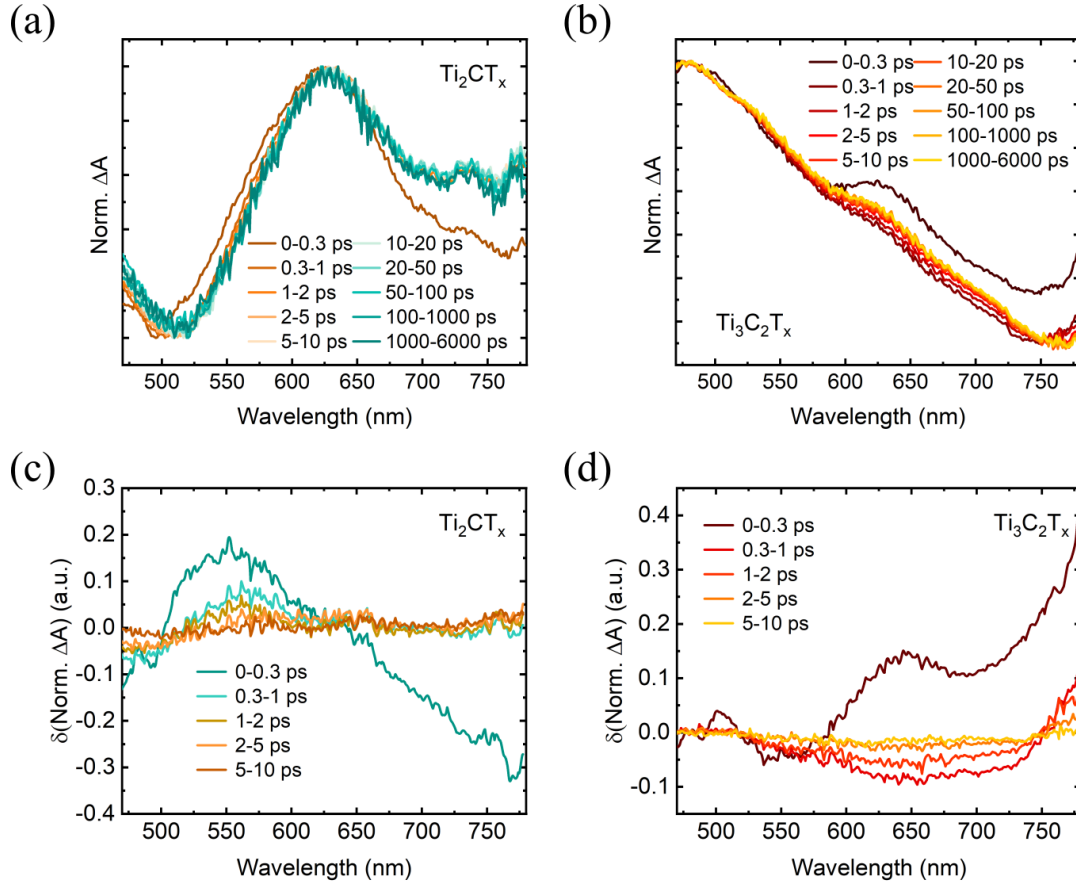


Figure 5.5 Comparison of TA spectra at early time and late time. (a) and (b) Normalised TA spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films with 450 nm excitation in the visible and NIR region. (c) and (d) TA signal difference at early times.

As shown in Fig 5.5 (a) and (b), the normalized TA spectra at long delay times (>10 ps) are identical, which is attributed to a hot lattice after reaching thermal equilibrium with hot carriers. However, the differences between the spectra at early times (<10 ps) and those at late times (>100 ps) are not clearly to be visualised. To better illustrate the subtle spectral evolutions at early delay times, the normalized TA spectra were subtracted at late times (100 ps to 1 ns) from those at early times, denoted as $\delta(\Delta A)$, as shown in Fig 5.5 (c) and (d). In both MXenes, the TA spectral differences evolve within 5 ps (i.e., $\delta(\Delta A)$ is non-zero), and no differences are observed after 10 ps (i.e., $\delta(\Delta A)$ approaches zero). Furthermore, for both MXenes, the $\delta(\Delta A)$ spectra within the first 300 fs differ from those observed between 0.3 ps and 5 ps. The resulting $\delta(\Delta A)$ spectra

within the first 300 fs are attributed to electron-electron scattering and hot carriers, while the $\delta(\Delta A)$ spectra from 0.3 to 5 ps represent signals induced by hot carriers towards reaching thermal equilibrium with the lattice. The TA spectra of studied MXenes do not change after 5 ps and are attributed to lattice heating effect. The details of dynamics are discussed in the following sections.

5.3.2.1 Hot carrier cooling in MXenes

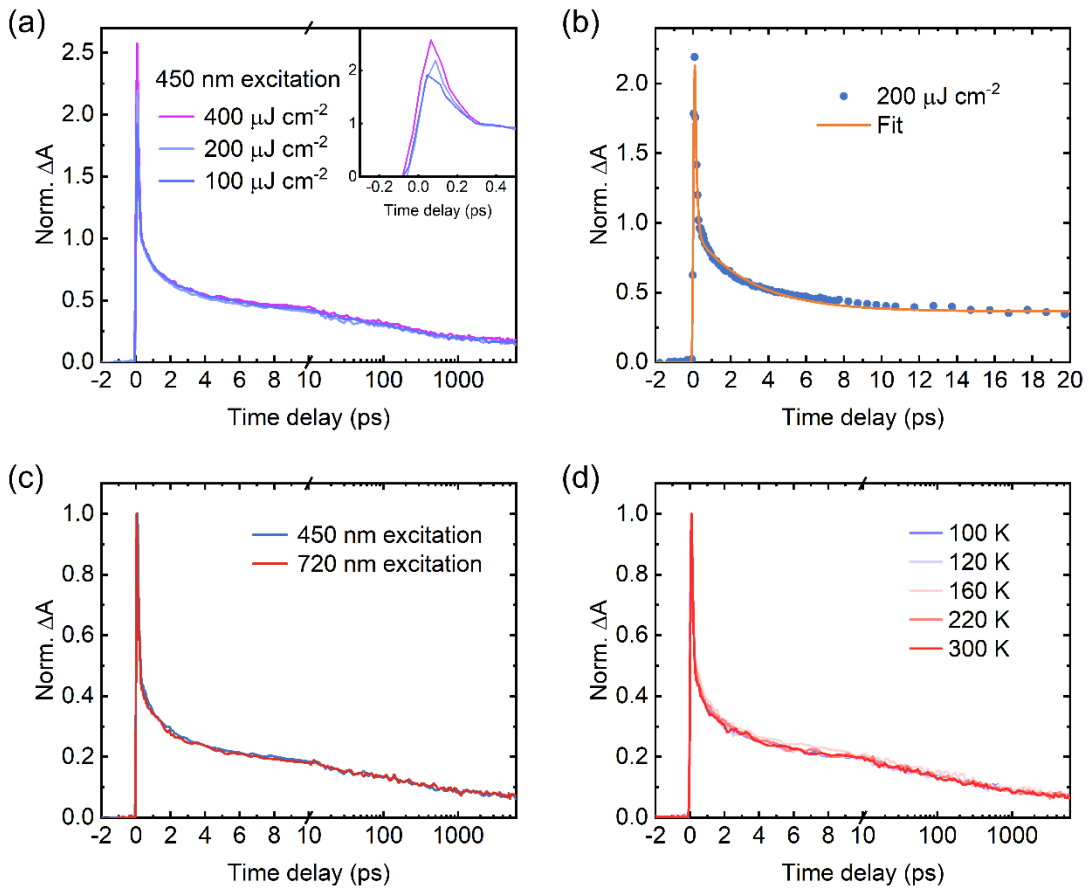


Figure 5.6 Ultrafast kinetics of Ti_2CT_x MXene film probed around 630 nm. (a) Kinetics of Ti_2CT_x MXene film excited at 450 nm at different fluences normalized at 0.3 ps. (b) Fit of the kinetics excited at 450 nm ($200 \mu\text{J cm}^{-2}$). (c) Comparison of the kinetics between excitation at 450 nm ($200 \mu\text{J cm}^{-2}$, in blue) and 720 nm ($350 \mu\text{J cm}^{-2}$, in red). (d) Normalized kinetics of Ti_2CT_x MXene film excited at 450 nm ($200 \mu\text{J cm}^{-2}$) at different environment temperatures.

Fig 5.6 presents the sub-ps-to-ns dynamics in Ti_2CT_x MXene film at different

experimental conditions. According to the spectral shape analysis, the TA signal at 630 nm for Ti_2CT_x MXene and 500 nm for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene are selected to represent the cooling dynamics in the studied films. The kinetics of Ti_2CT_x MXene film excited at 450 nm at different excitation fluences and probed at 630 nm are shown in Fig 5.6 (a). In Ti_2CT_x MXene, e-e scattering shows dependence on the fluence. Therefore, the TA kinetics is normalized at 0.3 ps after the fast component of the dynamics is complete.

As shown in Fig 5.6 (a), after 0.3 ps, the TA signal of Ti_2CT_x MXene shows two distinct decay components: one on ps timescale and the other on ns timescale. The ps-level decay is attributed as hot carrier cooling which refers to the process of thermal equilibrium between the photoexcited carriers and the material lattice.²⁰⁵ After reaching thermal equilibrium, the decay of the TA amplitude represents the heat dissipation from the hot lattice to the environment on ns- μ s timescale.¹¹¹ As shown in Fig 5.6 (a), the TA signal after 0.3 ps is independent on the laser fluence, which means that carrier cooling and subsequent lattice cooling in Ti_2CT_x MXene film are not affected by the excitation density.

To obtain hot carrier cooling time, the TA signal up to 20 ps is fitted by a biexponential decay plus a baseline, convoluted with the pump pulse duration, $G(t)$ (~ 100 fs):

$$\Delta A(t) = G(t) \otimes \left[A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_{e-ph}}\right) + c \right] \quad \text{Eq. 5.2}$$

where A_1 , τ_1 and A_2 , τ_{e-ph} represent the amplitudes and decay times of the fast decay component and carrier cooling process, and c is a constant value to estimate the long-lived component. The fitted curve is shown Fig 5.6 (b) and the carrier cooling time of Ti_2CT_x MXene is 2.6 ± 0.1 ps which is longer than the carrier cooling time of $\text{Ti}_3\text{C}_2\text{T}_x$

MXene (1.6 ± 0.2 ps, shown in Fig 5.7).

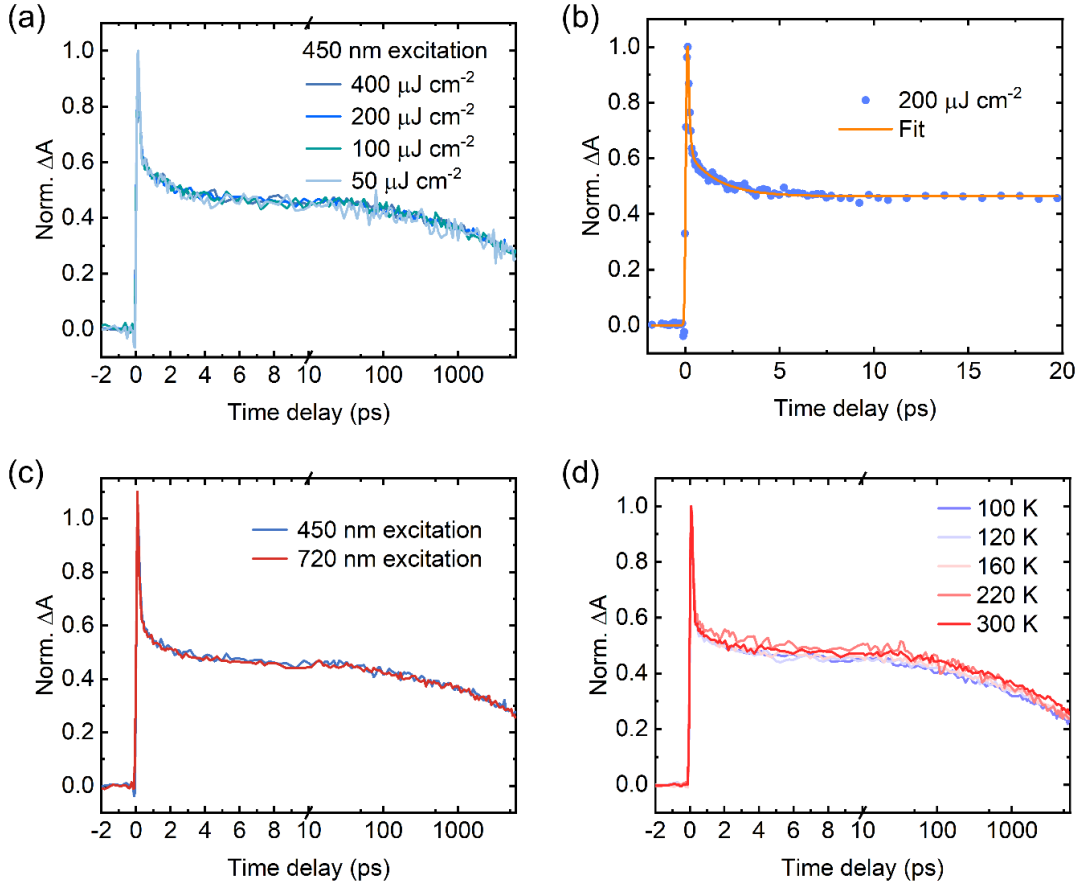


Figure 5.7 Ultrafast kinetics of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film probed around 500 nm. (a) Kinetics of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film excited at 450 nm at different fluences. (b) Fit of the kinetics excited at 450 nm (200 $\mu\text{J cm}^{-2}$). (c) Comparison of the kinetics between excitation at 450 nm (200 $\mu\text{J cm}^{-2}$, in blue) and 720 nm (350 $\mu\text{J cm}^{-2}$, in red). (d) Normalized kinetics of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film excited at 450 nm at different environment temperatures.

Furthermore, as shown in Fig 5.6 (c) and (d), apart from excitation density, the TA signal of Ti_2CT_x MXene is not affected by excitation laser wavelength and environmental temperature. These results highlight that hot carrier cooling in Ti_2CT_x MXene is not affected by HPB effect which is widely observed in other 2D materials like graphene and transition metal dichalcogenides (TMDs).^{95,148,181,220} In graphene and TMDs, the hot carrier relaxation time increases at higher hot carrier densities due to the

lack of longitudinal optical (LO) phonons. The absence of HPB effect has been extensively found in MXene family, including $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig 5.7 and previous literatures), Mo_2CT_x , V_2CT_x , $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$, and Nb_2CT_x .^{78,111,205,221–223} Although MXenes have different elemental compositions, the dissipation of the excess energy of hot carriers to the lattice via e-ph coupling is always efficient. This can be explained by the similar e-ph coupling constant in different MXenes, regardless of whether they are metallic or semiconducting.²⁶ The absence of the HPB effect in MXenes suggests that this material family has broad potential for applications particularly in cryogenic and high-power scenarios.

5.3.2.2 Thermochromic effect

When carrier cooling is complete, the TA response is assigned to the thermochromic phenomena – the increase in the temperature of electron gas and material lattice after photoexcitation leads to the modulation of absorption and transmission properties. This assignment is based on the line shape analysis of the steady-state absorption spectra at different temperatures, shown in Fig 5.8.

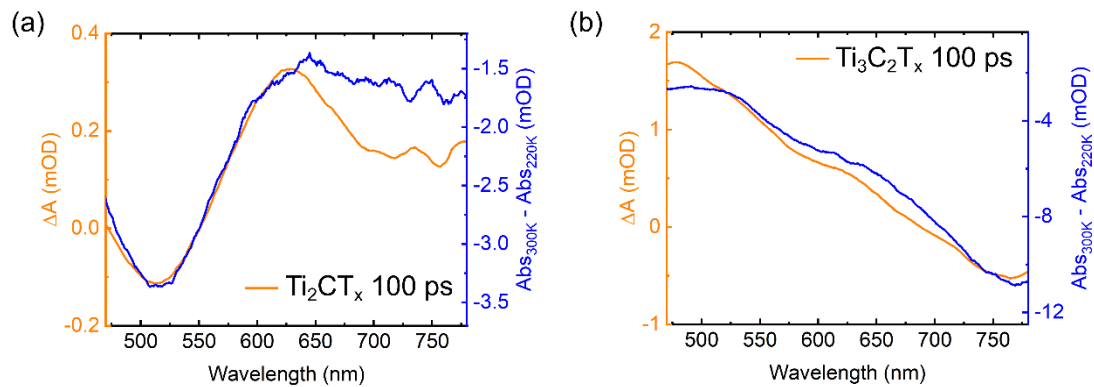


Figure 5.8 Comparison between TA spectra at 100 ps and difference of absorption spectra at two 300 K and 220 K of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films.

To gain insight into the origin of thermochromic effect, TA spectra at 100 ps of both

MXenes are compared to the first and second derivatives of respective absorption spectra (Fig 5.9 (a) and (b)). The line shape of the TA spectrum of Ti_2CT_x MXene at 100 ps can be well described as a linear combination of the first and second derivatives ($-\frac{dA}{d\lambda} + 100\frac{d^2A}{d\lambda^2}$) of the steady-state absorption spectrum, shown in Fig 5.9 (c). Therefore, the steady-state absorption spectrum of Ti_2CT_x MXene is shifted to the red and broadened at 100 ps after laser excitation. As shown in Fig 5.9 (d), it is found that the line shape of the TA spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at 100 ps can be represented solely by the inverse of the first derivative ($-\frac{dA}{d\lambda}$) of the steady-state absorption spectrum, without the need for second derivative, which agrees with literature.²⁰⁵ With analogy to the Stark effect, this may be an evidence that the dipole moment of Ti_2CT_x MXene can be modulated by temperature more easily compared with $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.^{224,225}

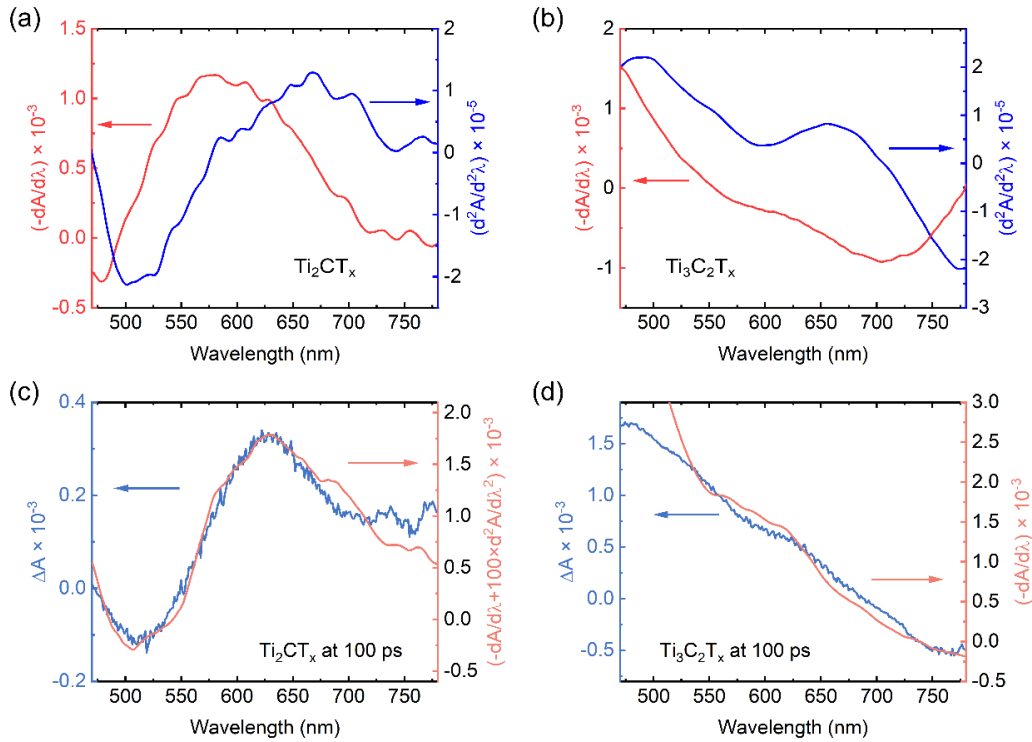


Figure 5.9 Differential spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. (a) and (b) first and second derivatives of UV-vis absorption spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. (c) and (d) comparison of TA spectra of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes at 100 ps and the

linear combination of the first and second derivatives of the UV-vis absorption spectrum.

5.3.3 Lattice cooling dynamics

5.3.3.1 Dynamics analysis

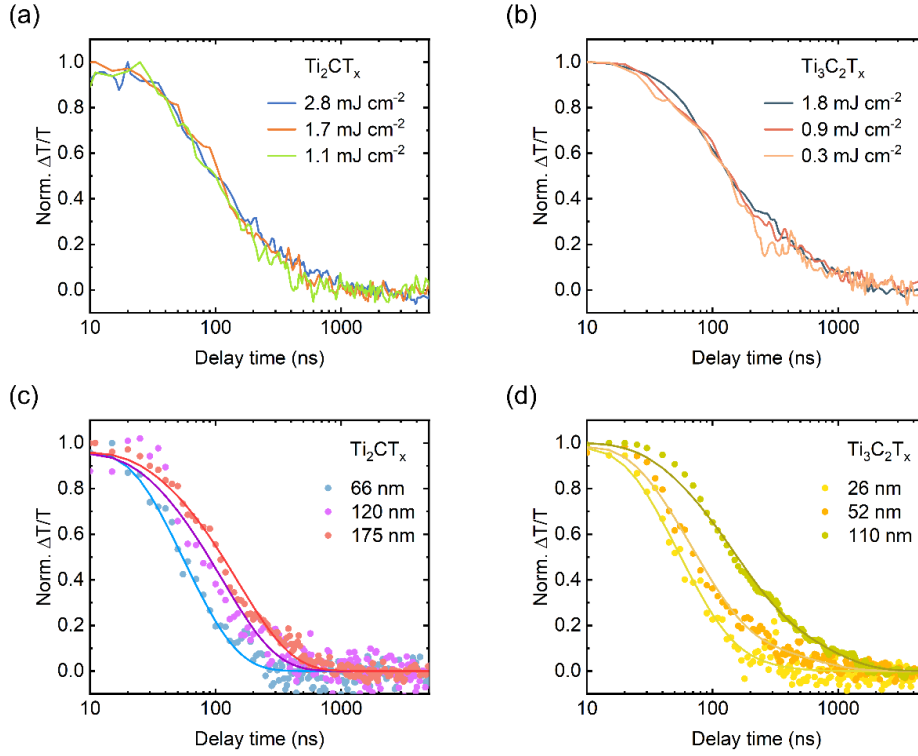


Figure 5.10 Lattice cooling dynamics of MXene films. (a) and (b) normalized ns-PP kinetics at Ti_2CT_x (175 nm) and $Ti_3C_2T_x$ (110 nm) MXene films different pump fluences. (c) and (d) normalized ns-PP kinetics of Ti_2CT_x and $Ti_3C_2T_x$ MXene films with different thicknesses.

As shown in Fig 5.6 and 5.7, in both MXene solid-state films, initial dynamics are followed by a much slower process with a lifetime > 6 ns, which is assigned to the heat dissipation from the hot lattice to the environment (i.e., lattice cooling).^{111,205} Li et al. have shown that the $Ti_3C_2T_x$ MXene flakes in liquid solution exhibit faster lattice cooling in picosecond timescale,^{208,209} but the lattice cooling kinetics for MXene films in solid state have not been studied previously. To investigate the lattice cooling

dynamics in thin films, PP experiments on ns to μ s timescales were performed for both MXenes films. Here, the transmittance change ($\Delta T/T$) of the probe was recorded.

Fig 5.10 presents the lattice cooling dynamics in Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films from ns to μ s timescale. Fig 5.10 (a) and (b) show the lattice cooling dynamics (i.e., ns-PP kinetics) of Ti_2CT_x (175 nm thick) and $\text{Ti}_3\text{C}_2\text{T}_x$ (110 nm thick) MXene films different pump fluences normalized at the maximum. No clear pump fluence dependence can be observed. However, the lattice cooling kinetics in both MXene films varies with the film thickness, shown in Fig 5.10 (c) and (d). The lattice cooling dynamics of Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films are fitted by a monoexponential decay, $A_1 \exp(-\frac{t}{\tau_1})$, and a biexponential decay, $A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2})$, respectively, convoluted with the pump pulse duration ($G_{ns}(t)$, ~ 15 ns). The fitted time constant is used as the heat dissipation (lattice cooling) time in Ti_2CT_x MXene film, while the heat dissipation time in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films is the average of the two components:²¹⁰

$$\tau = \frac{A_1 + A_2}{\frac{A_1}{\tau_1} + \frac{A_2}{\tau_2}} \quad \text{Eq. 5.3}$$

As shown in Fig 5.11, the heat dissipation time in both Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films linearly increases with the film thickness. The intercept for both linear fits is kept as 0. The error bar for the heat dissipation time is obtained by fitting and propagation via Eq. 5.3. The error bar for film thickness is obtained by the standard deviation of the thickness measured at several points on an individual sample. Fig 5.11 also shows that at a constant film thickness, the heat dissipation time in Ti_2CT_x MXene film is faster than $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film, suggesting a faster thermal transfer rate. The timescale of

heat dissipation process of the Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films indicates that the upper limit for optical modulation frequency is tens of megahertz without heat accumulation of these two MXene films.

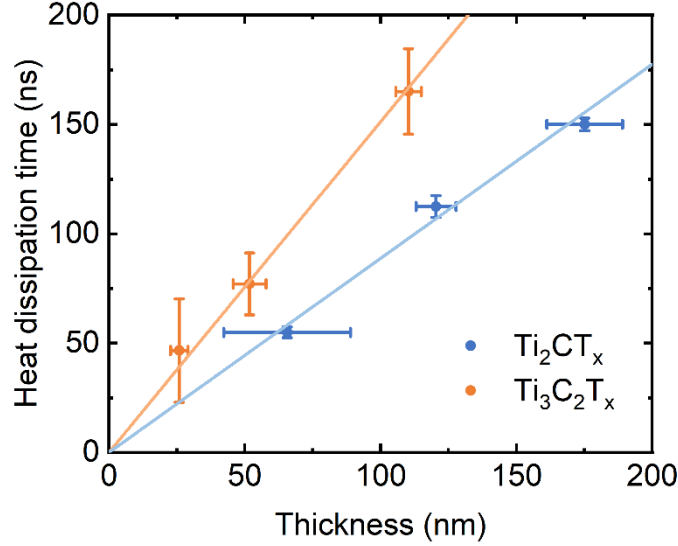


Figure 5.11 Lattice cooling time for Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films as a function of film thickness.

5.3.3.2 Thermal diffusion model

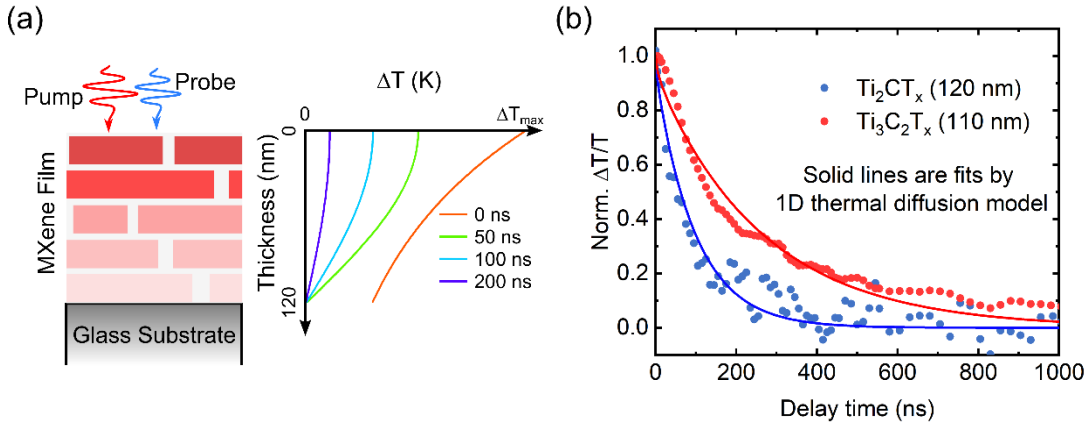


Figure 5.12 Thermal diffusion model to describe the ns-PP dynamics. (a) Scheme of 1D thermal diffusion model of heat dissipation in MXene flakes-based film on the substrate. The plot shows the temperature distribution in the MXene film at different times after photoexcitation. (b) Fitting results of Ti_2CT_x (120 nm, in blue) and $\text{Ti}_3\text{C}_2\text{T}_x$ (110 nm, in orange) films with the 1D thermal diffusion model.

To obtain better understanding of the heat dissipation in MXene films, a 1D thermal diffusion model was used, schemed in Fig 5.12 (a), to extract the thermal diffusivity (α) of the two MXenes films. According to a study of $\text{Ti}_3\text{C}_2\text{T}_x$ flakes, the micrometer-size MXene flakes prefer to stack almost parallelly to the substrate, with a tilted angle less than 5° .¹⁴ Fig 5.12 (a) illustrates the simulation of the 1D heat flow across the thickness of the MXene flake network.

For simplicity, the MXene films are considered as continuous medium for 1D thermal transport, which is an acceptable assumption given that individual chemical vapor deposition (CVD)-grown $\text{Ti}_3\text{C}_2\text{T}_x$ flakes and networks of individual $\text{Ti}_3\text{C}_2\text{T}_x$ flakes have shown to have the same electronic transport.¹⁴ The model describes the relative temperature difference caused by the incident laser pulse between the MXene film and the ambient environment, rather than the temperature of MXene film. As shown in Fig 5.10 (a), the lattice cooling is independent of the initial temperature (i.e., excitation density), therefore, the initial temperature distribution is assumed to be the same as the distribution of absorbed photon number. Dirichlet condition is used as the other boundary condition. All equations are given as follow:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad \text{Eq. 5.4}$$

$$T(x, 0) = ne^{-\frac{x}{a}} \quad \text{Eq. 5.5}$$

$$\frac{\partial T(x_0, t)}{\partial t} = 0 \quad \text{Eq. 5.6}$$

$$T(x_{\max}, t) = 0 \quad \text{Eq. 5.7}$$

where T is the temperature difference of the lattice from room temperature, t is the delay time, x is the thickness of the sample, α is thermal diffusivity, n is the initial temperature, which is linearly proportional to the incident photon number, and a is the absorption coefficient. x_0 is the interface between the MXene thin film and N_2 atmosphere, and x_{max} is the interface between the MXene thin film and the glass substrate. The equations are solved by pdepe solver function in MATLAB. The integral $T(t)$ as a function of x , $\int T(t) dx$, is used as the fitting function of the ns-PP kinetics. The absorption coefficient, a , is determined from the absorption at 1064 nm for both MXenes films by Eq. 5.8, shown in Table 5.1.

$$\alpha = \frac{\text{Absorbance}}{\text{thickness}} * 2.303 \quad \text{Eq. 5.8}$$

Table 5.1 Absorbance and absorption coefficient of MXene films

120-nm Ti_2CT_x MXene film		110-nm $Ti_3C_2T_x$ MXene film	
Absorbance	a (nm^{-1})	Absorbance	a (nm^{-1})
0.406	0.008	0.548	0.011

The best fits by the 1D thermal diffusion model of Ti_2CT_x MXene film (120 nm, in blue) and $Ti_3C_2T_x$ MXene film (110 nm, in orange) are shown in Fig 5.12 (b). It is noted that the thermal transfer to the N_2 atmosphere from the MXene film is not considered in the model. In addition, the in-plane heat dissipation is not considered in the 1D thermal diffusion model. Therefore, the estimated thermal diffusivity values for both MXenes films might be overestimated. However, the extracted α for Ti_2CT_x MXene film is ~ 0.06 mm^2/s and α for $Ti_3C_2T_x$ MXene film ~ 0.02 mm^2/s with error bars less

than 5%, which are orders of magnitude lower than typical metals ($\sim 10^4$ mm²/s at room temperature).²²⁶

According to the Wiedemann-Franz law and the definition of thermal diffusivity,

$$\frac{\kappa}{\sigma} = LT \quad \text{Eq. 5.9}$$

$$\alpha = \frac{\kappa}{\rho C_p} \quad \text{Eq. 5.10}$$

where κ is the thermal conductivity, σ is the electrical conductivity, L is Lorenz number, T is temperature, ρ is the material density, and C_p is the specific heat capacity, thermal diffusivity should scale linearly with the electrical conductivity. However, the thermal diffusivity for two metallic MXenes in this study deviates from the Wiedemann-Franz law. From the aspect of interactions between electrons and phonons, the deviation from the Wiedemann-Franz law can be caused by the strong e-ph scattering in MXenes, which can reduce the lattice thermal conductivity in these 2D metallic materials.¹¹² From the aspect of materials, the small thermal diffusivity in MXene films can be explained by slow inter-flake thermal transfer. As illustrated in Fig 5(d), the heat from the upper flakes will propagate across multiple flakes to the substrate be dissipated. The slow inter-flake thermal transfer may be a rate-limiting step due to the functional groups (such as -OH, =O, -Cl, and -F) on the surface of the flakes.²²⁷

5.4 Conclusions

This chapter demonstrates a systematical investigation of the energy dissipation dynamics in solid-state Ti_2CT_x MXene film, in comparison with $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film, from sub-ps timescale to μs timescale. Two plasmonic resonant bands in Ti_2CT_x MXene film were observed, one at ~ 500 nm and the other at ~ 1500 nm, using ultrafast TA spectroscopy. Carrier cooling time in Ti_2CT_x MXene is persistently ~ 2.6 ps, which is 1 ps longer than the cooling time in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. No evidence of hot-phonon bottleneck is observed even at high excitation densities, different excitation wavelengths, and low environmental temperatures. The main feature of TA spectra of Ti_2CT_x MXene film can be described as thermochromic effect without any absorption of electronic excited states. However, in both Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene films, the heat dissipation from the material lattice to the environment is a slow process, taking as long as hundreds of nanoseconds and scaling linearly with the film thickness. A 1D thermal diffusion model was used to fit the lattice cooling dynamics to extract thermal diffusivities in MXene films ($\sim 0.06 \text{ mm}^2 \text{ s}^{-1}$ in Ti_2CT_x and $\sim 0.02 \text{ mm}^2 \text{ s}^{-1}$ in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film). The low thermal diffusivities in MXene films can be caused by the inefficient inter-flake thermal transfer. This work unravels the energy dissipation mechanisms in the solid-state Ti_2CT_x MXene film, which is relevant for both fundamental studies and applications.

Chapter 6 Photophysics of Excited States in Multilayer MoS₂ Photodetector

Chapter 4 and 5 demonstrated the carrier cooling mechanisms in semiconducting and metallic 2D materials, respectively. In particular, Chapter 4 utilized a NIR push pulse to investigate and manipulate the cooling dynamics in the SL WS₂ film under open-circuit conditions. Building on the idea of using NIR push pulse to interact with the excited states, this chapter applies the pulse technique to multilayer MoS₂ photodetectors operating under short-circuit conditions, employing PPPc spectroscopy to investigate exciton dynamics. Combined with steady-state photocurrent spectroscopy to examine FC transport mechanisms, this chapter seeks to provide new insights into the photophysics of ESs in multilayer MoS₂.

6.1 Introduction and motivation

Previous chapters have introduced the photophysics in SL TMDs which have shown substantial potentials in (opto-)electronics and photonics. Although wafer-scale SL TMDs can be grown via CVD methods, high temperature and high vacuum are normally required and the subsequent microfabrication techniques involving photolithography, lift-off, and transfer processes are still difficult and expensive.²²⁸ Therefore, printable inks based on 2D material nanosheets have been developed, which can deposit the functional materials into customizable patterns on various substrates. For example, the conducting, semiconducting, and insulating materials have been developed to printable inks as building blocks for electrodes, channels, and dielectric layers in fully-printed FETs.²²⁹ Apart from electronics, printed TMDs have also been used in optoelectronics, such as photodetectors and photovoltaics.^{228,230–232} However, comparing to widely studied SL TMDs, the dynamics of photogenerated excitons and charge carriers is much less comprehensively investigated and understood, which is essential for light harvesting and sensing. In addition, different from SL TMDs with direct bandgaps which allow people to study either steady-state or time-resolved PL to understand the photophysics,^{107,108,233} printable TMD nanosheets are always a mixture of SL and multilayer TMDs whose PL efficiency is extremely suppressed by the indirect bandgap nature. This not only complicates the system making data interpretation more difficult, but also limits the available experimental methods.

This chapter aims to use steady-state and time-resolved photocurrent spectroscopies as a function of temperature to understand the photophysics of ESs in thin films made from multilayer MoS₂ flakes produced by electrochemical exfoliation. The

temperature-dependent steady-state photocurrent spectroscopy demonstrated an abnormal band-like transport, which indicates high density of photoexcited FCs. PPPc spectroscopy indicates that the exciton dissociation has negligible contribution of FC generation.

6.2 Experimental details

6.2.1 Sample preparation

All samples were prepared by Ao Yan (Imperial College London).

6.2.1.1 Preparation of the MoS₂ ink

The procedures of MoS₂ ink preparation were adapted from Wang et al.²³⁴ MoS₂ crystal (SPI Supplies) was cut into a 0.8*0.4*1 mm piece. The cut crystal was then electrochemically exfoliated with graphite or Pt as anode, 8V voltage applied and in 5 mg/mL THAB in MeCN electrolyte for 2 hours. Then the expanded crystal was washed with EtOH to remove the residual electrolyte. The rinsed expanded crystal was sonicated in PVP/DMF (0.8892 g PVP in 40 mL DMF) for 30 minutes. The as-produced dispersion was centrifuged (Beckman Coulter) at 400g for 5 minutes. The supernatant was pipetted out into two high-speed centrifuge tubes. To wash out the PVP The dispersion was then centrifuged at 12800g for 20 minutes and the supernatant was discarded. Then 30 mL IPA was added to the dispersion and the dispersion was sonicated for 1-3 minutes to disperse the precipitate. The washing process was repeated twice. 25 mL of IPA was added into the tube after the final washing step. The dispersion was then sonicated for 1-3 minutes and the centrifuged at 600g for 5 minutes. The top

80% of the supernatant was used for film deposition.

6.2.1.2 Film deposition

The substrates used in this study were sonicated in a 1:1 IPA and acetone mixture for 15 minutes, followed by additional 15 minutes sonication in IPA alone. Then the substrates were treated with ozone plasma using a UV Ozone Cleaner (UVOCS, T0606B) to enhance their surface hydrophilicity. The MoS₂ thin films were fabricated using a home-built automatic spray-coating system equipped with an airbrush on a three-axis platform and electronic gas flow control. To achieve comprehensive coverage in a single pass, the nozzle was positioned 40 mm above the substrate. Nitrogen gas was applied at 150 kPa as the atomisation gas, and a 0.4 mm nozzle traversed at 66.67 mm/s. Following spray-coating, the samples were annealed on a hotplate (Cole-Parmer, UC152D) inside a glovebox at 150°C for 2 hours to remove residual solvent.

The substrates used in photocurrents were commercial ITO glass substrate (Ossila, S161, 50 μm channel length), schemed in section 3.1.3. In the TA measurements the MoS₂ films were deposited on glass. In the Raman and AFM measurements, the MoS₂ flakes were deposited on Si/SiO₂ substrates.

6.2.2 Sample characterisation

6.2.2.1 UV-vis absorption spectroscopy

The steady-state UV-vis absorption spectrum was measured with a Cary 60 UV-vis spectrophotometer (Agilent) in ambient condition.

6.2.2.2 Raman spectroscopy

Raman spectroscopy was performed by Sihui Liu.

Raman spectrum was collected by a Reminder lab Raman with the 50× objective lens and 532 nm laser excitation in an incident power of 0.16 mW at the same spot.

6.2.2.3 Photocurrent spectroscopy

Photocurrent spectroscopy measurements were performed using the setup sketched in section 3.1.3. The devices were measured in a cryogenic probe state (Linkam Scientific, HFS350EV-PB4) under vacuum.

6.2.2.4 AFM

The AFM measurement was done by Shuwei Wu (Imperial College London).

AFM was performed using the Keysight 5500 SPM AFM (Keysight Technologies). The diluted MoS₂ ink was deposited on the pre-cleaned Si/SiO₂ substrate by drop casting.

6.2.2.5 Temperature dependent resistance

The MoS₂ photodetector was measured in dark environments within a cryogenic probe state (Linkam Scientific, HFS350EV-PB4) under vacuum. The dark current was scanned from -1 V to 1 V by a sourcemeter (Keithley 2450) controlled by a LabView code. The resistance at different temperatures was calculated according to Ohm's Law.

6.2.3 Time-resolved spectroscopy

TA measurements were carried out using the setup described in section 3.2.3. The samples were measured in N₂ atmosphere sealed in a quartz cuvette at room temperature. In all the measurements, the probe spectra when the pump is on and off were averaged for 1 second at each delay time. All the data was analysed after chirp correction.

The PPPc measurements were performed using the setup schemed in section 3.2.5. Since the device is semi-transparent and the pump and push beams are colinear, the PPPc setup was easily adapted to a PP configuration, keeping the probe as the same wavelength as 2000 nm. A PbSe photodetector (PDA20H-EC, Thorlabs) was placed behind the cryogenic probe station to measure the transmitted intensity, T , of the probe beam. A Si plate permits the probe to enter the PbSe photodiode but blocks the pump. The probe fluence was kept less than 0.1 mJ cm⁻². Note that in PP configuration, the chopper was place on the pump beam path, modulating at 2 kHz synchronised to the main laser. All PPPc and PP measurements were performed in a cryogenic probe state (Linkam Scientific, HFS350EV-PB4) under vacuum.

Due to the unavoidable baseline of the NIR push induced photocurrent, as shown in Fig. 6.9, PP configuration was used to confirm the spatial and temporal overlap between the visible and NIR pulses prior to the PPPc measurements. The chopper was moved from the visible pump beam to the NIR push beam (i.e., probe beam in PP configuration) to obtain the push-induced photocurrent signal.

6.3 Results and discussion

6.3.1 Steady-state characterisations

6.3.1.1 Non-optical characterisation

To estimate the number of layers in the MoS₂ flakes, AFM measurements were performed. According to the statistics of AFM results shown in Fig 6.1, the majority of the flakes have 6 or 7 layers (around 4 nm thick). As discussed in section 2.1.1, the multilayer MoS₂ has an indirect bandgap.

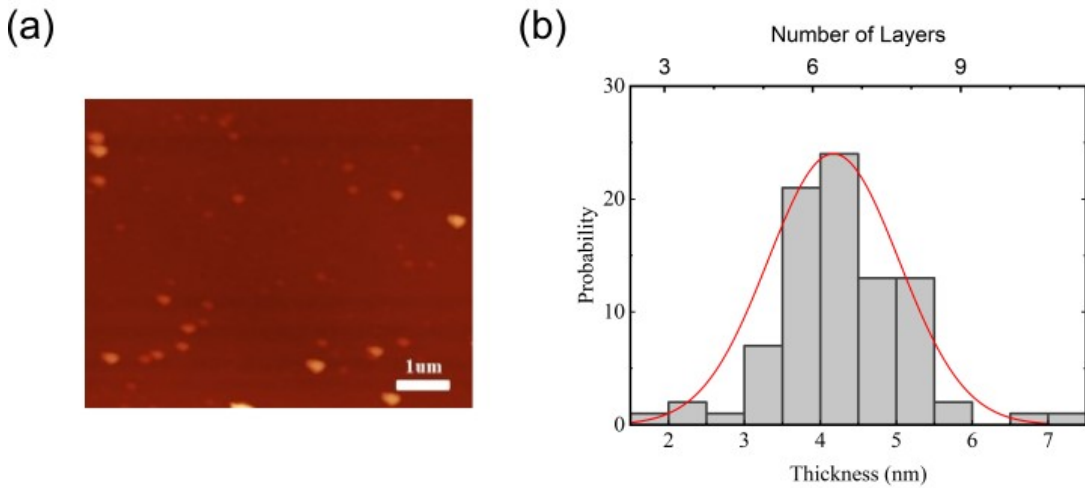


Figure 6.1 AFM measurements of the multilayer MoS₂ flakes. (a) AFM image of the multilayer MoS₂ flakes deposited on the Si/SiO₂ substrate. (b) statistics of flake thickness with the fit of Gaussian distribution.

To understand the hopping mechanism in the multilayer MoS₂ photodetector, the electrical conductivity, $\sigma(T)$, should be measured as a function of temperature, which normally requires four-probe measurement.

According to Ohm's law, the electrical conductivity can be written as:

$$\sigma = \frac{1}{\rho_R} = \frac{L}{R \times A} \quad \text{Eq. 6.1}$$

where ρ_R is the resistivity of the material, R is the electrical resistance, A is the cross-sectional area, and L is the length of the sample. As shown in Eq. 6.1, A and L are independent on temperature. Therefore, the electrical conductivity is proportional to the inverse of electrical resistance. For simplicity, in this thesis, the resistance was used to show the hopping transfer mechanism in the MoS₂ photodetector.

The hopping mechanism can be described as:¹⁴

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^p \right] \quad \text{Eq. 6.2}$$

where T_0 represents the characteristic temperature, σ_0 represents the conductivity as T approaches infinity, and p is an exponent determined by the specific hopping mechanism. In the nearest-neighbour hopping (NNH) mechanism, p is 1, while in variable-range hopping (VRH) mechanisms p is less than 1. The Mott VRH mechanism is defined by $p = 1/(1 + d)$, where d represents the dimensionality of the transport mechanism. According to Eq. 6.2, $-\ln(R)$ and $T^{-1/p}$ follow a linear relationship.

As shown in Fig 6.2, the resistance of the multilayer MoS₂ photodetector increases monotonically as the decrease of temperature. Due to the linear relationship between $-\ln(R)$ and $T^{-1/4}$, the electrons in the MoS₂ photodetector can be described by 3D Mott VRH.

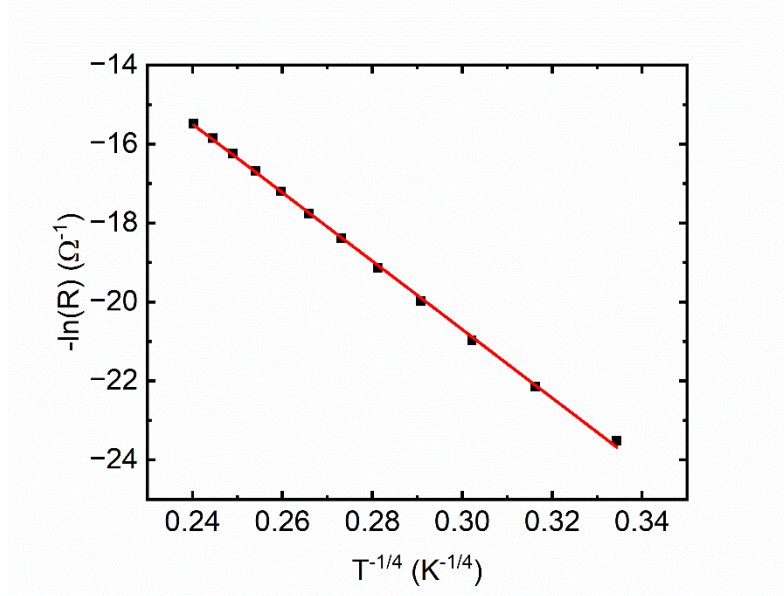


Figure 6.2 Resistance as a function of $T^{-1/4}$ for multilayer MoS₂ photodetector under dark condition.

6.3.1.2 Optical characterisation at room temperature

The UV-vis absorption spectrum of spray-coated multilayer MoS₂ film at 300 K is shown in Fig 6.3 (a). In Fig 6.3 (a), the UV-vis absorption spectrum can be reproduced by three Gaussian peaks and a second-order polynomial baseline (dashed grey curve). The resonances of A, B, and C excitons are around 661 nm (1.87 eV), 610 nm (2.03 eV), and 448 nm (2.77 eV), respectively. The A exciton resonant energy shows a bit higher energy than that reported in previous studies, which may be caused by different defect density, e-ph interactions, and flake size.^{14,44,235,236} This chapter only focuses on the A and B excitons. Fig 6.3 (b) shows the Raman spectra of multilayer MoS₂ with 532 nm excitation. The E_{2g}¹ mode (in-plane vibration) is around 384 cm⁻¹ and A_{1g} mode (out-of-plane vibration) is around 409 cm⁻¹, which also agree well with the literature.^{14,44}

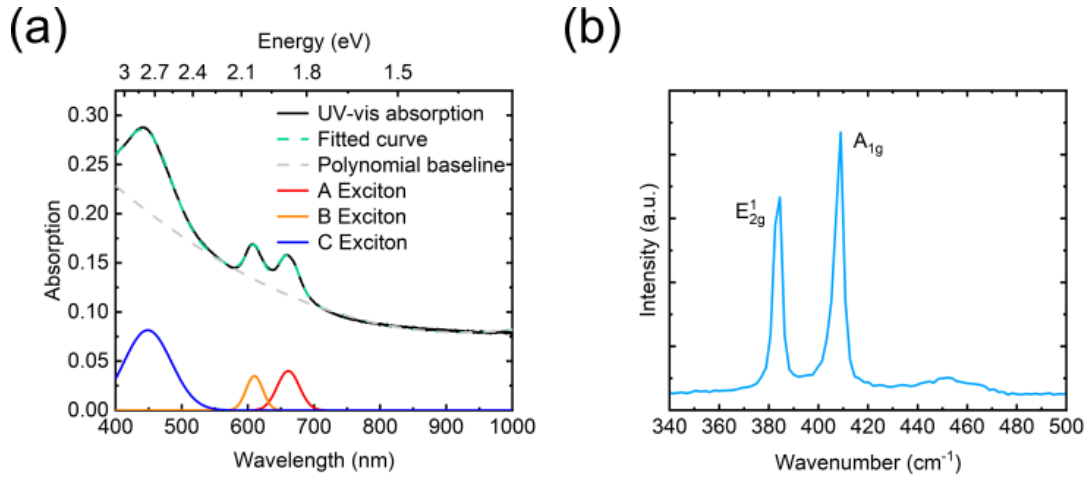


Figure 6.3 UV-vis absorption and Raman spectra of multilayer MoS₂ at room temperature.

The multilayer MoS₂ film shows some sub-bandgap optical absorption, for example 700 nm to 1000 nm, shown in Fig 6.3 (a). This can be caused by direct optical absorption caused by reflection, scattering artefact, and the trap states within the bandgap, which has been observed in perovskite solar cells.^{237,238} To confirm the origin of the sub-bandgap absorption, photocurrent spectroscopy was performed. If the sub-bandgap absorption originates from direct optical absorption caused by the trap states, these photoexcited carriers can contribute to photocurrent. In the contrary, if the sub-bandgap absorption is an artefact caused by scattering, no photocurrent can be observed with sub-bandgap photon excitation.

Fig 6.4 shows the photocurrent spectrum of a MoS₂ photodetector under 2V (field strength around 0.04 V μm^{-1}) as a comparison between dark measurements. Similar to the UV-vis absorption spectrum, the photocurrent spectrum also shows the three excitonic resonances of A, B, and C excitons, which agree well with the literatures.^{239,240} Expect for the excitonic resonant peaks, the broadband photocurrent response with sub-bandgap excitation is significantly higher than the noise level (i.e., dark current). It is noted that the photocurrent response calibration introduced in section

3.1.3.2 was performed on both photocurrent and dark current, which induces the curvature of the dark current. Without such a calibration procedure the dark current is flat. Therefore, the multilayer MoS₂ prepared by electrochemical exfoliation used in this chapter exhibits sub-bandgap absorption. The sub-bandgap absorption suggests unintentional doping of the multilayer MoS₂ (normally n-type doping) by introducing during the atomic vacancies and other defects the sample preparation process.^{4,241–243} This broadband sub-bandgap absorption will be further confirmed by the TA spectra.

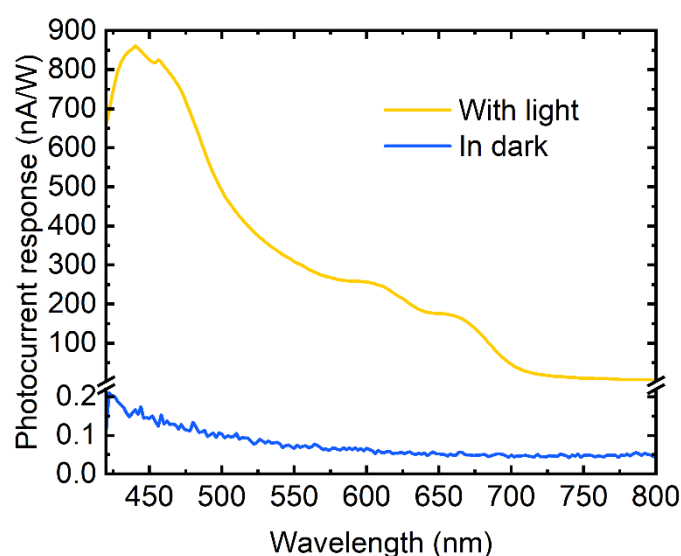


Figure 6.4 Photocurrent of multilayer MoS₂ at room temperature.

6.3.1.3 Temperature-dependent measurement

To obtain further understanding of e-ph interactions in the multilayer MoS₂, the photocurrent spectrum of the MoS₂ photodetector and UV-vis absorption were measured as a function of temperature. Fig 6.5 (a) presents the photocurrent response of the MoS₂ photodetector from 290 K to 80 K. The A and B excitonic resonances persist across all temperatures; however, their peak positions exhibit a blue shift as the temperature decreases. Similar blue shifts have been observed in UV-vis absorption spectra in Fig 6.5 (b), which are related to e-ph coupling.^{236,239,244,245} The A and B

exciton resonant peaks are broader than those in SL TMDs across the studied temperature range, suggesting a weak exciton binding energy.^{236,239,246} Furthermore, no additional peaks can be observed in the photocurrent spectra locating at lower energy than the A exciton peak even at 80 K. Therefore, different from SLs, the formation of exciton complexes, such as trions, can be ruled out in the multilayer MoS₂ photodetector.^{239,246,247}

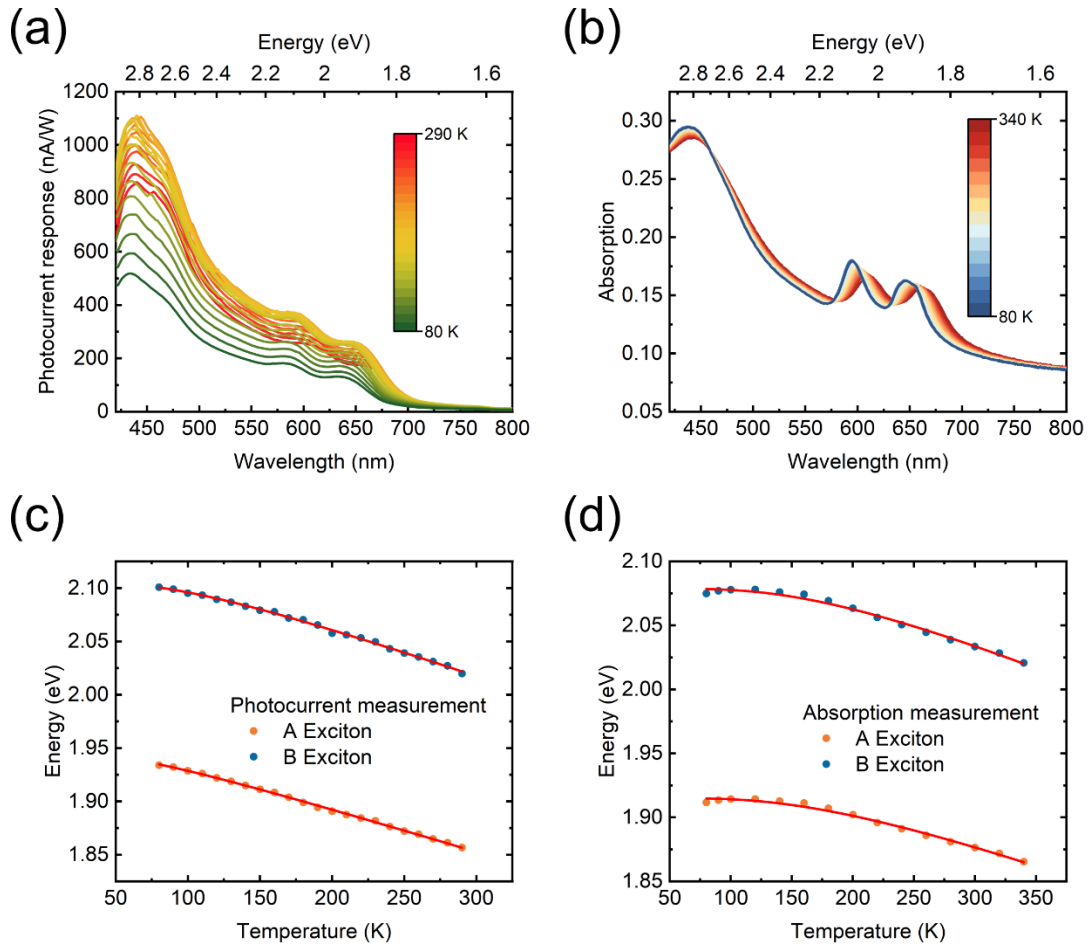


Figure 6.5 Temperature-dependent photocurrent response and absorption of multilayer MoS₂. (a) and (b) photocurrent response and UV-vis absorption spectra, respectively. (c) and (d) changes of the A and B excitonic resonant energies extracted from both measurements as a function of temperature. The solid lines are fitted by O'Donnell equation.

The A and B excitonic resonant energies are extracted with Gaussian peaks from the

photocurrent response spectra and UV-vis absorption spectra, as shown in Fig 6.5 (c) and (d), respectively. The A and B excitonic resonant energies as a function of temperature are fitted by O'Donnell equation:^{244,245,248}

$$E_x(T) = E_x(0) - SE_{ph} \left[\coth \left(\frac{E_{ph}}{2k_B T} \right) - 1 \right] \quad \text{Eq. 6.3}$$

where $E_x(0)$ is the exciton peak energy at zero temperature, S is a dimensionless constant that increases with the exciton–phonon coupling strength, and E_{ph} is the average phonon energy. The parameters used to fit the temperature-dependent A and B excitonic resonant energies from the two methods are listed in Table 6.1.

Table 6.1 The fitting parameters of the O'Donnell equation

	$E_x(0)$ (eV)	S	E_{ph} (meV)
A Exciton, photocurrent	1.94 ± 0.01	2.40 ± 0.05	15.1 ± 1.7
B Exciton, photocurrent	2.10 ± 0.01	2.79 ± 0.09	24.1 ± 1.6
A Exciton, absorption	1.92 ± 0.01	2.13 ± 0.19	47.5 ± 4.5
B Exciton, absorption	2.08 ± 0.01	2.51 ± 0.24	47.6 ± 4.6

The values of $E_x(0)$ and S , with the error bars, for A and B excitons does not show significant deviation in photocurrent and absorption measurements. However, the averaged phonon energies which are coupled to electrons depend on the methods. The E_{ph} extracted from absorption measurements coincide with the phonon energies in Raman spectra shown in Fig 6.3 (b). In photocurrent measurements, the carriers are coupled to the phonons with much lower average energies, which are 2 to 3 times lower than the energies obtained from absorption measurements. Since photocurrent

measurements involve photon absorption and photoexcited carrier transport, the deviation in e-ph interactions can be caused by temperature-dependent carrier transport within the multilayer MoS₂ film.

To investigate the e-ph interactions in charge transport, the photocurrent response intensities are plotted at different temperatures, shown in Fig 6.6 (a). Due to the spectral shift, the photocurrent responses are the integration from 550 nm to 750 nm, which are normalized at the maximum.

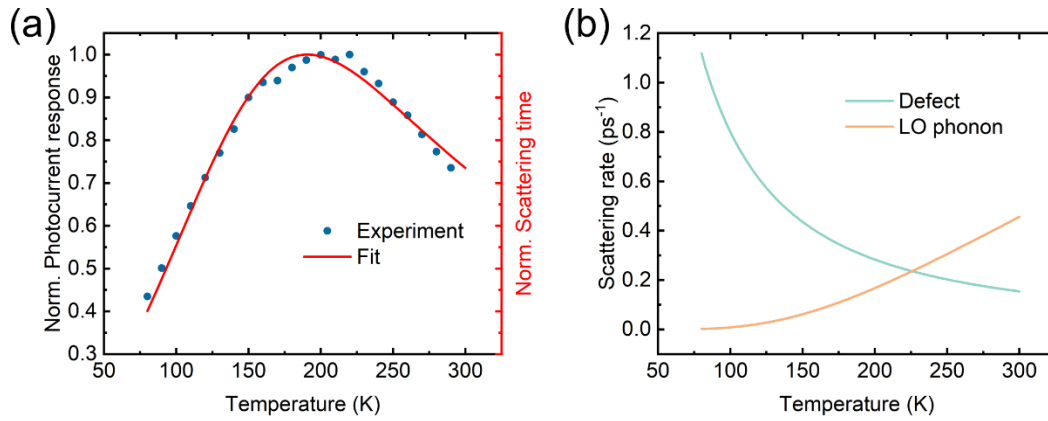


Figure 6.6 Correlation between photocurrent response and carrier scattering time at different temperatures. (a) normalised photocurrent response (blue dots) and fits by normalised carrier scattering time (red curve). (b) rates of carrier scattering with defects and LO phonons, reproduced from the fitting parameters obtained in (a).

Surprisingly, in Fig 6.6 (a), the temperature-dependent photocurrent response intensity shows a volcano shape: an increase from 290 K to 200 K followed by a decrease from 200 K to 80 K. The increased photocurrent responses indicate a band-like transport, suggesting an insulator-to-metal transition induced by the photoexcitation,²⁴⁹ which is different from the hopping transfer in dark environment (Fig 6.2). Similar band-like transport has been observed in multilayer MoS₂ based FETs when the gate voltage is greater than 1.4 V: current between the source and drain increases at lower temperatures.^{14,249} This similarity invokes the following model about carrier mobility.

The insulator-to-metal transition can be caused by generating substantial FC density, resulting to the Fermi level higher than the CB.²⁴⁹ However, in the studies of FETs, only the increasing current is discussed above 200 K, which can be fitted by a power law function of temperature.^{249,250} This chapter attempts to fully describe the volcano-shape photocurrent responses from 290 K to 80 K by electron scattering with LO phonons and defects.

Photocurrent, I_{ph} , is proportional to the carrier density, n_c , and carrier mobility, μ :

$$I_{ph}(T) \propto n_c(T) \times \mu(T) \quad \text{Eq. 6.4}$$

The $n_c(T)$ is proportional to the optical absorption at different temperatures, shown in Fig 6.5 (b). The change of optical absorption at different temperatures is negligible. Therefore, the temperature-dependent carrier mobility can represent the photocurrent responses. Previous studies have shown that the carrier mobility scales the e-ph scattering time, $\tau_{e-ph}(T)$.^{26,251}

$$\mu(T) = \frac{e}{m^*} \tau_{e-ph}(T) \quad \text{Eq. 6.5}$$

Therefore, the measured photocurrent scales linearly with the carrier scattering time. The e-ph scattering time shows the contributions from both phonons and impurities following Matthiessen's law.^{26,251,252}

$$\frac{1}{\tau_{e-ph}(T)} = \gamma_{e-ph}(T) = \gamma_{ac}(T) + \gamma_{LO}(T) + \gamma_{def}(T) \quad \text{Eq. 6.6}$$

where $\gamma_{e-ph}(T)$ is the total e-ph scattering rate, $\gamma_{ac}(T)$, $\gamma_{LO}(T)$, and $\gamma_{def}(T)$ are the e-

ph scattering rate due to acoustic phonons, LO phonons and defects, respectively. The contribution of $\gamma_{ac}(T)$ is negligible.^{26,252}

The term $\gamma_{LO}(T)$ can be simplified as:²⁶

$$\gamma_{LO}(T) = a_{LO} \exp\left(-\frac{E_{LO}}{k_B T}\right) \quad \text{Eq. 6.7}$$

where a_{LO} is a temperature-independent prefactor including polaron effective mass, LO phonon energy, and Fröhlich constant, and E_{LO} is the energy of LO phonon.

The defect scattering rate reads:

$$\gamma_{def}(T) = a_{def} \times T^{-3/2} \quad \text{Eq. 6.8}$$

where a_{def} is a temperature-independent prefactor characterizing the strength of defect scattering.

Following the above model (Eq. 6.5-6.8), as shown in Fig 6.6 (a), the normalised photocurrent responses can be well reproduced by the carrier scattering time. Carrier scattering with defects and LO phonons has been observed in the multilayer MoS₂ film by photoconductivity studies.²⁵² The parameters used in the fitting are listed in Table 6.2. The rates of carrier scattering with defect and LO phonon are reproduced in Fig 6.6 (b) with the parameters in Table 6.2.

Table 6.2 The fitting parameters of the carrier scattering time.

a_{LO}	3.4×10^{12}
E_{LO} (meV)	51.8
a_{def}	8×10^{14}

Fig 6.6 (b) shows that the carrier scattering with LO phonons dominates the charge transport above 220 K, and the carrier scattering with defects dominates at lower temperatures. As shown in Table 6.2, the fitted phonon energy is not significantly different from the LO phonon energy measured in Raman spectroscopy, as shown in Fig 6.3 (b). The low average phonon energies shown in Table 6.1 can be attributed to the effect of scattering with defects during the transport within the multilayer MoS₂ network.

However, this classic model cannot distinguish the contribution of LO phonons and zone-edge acoustic phonons which have similar energies and dominate intervalley scattering.^{83,177,178} Although zone-edge acoustic phonons can provide the momentum needed for carriers to scatter between valleys—thereby impacting carrier mobility—an external electric field was applied during photocurrent measurements. This field creates a potential difference between the two electrodes, enabling carriers to drift consequently. Therefore, carrier scattering with zone-edge acoustic phonons may not have substantial impact on the results shown in Fig 6.6 (a). Further studies are required to quantify the effect of electron-zone-edge-phonon scattering during the transport across the network of multilayer MoS₂ flakes and within an individual flake.

6.3.2 Time-resolved spectroscopy

The band-like transport and scattering of FC have been discussed in the previous sections. However, the origins of the FCs cannot be determined from steady-state measurements alone. Therefore, this section summarizes evidence from various types of ultrafast spectroscopy measurements, which can indicate the origins of the FCs in multilayer MoS₂.

6.3.2.1 Transient absorption spectroscopy

To investigate the photophysics of the multilayer MoS₂, TA spectroscopy with visible and NIR probes has been performed with 400 nm excitation at the fluence of 14.5 $\mu\text{J cm}^{-2}$. The TA results are shown in Fig 6.7 (a). In the visible region (450 nm to 750 nm), three negative peaks are observed around 670 nm, 610 nm, and 450nm, which are assigned to the GSB signal of A, B, and C excitons. The three positive peaks are assigned to the PIA signal of the three types of excitons. No significant peak shifts can be observed for A and B exciton GSB. In the NIR region (850 nm to 1400 nm), only broadband features can be observed but with sign change. At early time (< 1 ps) and late time (> 100 ps), a broadband PIA signal can be observed, which can be assigned to exciton and/or FCs. However, from 1 ps to 20 ps, the signal turns to a broadband GSB signal. The sub-bandgap GSB can be caused by depopulation of the carriers from the defects (i.e., locating within the bandgap) to the CB. This observation is different from previous studies which illustrate resonant sub-bandgap GSB peaks of some specific trap states, such as S vacancies and edge states.^{161,235,253} The sub-bandgap broadband GSB feature indicates a semi-continuous distribution of the trapped carriers within the bandgap, rather than locating on a narrow range of energy levels.

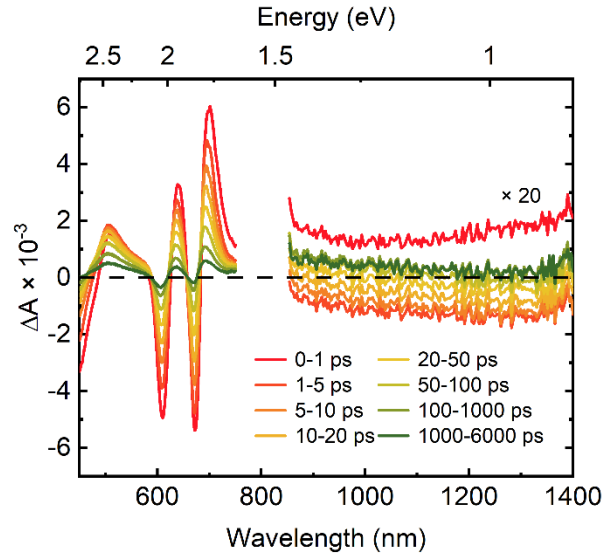


Figure 6.7 TA measurement of multilayer MoS₂ excited at 400 nm at room temperature.

TA response is a mixture of signals coming from substantial photophysical processes and quasiparticles, which always make the data interpretation complicated or even incorrect. For example, although FCs are the most logical assignment of the long-lived (> 6 ns) component in the TA measurements, this long-lived component can be caused by free and/or trapped carriers and indirect excitons.^{102,109,235,254} Therefore, this section does not aim to interpret the TA responses with more details. To selectively investigate the dynamics of some specific quasiparticles, other time-resolved spectroscopic methods have been developed.

6.3.2.2 Pump-push-photocurrent spectroscopy

Ultrafast photocurrent spectroscopy has been used in 2D material-based devices with the excitation by two laser pulses separated by a variable time delay.^{255–258} In many studies, the two laser pulses have the same photon energies (above the bandgap), which is similar to autocorrelation measurements.^{256,258} The typical signal observed in such experimental configuration is that a dip of photocurrent at the overlap of the two pulses and symmetric exponential recovery signal on the both negative and positive delays.

^{256,258} This nonlinear photocurrent response has been attributed to the depopulation of the GS by one pulse, which decreases the available carriers to be excited by the second pulse.^{256,258} However, high-order recombination of the carriers excited by the two above-gap pulses cannot be eliminated due to the high carrier density.

As discussed in section 3.2.5, PPPc spectroscopy consists of an above-bandgap pump and a sub-bandgap push. Ideally, the push pulse only interacts with the excited states generated by the pump. With the NIR push pulse, the bound states can be re-excited to generate more FCs and contribute to additional photocurrent. However, as discussed in Chapter 4, the FCs can only be thermalised and relax to the original excited state before the arrival of the push pulse within a few ps without increasing photocurrent.^{254,259} Therefore, PPPc spectroscopy is sensitive to the bound states rather than the FCs.

Fig 6.8 summaries the results of PP and PPPc dynamics of the MoS₂ photodetector with 600 nm excitation and 2000 nm push (or probe). Fig 6.8 (a) shows the PP dynamics of the multilayer MoS₂ probed at 2000 nm at different pump fluences. The PP dynamics is assigned to exciton dynamics.^{59,153} The excitons do not undergo exciton-exciton annihilation, which is different from SL TMDs.^{75,99–101} The absence of exciton-exciton annihilation indicates localised excitons which may be caused by strong e-ph coupling. The exciton dynamics can be fitted by a monoexponential decay convoluted with the pump pulse duration (~100 fs), shown in the solid line in Fig 6.8 (a). The extracted lifetimes at different fluences are shown in Fig 6.8 (b), scattering around 2 ps. Therefore, the exciton lifetime is determined around 2 ps in the multilayer MoS₂.

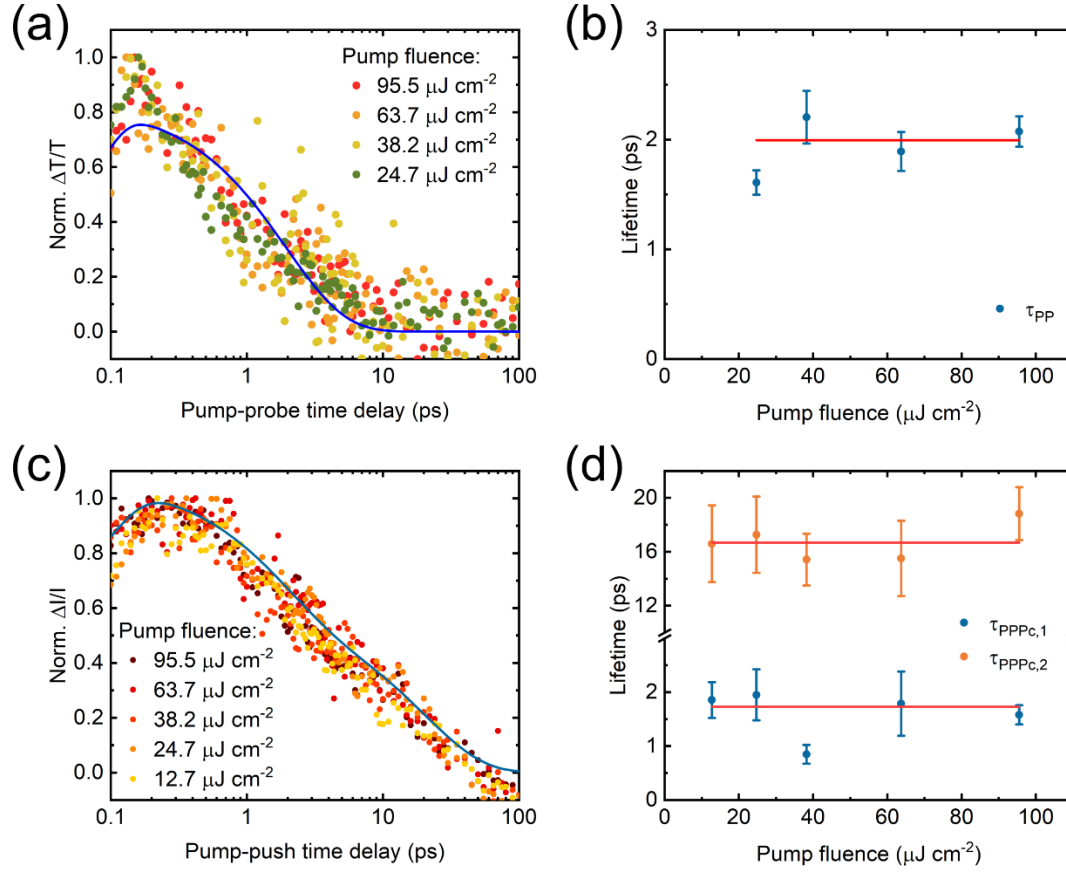


Figure 6.8 Normalised PP and PPPc dynamics of multilayer MoS₂ photodetector excited at 600 nm at room temperature. (a) PP dynamics with monoexponential fit. (b) PP lifetimes at different pump fluences. (c) PPPc dynamics with biexponential fit. (d) PPPc lifetimes at different pump fluences.

Fig 6.8 (c) shows the PPPc dynamics of the multilayer MoS₂ photodetector with 2V with the 2000 nm push fluence at 3.2 mJ cm⁻². It is noted that the push pulse by itself can generate a noticeable current in the device. This current is from the direct excitation of sub-bandgap states of the multilayer MoS₂ by the 2000 nm photons of the push pulse. This push-only induced current does not depend on the delay between the pump and push pulses (Fig 6.9).

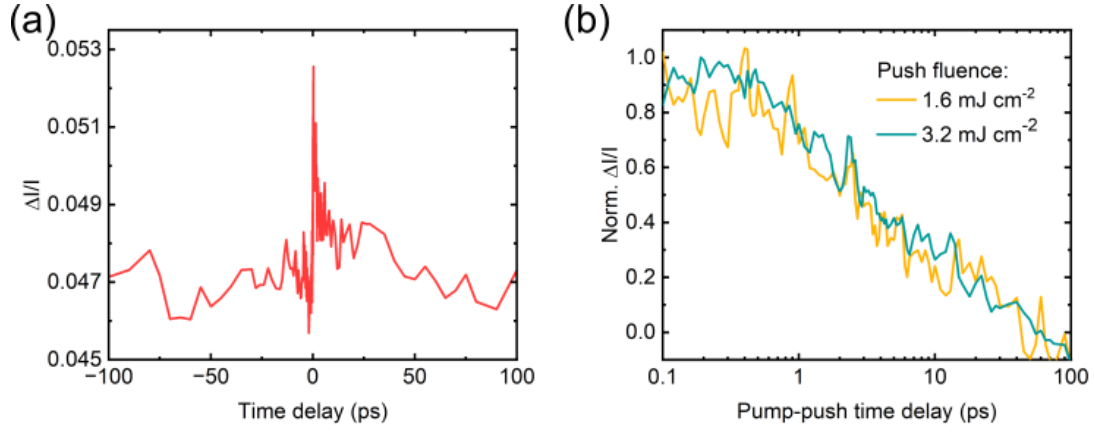


Figure 6.9 Baseline in PPPc measurement of multilayer MoS₂ photodetector. (a) PPPc signal without baseline correction. (b) PPPc signal with different push fluences.

Fig 6.9 (a) shows the PPPc signal with the 600 nm pump fluence at $95.5 \mu\text{J cm}^{-2}$ and 2000 nm push fluence at 3.2 mJ cm^{-2} without baseline correction. Before time zero (i.e., the overlap between the pump and push pulses), a push-only-induced photocurrent baseline can be observed, which is independent of the time delay between the two pulses. To further confirm that the push induced photocurrent does not change the PPPc signal, PPPc measurements with different push fluences (at constant pump fluence) are shown in Fig 6.9 (b). This pump-push delay time independent background signal is subtracted in the data presented in Figs 6.8 and 6.10.

Similar to the PP measurements, the PPPc dynamics is also independent on the pump fluences. However, comparing the PP dynamics, the PPPc dynamics shows an additional longer-lived component. The PPPc dynamics can be fitted by a biexponential decay, shown in the solid curve in Fig 6.8 (c). The fitted lifetimes are summarised in Fig 6.8 (d) at different pump fluences. The two lifetimes are around 1.7 ps and 17 ps, which do not depend on the pump fluences. Since the lifetime of the first component is similar to the exciton lifetime obtained in PP measurements, the first component is assigned to exciton, and the longer-lived component is assigned to trapped exciton.

In PP configuration, the excited states are detected by the transmittance change of the probe beam. Therefore, the excited states absorption at the probing wavelength cannot be too weak so that these states can be detected optically. However, trap states normally do not have strong optical absorption, which cannot be easily detected in PP method.²⁵⁴ Comparing to optical detection, in PPPc spectroscopy, photocurrent detection is more sensitive to the push-induced additional FCs from the bound states including excitons, polarons, and traps.^{130,254,259–264} In addition, the push fluence in PPPc method is orders or magnitudes stronger than the probe fluence in PP spectroscopy.

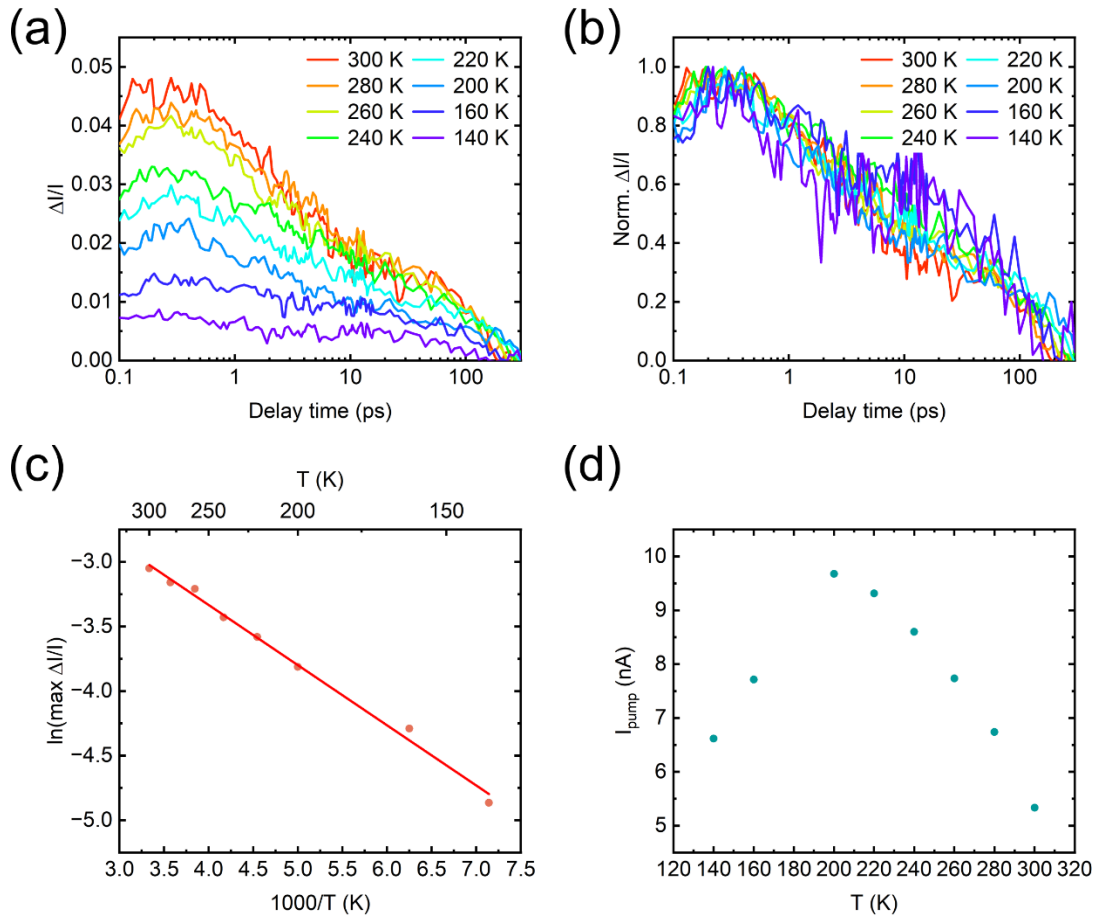


Figure 6.10 Temperature-dependent PPPc dynamics of multilayer MoS₂ photodetector. (a) and (b) PPPc dynamics and normalised dynamics measured from 300 K to 140 K. (c) Arrhenius plot of the maximum of PPPc signal of multilayer MoS₂ device. (d) pump induced photocurrent at the measured temperatures.

To understand the energetics of the excitons in the multilayer MoS₂, PPPc measurements have been performed from 300 K down to 140 K. Fig 6.10 (a) shows the PPPc dynamics of the device as a function of temperature. The PPPc dynamics is normalised at the maximum amplitude of each temperature, shown in Fig 6.10 (b). The dynamics does not show significant change with the temperature.

According to Eq. 3.11, $\Delta I/I$ is expected to increase at lower temperatures, because the exciton dissociation is suppressed due to the binding energy, resulting in an increased ratio of the population of the bound states to the population of free states, and the obtained activation energy is attributed to the binding energy of the excitons.^{130,260} However, the amplitude of the PPPc signal in the multilayer MoS₂ device decreases monotonically as the reduce of the temperature, which does not agree with the previous PPPc studies of excitonic states in organic solar cells.^{130,260} By using Arrhenius analysis,¹³⁰ $\ln(\max \Delta I/I)$ are plotted against $1/T$ with a linear fit, as shown in Fig 6.10 (c). The obtained activation energy is 40.1 ± 1.3 meV. However, this activation energy should not be assigned to the binding energy of the bound states (i.e., exciton).

To explain the decreased $\Delta I/I$ at lower temperatures in the multilayer MoS₂ device, there are two potential reasons: (i) push-induced FCs originating from the bound states have different mobility or extraction rate compared to pump-induced FCs, making Eq. 3.11 not applicable; (ii) the dissociation of the bound states to the free states is negligible, but the bound states interacting with the push pulse is converted to other states at lower temperatures, such as dark states or deep traps.

Fig. 6.8 (d) shows that the pump-induced photocurrent (I_{pump}) at different temperatures follows the same trend observed in the steady-state measurements presented in Fig. 6.4 (a). If the reason (i) is correct, the maximum of $\Delta I/I$ should not change monotonically

as the reduce of temperature, instead, the trend of $\Delta I/I$ is expected to follow the trend of I_{pump} . According to the studies of SL TMDs, bright excitons to dark exciton transition at lower temperatures has been widely observed with the energy barrier of tens of meV.^{107,108} Based on the understandings of SL TMDs, reduced $\Delta I/I$ at lower temperatures is attributed to the conversion of the excitons into dark states (including deep traps) in the multilayer MoS₂ and the dissociation of such excitons is negligible.

Considering the inhomogeneous distribution of defect states, temperature-dependent PPPc measurements were conducted on four different devices, including the device used in the measurements for Fig. 6.10. As shown in Fig. 6.11, while the activation energies obtained from the four devices vary, a consistent decrease in $\Delta I/I$ at lower temperatures is observed. These results further confirm the occurrence of exciton trapping in multilayer MoS₂ photodetectors.

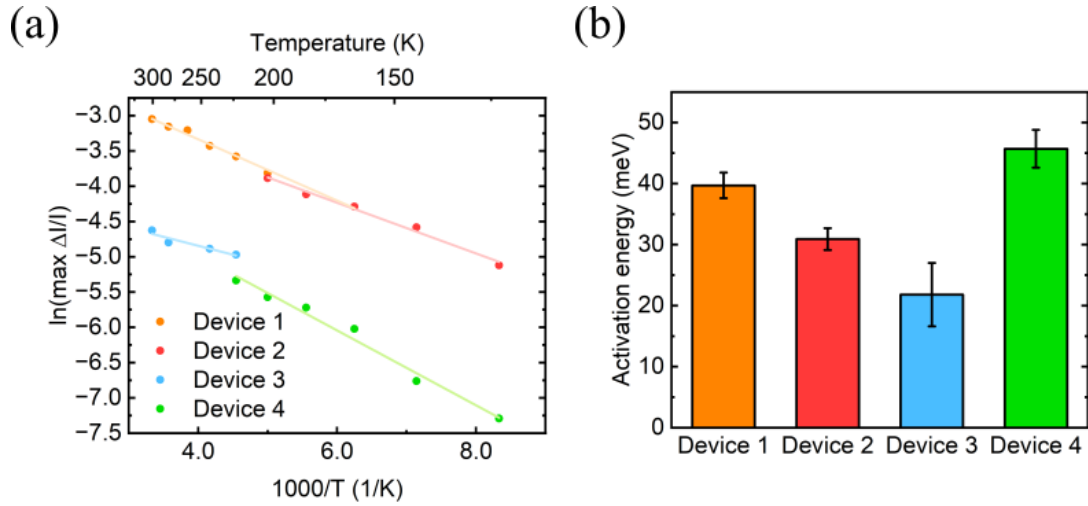


Figure 6.11 Reproducibility of temperature-dependent PPPc measurements of four MoS₂ photodetectors. (a) Arrhenius plot of the maximum of PPPc signal of four multilayer MoS₂ devices. (b) Summary of the activation energy from the four devices.

6.4 Conclusions

This chapter demonstrates the application of steady-state and time-resolved photocurrent spectroscopies to investigate the photophysics of ESs in the multilayer MoS₂ photodetector. Steady-state photocurrent spectroscopy proves the existence of sub-bandgap carriers indicating a defective material. However, in a flake-based network with noticeable defect density, photoexcited FCs exhibit band-like transport. Above 220 K, carrier-LO phonon scattering dominates, resulting in an increase in photocurrent as the temperature decreases. However, below 200 K, carrier-defect scattering becomes the dominant mechanism, leading to a reduction in photocurrent with further decreases in temperature. PPPc and PP spectroscopies were performed to study the dynamics of excitons in the multilayer MoS₂ photodetector. Exciton-exciton annihilation is absent at room temperature, which can be caused by strong coupling with phonons. The ratio of the population of excitons to that of FCs decreases monotonically as the reduce of temperature, which indicates that the excitons can be converted to dark states and exciton dissociation is negligible. Therefore, substantial FCs can be directly generated by optical excitation in the multilayer MoS₂. Fig 6.11 summarises the energy diagram of the multilayer MoS₂.

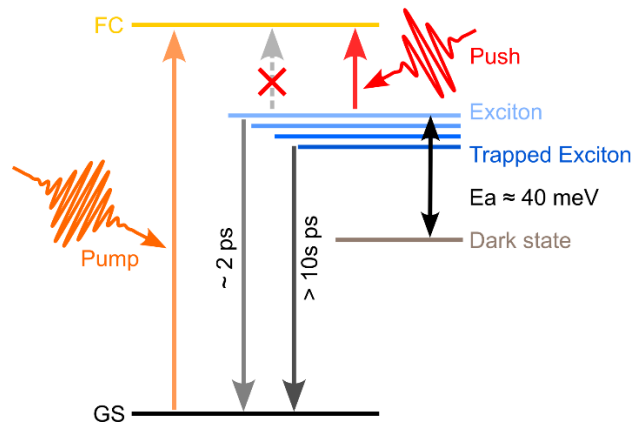


Figure 6.12 Energy diagram of excited states in multilayer MoS₂.

Chapter 7 Summary and Outlook

7.1 Key findings of this thesis

In this thesis, ultrafast spectroscopy methods have been implemented to investigate the photophysics of excited states in two classes of 2D materials: semiconducting TMDs (**Chapter 4 and 6**) and metallic MXenes (**Chapter 5**). The general characteristics of 2D materials, the principle photophysics their excited states, and the basic details of the spectroscopic methods used to study them are outlined in **Chapter 1 to 3**.

In **Chapter 4**, the PPP spectroscopy was used to investigate the hot carrier cooling dynamics in SL WS₂. Compared to the conventional PP (including TA) spectroscopy, PPP spectroscopy directly illustrates the impact of hot and cold carrier densities and hot carrier excess energy without contaminating the signal by many-body interactions, such as Auger recombination. At a constant cold carrier density (i.e., pump fluence), by increasing the hot carrier density (i.e., push fluence), the cooling dynamics in SL WS₂ slows down to a few picoseconds, which was attributed to the typical HPB effect. However, by carefully raising the cold carrier density, the HPB effect in SL WS₂ can be weakened, which was assigned to the carrier-carrier interactions. By altering the hot carrier excess energy (i.e., push photon wavelength), the hot carrier cooling rate scales linearly with the excess energy. Interestingly, when the excess energy is high enough,

a portion of hot carriers can be trapped without relaxing down to the band edge.

Chapter 5 examines carrier and lattice cooling dynamics in the metallic Ti_2CT_x MXene thin films, in comparison to the widely studied $\text{Ti}_3\text{C}_2\text{T}_x$ MXene thin films. Different from the semiconducting TMDs, PPP method is not applicable to study the carrier relaxation of the metallic MXenes. Conventional TA spectroscopy was used to investigate the carrier cooling in MXenes in from sub-picosecond to nanosecond timescale. The carrier cooling time in Ti_2CT_x is ~ 2.6 ps, which is 1 ps longer than the cooling time in $\text{Ti}_3\text{C}_2\text{T}_x$, without undergoing HPB effect. The main feature of TA spectra of both MXene films can be described as thermochromic effect (i.e., heated lattice after carrier cooling). To investigate the lattice cooling dynamics, PP spectroscopy from nanosecond to microsecond timescale was performed. In both Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ films, the heat dissipation from the material lattice to the environment takes as long as hundreds of nanoseconds. The thermal diffusivities of Ti_2CT_x ($\sim 0.06 \text{ mm}^2 \text{ s}^{-1}$) and $\text{Ti}_3\text{C}_2\text{T}_x$ ($\sim 0.02 \text{ mm}^2 \text{ s}^{-1}$) films were extracted by fitting with a 1D thermal diffusion model, which are orders of magnitude lower than typical metals.²²⁶ The small thermal diffusivity is attributed to the inefficient inter-flake heat transfer.

Chapter 6 investigates the photophysics of excited states in the multilayer MoS_2 photodetector by steady-state and ultrafast photocurrent spectroscopies. The steady-state photocurrent response spectrum exhibits the fact of trapped carriers locating within the bandgap in equilibrium, which can be caused by unintentional doping by the defects in the material. The photocurrent amplitude increases as the temperature cooling down from 290 K to 220 K, which was attributed to reduced electron-LO phonon scattering. Below 220 K, the photocurrent amplitude decreases at lower temperatures,

which was assigned to increased carrier scattering with the defects. To understand interplay between free carriers and excitons, PPPc spectroscopy has been performed to investigate the exciton dynamics in the multilayer MoS₂ photodetector. No evidence of exciton-exciton annihilation was observed by changing the exciton density (i.e., pump fluence). However, at lower temperatures, the ratio of the population of exciton to that of free carriers decrease monotonically, which was assigned to the transition from exciton to dark states rather than dissociation to generate free carriers. The activation energy between the exciton and dark states was estimated ~40 meV.

7.2 Outlook

As discussed in the previous chapters, ultrafast spectroscopy has emerged as a powerful technique for investigating the dynamic processes in 2D materials, offering valuable insights into their electronic and optical properties on femtosecond to picosecond timescales. This method is particularly advantageous for studying the rapid excited state dynamics, such as exciton formation, carrier relaxation, and energy transfer processes, that are crucial for the functionality of 2D materials in optoelectronic devices.^{67,70,265–}

²⁶⁷ The ability to resolve these ultrafast processes provides a deeper understanding of the material's intrinsic properties, which can lead to the development of more efficient photovoltaic cells, transistors, and other nanodevices. As research of 2D materials continues to advance, ultrafast spectroscopy is expected to play a central role in exploring new material systems, tuning their properties through various material engineering (such as strain and chemical doping), and guiding the design of next-generation applications.^{109,161,233}

Developing new ultrafast spectroscopic methods is crucial for the field, as they can

provide direct evidence of various photophysical processes. The studies presented in Chapters 4 through 6 highlight the potential of these advanced ultrafast spectroscopic techniques in understanding the photophysics of 2D materials, paving the way for further research in this area.

In Chapter 4, hot carrier trapping in SL TMDs has been observed with PPP spectroscopy. However, the study was unable to uncover the origin of these trap states. By controlling the variety and density of defects, more fundamental insights into the mechanisms of hot carrier trapping in SL TMDs are expected to be gained.

Although Chapter 5 highlights the slow thermal transport in MXene thin films, the PP methods used in the study are unable to detect in-plane heat dissipation. To investigate in-plane thermal transfer in MXene thin films or single flakes, ultrafast microscopy could be applied to measure in-plane heat diffusion directly.

In Chapter 6, PPPc spectroscopy with NIR push has been applied to investigate the bound state dynamics in the multilayer MoS₂ device. This approach can be extended to investigate the bound states in SL TMDs and other semiconducting 2D materials and heterojunctions. However, using NIR push does not reveal all details of the bound states' photophysics, such as the dynamics of trions and other exciton complexes, because the NIR photon energy is higher than their resonant energies. Therefore, reducing the push photon energy down to mid-IR or THz range, one can observe more details about the bound state dynamics with the acquisition of spectral resolution.^{59,268–}

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