



DPhil THESIS

Tuning the Electrical and Optical Properties of Two Dimensional Materials

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*A thesis submitted in fulfilment of the requirements
for DPhil Degree*

in the

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Department of Materials

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Declaration of Authorship

I, Zhengyu HE, declare that this thesis titled, 'Tuning the Electrical and Optical Properties of Two Dimensional Materials' and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

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Abstract

Tuning the Electrical and Optical Properties of Two Dimensional Materials

by Zhengyu HE

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in pursuit of DPhil Degree, Trinity Term, 2016

The emergence of 2D materials inspires the pursuit of all-2D materials based devices which are predicted to outperform those with conventional architectures and materials. To achieve this goal, thorough understanding of the fundamental electrical and optical properties of 2D materials separately and the ability to manipulate these properties *via* external modulation methods are essential.

Graphene can perform as transparent electrodes, yet suffering from its high sheet resistance. It was demonstrated that it can be greatly reduced *via* doping iron (III) chloride solution onto graphene film with high optical transmission at visible range if an optimal dopant solution concentration was employed. Doping with nanoscale spatial resolution was then achieved with the help of aberration-corrected transmission electron microscope, allowing *in-situ* observation of the atomic structures of doped regions, which possess unique properties predicted by DFT calculations.

Transition metal dichalcogenides (TMDCs) can perform as active materials due to their sizeable bandgap. Therefore, the focus of this thesis then shifted to the investigation of WS₂. Three different methods were employed to alter the optical properties of WS₂. Firstly, the photoluminescence (PL) of WS₂ presents layer dependent response towards lateral electric field, with PL quenching in monolayer and PL enhancement in bilayer. The results of temperature dependent PL measurement ruled out the joule heating effect. A possible mechanism based on the inter-valley electron transfer induced recombination pathways modification was then proposed.

Secondly, high optical pump power was used to create dense excitons environment to explore the higher order excitonic species in WS_2 with focus on the discussion on bilayer case. It showed that bright biexcitons could be formed in as-grown bilayer WS_2 but was absent in transferred sample due to the release of strain. This work demonstrated the strong many-body interaction even in bilayer WS_2 and the effect of strain on the band structure of TMDCs.

The stability of TMDCs in ambient conditions is of great importance for their future applications. The last part showed that monolayer WS_2 stored in ambient conditions for 2 months went through severe degradation yet without additional PL peak emerging even under cryogenic environment. It was then demonstrated that the degradation related PL peak was buried by the adsorbents on WS_2 surface and could be revived after a novel cryogenic laser processing technique, which could be a non-invasive method to probe the defect states in monolayer TMDCs.

Acknowledgements

I want to express my greatest gratitude to my supervisors because this DPhil project cannot be accomplished without their patient guidance. First and foremost, I want to thank my principal supervisor, Professor Jamie Warner. He offered me sufficient freedom in the project so that I can develop my own research interest. Meanwhile, he can always provide constructive and visionary suggestion and supervision when I get lost. I also want to thank Professor SeungNam Cha and Dr. Jung Inn Sohn for sharing their knowledge and expertises in devices fabrication, which greatly expands my skill sets. I would also like to thank professor Angus Kirkland for his insightful discussion.

The project has been supported by many other people, without which it will be much harder for me to complete it. Special thanks should be given to Professor Jason Smith for his generosity of lending the cryostat and liquid nitrogen Dewar to me, which played an important role in the last two chapters of this thesis. I also want to thank Dr. Mercè Pacios Pujadó and Professor Harish Bhaskaran for allowing me to get access to their fantastic AFM. Professor Gun-Do Lee from Seoul National University and Mr. Shaoqiang Guo and Professor Junying Zhang from Beihang University performed DFT calculations which provided sound theoretical backup for this thesis. I would also like to thank all my dear group members for their help, cooperation and collaboration. In particular, I want to thank Dr. Kuang He and Dr. Alex Robertson for their TEM characterization, Mr. Xiaochen Wang for the AFM characterization and Dr. Youmin Rong, Ms. Wenshuo Xu and Ms. Yingqiu Zhou for the WS₂ preparation.

Last but not least, I want to thank my parents and my grandmother for their unconditional support and love, which offer me the courage and confidence to overcome any difficulties and challenges that I come across. I would also like to thank my wife, Ms. Weiyue Chen, for her understanding and love, which has been one of my biggest motivation to achieve the greatness. Weiyue will also finish her PhD project soon and I wish everything goes very smooth with her.

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Publications

This section lists the publications produced during the DPhil research projects. The results part of this thesis are mainly based on the 4 first-author publications and the co-author publications are beyond the purview of this thesis.

First Author Publications

1. **Z. He**, X. Wang, W. Xu, Y. Zhou, Y. Sheng, Y. Rong, J. M. Smith, J. H. Warner, Revealing Defect-State Photoluminescence in Monolayer WS₂ by Cryogenic Laser Processing, **Just Accepted in ACS Nano**.
2. **Z. He**, W. Xu, Y. Zhou, X. Wang, Y. Sheng, Y. Rong, S. Guo, J. Zhang, J. M. Smith, J. H. Warner, Biexciton Formation in Bilayer WS₂, *ACS Nano*, 10(2), **2016**, 2176-2183.
3. **Z. He**, Y. Sheng, Y. Rong, G-D. Lee, J. Li, J. H. Warner, Layer-Dependent Modulation of Tungsten Disulfide Photoluminescence by Lateral Electric Fields, *ACS Nano*, 9(3), **2015**, 2740-2748.
4. **Z. He**, K. He, A. W. Robertson, A. I. Kirkland, D. Kim, J. Ihm, E. Yoon, G-D. Lee, J. H. Warner, Atomic Structure and Dynamics of Metal Dopant Pairs in Graphene. *Nano Letters*, 14(7), **2014**, 3766-3772.

The results chapters are based on the corresponding references shown as follows:

- Reference 1: Chapter 4
- Reference 2: Chapter 5
- Reference 3: Chapter 6
- Reference 4: Chapter 7

Co-Author Publications

1. L. C. Flatten, D.M. Coles, **Z. He**, D.G. Lidzey, R.A. Taylor, J.H. Warner, J.M. Smith, Electrically Tunable Mixing of Organic-Inorganic Hybrid Polaritons with Two-Dimensional WS₂, **In preparation**
2. L. C. Flatten, **Z. He**, D.M. Coles, A.W. Powell, R.A. Taylor, J.H. Warner, J.M. Smith, Room-Temperature Exciton-Polaritons with Two-Dimensional WS₂ in an Open Microcavity, **submitted to Scientific Report**.
3. M. Pacios, P. Hosseini, Y. Fan, **Z. He**, O. Krause, J. Hutchison, J. Warner, H. Bhaskaran, Direct manufacturing of ultrathin graphite on three-dimensional nanoscale features, *Scientific Report*, 6,**2016**,22700.
4. Y. Sheng, W. Xu, X. Wang, **Z. He**, Y. Rong, J. H. Warner, Mixed Multilayer Vertical Heterostructures Utilizing Strained Monolayer WS₂, *Nanoscale*, 8, **2016**, 2639-2647.
5. H. Tan, Y. Fan, Y. Rong, B. Porter, C. S. Lau, Y. Zhou, **Z. He**, S. Wang, H. Bhaskaran, J. H. Warner, Doping Graphene Transistors Using Vertical Stacked Monolayer WS₂ Heterostructures Grown by Chemical Vapour Deposition. *ACS Applied Materials and Interfaces*, 8(3), **2016**,1644-1652.
6. Y. Rong, Y. Sheng, M. Pacios, X. Wang, **Z. He**, H. Bhaskaran, J. H. Warner, Electroluminescence from Grain Boundary Regions in Monolayer WS₂, *ACS Nano*, 10(1), **2016**, 1093-1100.

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7. Y. Sheng, Y. Rong, **Z. He**, Y. Fan, J. H. Warner, Uniformity of Large-Area Bilayer Graphene Grown by Chemical Vapour Deposition, *Nanotechnology*, 26(39), **2015**, 395601.

Chapter 1

Introduction

1.1 Project Aims

This doctorate research project aims to characterize and modulate the electrical and optical properties of two different types of 2D materials, graphene and transition metal dichalcogenides in which WS_2 is chosen as an typical example.

1.2 Thesis Scope

This thesis covers the research results I obtained in the past 3.5 year DPhil course funded by China Scholarship Council (CSC) and China Oxford Scholarship Fund (COSF) in the Department of Materials, University of Oxford.

Chapter 2 presents a literature review on the latest progress of 2D materials, which can be separated into two parts. The first part starts with a brief introduction to the history and properties of graphene and propose the most reachable graphene based application, transparent conductive electrodes (TCEs), followed by the discussion of the challenges and the possible methods to overcome them by doping. The second part emphasizes on

the review of the properties of TMDCs, with a particular focus on optical properties and the possible methods that can modulate the PL of TMDCs.

The details of experimental methods are briefly described in chapter 3, including important operation procedures, instruments models, experimental parameters and data analysis software and techniques.

The first section of chapter 4 mainly investigates the electrical and optical properties FeCl₃ doped graphene. The doped graphene sample was then transferred to TEM grid and handed over to Dr. Kuang He and Dr. Alex Robertson, from which they obtained very high quality atomic resolution TEM data. The second section of this chapter focuses on the analysis the AC-TEM data and the construction the initial atomic models. These models were then sent to Professor Gun-Do Lee who performed DFT calculations on these structures. The analysis of the DFT calculation results provides insights into understanding the unique properties of these structures.

The development of 2D materials leads to the emergence of many other materials including black phosphorus and metal dichalcogenides, which possesses even more exciting properties than graphene, rendering them promising candidates as active materials in optoelectronics. Therefore, the research interest is then shifted to WS₂, a typical example of metal dichalcogenides. WS₂ samples were prepared by chemical vapour deposition (CVD). The CVD parameters were developed by Dr. Youmin Rong and further optimized by Ms. Wenshuo Xu and Ms. Yingqiu Zhou who provided many high-quality samples, which is crucial to the completion of this project. The design and construction of an user-friendly PL micro-spectrometer by myself under the supervision of Professor Jamie Warner forms a keystone for this project. The high flexibility of this home-built instrument allows the integration of other system such as electrical unit or a cryostat. Meanwhile, the measurement program based on LabVIEW designed and coded by myself realizes the synchronization of the optical and electrical measuring systems.

Chapter 5 investigates the modulation of photoluminescence of tungsten disulphide with lateral electric field and its possible theoretical explanation. This reveals the behaviour of ground-state excitons towards electric field. The experiment idea is firstly proposed by Professor Jamie Warner and the further experiments design and data analysis are done by myself. Chapter 6 mainly focuses on monitoring the PL response of TMDCs under high optical pump and influence of strain on this effect. The DFT calculations were performed by Mr. Shaoqiang Guo and Professor Junying Zhang from Beihang University, which provides sound theoretical backup to this work. Chapter 7 discusses the effect of the degradation and adsorbents on the PL monolayer WS₂ in air. A novel laser processing technique was adopted to revive the defects related PL peak under cryogenic environment by removing the adsorbents. The last two projects relies heavily on the cryostat borrowed from Professor Jason Smith, to whom I would like to express my greatest gratitude for his generosity.

The last chapter briefly summarizes and concludes the whole thesis. Based on the results obtained, a brief plan for the future work as extension to this project is proposed.

Chapter 2

Literature Review

2.1 Introduction

The ever-increasing demands for faster, lighter and more energy efficient electronic and optoelectronic devices have almost exhausted the potentials of the existing materials, which will result in a huge gap between need and actual device performance in the near future. This calls for the revolution in the materials industries. The emergence of two-dimension family including graphene and transition metal dichalcogenides (TMDCs) are expected to close this gap. This chapter presents a review of the nascent development of 2D materials with a particular focus on the graphene and TMDCs. The researches of past decades on graphene pointed out the most promising and close-to-target application is transparent conductive electrodes (TCEs). Therefore, rather than being a broad review, the first part of this chapter emphasizes on the discussion related to TCEs applications, including the exploration of the intrinsic electrical and optical properties and the possible routes to improve them by either doping or proper fabrication methods.

Compared with graphene, the research of atomically thin TMDCs are still in its infancy with much more uncertainty. Therefore, a broader scope is included in the second part, which mainly focus on the review of TMDCs. Starting from the history of TMDCs, the discussion then shifts to the properties of TMDCs with a particular emphasis placed on the optical properties and the ability to modulate the luminescence ability *via* various external modulation methods, followed by the review of existing synthesis methods. At the end of this part, possible applications based on TMDCs or the combination of graphene and TMDCs listed here are discussed.

2.2 Graphene

Graphene is single atomic layer of graphite with carbon atoms in a hexagonal lattice, which is first isolated from highly oriented pyrolytic graphite (HOPG) using mechanical exfoliation method.[1] It possesses exotic mechanical, electrical, optical and magnetic properties[2, 3, 4, 5], which allow it to become an ideal platform for physicists to observe physical phenomena experimentally, which once only lived in theoretical prediction. For example, Novoselov *et al.*[6] reported their experimental observation of quantum hall effect (QHE) at room temperature on graphene. This observation dramatically extends the QHE temperature from the previous value limited to the boiling temperature of liquid helium[7], to an unprecedented high point, which not only satisfies people's innate desire to observe quantum effect at ambient condition, but also fulfils the practical need to carry out precise metrology at room temperature. In addition, Schedin *et. al.*[8] claims that the transport of carriers in graphene are ballistic within sub-micrometer even with high charged impurities concentrations ($>10^{12}\text{cm}^{-2}$), and thus raises a fundamental question about whether charged impurities act as scattering centres thus the limiting factor to carrier mobilities. Other extensive studies on digging out the scientific values of graphene have been carried out, such as fractional quantum hall effect(FQHE)[9], flat low absorption over broad wavelength range[10],

direct observation of crystal lattice from suspended graphene[2] and so on. The discovery of graphene also brings great breakthrough to our knowledge of materials and thus, the fabrication and characterization of new 2D materials, which were theoretically predicted to be unstable[11], become an important ramification in materials research area. A lot of other 2D crystals have been isolated from bulk materials such as boron nitride (BN)[12], and TMDCs including molybdenum disulphide (MoS_2)[13] and tungsten disulphide (WS_2)[14], the progress of which will be discussed in section 2.3. In a word, graphene and other 2D materials have raised global interest and are becoming one of the most cutting-edge topic in today's scientific world.

In addition to the wealth that graphene brings to the scientific community, it has great potential for various practical applications[15]. Graphene was once predicted to be one of the most prospective alternatives to silicon in integrated circuits because of the ballistic transport property. People believe that logic transistors based on graphene, with higher speed and lower energy consumption, can be fabricated[16]. However, graphene based logic transistors cannot surpass the silicon-based ones in the short term because of its disadvantages such as poor on-off ratio[17] caused by its zero band gap. Although a lot of methods have been raised to open a band gap in graphene[18, 19], it can inevitably deteriorate other good properties such as high mobility.[20] Thus more feasible applications based on graphene are advanced including high frequency transistor, THz detector and generator and so on[21, 22, 23] which are all very promising. Yet there is still a very long way to go ahead for these applications. Another important and more close-to-target application is graphene based transparent conductive electrodes.[24] Due to its extremely low mass and high stiffness, graphene has also been demonstrated as an ideal active material for nanoelectromechanical resonator.[25]

Transparent conductive electrodes(TCEs) are now widely used in modern electronic products, such as organic light emitting diodes (OLEDs), solar cell, touch screens on smart phones and so on, and thus very important to our everyday life. It requires

materials with very low sheet resistance (less than $70 \Omega/\square$) and high optical transmittance (over 90% at 550 nm). Currently, metal oxide-based TCEs like doped indium oxide (In_2O_3), zinc oxide are the only products commercially available. Among these semiconductor TCEs, indium tin oxide (ITO) [26] is the most favourable material. ITO is an n-type semiconductor containing $\sim 90\% \text{In}_2\text{O}_3$, $\sim 10\% \text{SnO}_2$ and impurities Tin atoms, the concentration of which and the film thickness are the two main factors that determine the electrical and optical properties. Typically, the commercially available product is a layer of 140 nm ITO sputtered onto glass substrate with sheet resistance and transmittance of $\sim 10 \Omega/\square$ and 85% at 550 nm [27]. The excellent electrical and optical performance allow ITO to dominate the TCEs field for over 4 decades [28] despite of its disadvantages such as ever increasing cost of indium due to its scarcity, complicated deposition process, brittleness and so on. However, this trend is going to stop, because ITO fails to satisfy demand of the next-generation optoelectronic devices that TCEs should be lightweight, cheap, environment friendly and flexible in addition to transparent and conductive. For example, ITO based devices fails in bending tests easily, decaying severely after 200 cycles [29]. Additionally, the sheet resistance of ITO coated on flexible substrates like polyethylene terephthalate (PET) is $\sim 60\text{--}300 \Omega/\square$ [30], which is above the industrial threshold. Hence an alternative to ITO for next-generation flexible electronics is needed. There are a lot of candidates, including other metal oxide materials [31], metal grids [32], metallic nanowires [33], carbon nanotubes (CNTs) film [34] and graphene. Metal nanowire networks exhibits extremely high dc to optical conductivity ratios ($\sigma_{DC}/\sigma_{Op}=500$, see section 2.2.1.3), which is comparable with ITO, as well as electromechanical robustness under flexing [33]. However, non-uniformity and poor adhesion to PET substrate are likely to become big obstacles on its way to commercialization. Similarly, metal grids with well-defined grating structure represented an promising configuration as TCEs with sheet resistance as low as $\sim 20 \Omega/\square$ and $\sim 80\%$ transmittance at 550 nm, high film uniformity and tunable work function. [32] However, it is very likely to suffer from the high surface roughness and the complicated

preparation process, which may limit its production scale. In contrast, CNTs films are comparatively inexpensive and simple to fabricate, thus suitable for mass production, but favourable sheet resistance can only be achieved by increasing film thickness, which can severely suppress its transparency[35]. Graphene is another competitive contender[36], which can surpass other three competitors in several aspects. First of all, single layer of graphene possesses uniform transparency of 97.7% from near infrared to UV (figure 2.1a)[10]. The feature ensures that graphene has the capability to work for all visible range devices. Secondly, since graphene is only one atomic layer thick, the surface roughness(167 pm if transferred onto SiO₂[37]) can be almost neglected. The ultraflatness of graphene can therefore avoid electrical shorts and leakage current even without a buffer layer[24]. Thirdly, graphene has excellent mechanical properties[38] and therefore graphene based TCEs are very suitable for bendable and rollable optoelectronic devices. Last but not least, it is relatively easy and cheap to produce large area graphene sheet by employing different methods like liquid phase exfoliation[39], reducing graphene oxide[40] and CVD[41]. However, graphene film perform poorly on conductivity, as shown in figure 2.1b. The sheet resistance of the best as-prepared CVD graphene is 125Ω/□ with 97.4% transmittance[36]. Although the transparency is very high, the sheet resistance is still one order higher than the industrial entrance threshold. Another drawback of graphene is its relatively low work function(~ 4.6 eV[42]) compared with that of ITO(~ 4.7 - 4.9 eV). However, a lot of effective methods have been proposed to overcome these difficulties, from both preparation and post-processing aspects, which all produce promising results[43, 44, 36]. Therefore, we have every reason to believe that graphene is very likely to stand out above other competitors and become the first choice as TCEs for next-generation optoelectronic devices. In order to fabricate efficient graphene based TCEs, deep understanding of the electrical and optical properties and possible routes to improve them are essential, which will be reviewed in the following section.

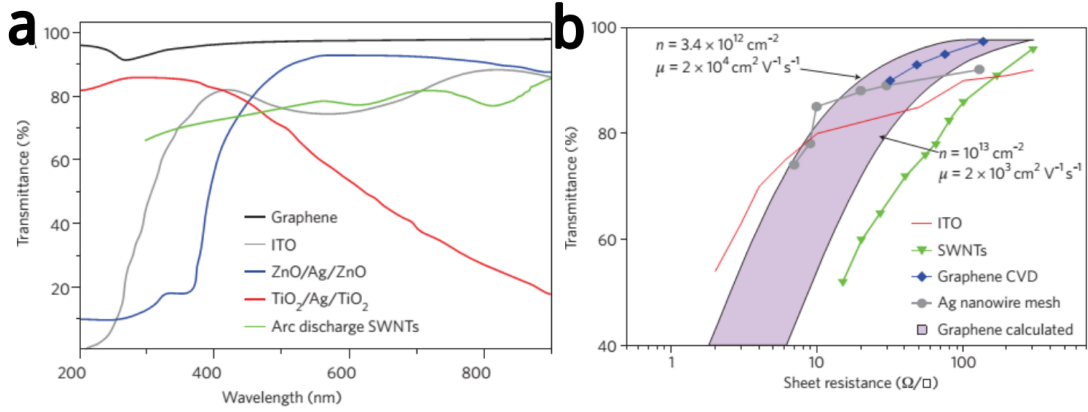


FIGURE 2.1: Comparison of optical and electrical properties among next-generation TCEs candidate. **a.** Comparison of optical transmittance in visible range. **b.** Comparison of sheet resistance VS transmittance. Figure reproduced with permission from ref. [15], Copyright Macmillan Publishers Limited 2010

2.2.1 Optical transmittance and sheet resistance

2.2.1.1 Optical transmittance

The optical conductance of graphene has been studied extensively both theoretically and experimentally. Ando *et al.*[45] predicted that carbon atoms structured in honeycomb lattice possess universal high frequency conductance over broad band. Kuzmenko *et al.*[46] confirmed this conclusion by analysing the reflectance spectra of graphite. In this letter, Kuzemenko and his co-workers also asserted that graphene possesses a fixed universal optical conductance, $G_0 = e^2/(4\hbar) \approx 6.08 \times 10^{-5} \Omega^{-1}$, derived from Fresnel equations in the thin-film limit. Based on it, they claimed that the transmittance of free-standing single layer of graphite is determined solely by the fine structure constant $\alpha = e^2/\hbar c = G_0/(\pi\epsilon_0 c) \approx 1/137$ which describes the coupling between light and relativistic electrons:

$$T = \left(1 + \frac{\pi\alpha}{2}\right)^{-2} \approx 1 - \pi\alpha \approx 97.7\% \quad (2.1)$$

This value is surprisingly in agreement with what Nair and his co-workers derive from the experiment measuring the transmittance of free standing mono- and bi-layer

graphene[10], as illustrated in Figure 2.2. Figure 2.2a is the optical image of their sample design for the experiment. With the help of an additional layer of PMMA on substrate, they prepared graphene single crystal exceeding $100\ \mu m$ in size which is then transferred on to copper-gold film with 9 apertures. By performing transmission experiment on this sample, they confirmed that the optical transmittance is universal in the full visible range(see Figure 2.2b). This allows graphene based TCEs to perform as good as ITO based TCEs even in conventional blue LED, although the sheet resistance is 20 times higher than ITO [47]. Moreover, in this letter, they also proved that graphene only reflects less than 0.1% of the incident light in the visible region and this value increases to about 2% for as many as 10 layers[48]. Thus, the optical transmittance has linear relationship with the number of graphene layers(see Figure 2.2a and the inset of Figure 2.2b):

$$T_{MLG} \approx 1 - N\pi\alpha \quad (2.2)$$

in which N is the number of graphene layers and $N < 10$. Tony Heinz and his collaborators [4] then extended the observation wavelength from visible to mid-infrared. In visible to near infrared range, their observation is consistent with results previous works[45, 46, 10], again confirming the existence of the fixed universal optical conductance of graphene (Figure 2.2c) while this result breaks down at lower photon energies (Figure 2.2d). This "non-universal" effect is elucidated by considering doping effects and contributions from intraband transitions, indicating that it is possible to manipulate the optical properties of graphene by controlling the doping level, which can also affect the DC conductance,[49, 50] as discussed in the following section.

2.2.1.2 Sheet resistance

Relatively high sheet resistance of graphene is one of the biggest obstacles for graphene to be applied into next-generation TCEs[51]. Therefore, an easy and effective method is

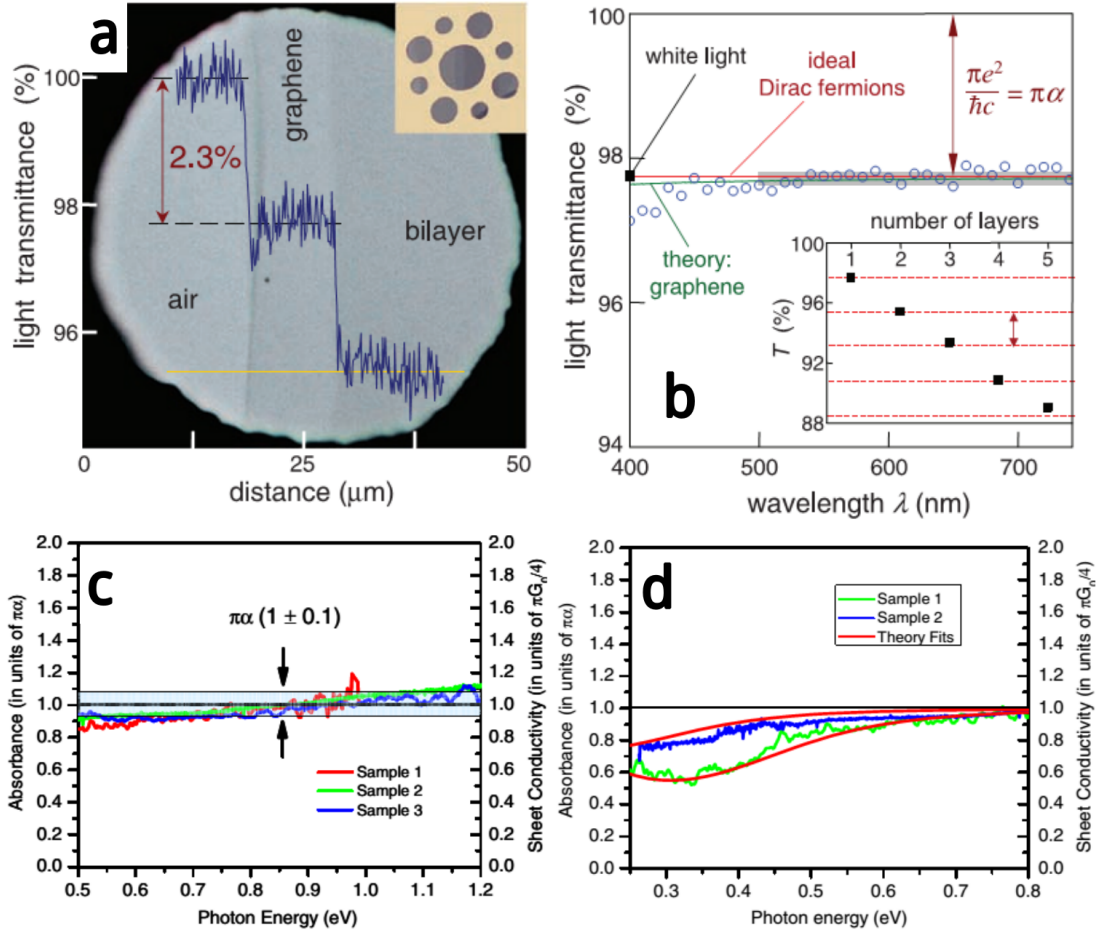


FIGURE 2.2: **a.** Graphene transferred onto specially designed metal support with several apertures. **b.** Flat optical transmittance curve in visible range. Inset: average transmittance for different graphene layers. **c.** Flat transmittance curve of graphene in visible to near-infrared range. **d.** Transmittance of graphene in the wavelength ranging from near-infrared to mid-infrared. **a,b** Reprinted with permission from ref. [10], Copyright American Association for the Advancement of Science 2008. **c,d** Reprinted with permission from ref.[4]. Copyright American Physics Society 2008.

needed to improve its DC conductivity. This requires us to have a deep understanding of the origin of the high sheet resistance of graphene as well as the factors that can influence the sheet resistance of graphene. In a very thin film, the resistance is still determined by the 3D conductance, σ_{DC} :

$$R = \frac{\rho}{t} \times \frac{L}{W} = \frac{1}{\sigma_{DC}t} \times \frac{L}{W} \quad (2.3)$$

in which ρ is the resistivity, t is the film thickness, L and W is the length and width of the film. In eq. 2.3, the reciprocal of $\sigma_{DC}t$ is defined as sheet resistance, R_s .

$$R_s = (\sigma_{DC}t)^{-1} \quad (2.4)$$

The derivation above is suitable for general thin film case. For graphene, eq. 2.4 can be written as:

$$R_s = (\sigma_{DC}t_0N)^{-1} = (\sigma_{2D}N)^{-1} \quad (2.5)$$

in which t_0 is the thickness of monolayer of graphene, N is the number of layers of graphene sample and σ_{2D} is the 2D conductance. Here it is assumed that the thickness of graphene film increases linearly with the number of layers. In graphene, 2D conductance can be expressed as:

$$\sigma_{2D} = ne\mu \quad (2.6)$$

In this equation, n is the concentration of carriers, μ is the carrier mobility. Therefore, the sheet resistance of graphene can be expressed in terms of

$$R_s = (ne\mu N)^{-1} \quad (2.7)$$

Therefore an important factor that have large impact on the sheet resistance of graphene, is the carriers concentration. As inspired by the silicon industry, the carriers concentration can be modulated *via* doping technique, which will be discussed later.

A noteworthy point is the non-zero 2D conductance for undoped graphene[3] and corresponding sheet resistance is

$$R_s = \left(\frac{4e^2}{h}N\right)^{-1} \quad (2.8)$$

Hence the sheet resistance of undoped monolayer graphene is $\sim 6500 \Omega/\square$, which is at least two orders higher than that of ITO. Again, this points out that doping process is essential to prepare graphene film with high conductance.

2.2.1.3 Correlation between optical transmittance and sheet resistance

It is important to understand the relationship between sheet resistance and optical transmittance, which are both the response of electrons to electrical fields. This relationship can be a guideline for the fabrication of graphene based TCEs with outstanding electrical and optical properties. In the text above, we have derived that transmittance of single layer graphene is solely determined by fine structure as eq. 2.1 describes. Therefore, for multilayer graphene, the transmittance is

$$T_{MLG} = \left(1 + \frac{\alpha\pi}{2}N\right)^{-2} \quad (2.9)$$

The fine structure α can be expressed in terms of the fixed universal optical conductivity, G_0 :

$$\alpha = \frac{G_0}{\pi\epsilon_0 c} \quad (2.10)$$

in which ϵ_0 is vacuum permittivity, c is the speed of light in vacuum. Therefore, optical transmittance can be written as:

$$T_{MLG} = \left(1 + \frac{G_0}{2\epsilon_0 c}N\right)^{-2} = \left(1 + \frac{G_0 Z_0}{2}N\right)^{-2} \quad (2.11)$$

in which $Z_0 = 1/\epsilon_0 c = 377 \Omega$ is free-space impedance. Combining eq. 2.7, eq. 2.5 and eq. 2.11 and eliminating number of layers, N produce:

$$T = (1 + \frac{Z_0}{2R_s} \frac{G_0}{\sigma_{2D}})^{-2} = (1 + \frac{Z_0}{2R_s} \frac{G_0}{ne\mu})^{-2} \quad (2.12)$$

From eq. 2.12, we can draw a conclusion that the relationship between transmittance and sheet resistance is controlled by the ratio between 2D DC and optical conductance (OC), $\sigma_{DC}/\sigma_{OC}(\sigma_{2D}/G_0)$. This is a very important parameter which can be used as a figure of merits for graphene based TCEs[52]. For the industrial entrance threshold, the value is ~ 49.8 ($70 \Omega/\square$ @ 90%), while for single crystal pristine monolayer graphene this value is ~ 11.5 (the in-plane conductivity of single crystal graphite is 2×10^6 S/m[53]), still 5 times smaller than the threshold. For some current-driven applications like OLEDs, the condition is more stringent that sheet resistance should be less than $10 \Omega/\square$ so that the RC delay can be neglected while the transmittance should be no less than 85%, yielding the conductance ratio as high as 220. For CVD graphene on copper, the best result is that sheet resistance and optical transmittance are $125 \Omega/\square$ and 97.4%, giving the ratio of 113.7 which is still not high enough to be applied to current-driven optoelectronic devices like OLEDs. However, if considering doping graphene intentionally, it is possible reach this criteria. For example, if $n\mu$ reaches $10^{17} \text{ V}^{-1}\text{s}^{-1}$, the conductance ratio can be as high as ~ 263.2 . In a short summary, based on the discussion above, in order to fabricate graphene film which can outperform ITO, doping method is inevitable to reach an optimal σ_{DC}/σ_{OC} of graphene.

2.2.2 Doping of graphene

2.2.2.1 Improving DC to OC ratio

Blake *et al.*[54] first reported that by n-type doping graphene of about $3 \times 10^{12} \text{ cm}^{-3}$ using polyvinyl alcohol (PVA), they prepared a piece of mechanical cleaved graphene

film with sheet resistance and optical transmittance of $400 \Omega/\square$ and $\sim 98\%$ (Figure 2.3a), yielding the conductance ratio $\sigma_{2D}/G_0 \approx 46.4$. Although this result is still below the industrial threshold, it provides a very good starting point, proving the validity of doping method. Kim *et al.* [55] then reported that they managed to enhance the conductivity of centimetre-sized CVD graphene by spin coating AuCl_3 dissolved in nitromethane onto graphene. They investigated the relationship between sheet resistance and doping level monitored by Raman spectroscopy which can provide insights into the concentration of AuCl_3 solution and concluded that AuCl_3 can effectively decrease the sheet resistance from the original value, $\sim 550 \Omega/\square$ to a saturated value, $112 \Omega/\square$ with 87% transparency if an optimized concentration was employed (Figure 2.3b). This corresponds to a conductance ratio of 23.3, well below the industry threshold, due to the low efficiency of top doping. In order to increase the doping efficiency, Gu *et al.* [56] advanced that the conductivity can be further improved by adopting layer-by-layer doping technique (Figure 2.3d). In their report, they produce a 4-layer graphene film with sheet resistance and transmittance of $58 \Omega/\square$ and 83.5%, yielding the conductance ratio of 35 which is close to the threshold. However, in both two articles, the improvement of conductivity is caused by the formation of Au particles on graphene surface, which greatly increased the local roughness of graphene film to as high as 90 nm (inset in figure 2.3c). This will lead to severe current leakage or even electrical shorts if working as anode in a device. In addition, the stability of the doped graphene film is also relatively poor (Figure 2.3c, d).

In order to achieve the surface flatness and high conductance after doping, Kasry *et al.* [57] proposed that nitric acid was an effective p-type dopant for graphene. By layer stacking and exposing CVD graphene sample to nitric acid environment (figure 2.3e), they reduced the sheet resistance from $2100 \Omega/\square$ to $90 \Omega/\square$ at a transmittance of 80%, producing the conductance ratio of 17.7. They also investigated the difference between last-layer doping and interlayer doping (Figure 2.3f,g). Surprisingly, they found that interlayer doping had almost the same effect as last-layer doping on sheet resistance

but outperformed on transmittance (Figure 2.3f,g). Since the mechanism of doping is the formation of carbon-nitric acid charge-transfer complex, it will not roughen the surface of graphene at all. Furthermore, Bae *et al.*[36] improved the treatment process and reduced the sheet resistance to $30 \Omega/\square$ at transmittance of 90 %, corresponding to conductance ratio of 116 which was far above the industrial threshold. However, the nitric acid is very easy to decompose if it is exposed to light, which will downgrade the doping effect greatly under ambient environment. Therefore, albeit nitric acid doped graphene presents the excellent optical and electrical performance, it still cannot be applied into practical devices due to the stability issue.

To improve the stability, Khrapach *et al.* [58], motivated by the intercalation of graphite [59], advance that ferric chloride intercalation between two layers of graphene can improve the conductance greatly. They prepare the sample by using two-zone vapour transport method. The doping level was revealed by Raman spectroscopy, which showed a splitting G peak after intercalation. Surprisingly, the intercalated sample has sheet resistance as low as $8.8 \Omega/\square$ and transparency of 84% (Figure 2.3h,i) and very high carrier density of $8.9 \times 10^{14} \text{ cm}^{-2}$, yielding conductance ratio of 235.2, even higher than the threshold for current driven devices. By showing the change of Raman spectrum with time, they also confirmed the very high stability of intercalated graphene sample. Although the ferric chloride intercalated graphene film presented excellent optical and electrical properties, the characterization was carried out on a sample with size of $5 \mu\text{m} \times 20 \mu\text{m}$, which raised a question whether this method can be scalable or not. The FeCl_3 intercalated graphene also suffered from non-uniformity. Kim and his colleagues[60] measured Shubnikov de Haas (SdH) oscillation measurement, where two different periodicity were observed, indicating two different Fermi level co-existence in one sample, thus suggesting that ferric chloride intercalated graphene film is made up of two different types of domains, intercalated and unintercalated, consistent with the result from intercalated graphite[59]. The non-uniformity is very possible to downgrade the performance of devices. Other problems like film roughness may

arise, which requires more characterization. Other potential chemical dopants like Na-NH₂[61], tetrasodium 1,3,6,8-pyrenetetrasulfonic acid (TPA)[61], tetrafluorotetracyanoquinodimethane (F4-TCNQ)[62], poly(ethyleneimine) (PEI)[63] and so on. These dopant have been demonstrated to be able to dope graphene effectively and therefore are potential candidates to improve the conductivity of graphene.

Apart from doping, people also tried to use graphene hybrid structures to improve its performance. Kholmanov *et al.*[64] reported that they reduced the sheet resistance of graphene from 1050 $\Omega/\square$ to 64 $\Omega/\square$ while the optical transmittance as high as 93.6% was maintained (Figure 2.3j) by employing the metal nanowire to repair the defects like foldings and cracks introduced in CVD cooling process and transfer process (inset in figure 2.3j). Although this graphene-nanowire hybrid structure possesses excellent optical and electrical properties, this method is almost impossible to be employed by industry at present because of the expense issue (1600 dollar per gram[52]). Similar work has also been published by Zhu *et al.*[65]. In their work, they combined graphene with metal grids, which greatly improve the conductivity of graphene film. By tuning the pitch periodicity, the resultant sheet resistance and transparency can be achieved within a range from 20 $\Omega/\square$ and over 90% to 3 $\Omega/\square$ and $\sim$ 80%. However, as we have pointed out in the previous text, the surface roughness is a key parameter to judge the quality of transparent film while metal grid performs poorly on it. Therefore we have every reason to be critical about the effectiveness of these graphene hybrid structures because of their roughness, which the author did not give any details on.

2.2.2.2 Introducing magnetic moments

Making graphene magnetic raises particular interest from the technological aspect because it can potentially lead to high-Curie-temperature diluted magnetism and therefore satisfy the demands of the continuously increasing magnetic information storage

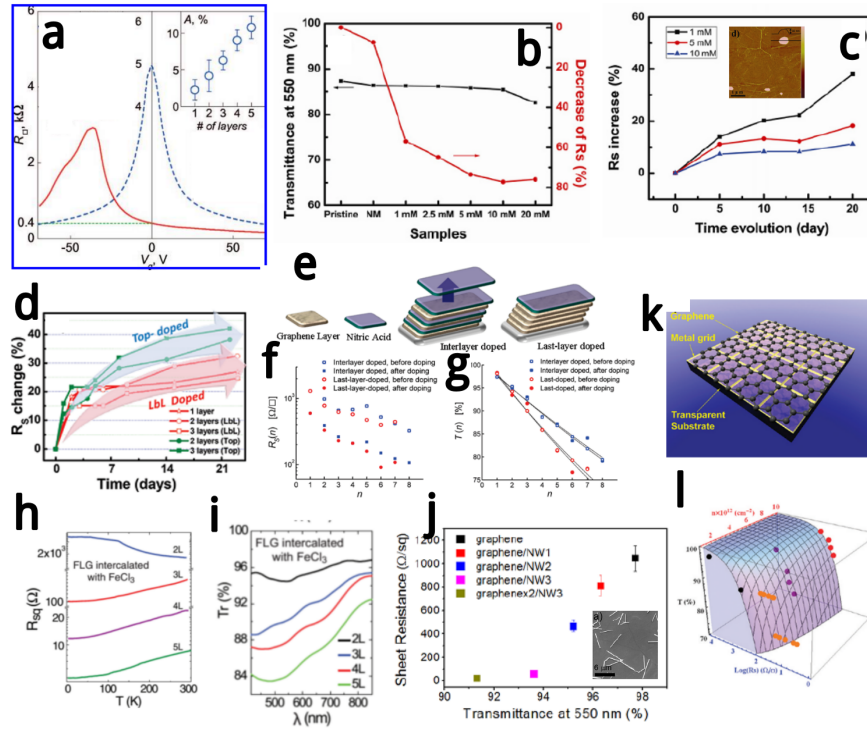


FIGURE 2.3: **a.** Transport properties of graphene doped by PVA. Inset: Optical absorption of doped graphene as a function of layer number. **b.** Relationship between AuCl_3 solution concentration and change of sheet resistance and optical transmittance. **c.** Stability of AuCl_3 doped graphene. Inset: AFM image of AuCl_3 doped graphene sample. **d.** Comparison of the stability between the stacked graphene doped by AuCl_3 on top and layer by layer. **e.** Schematic diagram of layer-by-layer and top-layer doping using nitric acid. **f,g.** **f** Sheet resistance and **g** optical transmittance *versus* number of layers using two different doping method in **e**. **h.** Sheet Resistance VS temperature and number of layers of FeCl_3 intercalated graphene. **i.** Effect of number of layers on optical transmittance of FeCl_3 intercalated graphene. **j.** Sheet resistance as a function of optical transmittance of graphene-silver nanowire hybrid structure with different density of nanowire. Inset: SEM image of graphene-metal hybrid nanowire hybrid structure. **k.** Schematic diagram of graphene hybrid structure. **l.** Optical and electrical properties of graphene-metal grid hybrid film. Mesh surface: theoretical modelling of optical and electrical properties with graphene mobility of $5000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Orange dots: optoelectrical properties of graphene-metal grids. Black dots: Undoped graphene. Red dots: Data from HNO_3 doped graphene. Purple: Data from AuCl_3 doped graphene. **a** Reprinted with permission from ref. [54], copyright American Chemistry Society 2007. **b,c** Reprinted with permission from [55], copyright IOP-Science 2010. **d** Reprinted with permission from [56], copyright American Chemistry Society 2010. **e-g** Reprinted with permission from [57], copyright American Chemistry Society 2010. **h,i** Reprinted with permission from [58], copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2012. **j** Reprinted with permission from [64], copyright American Chemistry Society 2012. **k,l** Reprinted with permission from [65], copyright American Chemistry Society 2011.

density. [66] Yet similar to graphite, pristine graphene is strongly diamagnetic. Therefore, it is of vital importance to introduce magnetic moment into graphene, which is, however scientifically challenging because graphene does not possess either d or f electrons, which common ferromagnetic materials have. This can be solved *via* doping by introducing transitional metal atoms into graphene lattice. Chan *et al.* [67] proposed that transition metal surface adatom on graphene can efficiently magnetize the graphene according to first principal calculations. For example, placing an Fe at the centre of the carbon ring in graphene can introduce an magnetic moment of $2.03 \mu_B$. The magnetic moment can be further increased to $3.41 \mu_B$ if the Fe atom is replaced by Ti atom. However, due to the low binding energy and migration barrier, the surface adatom cannot serve as a reliable building block for electronics. In order to achieve a highly stable structure, the metal dopant must be embedded into the graphene lattice. Krashennnikov *et al.* [68] theoretically predicted the magnetic property and stability of graphene with metal atom embedded in the lattice. All the metal atoms can form covalent bonds with surrounding carbon atoms and the binding energy is more than - 3 eV, indicating that these structures are highly stable. However, the magnetic properties is heavily dependent on the structural configurations. For example, a single Fe atom embedded in a graphene monovacancy (the single Fe atom interstitially substitute one carbon atom) can induce a localized magnetic moment of over $3 \mu_B$ while in a divacancy the doped graphene is non-magnetic. [68] This indicates that in order to achieve a reliable magnetized graphene, a doping technique with high spatial resolution and the corresponding *in-situ* structural characterization method are highly desired, which will be discussed in section 2.2.4.2.

2.2.3 Fabrication method

The sheet resistance of graphene is also strongly affected by its surface morphology and crystal quality[51], which is determined by its growth and preparation method. In this

section, I will discuss four different graphene fabrication methods that are suitable for future mass production in industry and evaluate their performance based on the figure of merit of DC/OC ratio.

Wang *et al.*[69] prepared transparent graphene-constructed films via cross-linking of carbon-rich molecules. Figure 2.4a,b presents the optical, electrical and morphology information of this sample. The sheet resistance is still as high as $1\text{ k}\Omega/\square$ even if thickness of the film reaches 30 nm (Figure 2.4a), which sacrifices the transmittance severely (Figure 2.4b), corresponding to a conductance ratio of 0.46. This is very likely due to the amorphous nature of the film.

To improve the crystallinity, Hernandez *et al.*[39] advanced another low-cost and effective way to fabricate graphene films. They first exfoliated graphene by sonicating graphite in organic solvents like NMP and then spray-coating dispersion onto target substrate. By controlling the concentration of dispersion and parameters used for spray-coating, films with desired thickness can be prepared. However, the electrical properties is still far from satisfactory. The sheet resistance and transmittance of as-prepared graphene film is $7.2\text{ M}\Omega/\square$ and 61%(figure 2.4c), corresponding to a conductance ratio of as low as 9.5×10^{-5} . Post-treatment like vacuum drying and annealing greatly decrease sheet resistance to $5.1\text{ k}\Omega/\square$ and therefore improve the conductance ratio by 1000 times, but it is still far from industrial threshold. It is mainly due to the large contact resistance between adjacent graphene flakes (Figure 2.4d,g) and residual solvent molecules and surfactant adsorbed on graphene sheets. Other coating techniques such as vacuum filtration have been proposed to help eliminate the effect of surfactants and adsorbed solvent molecules. However, the sheet resistance is still as high as $\sim 4\text{ k}\Omega/\square$ and average transmittance of 80 %, corresponding to a conductance ratio of 0.4.[52] Therefore, the high contact resistance between adjacent flakes is possible to be the dominant limiting factor to the low conductance.

Another low cost and solution based method to fabricate graphene film is to reduce graphene oxide into graphene. Graphene oxide is prepared by oxidizing graphite in strong acids[70], which is then exfoliated in water by sonication. In this procedure, sp^2 network is damaged severely, which needs to be repaired in the reduction process to restore its conductivity. Subsequently, the water-graphene oxide diluted dispersion is centrifuged to get graphene oxide dispersion with favourable concentration, which is then coated onto substrates to form graphene oxide film using different techniques like spray-coating[40], dip coating[71], spin-coating[72], vacuum filtration[73] and so on. The most conductive film from reduced graphene oxide was reported by Bao and her collaborators[72]. In this article, they anneal the sample at 1100 °C in vacuum environment, which then produces graphene film with sheet resistance of $\sim 800 \Omega/\square$ with low transmittance ($\sim 60\%$)(Figure 2.4e,f). This corresponds to a conductance ratio of about 0.81. Similarly, the high sheet resistance mainly comes from the large contact resistance between two contacting flakes (Figure 2.4g). Therefore graphene film prepared by GO reduction method still has a long way to go before it can outperform ITO and other candidates.

Graphene films prepared by the above three methods all suffer from the poor crystal quality, therefore introducing very high contact resistance between two adjacent flakes. Chemical vapour deposition (CVD) provides an excellent solution to this problem. Different metal substrates as catalysts have been used to grow graphene including Pt[74], Ru[75], Ni[76] and Cu[41, 77, 78, 79]. Copper is now the dominant substrate in CVD growth graphene because of its low price, large grain size after high temperature annealing and low carbon solubility, which is essential for forming large area monolayer graphene with high uniformity[80]. The sheet resistance of CVD graphene is $\sim 10^3 \Omega/\square$, which is still relatively high compared with that of ITO. This is due to the polycrystalline nature of CVD graphene and therefore electron experience strong scattering effect at numerous grain boundaries and defects introduced during transfer process[24]. Indeed, Zhou *et al.* [81] reported large discrepancy between the sheet resistance of

graphene film composed of large domain (0.5 mm in lateral size) and small domain, as shown in figure 2.4i. The larger domains greatly reduces the sheet resistance by over 60 % which can reach as low as about $300 \Omega/\square$, corresponding to a conductance ratio of about 45.6. Stacking CVD graphene layer by layer is another effective way to reduce the sheet resistance. Bae *et al.*[36] claimed that by stacking four layers of graphene layers (Figure 2.4j), they reduces the sheet resistance to as low as $40 \Omega/\square$ over 90 % transmittance at 550 nm, yielding a conductance ratio of as high as 87.1 which have almost the same performance as ITO does. In addition, CVD has been employed in industry for decades, which ensures the compatibility with present production line straightforward, indicating that CVD is likely to be the dominant way to produce graphene film for the purpose of TCEs in industry although the energy cost is very high and the transfer process is complicated, which will be solved through future research[51]. Apart from growing graphene on flat substrates, a recent work showed that it was also possible to grown graphene on uneven nanoscale surfaces, which could be applied into many scanning probe microscopy techniques.[82]

2.2.4 Characterization of Graphene

2.2.4.1 Raman

Raman spectroscopy is a powerful and non-invasive technique to probe the electronic, vibrational and structural properties of graphene. Figure 2.5a presents the Raman spectra of both graphene and graphite. There are two pronounced features in both spectra, which are attributed to *G* peak at around 1580 cm^{-1} and *2D* peak locating at $\sim 2700 \text{ cm}^{-1}$. The *G* peak originates from the doubly degenerate Brillouin zone centre E_{2g} mode which is the characteristic signature of carbon-carbon bond stretching in sp^2 configuration. The 2D band is associated with two zone edge phonons with opposite momentum. The prominent intensity of 2D peak is due to the double resonance process, which can provide link between phonon wave vectors and the electronic band structure.

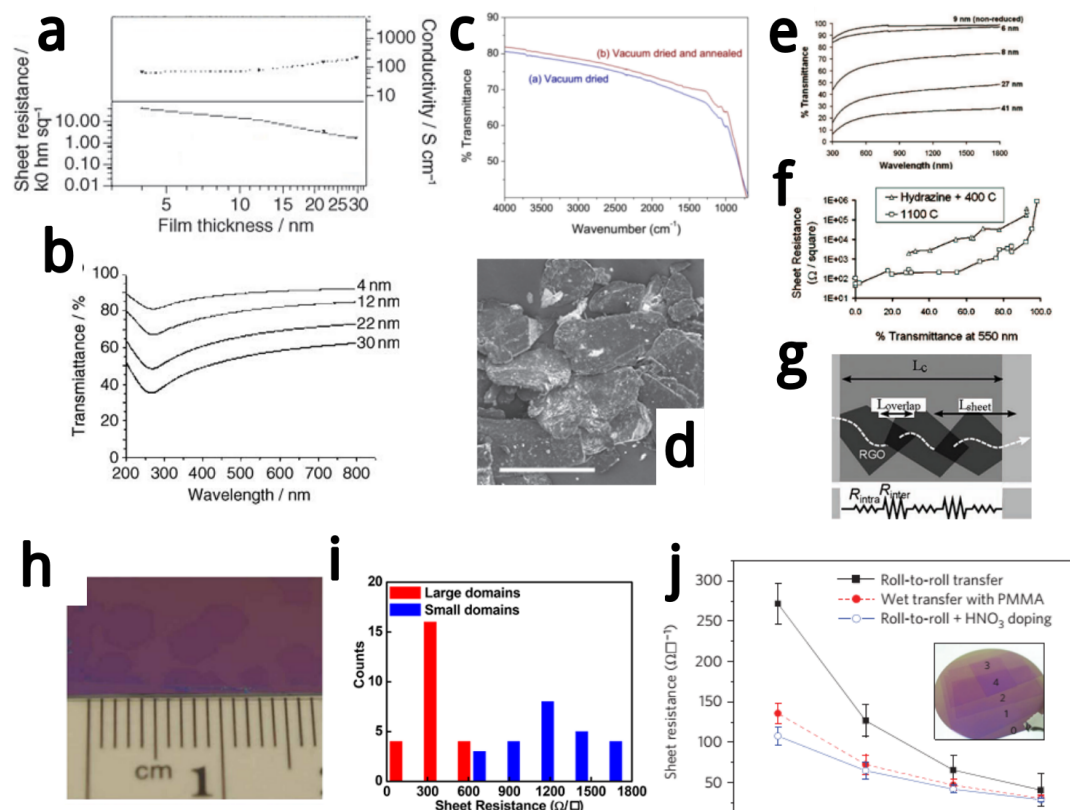


FIGURE 2.4: **a.** Sheet resistance VS thickness of the film prepared by cross-linking carbon-linking molecules. **b.** Transmittance curve of film prepared by the method in **a** with different thickness. **c.** Transmittance curve of graphene film prepared by liquid exfoliation method. **d.** SEM image of liquid exfoliated graphene flakes. **e.** Transmittance curve of graphene film prepared by reduced graphene oxide with different thickness. **f.** Sheet resistance *versus* transmittance of reduced graphene oxide film. **g.** Schematic diagram large contact resistance between two adjacent flakes. **h.** Photograph of large area single crystal hexagonal graphene domains prepared by CVD. **i.** Sheet resistance distribution graph for two types of graphene. **j.** Sheet resistance VS number of stacked layers. Inset: photograph of stacked graphene on silicon wafer. **a,b** Reprinted with permission from ref. [69], copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2008. **c,d** Reprinted with permission from [52], copyright American Chemistry Society 2010. **e-g** Reprinted with permission from [72], copyright American Chemistry Society 2008. **h,i** Reprinted with permission from [81], copyright Macmillan Publishers Limited 2010. **j** Reprinted with permission from [36], copyright Macmillan Publishers Limited 2010.

Therefore, $2D$ peak is sensitive to the electronic structure change and can be utilized as an indicator for layer number identification. Ferrari *et al.* [83] reported the variation of $2D$ peak with increasing number of layer, as shown in figure 2.5b. In monolayer graphene, $2D$ band is a single sharp peak. The additional layer leads to an obvious peak position blue-shift and width broadening, which consists four sub-bands due to the electronic band splitting.[83] Further increasing the layer number up to five leads to different spectral weight distribution among the four sub-bands. If the layer number exceeds five, it can hardly be distinguished from bulk graphite. The peak positions of $2D$ band can also be affected by the excitation wavelength because of the double resonance, which experiences redshift with smaller incident photon energy. The first order of $2D$ band, D band is the breathing modes of sp^2 bonded aromatic ring in graphene, which is Raman inactive in perfect graphene lattice. However, if the ring structure is severely damaged, the D band can be Raman active, which, therefore, provides an way to evaluate the lattice quality of graphene. Indeed, the D peak is observed locating at 1350 cm^{-1} at the edge of both graphene and graphite, as shown in figure 2.5c. In defective monolayer graphene, D peak exhibits a single peak while in graphite it possesses two components.[84] The Raman spectra can also be used to monitor the doping level of graphene. Yan *et al.*[85] fabricated a monolayer graphene based FET and monitored its Raman spectra under different gate voltage in order to figure out the relationship between phonon structures and doping level. Figure 2.5d shows the carriers concentration dependence of G band and D^* (equivalent to $2D$ band), with the response of G peak more prominent. Figure 2.5e depicts both the peak positions and width as a function of carriers concentration. It clearly shows that the increase in either electrons or holes concentration leads to the stiffening and sharpening of G mode. Therefore, the G band can serve as an indicator for doping level monitoring. The Raman spectrum has also been used to monitor other properties such as strain and [86] interlayer stacking order.[87, 88]

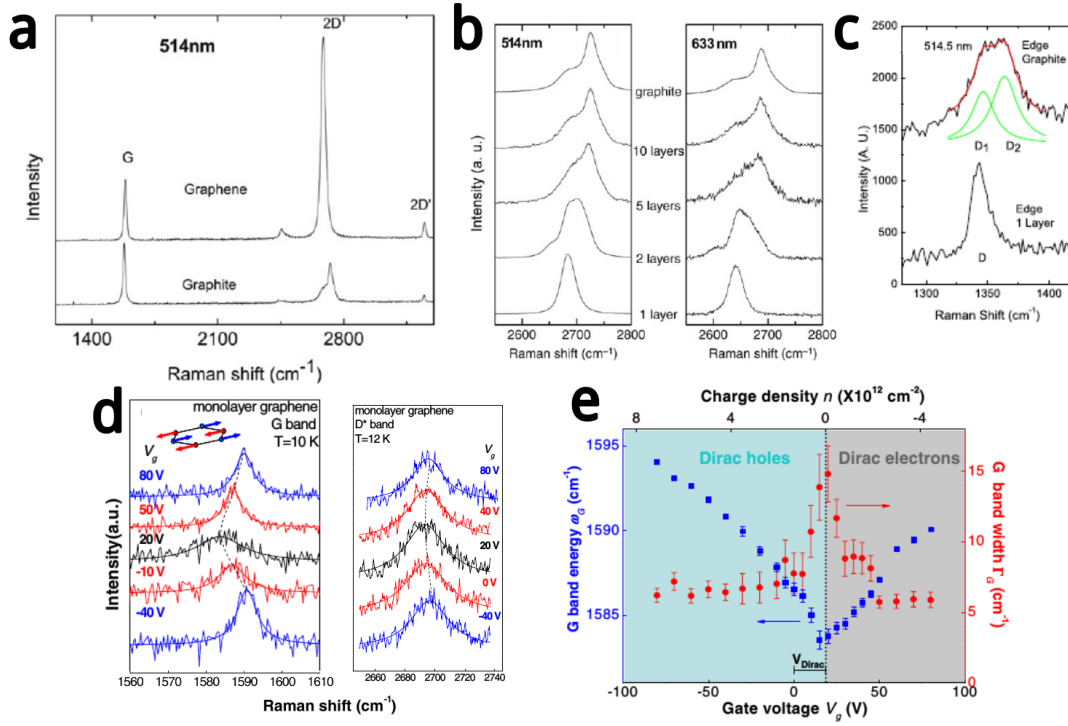


FIGURE 2.5: **a.** Raman spectra of both graphene and graphite. **b.** $2D$ band variation as a function of layer number under two excitation wavelengths. **c.** D band of graphene and graphite edges. **d.** G and $2D$ band of graphene as a function of gate voltage. **e.** G peak position and FWHM of graphene as a function of carriers concentration. Reprinted from [84] Copyright Elsevier Ltd. 2007. **b,c** Reprinted with permission from ref. [83]. Copyright American Physics Society 2006. **d,e** Reprinted with permission from ref. [85]. Copyright American Physics Society 2007.

2.2.4.2 HRTEM

High resolution transmission electron microscopy (HRTEM) provides another useful way to characterize the structure of graphene with high spatial resolution. Unlike optical microscopy which provides the information of target by monitoring the light amplitude variation, the image of HRTEM is reconstructed according to the interference of electron beams transmitted through the target sample, which presents the phase variations of the electron beam. This renders the interpretation of the HRTEM image and proper sample preparation challenging. Thanks to its single atomic layer thickness,

graphene can be viewed as a weak-phase object. Therefore, at proper defocus value, the region with dark contrast in a HRTEM image can be directly linked to high electron density. That is to say, the HRTEM image of graphene can directly be viewed as its atomic structure. With the development of aberration-corrected TEM (AC-TEM) which can minimize the spherical aberration of electromagnetic lenses, graphene TEM image with atomic resolution can be achieved. Figure 2.6a presents the typical contrast-inverted AC-TEM image of graphene with perfect lattice, in which dark spots stand for carbon atoms. Since the contrast of TEM image directly correlates to the electron density variation, this technique must have the ability to distinguish the foreign atom, especially those with heavy atomic mass like transition metal atoms, from the carbon atoms. Cretu *et al.* [89] have observed W atom adsorbed on the graphene sheet showing much darker contrast than surrounding carbon lattice, as presented in figure 2.6b1-8. Thanks to the high temporal resolution of HRTEM, the dynamics of the foreign atoms can also be monitored. A large spatial oscillation of the W atom on the graphene sheet between two reconstructive defects and a smaller vibration localized at one trapping centre are observed, revealing that the mechanism of atom adsorption on graphene can be facilitated by defects induced strain.

One of the most important consideration during TEM image capturing is the effect of electron irradiation on the target sample, in which the energy that the electron beam transfers to target sample must not exceed the knock-on threshold. For graphene, an accelerating voltage of 80 kV is believed to be safe. However, Robertson *et al.* [90] reported that the defects creation can still exists even under 80 kV electron beam if electron beam dose increases. However, unlike direct knock-on damage, this process is much more controllable and therefore paves a way for atomic resolution doping technique. In this method, a vacancy is first created in graphene within a typically $10 \times 10 \text{ nm}^2$ area by focused electron beam irradiation using an aberration-corrected transmission electron microscope (AC-TEM) operated at an accelerating voltage of 80kV, as shown in figure 2.6c2.[90] These vacancies show enhanced chemical reactivity

and are able to trap mobile atoms. Robertson *et al.* [91] reported that an Fe atom introduced during transfer process can be trapped by the vacancies created. Figure 2.6d1,2 show the contrast inverted AC-TEM image of single Fe atom trapped by either monovacancy or divacancy, in which bright spots in the middle represent the Fe atom. Figure 2.6d5,8 present the simulation images according to the atomic models in figure 2.6d4,7, which are used to compare with obtained TEM images to confirm the validity of guessed structure.[91] Additionally, HRTEM can also provide information about the dislocation,[92] exotic edge structure,[93] vacancies[94] and grain boundaries[95] which are beyond the scope this thesis and will not be reviewed here.

2.2.5 Applications

This section will focus on the review of the development of graphene based TCEs. However, rather than discussing the pros and cons of graphene based TCEs (GTCEs) as an isolated component, it is more meaningful to incorporate it into a working device. GTCEs has been proved to be highly desirable in many applications, including highly functional NEMS,[96] Here light emitting diode (LED) is used as a platform, which sets the highest industrial entry threshold for TCEs, to evaluate the viability of graphene based TCEs. LEDs are devices designed to convert the electrical power into electromagnetic irradiation in the visible range. Compared with conventional light sources such as incandescent light bulbs, LEDs are more efficient and therefore become very promising candidate for the next-generation energy-saving light sources. LEDs can be classified in two category in general: inorganic LEDs and organic LEDs (OLEDs), determined by the light emitting materials used in the devices. In these devices, transparent electrodes are one of the key components for carriers injection and light out coupling. In the following part, I will review the recent progress on GTCEs based LEDs.

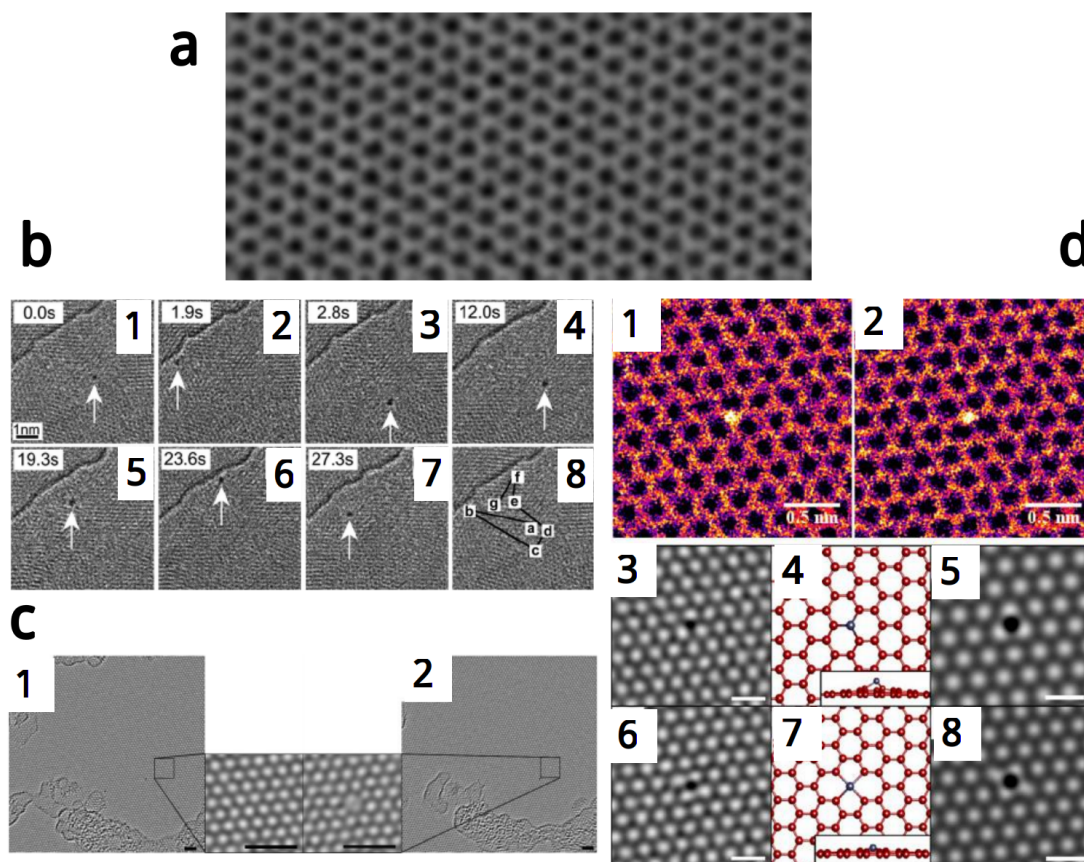


FIGURE 2.6: **a.** Contrast inverted AC-TEM image of monolayer graphene with perfect lattice. **b.** Time evolution of HRTEM images of W atom on graphene. **c.** Controllable defects creation using focused electron beam under acceleration voltage of 80 kV. **d.** AC-TEM assisted doping of graphene with single Fe atom. **b.** Reprinted from [89] Copyright American Physics Society 2010. **c.** Reprinted with permission from ref. [90]. Copyright Macmillan Publishers Limited 2012. **d.** Reprinted with permission from ref. [91]. Copyright American Chemistry Society 2013.

Inorganic LEDs have been widely used as indicators for over four decades. The simplest schematic structure of inorganic LEDs is that light emitting layer (usually semiconductor p-n junction) on sapphire substrate is covered by ITO (figure 2.7a). However, ITO presents relatively low transparency in the blue range and therefore can downgrade the blue light outcoupling, which can be overcome by employing graphene as TCEs. Jo *et al.* [47] report the first GaN blue LEDs with graphene TCEs, which was prepared by CVD using Ni as catalyst and methane as carbon precursor. The sheet resistance and

optical transmittance are $\sim 520 \Omega/\square$ and $\sim 85\%$, corresponding to a conductance ratio of about 4.28. This device performed as good as ITO based one if the input current is below 10 mA but it was defeated if the current is larger than 10 mA, due to the high sheet resistance of graphene (Figure 2.7b). In addition to single LED, Kim *et al.*[97] proposed that graphene can be utilized as interconnect TCEs for stretchable LED array, which showed very high mechanical stability, surviving even after 85% stretching (Figure 2.7c). Although some works have been reported to confirm its validity in inorganic LED, more promising applications for graphene based TCEs are OLEDs because OLEDs possess superior flexibility to that of inorganic LED, which can take the advantage of the excellent mechanical properties of graphene.

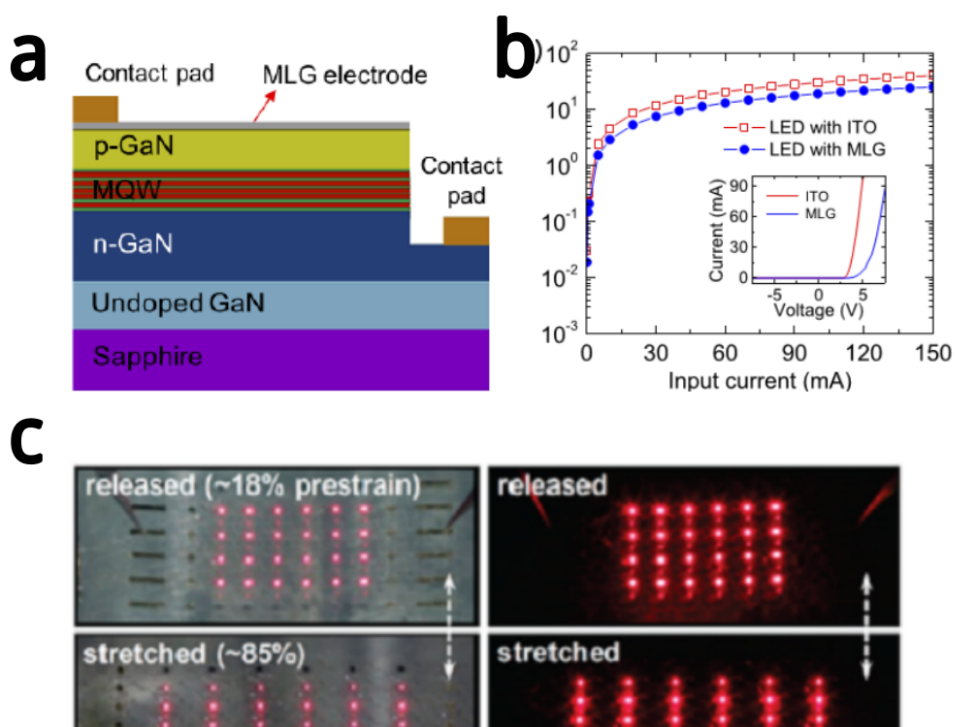


FIGURE 2.7: **a.** Schematic diagram of structure of graphene based inorganic light emitting diode. **b.** Input current VS output power of graphene and ITO based devices with structure in **a.** **c.** Photograph of graphene based LED on flexible substrates before and after stretching. **a,b** Reprinted with permission from ref. [47], copyright IOPScience 2010. **c** Reprinted with permission from [97], copyright American Chemistry Society 2010.

OLEDs are attracting worldwide attentions because of their high image quality and lower energy consumption compared with traditional LEDs, which will find great applications in ultrathin displays. The structure of OLED is quite simple, with one electroluminescent layer sandwiched by two electrodes and at least one of the electrodes should be transparent. When applying a certain voltage onto the device, electrons from cathode are driven into the lowest unoccupied molecular orbital (LUMO) of the emissive layer while holes are injected into its highest occupied molecular orbital (HOMO). For highly efficient OLED, the work function of the anode and cathode should match the LUMO and HOMO of active layer, respectively[98].

Normally people use graphene as anode for hole injection in OLED devices because of its relatively high work function (~ 4.5 eV[42, 99]) which is very close to that of ITO (4.5 eV - 4.8 eV [27]). Wu *et al.*[100] reported that they fabricate OLED based on solution based reduced graphene TCEs with conductance ratio of 2.26 (sheet resistance: $\sim 800 \Omega/\square$, optical transmittance: 82% at 550 nm). The structure of the OLED devices are presented in the inset of Figure 2.8a. For comparison, they also fabricate OLED devices with same structure with ITO as TCEs. The performance of two devices are presented in Figure 2.8b. The performance of graphene based device is slightly below that of ITO based devices despite of the two magnitude higher sheet resistance of graphene than ITO, possibly due to the effect of conductive polymer PEDOT:PSS. Although the performance of devices is comparable to the ITO based ones, OLEDs based on reduced graphene film prepared by reduction of graphene oxide cannot make too much further improvement because the intrinsic poor conductance. An alternative way is to use CVD method to fabricate graphene film.

Sun *et al.* [101] reported the fabrication of OLED devices based on multilayer CVD graphene as anode with conductance ratio of ~ 7.18 (sheet resistance: $3.1 \times 10^2 \Omega/\square$, transmittance: $\sim 85\%$ at 550 nm). Figure 2.8c illustrates the structure of the devices and the energy level diagram is shown in figure 2.8d. I-V curve and power efficiency

of the device are presented in figure 2.8e,f, revealing the turn-on voltage and the corresponding voltage to maximum power efficiency are 4 V and 5.8 V. The efficiency is well below the ITO based devices, which is very likely due to two issues. One is the structure of the device, which can decrease the light out coupling efficiency severely. The other is the poor conductance of graphene and the mismatch of work function between graphene and hole injection layer, which is likely to be the main factor, as confirmed by the work of Han and his co-workers[29]. In this letter, CVD graphene TCEs transferred onto flexible substrate are doped by HNO_3 , which reduce the sheet resistance to as low as $\sim 30 \Omega/\square$ and increase the work function to $\sim 4.6 \text{ eV}$. A conducting polymer composition is employed to modify the surface of graphene, leading to a gradient work function from graphene surface to organic layer in order to bridge the $\sim 1 \text{ eV}$ work function gap (Figure 2.8g). The graphene based green fluorescent OLED (Figure 2.8h) showed an extremely high efficiency with current efficiency (CE) of 30.2 cd/A and luminance efficiency (LE) of 37.2 lm/W, much higher than ITO based devices with GraHIL (CE: 18.4 cd/A, LE: 24.1 lm/W) despite the higher sheet resistance of graphene. Phosphorescent green OLED devices have also been demonstrated, which shows even higher efficiency. (CE $\approx 98.1 \text{ cd/A}$, LE $\approx 102.7 \text{ lm/W}$) while CE and LE of ITO based devices with same structure are 81.8 cd/A and 85.6 lm/W. Figure 2.8h presents the increasing device efficiency with additional graphene layer number. Graphene based devices also outperformed ITO based devices in bending test, indicating promising prospect of graphene to replace ITO as TCEs in the next generation flexible OLEDs (figure 2.8i). The key point is to find suitable chemicals to reduce the sheet resistance as well as to align its work function with organic layer.

The conventional structure of OLED ask for the match between work function of anode and LUMO of organic layer while most of the electrodes including graphene cannot meet this requirement. Therefore post-treatment is required, which brings complexity to the processing procedure. To overcome this difficulty, Matyba *et al.* [102] incorporated graphene into a frequently overlooked electroluminescence device structure:

light-emitting electrochemical cell (LEC)[103]. The structure of LEC is similar to that of a polymer OLED but in LEC devices, the light-emitting polymer or small molecule compound is blended with an electrolyte. When applied an external voltage between the electrodes, the mobile ions in the electrolyte rearrange, forming high charge-density layers at each interface of electrodes (Figure 2.8j). Therefore LEC allows efficient and balanced carriers injection even without work function alignment. Despite the poor efficiency demonstrated here(Figure 2.8k,l) due to the high sheet resistance ($\approx 5000 \Omega/\square$) and high surface roughness of graphene film, this work suggests a new way to fabricate metal-free all solution processed electroluminescent devices, which cannot only simplify the processing procedure, but also avoid the severe chemical side reactions involving metal or metal oxide electrodes, which can downgrade the performance and life time of LEC devices.

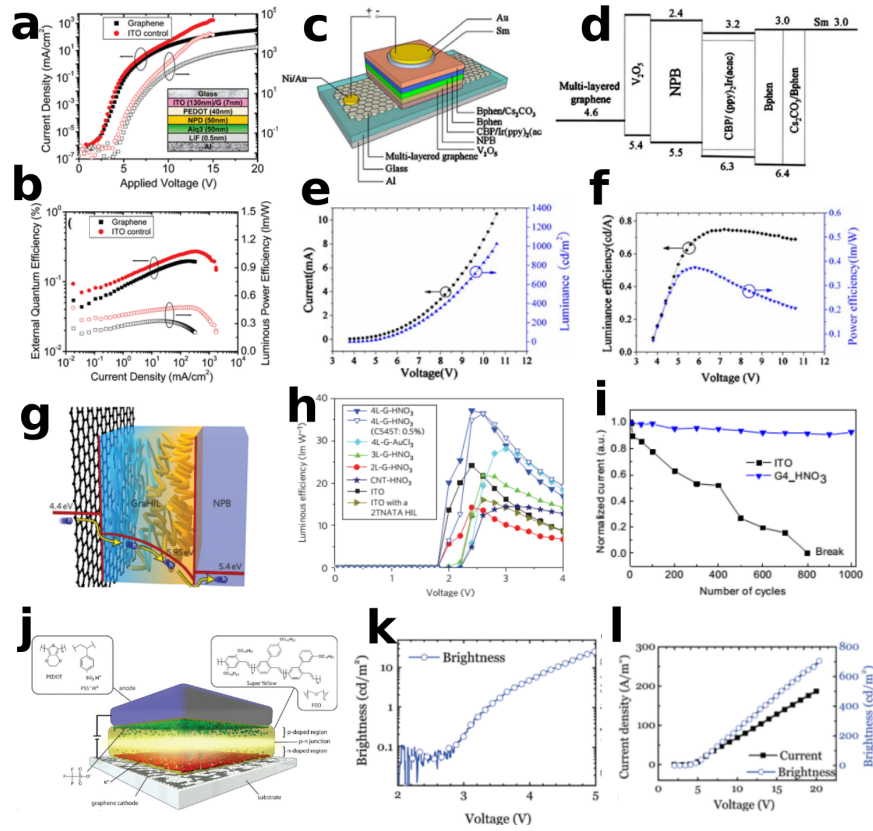


FIGURE 2.8: **a.** Comparison of current density-voltage and luminance-voltage between graphene based and ITO based OLED devices. Inset: schematic diagram of the structure of OLED. **b.** External quantum efficiency and luminous power efficiency VS current density of graphene and ITO based OLED devices in **a.** **c.** Schematic diagram of graphene based OLED devices. **d.** Energy level diagram of graphene based OLED devices in **c.** **e,f.** **e)** Current and luminance and **f)** luminance and power efficiency *versus* voltage of OLED in **c.** **g.** Schematic diagram of OLED with anode based on p-doped CVD graphene with GraHIL. **h.** Comparison of Luminous efficiency of fluorescent OLED devices based on different anodes. **i.** Bending test comparison between graphene and ITO based OLED devices in **g.** **j.** Schematic diagram of the structure of graphene based LEC. **k.** Brightness *versus* voltage near turn-on voltage region of graphene based LEC devices. **l.** Current and brightness *versus* voltage of graphene based LEC. **a,b** Reprinted with permission from ref. [100], copyright American Chemistry Society 2009. **c-f** Reprinted with permission from [101], copyright IOPScience 2010. **g-i** Reprinted with permission from [29], copyright Macmillan Publishers Limited 2012. **j-l** Reprinted with permission from [102], copyright American Chemistry Society 2010.

2.3 Transition Metal Dichalcogenides

Starting from decades ago, extensive researches have been carried out on the bulk TMDCs to investigate the structural[104], chemical[105], electronic[104, 106, 107, 108, 109, 110] and optical[104, 111, 112, 113, 114] properties. Yet the major applications of bulk TMDCs until now only include dry lubricant, hydrodesulphurisation catalysts and cathode materials for lithium ion batteries, partly due to their indirect bandgap[108, 109, 110]. Until very recently, inspired by the mechanical cleavage method employed to isolate graphene[1] from bulk graphite, Novoselov *et al.*[115] first isolated atomically thin TMDCs from their bulk form and exhibit very different electronic structures and optical properties, which opens up new pathways for the applications of TMDCs in electronic and optoelectronic industries.[116, 117, 118, 119]. In this section, a review of the recent progress of the development of 2D TMDCs is presented with emphasis on the optical properties of TMDCs. This section starts from The crystal structures of 3 kinds of TMDCs polytypes, which is then followed by the detailed review of the exotic optical properties of monolayer TMDCs. Considering the future industrialization of TMDCs, different fabrication methods and potential applications are also discussed.

2.3.1 Crystal structure

One typical class of TMDCs with chemical formula MX_2 are combinations of transition metal in either group IV (Ti, Zr, Hf and so on) or group V (V, Nb or Ta) or group VI (Mo, W) and chalcogen (S, Se or Te) with 3 different polytypes, 1T, 2H and 3R, which are different from each other in either stacking order of different layers or the coordination of chalcogen atoms relative to the transition metal atoms. The denotation of each polytypes is composed of a number and a letter, in which the number represents the number of layer involved in the crystal unit cell and the letter stands for the crystallographic structure (T: trigonal, H: hexagonal and R: rhombohedral).

1T TMDCs are metastable which can only be synthetic and show metallic behaviour. Their crystallographic unit cell consist of only one layer. The transitional atoms in 1T-TMDCs are arranged in octahedral coordination (O_h). Two metal atoms in adjacent layers are aligned along the c-axis and therefore it has a stacking order of AbC, AbC..., in which the capital letters represent chalcogen atom and letters with lower case stand for the metal atom. The same alphabet indicates that two atomic planes are aligned vertically along the c-axis. [120, 121] The semiconducting 2H-TMDCs are the most abundant polytype in nature. The crystallographic unit cell of 2H TMDCs are composed of two layers with stacking order of AbA, BaB, AbA..., with the metal atoms arranged in trigonal prismatic coordination. 3R-TMDCs can also be found in the natural minerals with much lower abundance than 2H-TMDCs. The metal atoms in 3R-TMDCs also has the same coordination as those of 2H-TMDCs while the layer stacking order is different, which is AbA, BcB, CaC, AbA... The atomic models of 3 polytypes TMDCs are presented in figure 2.9.

Different combinations with different crystal structures can yield materials with distinct electronic properties, which are determined to a large extent by the coordination environment of the transition metal and its d -electron,[116] the details of which requires complex computational calculations to reveal the details. However, the basic properties (semiconducting or metallic) can be predicted from the ligand field splitting and filling of the d -orbit related bands.[122] The metal-chalcogen bands of TMDCs are composed of bonding bands (σ), anti-bonding bands (σ^*) and non-bonding bands. According to ligand field theory, the non-bonding bands can be splitted into three groups, d_{z^2} (a_1'), $d_{x^2-y^2}$ (e') and $d_{xz,yz}$ (e''). For the group VI 2H-TMDCs, only two d electrons can fully fill the a_1' band, rendering them semiconductors, as shown in figure 2.9d. In this thesis, 4 group VI transition metal based 2H TMDCs (MoS_2 , $MoSe_2$, WS_2 and WSe_2) are paid particular interest to because of their semiconducting nature and the ease of fabrication compared with others.

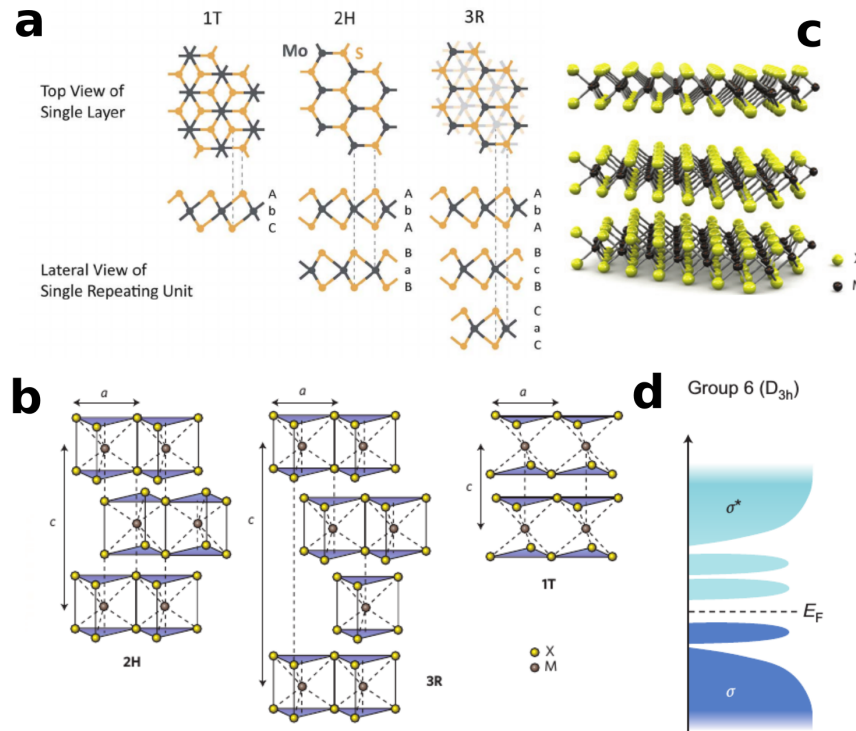


FIGURE 2.9: **a.** Top-view and side-view of TMDCs. **b.** 3D view of TMDCs. **c.** Atomic models of multilayer 2H-TMDCs. **d.** Schematic band diagram of *d*-electron filling of 2H group VI TMDCs band. **a,c** Reprinted with permission from ref. [123]. Copyright Royal Society of Chemistry 2015. **b.** Reprinted with permission from ref. [116]. Copyright Nature Publishing Group 2012. **d.** Reprinted with permission from ref. [124]. Copyright Macmillan Publishers Limited 2013.

2.3.2 Electronic structures

Compared with bulk TMDCs, the electronic structures of atomically thin TMDCs are determined not only by the atomic compositions and structural arrangement, but also by the dimensionality.[116] To better illustrate the evolution of band structures from bulk to monolayer, density functional theory calculated band structures and Brillouin zone of WS₂ are presented in figure 2.10. Clearly, the most prominent effect of the decreasing layer number is indirect-to-direct band gap transition with the band gap increasing from 1.3 eV for bulk to 2.1 eV for monolayer. This is manifested as strong excitonic photoluminescence of WS₂ and other group VI 2H-TMDCs even at room temperature, which will be discussed in the later section.[125, 126, 127]. Carefully

looking into the details of these band diagrams, it can be concluded that such indirect-to-direct gap transition is the result of the upshift of the conduction band (CB) valley at T point (middle point along the K - Γ symmetry line) and the downshift of the valence band (VB) hill while the CB hill and VB valley at K point change little. To understand the different layer number effect on the electronic bands at different symmetry points, it is essential to figure out the origins of these bands. In figure 2.10c, partial density of states (PDOS) diagram shows that the electronic bands around Fermi energy are mainly contributed by the $5d$ electrons of W atom and $3p$ electrons of S atoms. Detailed analysis of the charge spatial distribution (see figure 2.10d) reveals that the electronic bands at T and Γ points are composed of both the d orbitals of W atoms and the chalcogen p_z orbital. Therefore they can extend to the outer surface the layer. In contrast, the electronic bands at K point mainly stem from the localized d orbitals which are sandwiched in the middle of S-W-S layer. Thus they are less influenced by the interlayer coupling. The electronic structures of other TMDCs can mimic the description above and the difference lies in the band gap value. In general, the band gap decreases from sulphides to selenides of transition metals (Mo and W) due to the increase of orbit radius and the decrease of electronegativity.[128]

The indirect-to-direct transition from bulk to monolayer has been confirmed directly by the angular resolved photoemission spectroscopy (ARPES) [131] apart from optical spectroscopic methods.[125, 126] Zhang *et al.* [131] first performed the ARPES measurement on the monolayer MoSe_2 , presented in figure 2.11a. It is well known that ARPES can only detect the electron filled bands, corresponding to valence band in undoped semiconductors. In order to probe the CB minimum (CBM), strong electron donor, potassium, was employed to heavily n dope the MoS_2 , which enabled the detection of CBM, as shown in figure 2.11c. It clearly shows the that monolayer MoSe_2 is a direct gap semiconductor. Furthermore, carefully comparing the valence band maximum (VBM) at K point in figure 2.10a and figure 2.11a,b, an obvious difference observed is the valence band splitting of about 180 meV at K point. This is omitted

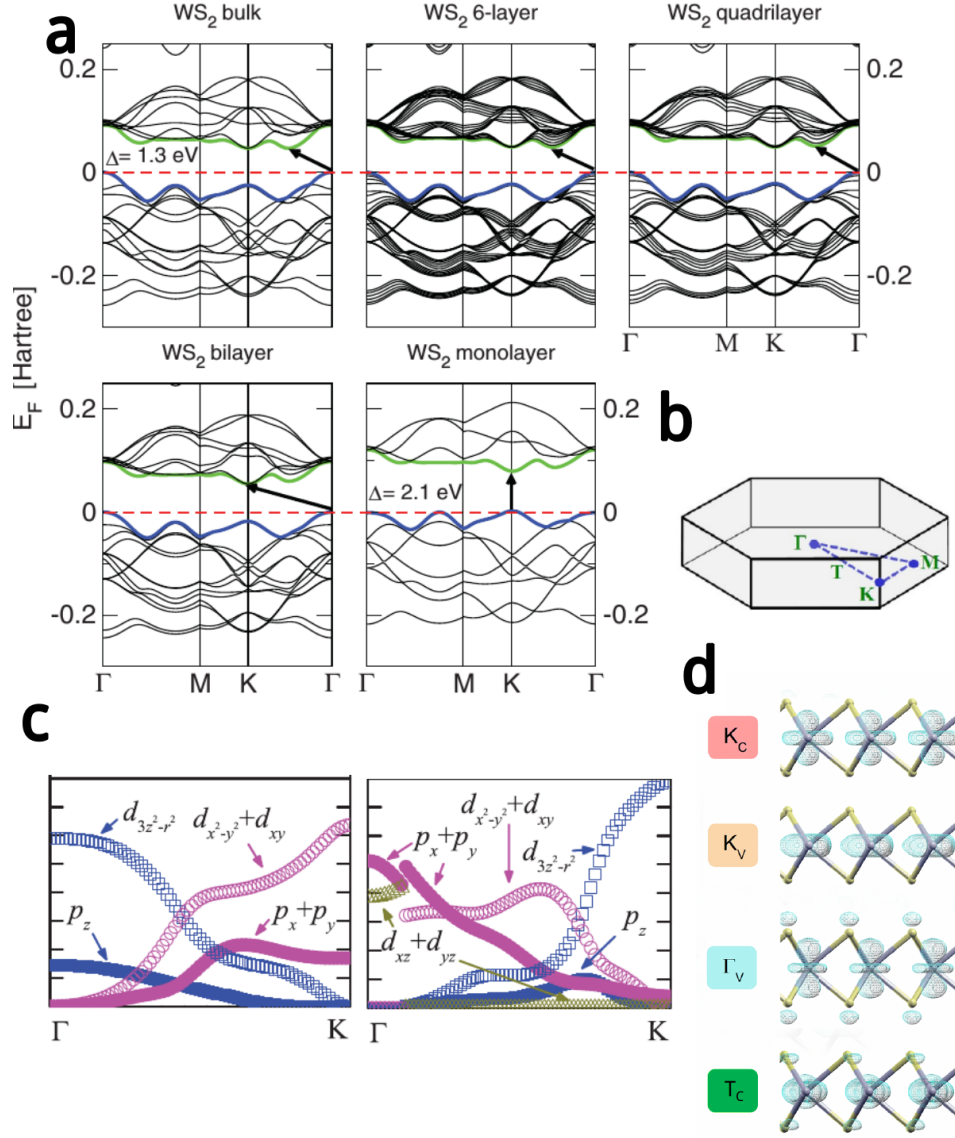


FIGURE 2.10: **a.** Evolution of band structures of WS₂ from bulk to monolayer according to DFT calculations. **b.** Brillouin zone for monolayer WS₂. **c.** Orbital contributions of Se and W along the symmetry line $\Gamma - K$ of valence band top (left) and conduction band minimum (right) in monolayer WSe₂. **d.** Schematic diagram of the spatial distribution of charge density corresponding to the CB valley at K and T points and the VB hills at K and Γ points. **a.** Reprinted with permission from ref. [129]. Copyright American Physics Society 2011. **b.** Reprinted with permission from ref. [127]. Copyright American Chemistry Society 2013. **c.** Reprinted with permission from ref. [130]. Copyright American Physics Society 2011. **d.** Reprinted with permission from ref. [122]. Copyright American Chemistry Society 2015.

in the early theoretical calculation due to the underestimate the strength of spin-orbit coupling (SOC).[131] Similar VBM splitting can be observed in other TMDCs, which are ~ 100 meV for MoS₂[132], ~ 400 meV for WS₂ [133] and for 230 meV WSe₂[134]. In monolayer TMDCs, the combination of inversion symmetry breaking and sizeable VBM splitting results in the non-degenerative spin states at K point (figure 2.11d) while in bilayer TMDCs, the degeneracy of the spin states are preserved at K point because the inversion symmetry is restored (figure 2.11e). Additionally, since K point is not a time reversal invariant point, this generates two inequivalent valleys (K and $-K$ valleys) with band edge electrons possessing opposite spin orientations. Therefore, the electrons in a certain valley can be excited selectively using circular polarized light, rendering another degree of freedom to carry and manipulate information in monolayer TMDCs.

2.3.3 Optical properties

The exotic optical properties of 2D TMDCs are the not only result of their unique electronic structures, but also due to the exceptional excitonic effect, which is caused by the reduced z dimension that greatly enhance the quantum confinement and therefore the electron-hole interaction, characterized by the exciton binding energies. The unique electronic structures and excitonic effect can therefore lead to the strong excitonic photoluminescence even at room temperature, which can be altered through various external modulation methods.

2.3.3.1 Excitonic effect

The absorption of an incoming photon excites an electron in a semiconductor to transit from valence band to conduction band and leave a positively charged hole in the conduction band, forming an electron-hole pair. At room temperature in many 3D semiconductors, the Coulomb interaction within the electron-hole pair is comparable to or

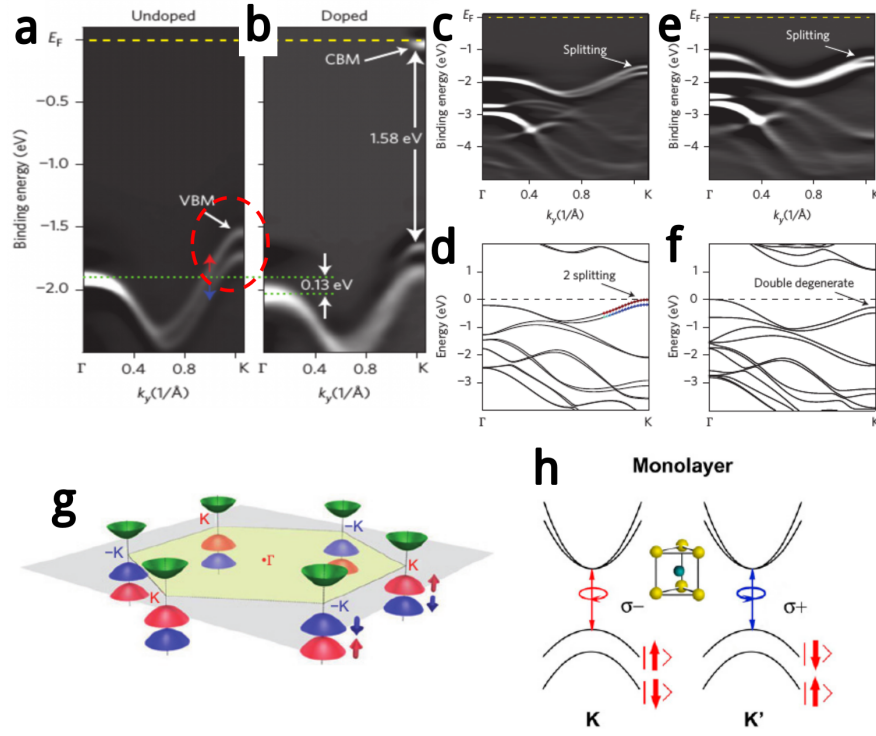


FIGURE 2.11: Second-derivatives of ARPES spectra of **a)** undoped and **b)** doped monolayer MoSe_2 . **c.** Second-derivatives of ARPES spectra of monolayer MoSe_2 . **d.** Calculated band structure of monolayer MoSe_2 . The different colour of the bands at K point indicate different spin orientation. **e.** Second-derivatives of ARPES spectra of bilayer MoSe_2 . **f.** Calculated band structure of bilayer MoSe_2 . **g.** Schematic diagram of spin state non-degenerate within the valley and opposite spin states assignment in two valleys. **h.** Schematic diagram of selective excitation of band edge electrons in certain valley. **a-f.** Reprinted with permission from ref. [131]. Copyright Macmillan Publishers Limited 2014. **g.** Reprinted with permission from ref. [124]. Copyright Macmillan Publishers Limited 2013. **h.** Reprinted with permission from ref. [135]. Copyright National Academy of Sciences 2014.

smaller than the room-temperature perturbation and thus, the electron-hole pair can be easily dissociated into free carriers. When considering the absorption rate, the only changing parameter is associated with band structure if the condition of incident light is fixed. Therefore, the optical properties of most conventional 3D bulk semiconductors at room temperature are mainly determined by their electronic band structures. However, if the temperature of a semiconductor is sufficiently low so that the electron-hole can maintain bounded, the electron-hole interaction cannot be neglected, the optical properties is not solely determined by the electronic band structure, but also by the

mutual Coulomb attraction between electron and hole, which is called excitonic effect and the bounded electron-hole pair is called exciton, a kind of quasi-particles. For example, the absorption spectrum of GaAs at room temperature is mainly dominated by electronic interband transition of photoexcited electrons from VBM to CBM, as shown in figure 2.12a. The lowest energy value of the solid line in the figure represents the electronic bandgap. With decreasing temperature, the whole absorption spectrum undergoes blue shift due to the bandgap expansion caused by lattice shrinkage.[136] Additionally, a new absorption peak emerges with photon energy below the electronic bandgap.

Stable excitons appear more frequently in semiconductors with reduced physical size since the Coulomb interactions within the exciton becomes stronger enough to survive after its collision with phonon even at room temperature due to the quantum confinement effect and reduced dielectric screening. For instance, the absorption spectrum of a GaAs quantum well with the width of about 10 nm experience presents several characteristic resonant peaks with energy lower than the band gap (the bandgap of GaAs quantum well increases with decreasing thickness), shown in figure 2.12b. The quantum confinement along the direction perpendicular to layer plane of monolayer TMDCs reaches the limit of the single molecular layer thickness (~ 0.7 nm)[125]. Therefore, the excitonic effect should play an even bigger role in the optical properties of atomically thin TMDCs compared with quantum well.[125] In figure 2.12c, the absorption spectrum at room temperature of monolayer MoS₂ is presented, where two obvious excitonic features locating at 627 nm and 670 nm originated from sub-bandgap transition, respectively. It can be concluded from the above discussion that the creation of stable excitons allows the absorption of photons with energy lower than the electronic bandgap and the lowest energy of absorbed photon is called optical bandgap. This leads to not only the redshift of the onset of absorption, but also one or several resonant absorption peaks in the spectrum.[137, p.77-82] The exciton binding energy is equal to the electronic bandgap less the optical bandgap. The electronic band gap characterizes

the single-particle excitations and its definition is the sum of the energies required to tunnel an electron and a hole separately into the material, while the optical band gap is defined as the energy needed to create an exciton. [138] It is an important parameter which can evaluate the Coulomb interaction within the excitons and the extent of excitonic effect. It can also provide insights into the design of photovoltaic where excitons must be broken for efficient charge extraction.[116] Therefore, the accurate determination of exciton binding energy of the atomically thin TMDC is of great importance, which will be introduced in the next part. Another important exciton related concept are the so-called bright and dark excitons. The difference between bright and dark excitons is that bright exciton can be probed in the linear optical spectrum while dark excitons can only be probed in the non-linear optical excitation method such as two-photon excitation.[157] The physical origin of the different behaviour between two kinds of excitons is the conservation of the orbital angular momentum.[144]

2.3.3.2 Exciton binding energy

In the conventional method, the exciton binding energy is determined by the energy difference between the onset of band edge absorption and the photon energy of first excitonic absorption peak. For example, the exciton binding energy in bulk GaAs extracted from figure 2.12a is 4.2 meV and the that of GaAs quantum well in figure 2.12b is about 10 meV. However, similar strategy cannot be applied to the determination of the exciton binding energies of monolayer TMDC due to two reasons: strong electron-phonon coupling and the overlap between higher excitonic peaks and the onset of inter-band transition. In order to tackle this problem, different research groups have advanced many novel methods from both experimental and theoretical aspects. It should be made clear here that the exciton discussed in the following text is the band-edge exciton at K point if not specified.

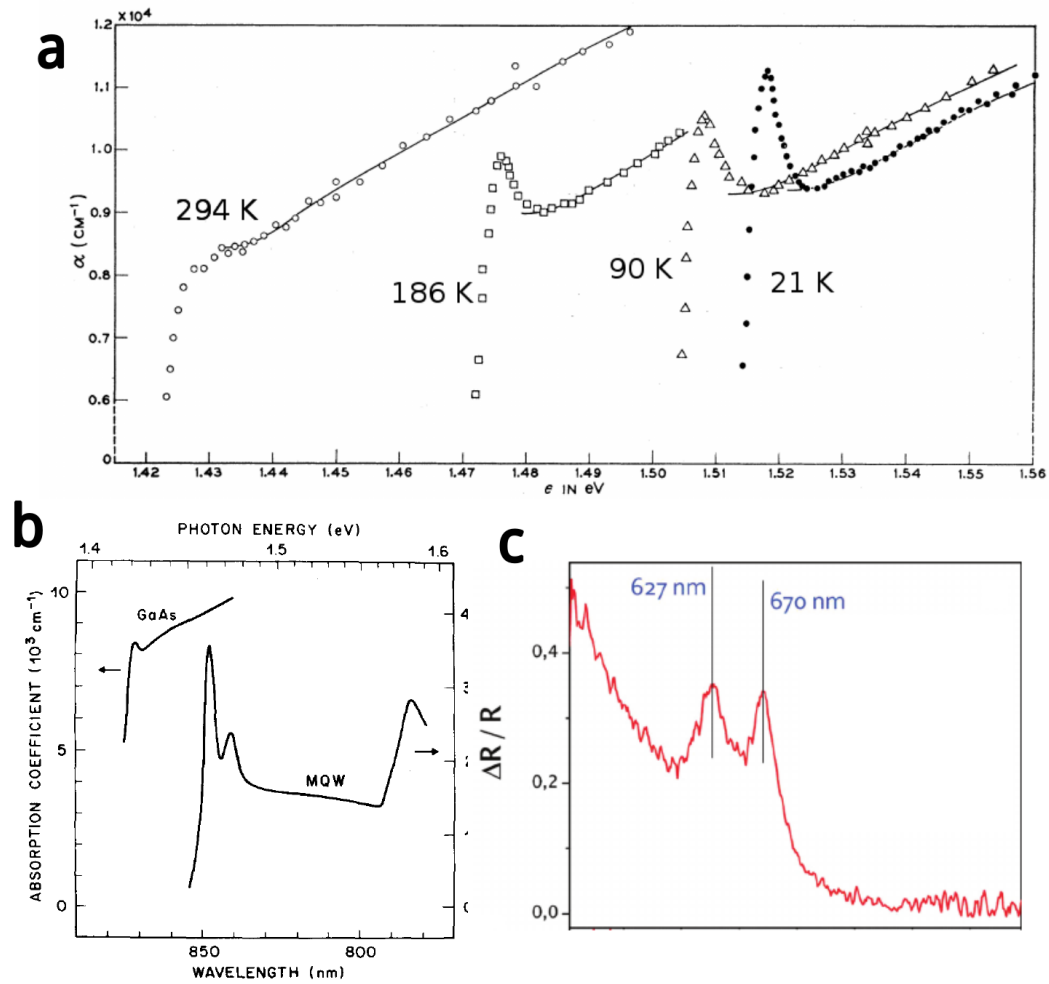


FIGURE 2.12: **a.** Optical absorption of bulk GaAs at different temperature. **b.** Optical absorption of GaAs quantum well. **c.** Optical absorption of monolayer MoS₂. **a** Reprinted with permission from ref. [139]. Copyright American Physics Society 1962. **b** Reprinted with permission from ref. [140]. Copyright American Institute of Physics 1982. **c** Reprinted with permission from ref. [125]. Copyright American Chemistry Society 2010.

Peimyoo *et al.* [141] derived the exciton binding energy by fitting the temperature dependence of PL integrated intensity with a modified Arrhenius law [142] based on the assumption that the temperature dependence of PL intensity was mainly due to thermal dissociation, presented in figure 2.13a. Based on their result, the exciton binding energy was determined to be ~ 0.53 eV. Their assumption is certainly not accurate because the temperature dependence of PL intensity is associated with other factors than exciton dissociation, *i.e.*, charged exciton formation.[143] However, their value is very close to what have been reported in other literature that will be introduced later, indicating thermal dissociation plays an important role.

Chernikov *et al.* [144] reported their observation of high order excitonic states of WS₂ with quantum principal number up to 5 *via* derivative reflectance spectrum. By fitting the excitonic peak positions as a function of quantum principal number according to hydrogenic Rydberg series in the 2D form, the electronic bandgap can be derived, [145] which is 2.41 ± 0.04 eV. By comparing with the first excitonic transition energy, they claimed the exciton binding energy of monolayer WS₂ to be 0.32 ± 0.04 eV. In figure 2.13c, it clearly shows that the first two excitonic peaks deviate from hydrogenic Rydberg series which is probably due to the different effect dielectric constant experienced by the excitons with different Bohr radius. To fix this problem, the authors apply a revised hydrogenic Rydberg model [146] to fit the experimental results which, surprisingly, yielded similar exciton binding energy. Zhu *et al.* [147] advanced that by taking the advantage of the different selection rules of linear and nonlinear optical transition, a combination of one-photon absorption and two-photon photoluminescence excitation (TP-PLE) spectroscopy can probe both the electronic bandgap as well as optical bandgap. The TP-PLE is an optical technique where the intensity of band-edge exciton PL is recorded as a function of two photons absorption which is a third-order optical process where the material absorbs two incident photons simultaneously. In linear absorption spectrum, the optical bandgap can be easily determined while the onset of band-edge absorption cannot due to its overlap with other high energy exciton

C. Due to the different selection rule, in TP-PLE the exciton C is a dark state and therefore the electronic bandgap can be determined, shown in figure 2.13d. According to their result, the exciton binding energy of monolayer WS₂ is 0.71 ± 0.01 eV.

It can be concluded from the previous discussion that the most difficult point in determining the exciton binding energy of TMDCs is the accurate measurement of the electronic bandgap. Ugeda *et al.*[148] reported that scanning tunnelling spectroscopy can be employed to determine the electronic bandgap of MoSe₂ while the optical bandgap is extracted from PL, shown in figure 2.13e,f. The exciton binding energy of MoSe₂ is about 0.55 ± 0.04 eV. Additionally, they also compared the exciton binding energy of monolayer MoSe₂ on two different substrates, bilayer graphene and HOPG, and found that the exciton binding energy of MoSe₂ on HOPG is 51% lower than that on bilayer graphene and the reduction comes from the decrease of the electronic bandgap. This indicates that the external dielectric environment can strongly modify the exciton binding energy. In order to eliminate the substrate induced effect, Klots *et al.*[149] performed their wavelength dependent photo-current measurement on suspended TMDC samples, from which they extracted the optical band gap and the lower bound of electronic band gap, shown in figure 2.13g. Based on their experimental results, the lower bound of exciton binding energy for monolayer suspended MoS₂ was claimed to be 0.57 eV.

Theoretical work has been carried out to predict the exciton binding energy of monolayer TMDC. Ramasubramaniam [150] performed calculations based on GW approximation in conjunction with BSE. Cheiwchanchamnangij *et al.*[151] reported the exciton binding energy of monolayer MoS₂ of 0.897 eV based on the quasiparticle self-consistent GW method. There are tons of work from either theoretical or experimental aspect, which certainly cannot be listed in details here. Instead, a table summary the recent work on exciton binding energy is presented, shown in table 2.1. For bilayer TMDCs, the binding energies for direct transition excitons are slightly less than half of the value

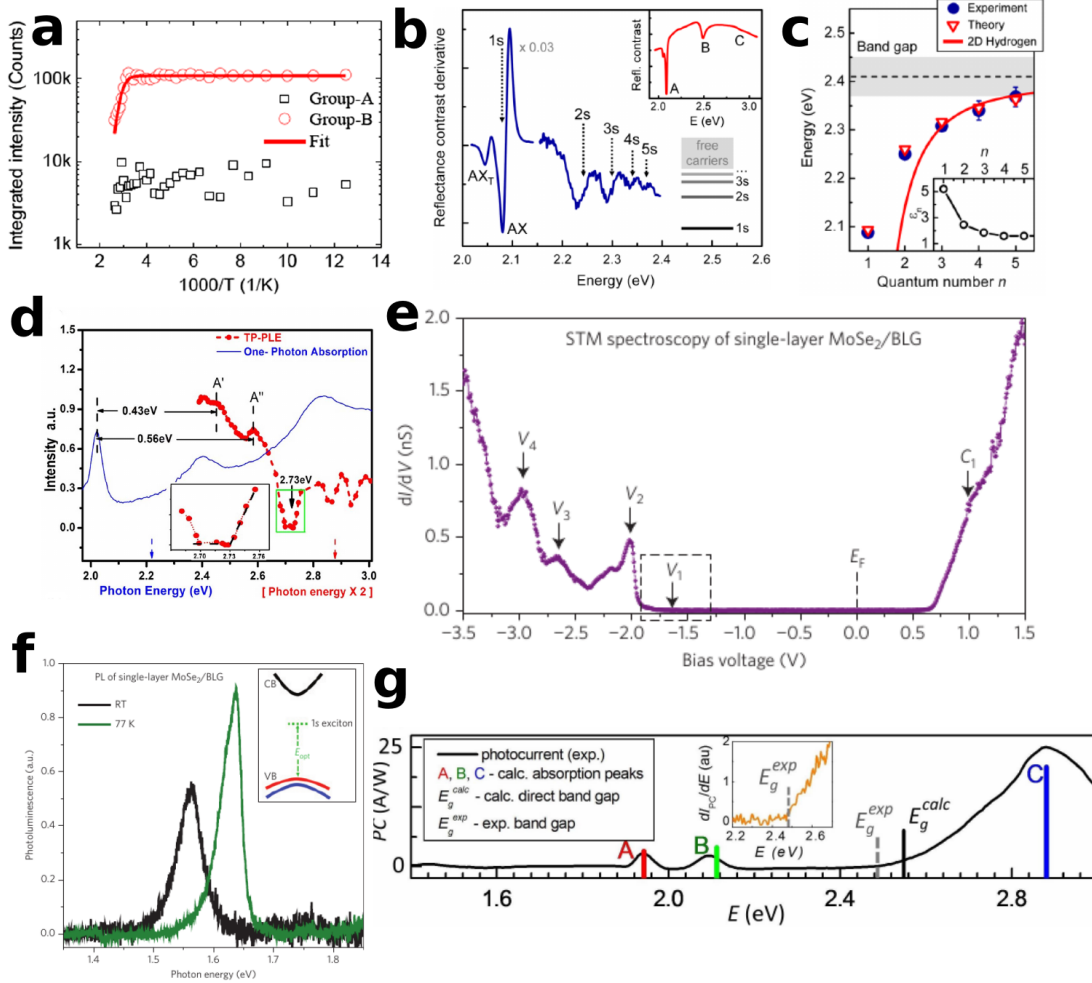


FIGURE 2.13: **a.** Temperature dependent PL intensity of monolayer WS₁. The solid line is the fitting curve according to a modified Arrhenius law. **b.** Derivative reflectance of monolayer WS₂. **c.** Experimentally and theoretically derived transition energies for excitons as a function of quantum number. **d.** Linear optical absorption spectra and two-photon photoluminescence excitation spectrum of monolayer WS₂. **e.** Scanning tunnelling spectroscopy (STS) of monolayer MoSe₂. **f.** PL spectra of monolayer WS₂. **g.** Photo-current as a function of excitation wavelength of suspended monolayer MoSe₂. **a** Reprinted with permission from ref. [141]. Copyright American Chemistry Society 2013. **b,c** Reprinted with permission from ref. [144]. Copyright American Physics Society 2014. **d** Reprinted with permission from ref. [147]. Copyright Nature Publishing Group 2014. **e,f** Reprinted with permission from ref. [148]. Copyright Nature Publishing Group 2014. **g.** Reprinted with permission from ref. [149]. Copyright Nature Publishing Group 2014.

in monolayer. For example, the binding energy of direct transition excitons in bilayer MoS₂ is 0.424 eV. [151]

2.3.3.3 Photoluminescence

PL is an inelastic optical process where a semiconductor emits light after it absorbs photons with higher energy. Typically, the energy of absorbed photon should exceed electronic band gap of the semiconductor. However, in low dimensional materials like atomically thin TMDCs with strong excitonic effect (see section 2.3.3.1), sub-electronic-band-gap excitation can also induce the PL process.[160] Due to its close relationship with the electronic band gap and excitonic effect, the characterization of the PL of TMDCs provides a convenient tool to monitor the electronic structure evolution with reducing dimensionality. Figure 2.14a shows the normalized PL spectra of MoS₂ with layer number ranging from 1 to 6. With additional layer, the PL peak at ~ 1.9 eV originated from K-K recombination in monolayer experience small spectral redshift. Meanwhile, a new peak emerges at lower energy, which corresponds to the indirect K- Γ recombination (left panel in figure 2.14d). Figure 2.14b presents the lowest peak energy as a function of layer number, which coincides with the electronic band gap shrinkage described in section 2.3.2. Similar PL evolution can also be observed in WS₂, as shown in figure 2.14c. It should be pointed out that the low energy peak of multilayer WS₂ stems from the indirect recombination of T- Γ , slightly different from the case of MoS₂.

The unique indirect-to-direct band gap crossover from multilayer to monolayer TMDCs leads to the sudden increase of the PL intensity, indicating the enhancement of PL efficiency in monolayer TMDCs. A specific term called quantum yield (QY) is used to evaluate the PL efficiency, which is defined as the ratio of the number of photons emitted over the number of photons absorbed.[161] Figure 2.15a shows the comparison of PL of monolayer and bilayer WS₂, which clearly shows the sudden increase in PL intensity

TABLE 2.1: Summary of exciton binding energy (E_b)

	E_b (eV)	Experiment or Theory	Method	Substrate
MoS₂	1.03[150]	Theory	GW+BSE	Suspended
	0.897[151]	Theory	Quasiparticle self-consistent GW	Suspended
	>0.57[149]	Experiment	Photocurrent	Suspended
	0.62[152]	Theory	Self-consistent GW + BSE	Suspended
	0.22±0.1[153]	Experiment	STS + PL	Graphite
	0.5265[154]	Theory	Path integral Monte Carlo (PIMC)	Suspended
	0.96[155]	Theory	G ₁ W ₀ -BSE	Suspended
	0.555[156]	Theory	Stochastic Variational Method	Suspended
MoSe₂	0.91[150]	Theory	GW+BSE	Suspended
	0.55[148]	Experiment	STS + PL	Bilayer graphene on 6H-SiC(0001)
	0.27[148]	Experiment	STS + PL	HOPG
	0.4769[154]	Theory	Path integral Monte Carlo (PIMC)	Suspended
	0.48[156]	Theory	Stochastic Variational Method	Suspended
WS₂	1.04[150]	Theory	GW+BSE	Suspended
	0.71[157]	Experiment + Theory	TP-PLE + GW-BSE	Fused-quartz
	0.44[158]	Experiment	PLE	Fused-silica
	0.32±0.04[144]	Experiment + Theory	Reflectance spectroscopy + hydrogenic Rydberg mode	SiO ₂ (300 nm)/Si
	0.53[141]	Experiment + Theory	Temperature dependent PL + Arrhenius law	Quartz
	0.63[152]	Theory	Self-consistent GW + BSE	Suspended
	0.71[147]	Experiment	TP-PLE + Absorption	Mica
	0.5098[154]	Theory	Path integral Monte Carlo (PIMC)	Suspended
	0.523[156]	Theory	Stochastic Variational Method	Suspended
WSe₂	0.9[150]	Theory	GW+BSE	Suspended
	0.4564[154]	Theory	Path integral Monte Carlo (PIMC)	Suspended
	0.47[156]	Theory	Stochastic Variational Method	Suspended
	0.37[159]	Experiment	TPPL + Fitting of band-to-band TP absorption	Quartz

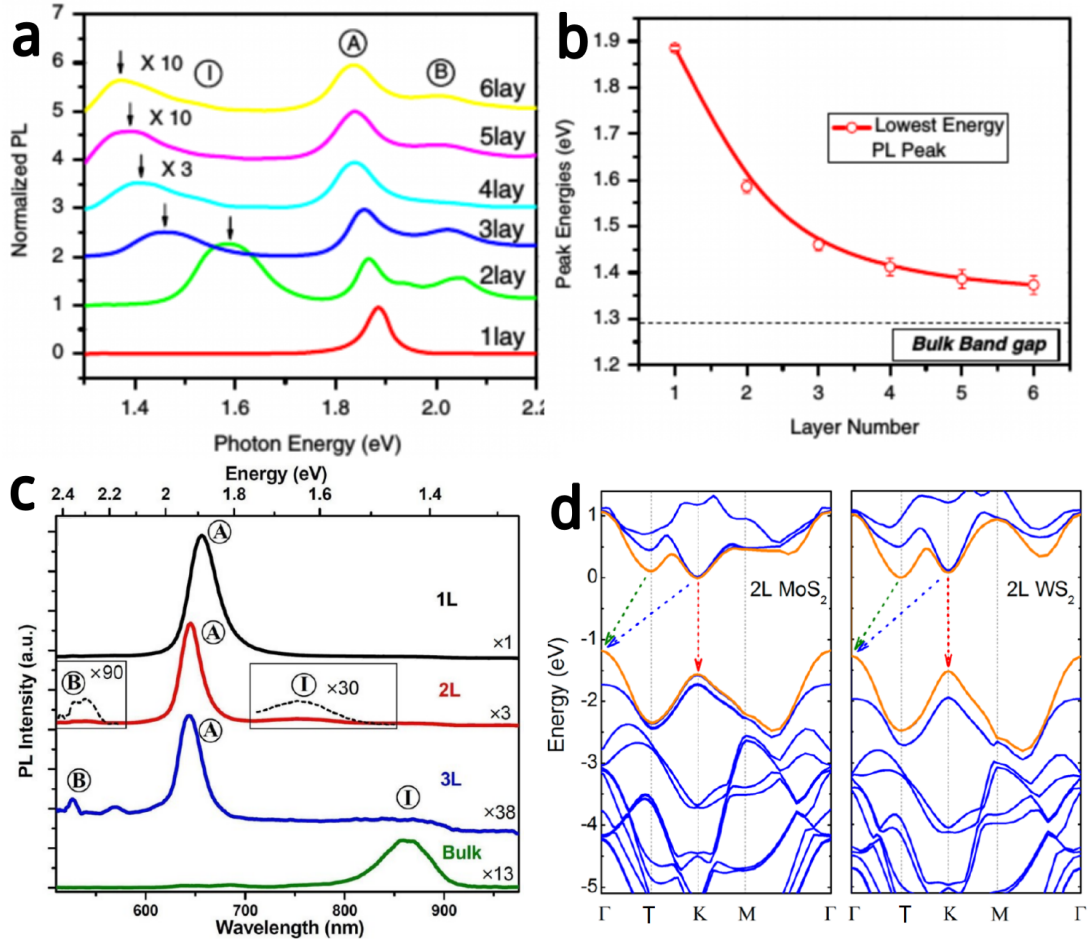


FIGURE 2.14: **a.** Normalized PL spectra of MoS₂ with different number of layers. **b.** Lowest peak energy as a function of number of layer. **c.** Normalized PL spectra of WS₂ with different number of layers. **d.** Band structures of bilayer MoS₂ and WS₂. **a,b.** Reprinted with permission from ref. [131]. Copyright Macmillan Publishers Limited 2014. **c.** Reprinted with permission from ref. [126]. Copyright American Physics Society 2010. **d.** Reprinted with permission from ref. [127]. Copyright American Chemistry Society 2013. **e.** Reprinted with permission from ref. [133]. Copyright American Chemistry Society 2013.

in monolayer. In figure 2.15b, the relative QY of WS₂ as a function of layer number is presented. It clearly reflects that the QY decrease with additional layers and the QY ratio between monolayer and bilayer WS₂ can reach more than 100. Similar trend has also been observed in MoS₂, shown in figure 2.15c. The dramatic drop in QY from monolayer to bilayer can be qualitatively explained by the simple band diagram in figure 2.15d,e. The pre-requisite for an optical transition is the conservation of momentum. Considering that the momentum of the emitted photon can be negligible compared with the momentum of electron (hole), an effective optical transition requires that the electron and hole have the same momentum. In direct gap monolayer TMDCs, the photoexcited electrons (holes) stay at VBM(CBM) with same momentum, leading to a high QY. However, in indirect gap multilayer TMDCs, the photoexcited electrons and holes relax to another band extrema due to the favourable energy, an additional phonon is required to facilitate the optical transition and therefore leads to the diminished QY. Although the emission ability of monolayer TMDCs is much better than multilayer TMDCs, their absolute QY is still very low compared with other efficient emitter. The inset in figure 2.15c shows that the QY of monolayer MoS₂ is only 1%.^[126] WS₂ is a better emitter compared with other TMDCs, but its QY can only reach 6%.^[162], which is unfavourable for many optoelectronic applications and needs to be improved.^[117]

Before any measures can be implemented to improve the QY of monolayer TMDCs, it is important to understand the factors that can affect the QY. Typically, a PL process involves three steps: 1) absorption, 2) relaxation and 3) recombination. Kozawa *et al.* ^[165] reported that the carrier relaxation path is excitation photon energy dependent, which can also affect the QY of monolayer TMDCs. The left panels of figure 2.16a,b present the PLE of monolayer MoS₂ and WS₂. It clearly shows that the emission brightness decreases with the increasing incident photon energy albeit the absorption is enhanced at these excitation energies (right panels in figure 2.16a,b), indicating that the QY in both monolayer MoS₂ and WS₂ decrease with excitation energy. This is due to the fact that the *C* absorption peak is associated with band nesting,^[166]

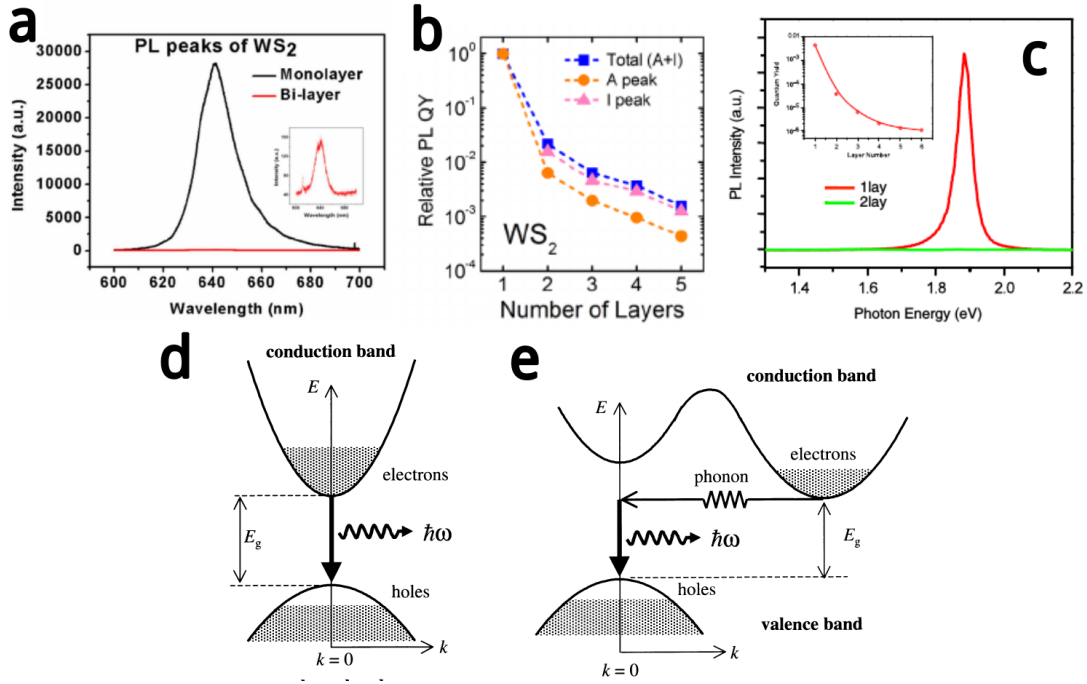


FIGURE 2.15: **a.** PL spectra of mono- and bilayer WS₂. Inset: details of PL spectrum of bilayer WS₂. **b.** Relative QY of WS₂ as a function of number of layer. **c.** PL spectra of mono- and bi-layer MoS₂. Inset: QY of MoS₂ as a function of number of layer. **d,e** Schematic diagram of electron-hole recombination in both **d**) direct and **e**) indirect band gap materials. **a.** Reprinted with permission from ref. [131]. Copyright Macmillan Publishers Limited 2014. **b.** Reprinted with permission from ref. [163]. Open Access Macmillan Publishers Limited 2015. **b.** Reprinted with permission from ref. [164]. Copyright American Chemistry Society 2013. **d,e.** Reprinted with permission from ref. [137]. Copyright Oxford University Press 2011.

where the CB and VB are parallel to each other. The photoexcited electrons (holes) associated band nesting first relax to CB valley at T (VB hill at Γ) point and part of them can be trapped there instead of relaxing to K point, leading to the suppression of QY, as shown in figure 2.16d.[167, 165] The QY of TMDCs can also be affected by the recombination pathways with two possible routes: radiative and non-radiative recombination. Yuan *et al.* [162] performed time-resolved photoluminescence (TR-PL) on monolayer WS₂, which showed that the decay time (τ_{ob}) of monolayer WS₂ is about 856 ps, longer than that in bilayer and trilayer. QY, τ_{ob} , radiative decay lifetime τ_r and non-radiative decay lifetime τ_{nr} can be correlated by the following equation:

$QY = \frac{\tau_{ob}}{\tau_r}$ and $\frac{1}{\tau_{ob}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}$. Combined with the QY of WS₂ of $\sim 6\%$, the τ_r and τ_{nr} are determined to be 13 ns and 900 ps, which indicates that more electron-hole pairs recombine non-radiatively before they can emit light.[162] Similar analysis can be applied to other TMDCs, which all shows that the low QY is the result of the dominated non-radiative decay.[168, 169] Wang *et al.* [170] further investigated the origin of the non-radiative decay, which suggested that the non-radiative electron-hole recombination in as-exfoliated TMDCs is directly associated with defects-related states, which can efficiently trap the photoexcited electrons and holes.[169] Therefore, it is important to minimize the defect-assisted recombination before optimized QY can be achieved. Chemical passivation has been proved to be effective to restore the QY, which will be discussed in details later.[171]

Carefully examining the details of the PL spectra of TMDCs reveals that it is comprised of more than one contributor. Figure 2.17a shows the PL spectrum of exfoliated monolayer MoS₂ with three components which are attributed to A peak (A exciton), B peak (B exciton) and A⁻ peak (trion). The schematic diagram of the optical processes of three components is presented in figure 2.17c. The A exciton peak stem from the band edge exciton associated with CBM and VBM at K point. B exciton originates from the valence band splitting at K point due to the strong spin-orbit-coupling.[126] Trion is a charged exciton, leading to the modification of the resultant PL emission energy which is lower than the that of exciton. The binding energy of a trion is defined as the energy to take the additional carrier away from the exciton and can be expressed as: $E_{b,A-} = \epsilon_A - \epsilon_{A-} - E_F$, in which $E_{b,A-}$ is the trion binding energy, ϵ_A is the exciton emission energy and ϵ_{A-} is the emission energy of trion and E_F is Fermi energy. Typically, $E_{b,A-}$ is in the range of 20-40 meV in TMDCs.[172, 143, 173, 174] Compared with the $E_{b,A-}$ in quantum well which is about few meV. The large trion binding energy infers the strong many-body effect in monolayer TMDCs.[175] In the PL spectrum of WS₂ shown figure 2.17b, only exciton and trion related emissions are observed, possibly due to the below-gap excitation for the B exciton. In many literatures, peak assignments

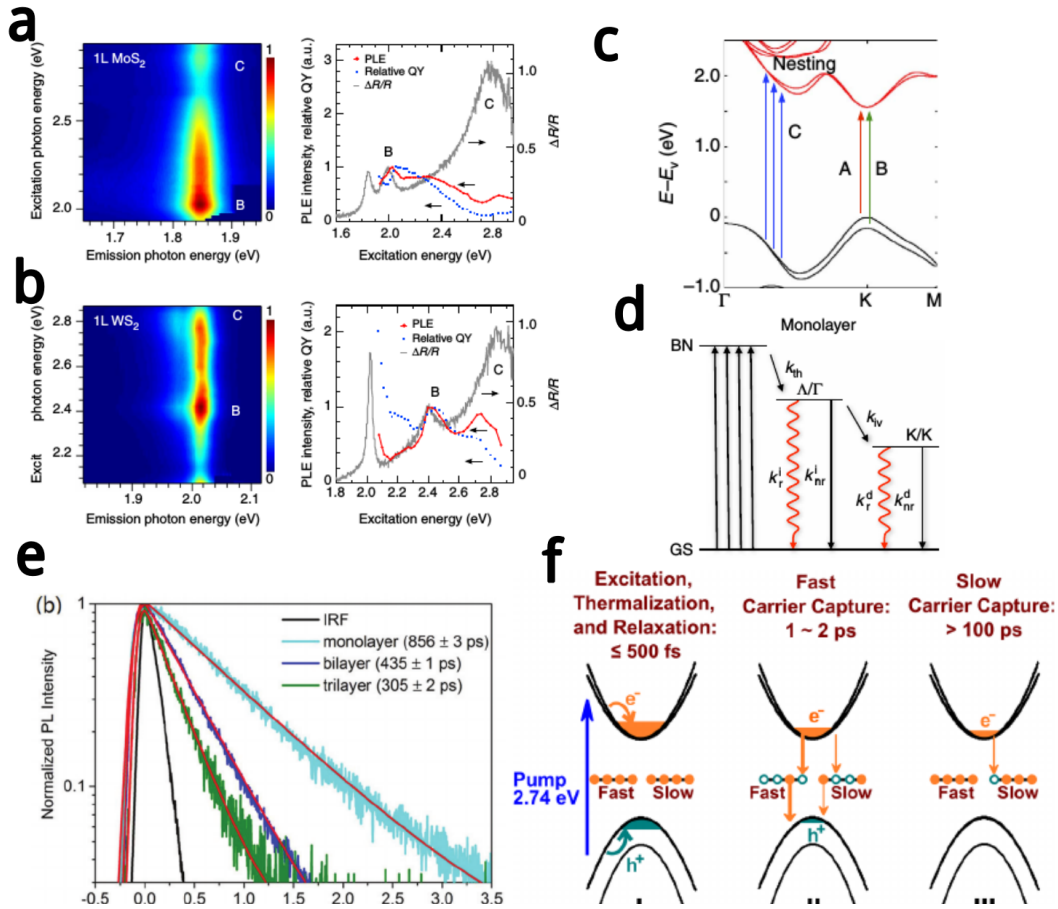


FIGURE 2.16: **a**. Photoluminescence excitation spectroscopy (PLE) of monolayer MoS₂ (left) and the PLE intensity (red), QY (blue) and reflection spectrum (grey) as a function of excitation photon energy. **b**. PLE of monolayer WS₂ (left) and its PLE intensity (red), QY (blue) and reflection spectrum (grey) as a function of excitation photon energy. **c**. Band diagram of monolayer TMDCs shows the transition originated from band nesting. **d**. Schematic diagram of photoexcited carrier relaxation and recombination pathways. **e**. Time-resolved PL spectroscopy of monolayer, bilayer and trilayer WS₂. **f**. Schematic diagram of the dynamics of photoexcited carriers in monolayer MoS₂. **a-d**. Reprinted with permission from ref. [165]. Copyright Macmillan Publishers Limited 2014. **e**. Reprinted with permission from ref. [162]. Copyright Royal Society of Chemistry 2015. **f**. Reprinted with permission from ref. [170]. Copyright American Chemistry Society 2015.

are only based on the peak positions, which can lead to many discrepancies. For example, the peak positions of A, A⁻ and B in figure 2.17a and the spectrum in red in figure 2.17d are very different, with spectral shift of about 30 nm. Similar situations can also be found in literatures about WS₂ photoluminescence. Therefore, knowing the exact peak positions of different excitonic transition is definitely non-trivial.[176] One of the discrepancies can happen between the spectra of exfoliated and CVD grown TMDCs. For example, the black curves in figure 2.17e,f present the PL spectra of exfoliated and CVD grown WS₂, which are distinct from each other. The PL of exfoliated sample possesses two features which locate at 2.01 eV and 1.96 eV while CVD grown sample only has one peak at 1.97 eV. Intuitively, one might attribute the peak in CVD sample to trion recombination. However, trion emission intensity should change little with gate voltage (figure 2.17g) [172] while the PL intensity of CVD sample in figure 2.17e has obvious dependence with gate voltage. Therefore, the PL peak of CVD WS₂ should be assigned to exciton emission. The redshift of exciton peak in as-grown CVD sample is very likely to come from the strain accumulated during growth due to the different thermal expansion between WS₂ and substrate. Indeed, after transfer process, the PL spectra of CVD WS₂ (figure 2.17b) looks almost the same with that of the exfoliated sample (figure 2.17h) since strain can be released after transfer.[177]

2.3.3.4 PL under different conditions

Chemical modification

For many applications, the ability to tune the electrical and optical properties of semiconductors is highly desired. In conventional bulk semiconductor industries, dopant diffusion and ion implantation are the most common techniques to achieve this goal, which, however, are not suitable for 2D TMDCs because they will inevitably damage the crystal structures, leading to the loss of exotic electrical[118] and optical properties[126] of these 2D crystals. As an alternative, chemical functionalization methods are usually

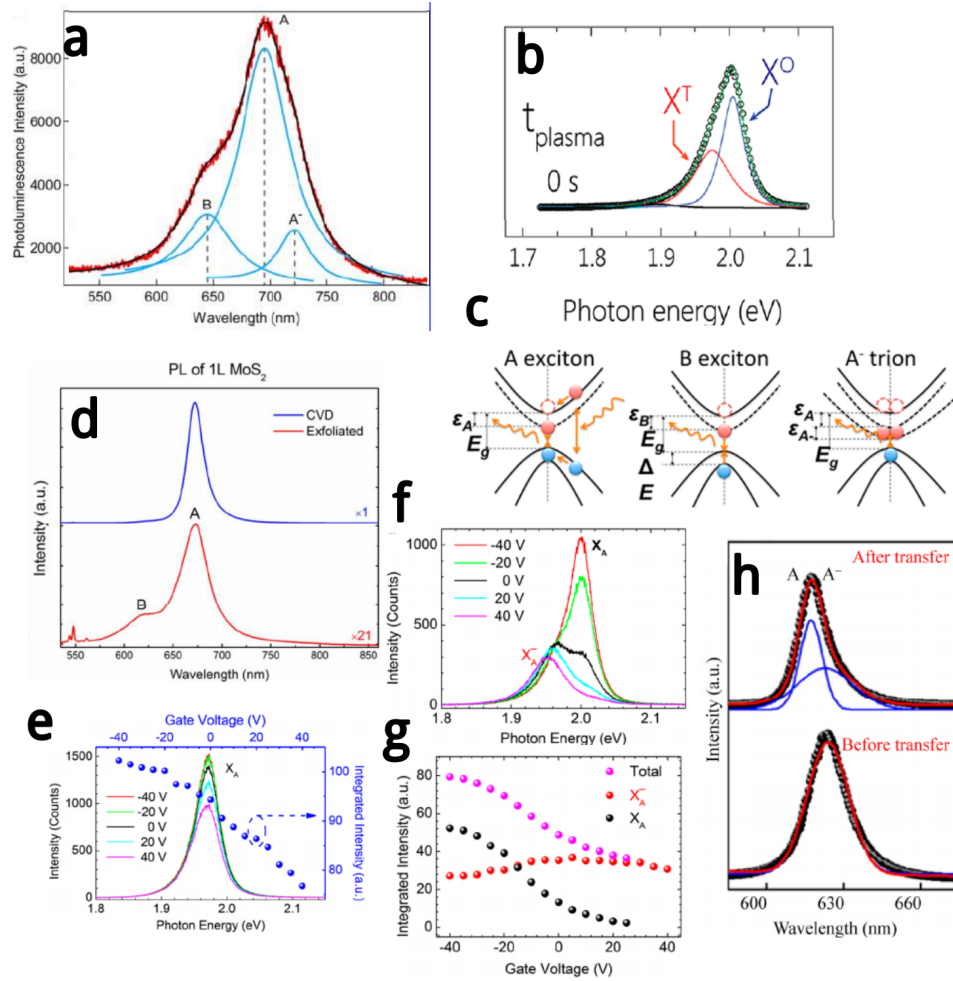


FIGURE 2.17: **a.** PL spectrum exfoliated monolayer MoS₂. Red curve: raw data. Blue curves: Lorentzian fitting curves for B exciton, A exciton and A⁻ exciton. **b.** PL spectrum of exfoliated monolayer WS₂. **c.** Schematic diagram of three excitonic transition in TMDCs. **d.** Comparison of PL spectra of between CVD (blue) and exfoliated (red) monolayer WS₂. **e.** Gate dependent PL spectra and integrated intensity of monolayer WS₂ from CVD sample. **f.** Gate dependent PL spectra and integrated intensity of monolayer WS₂ from exfoliated sample. **g.** Integrated intensity of PL components in **f** as a function of gate voltage. **h.** PL spectra of monolayer WS₂ comparison before and after transfer. **a.** Reprinted with permission from ref. [178]. Copyright American Chemistry Society 2014. **b.** Reprinted with permission from ref. [179]. Copyright American Chemistry Society 2015. **c.** Reprinted with permission from ref. [180]. Copyright American Chemistry Society 2014. **d.** Reprinted with permission from ref. [181]. Copyright American Chemistry Society 2014. **e-g.** Reprinted with permission from ref. [173]. Copyright American Chemistry Society 2015. **h** Reprinted with permission from ref. [182]. Open Access Springer 2015.

employed to manipulate the electrical and optical properties of TMDCs, the latter of which will be reviewed here. There are typically 4 routes to realize the goal, which are 1) charge transfer,[183, 184, 185, 186] 2) chemical passivation, [171, 187] 3) chemically induced phase transition,[188, 189] and 4) metal particles induced plasmonic effect[190]. Because of the strong many body effect caused by the quantum confinement, PL emission of atomically TMDCs is very sensitive to their carrier densities. Therefore, charge transfer between TMDCs and strong electron donor/acceptor can effectively modify the PL emission. Peimyoo *et al.*[186] demonstrated that the PL of monolayer WS₂ can be tuned *via* doping with F₄TCNQ, which is a strong electron acceptor. The PL emission of as-exfoliated monolayer WS₂ was dominated by trion emission while after it was doped by F₄TCNQ, another feature locating at higher energy emerged, which was believed to be the A exciton emission. Figure 2.18b shows the PL spectrum evolution with doping steps, which shows the A exciton emission gradually dominates the whole spectrum, indicating that the electrons are transferred from WS₂ to F₄TCNQ. Quantitative analysis of the contribution of different components indicates that the PL intensity of trion remains the same while emission intensity of exciton is greatly enhanced, which is similar to the gating effect on PL in MoS₂ and WS₂ as shown in figure 2.21e,g and figure 2.17f,g. Similar effect can also happen to monolayer MoS₂. On the contrary, if strong electron donor is applied, the PL intensity of monolayer MoS₂ can be quenched. (see figure 2.18d)[185] Additionally, Tongay *et al.* [183] reported that the emission intensity of monolayer MoS₂ can be broadly tuned by physisorbed oxygen molecules, and the highest intensity can reach 100 times of the intensity of the original value. Apart from that, it is also an reversible process, as shown in figure 2.18e. However, monolayer WSe₂ shows opposite response towards the oxygen adsorption, the PL of which can be greatly suppressed. A possible explanation is the difference in the initial transportation type with MoS₂ being n-type and WSe₂ p-type.

As described in section 2.3.3.3, the QY of monolayer TMDCs is very low compared with other direct gap semiconductor due to the defects enhanced non-radiative decay,

[170] which is unfavourable for optoelectronic applications. Han *et al.*[187] proposed that the PL of monolayer MoSe₂ can be greatly enhanced by hydrohalic acid treatment and the possible mechanism is probably the structural repairing. Recently, Bash *et al.* [171] reported that the defects in monolayer MoS₂ can be passivated by a non-oxidizing organic superacid:bis(trifluoromethane) sulfonimide (TFSI) and achieve a surprisingly high QY of over 95 %. Figure 2.18g presents the PL emission of monolayer MoS₂ before and after treatment. Clearly, the PL emission intensity of treated sample is greatly enhanced by about 190 folds compared with as-prepared sample. The fluorescence images in figure 2.18h demonstrate luminescence uniformity of the treated sample. They have also investigated the stability, which suggest that the high QY can be maintained after over one week in ambient condition. However, the detailed passivation mechanism is still not fully understood, which should be the target in the next stage.

In TMDCs, two of the possible polymorphs, 1T and 2H can be mutually transformed. Because of their different transport types with 1T being metallic and 2H being semiconducting, PL can thus be manipulated *via* phase engineering. Wang *et al.*[191] advanced that the phase of liquid exfoliated MoS₂ can be manipulated controllably through electrochemical reaction. In this report, the MoS₂ nanosheets are drop casted on transparent conductive electrodes as cathode and Pt wire as anode, which are then connected to an external power source. Both electrodes are then inserted into electrolyte with Li⁺ to form electric circuit. Depending on the polarity of bias, Li⁺ intercalation/deintercalation into MoS₂ can be controlled, and therefore the phase of the MoS₂. Figure 2.18i shows that reversible control of the PL intensity is achieved. Kappera *et al.*[188] also shows that selective area phase transformation within a single crystal domain of monolayer MoS₂ can be achieved, as shown by the PL map in figure 2.18j.

PL intensity of TMDCs can also be enhanced by the increasing absorption. One possible route is to employ the plasmonic structures, which can greatly strengthen the electric

field locally and thus the absorption. Figure 2.18k shows the schematic diagram of monolayer MoS₂ decorated with silica-gold nanoparticles, and the PL is enhanced by two folds.[190]

Temperature

Since the electronic structures of semiconductors are highly sensitive to the lattice temperature[136], temperature provides another effective tool to manipulate the PL emission of TMDCs. Figure 2.19a presents the PL spectra of monolayer MoSe₂ at various temperatures ranging from 15 K to 295 K.[143] At 15 K, two peaks can be resolved, locating at ~ 1.66 eV and ~ 1.625 eV, which are attributed to exciton and trion emission, respectively. With increasing temperature, one remarkable phenomenon is that the trion emission diminishes gradually until 150 K and then becomes hardly resolved. One possible reason is the thermal dissociation of the electron attached to the exciton in a trion. However, considering that the binding energy of an trion in monolayer MoSe₂ is about 30 meV, which is larger than the thermal perturbation at 150 K ($k_B T \approx 13$ meV), the quenching mechanism of trion should not be the thermal dissociation of the excessive carrier. Possible explanation might be the increased non-radiative decay of trion recombination. Another noticeable phenomenon is the pronounced redshift of exciton peak with elevated temperature, as depicted in figure 2.19b. The temperature induced spectral redshift is due to the shrinkage of the band gap, which can be simulated by an empirical equation:[136]

$$E_g(T) = E_g(0) - S\hbar\omega[\coth(\frac{\hbar\omega}{2kT}) - 1] \quad (2.13)$$

in which $E_g(T)$ is the band gap at temperature T, $E_g(0)$ is the band gap at 0 K, $\hbar\omega$ is an average phonon energy and S is a dimensionless coupling constant. Since the exciton binding energy changes little with temperature, Eq. 2.13 can also be employed to describe the temperature dependence of PL emission energy, as shown in figure 2.19b.

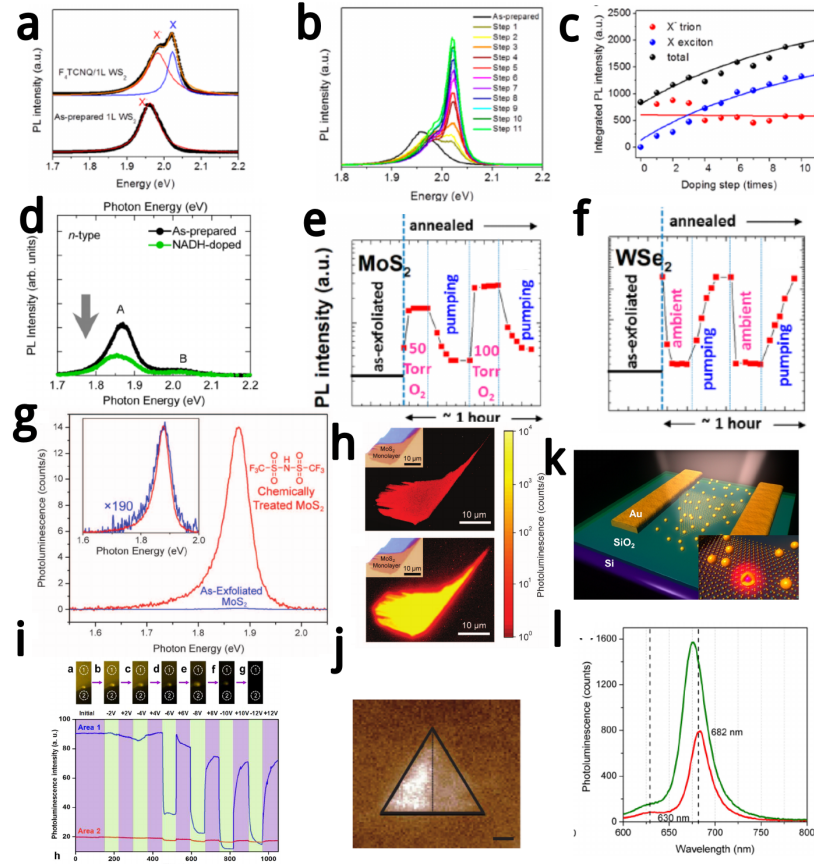


FIGURE 2.18: **a.** PL spectra of monolayer WS_2 before and after F_4TCNQ doping. **b.** PL spectra of monolayer WS_2 as a function of doping times. **c.** PL emission intensity of exciton X (blue), trion X^- and total spectra as a function of doping steps. **d.** PL of monolayer MoS_2 before and after doped electron donor NADH doping. **e,f.** PL peak modulation of **e)** monolayer MoS_2 and **f)** WSe_2 via oxygen adsorption and de-adsorption by pumping. **g.** PL spectra of monolayer MoS_2 before and after chemical passivation. **h.** Fluorescence image of monolayer MoS_2 before and after chemical passivation. **i.** Reversible modulation of PL intensity of monolayer MoS_2 via lithium intercalation and de-intercalation induced phase transition. **j.** PL mapping of partly phase transformed monolayer MoS_2 . Bright area in the triangle: High PL intensity, 2H phase. Dark area in the triangle: low PL intensity, 1T phase. **k.** Schematic diagram of monolayer MoS_2 coated with silica-gold nanoshell. **l.** PL spectra of MoS_2 before and after the decoration of nano-particles **a-c.** Reprinted with permission from ref. [186]. Copyright American Chemistry Society 2014. **d.** Reprinted with permission from ref. [185]. Copyright American Chemistry Society 2013. **e,f.** Reprinted with permission from ref. [183]. Copyright American Chemistry Society 2013. **g,h.** Reprinted with permission from ref. [171]. **i.** Reprinted with permission from ref. [191]. Copyright American Chemistry Society 2013. **j.** Reprinted with permission from ref. [188]. Copyright Macmillan Publishers Limited 2014. **k,l.** Reprinted with permission from ref. [190]. Copyright American Institute of Physics 2014.

Zhao *et al.* [133] also investigated the temperature dependence of few-layer TMDCs. Figure 2.19d shows the PL variations of bilayer WS_2 with temperature, in which two features originated from indirect transition (I) and A exciton are well resolved. The peak emission energies of the two features possess opposite response towards increasing temperature, where A peak redshifts while I peak, surprisingly, experience blueshift. The spectral shift is caused by change of band gap with temperature, which can be the result of two mechanisms: thermal expansion induced lattice constant increase and enhanced electron-phonon coupling. The authors then performed DFT calculation to explore the band gap change solely depend on the lattice constant elongation, from which they concluded that the effect of lattice constant change dominates the temperature dependence of indirect gap, while the enhanced electron-phonon coupling should account for the temperature dependent direct band gap. Temperature cannot only tune the emission energy, but also change the emission QY. Figure 2.19f-j demonstrate how PL intensities of TMDCs vary with temperature. The emission intensity in both monolayer and few-layer MoS_2 decrease because of the enhanced non-radiative rate with increasing temperature. Similar quenching effect also happens to the monolayer MoSe_2 , as shown in figure 2.19f. However, the multilayer MoSe_2 presents strikingly opposite temperature dependence, with the emission intensity being enhanced by about 10 times, which is believed to be the result of layer decoupling caused by thermal expansion along c -axis. The discrepancy of the temperature dependence of PL intensity between few-layer MoS_2 and MoSe_2 might come from the different direct and indirect band gap difference, with MoSe_2 possessing near degenerate direct and indirect gap.[192]

Strain

Applying strain to semiconductor can directly change the lattice constant and therefore the electronic structure,[138] which can be reflected by the change photoluminescence consequently. Conley *et al.* [193] first reported the strain effect on the PL of monolayer

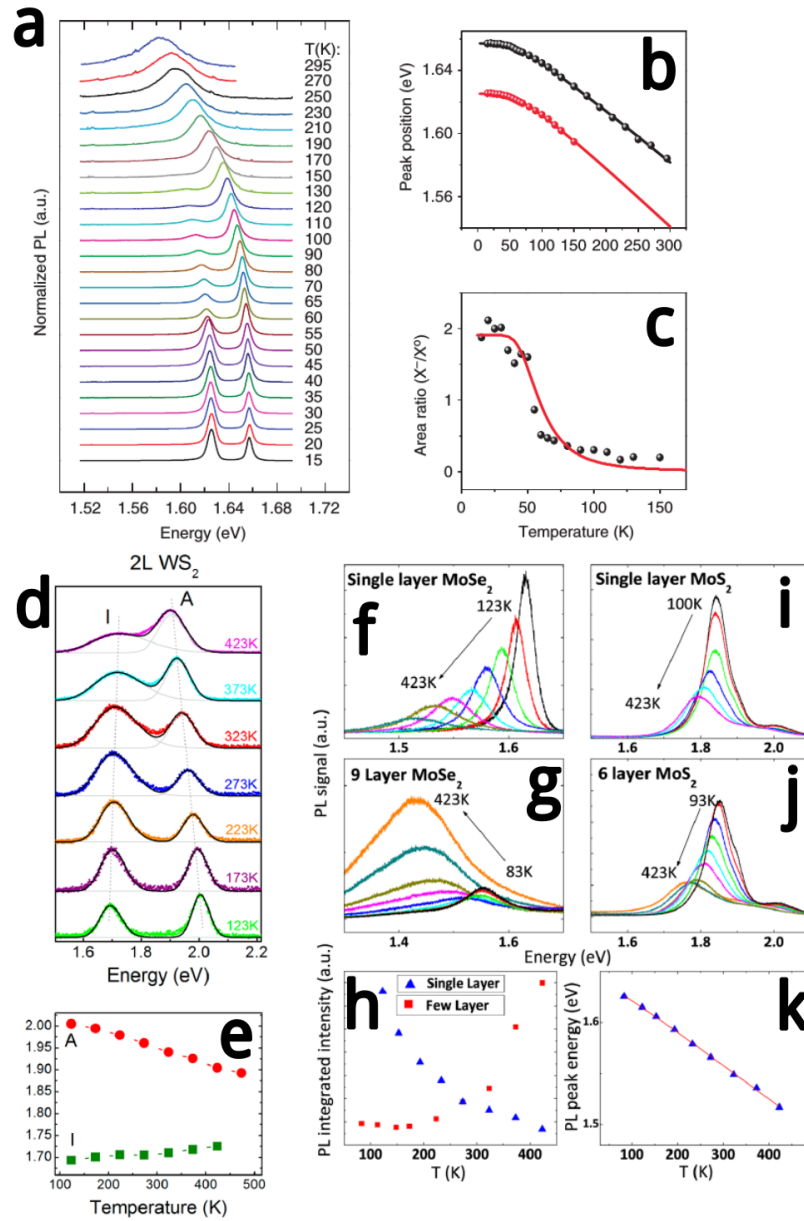


FIGURE 2.19: **a.** PL spectra of monolayer MoSe_2 under different temperature. **b.** Temperature dependence of peak emission energies of exciton and trion. Black spheres: exciton. Red spheres: trion. Solid line: fitting results according to eq. 2.13 **c.** Ratio of trion emission intensity over that of exciton. Solid line: curve fitting according to mass law. **d.** PL variation with temperature of bilayer WS_2 . **e.** Peak emission energies of A exciton and indirect transition as a function of temperature. **f,g.** PL spectra of **f** monolayer and **g** few-layer MoSe_2 at different temperatures. **h.** PL integrated intensity of monolayer and few-layer MoSe_2 as a function of temperature. **i,j.** monolayer and **g** few-layer MoS_2 at different temperatures. **k.** Peak energy of monolayer MoSe_2 as a function of temperature. **a-c.** Reprinted with permission from ref. [143]. Copyright Macmillan Publishers Limited 2013. **d,e.** Reprinted with permission from ref. [133]. Copyright American Chemistry Society 2013. **f-k.** Reprinted with permission from ref. [192]. Copyright American Chemistry Society 2012.

and bilayer MoS₂. In monolayer MoS₂, PL intensity decrease with increasing uniaxial strain applied and the emission energy of A exciton peak also decrease from 1.82 eV to 1.7 eV with a approximate linear dependence with strain of about 45 meV/%. The authors attribute the pronounced PL intensity drop to the direct-to-indirect band gap transition, as shown in the inset of figure 2.20a, which coincides with the theoretical prediction.[194, 195] However, indirect transition related peak is not observed even under the highest strain applied, which could be a strong evidence to oppose the argument of direct-to-indirect transition. In bilayer MoS₂, the PL intensity remains almost unchanged even at the highest strain (0.6%) applied. Both A exciton and indirect transition peak energy decrease linearly with rates of 53 meV/% for A exciton and 129 meV/% for indirect transition. Similar measurement has also been carried out on monolayer WS₂, which presents similar trend as MoS₂, but the emergence of indirect gap related peak is observed. [182] Another notable phenomenon is decreasing dissociation energy of trion, which may partly explain the absence of trion emission in as-grown CVD WS₂. [127]

WSe₂ presents very different response towards strain. Figure 2.20g shows that the PL intensity of bilayer can, surprisingly, be greatly enhanced under uniaxial strain and can reach the emission intensity as high as that of strain-less monolayer (dashed curve in figure 2.20g), which is believed to an indicator of indirect-to-direct gap transition. Careful analysis of the PL peak evolution with strain in figure 2.20g reveals the opposite response between direct and indirect band gap towards strain. Under 0% strain, the PL should be dominated by indirect transition. With 0.7% strain applied, there are two pronounced features in the PL spectra locating at 1.53 eV and 1.61 eV. Further increasing the strain leads to only one peak left which locates between 1.53 eV and 1.61 eV. Combined with the strain dependence of PL intensity, it can be concluded that the direct band gap shrinks with strain while the indirect band gap expands, which is opposite to what happens in MoS₂. This is possibly due to the different bands involved for indirect transition in the two materials. In MoS₂, the indirect transition

come from CBM at K to VBM at Γ while in WSe₂ it originates from CBM at T to VBM at K. Monolayer WSe₂ also behaves differently from monolayer MoS₂. Figure 2.20h demonstrate that the PL emission from monolayer WSe₂ is greatly enhanced by 5 times after strain is applied, which is the result that the direct band gap shrinks faster than indirect gap with strain, leading to more photoexcited carriers relaxing to CBM at K point.[196] Theoretical calculation also predicted that sufficiently high strain (10 %) could even lead to the transition from semiconducting nature to metallic behaviour.[194] Based on these results, Feng *et al.* [197] advanced theoretically that TMDCs with spatial variant strain field can be a basic building block for photovoltaic applications which can efficiently absorb a broad spectrum ranging from 2.0 eV to 1.1 eV. Two possible device architectures are proposed in figure 2.20i.

Electric field

Because of the maturity of the electronics industry, manipulating the optical properties of TMDCs through electrical method is a more desirable way than other methods like strain[199], temperature[192] and so on. Ross *et al.*[143] reported their observation of gate tunable PL in monolayer MoSe₂. Exfoliated MoSe₂ is implemented into an FET setup, as shown in figure 2.21d. At zero voltage, the PL spectrum was dominated by neutral exciton X^0 and X^I which was believed to related to impurities introduced during device fabrication. With increasing (decreasing) gate voltage, the intensity of X peak decreased continuously, while another peak, X^- (X^+) emission was enhanced. Such transition is very likely due to the electrostatic charging of MoSe₂ induced by the applied back gate voltages. Figure 2.21c shows the quantitative relationship between PL intensities of different components and back gate voltages. Clearly, it shows an opposite gate voltage response between neutral and charged excitons. Mak *et al.* [172] performed similar measurement on exfoliated monolayer at room temperature MoS₂, from which the gate tunable PL emission was also observed. Figure 2.21e shows the spectra of monolayer MoS₂ under different gate bias. However, the PL intensity

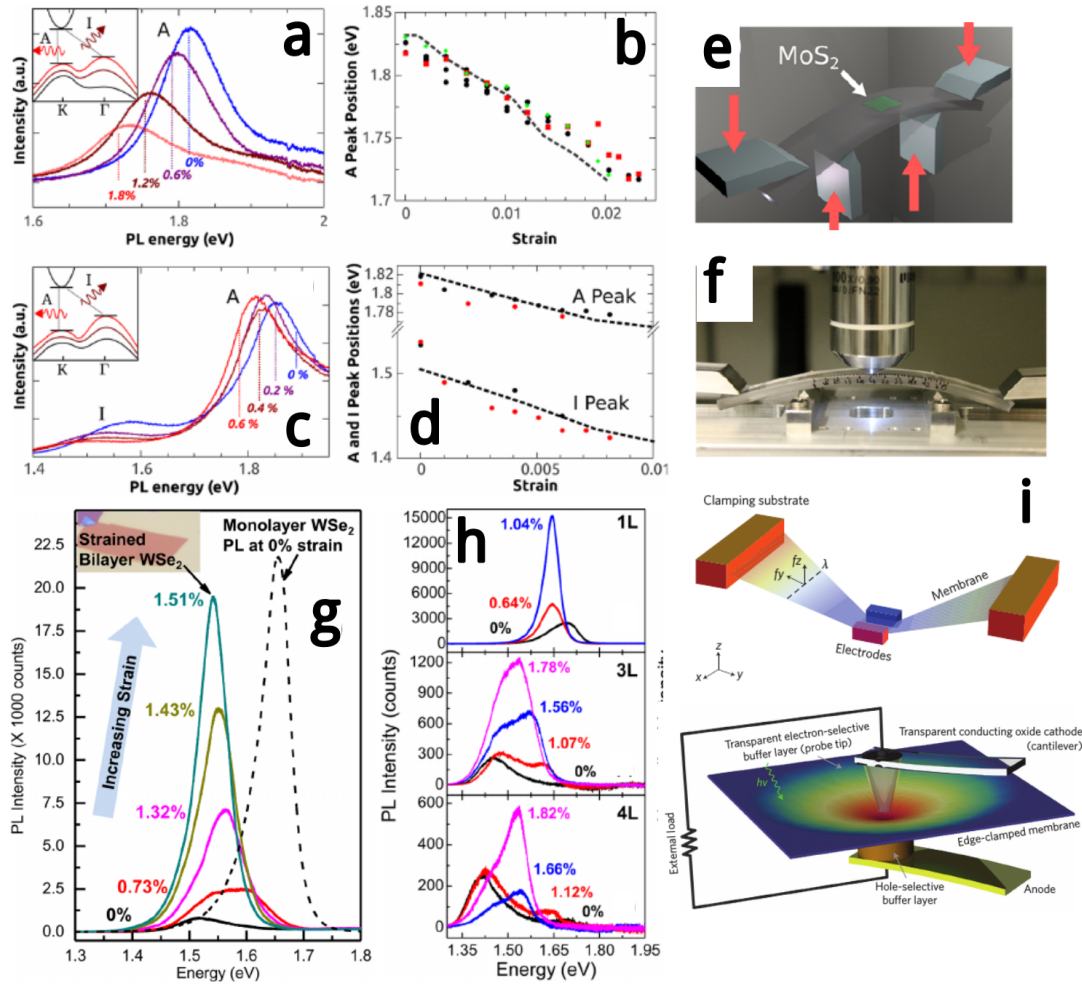


FIGURE 2.20: **a.** PL spectra of monolayer MoS₂ under different strain. **b.** A exciton peak energy of monolayer MoS₂ evolution with strain. **c.** PL spectra of bilayer MoS₂ under different strain. **d.** PL peak energy of A exciton and indirect transition of bilayer MoS₂ as a function of strain. **e,f.** Schematic diagram and photograph of experimental setup to apply uniaxial strain to MoS₂. **g.** PL spectra of bilayer WSe₂ under different strain. Dashed curve: PL spectrum of monolayer WSe₂ for comparison. **h.** PL response toward strain within monolayer, trilayer and quadlayer WSe₂. **i.** Schematic diagram of two possible device architecture for photovoltaic applications based on strained TMDCs. **a-f.** Reprinted with permission from ref. [193]. Copyright American Chemistry Society 2013. **g,h.** Reprinted with permission from ref. [198]. Copyright American Chemistry Society 2014. **i.** Reprinted with permission from ref. [197]. Copyright Macmillan Publishers Limited 2012.

presents different response toward gate voltage compared with MoSe₂. The intensity of excitons PL decreases monotonically with gate voltage while the trion emission intensity remains almost unchanged. The author also claim that the low temperature data also show similar trend. This phenomenon can also be observed in WS₂ (See figure 2.17f,g), [173] while monolayer WSe₂ presents similar intensity variation as that of monolayer MoSe₂. Such discrepancy is very likely due to the fine difference in the excitonic properties between S and Se based TMDCs, which requires further investigation to confirm. Another noticeable fact is the enhanced binding energy of charged excitons with increasing gate voltage, which is probably the result of quantum stark effect.[200]. Further increase in the vertical electric field can even modify the electronic structures of TMDCs. Theoretical calculations predicted that the band gap of TMDCs can be reduced, or even closed with sufficiently high electric field, as shown in figure 2.21j. [201, 202, 203, 204] The bilayer TMDCs can exhibit more interesting response due to the inversion symmetry breaking after electric field is applied, leading to the revival of optical circular dichroism [205] or Zeeman-like splitting[206].

High power optical excitation

The previous review mainly focuses on the optical properties of TMDCs under low excitation density, where the injected exciton densities are diluted enough so that the exciton - exciton interaction can be neglected. It is also called the linear optical response regime. Considering that the atomically thin TMDCs possess enhanced quantum confinement,[126] they provide an ideal platform to observe electronic as well as excitonic many-body effect, which naturally raises an question: what does the photoluminescence look like under high optical pump?

Figure 2.22a presents the PL spectra of monolayer WSe₂ under different excitation fluence and the spectra have been normalized according to the excitation power. It clearly shows that the PL intensity per incident fluence drops dramatically without

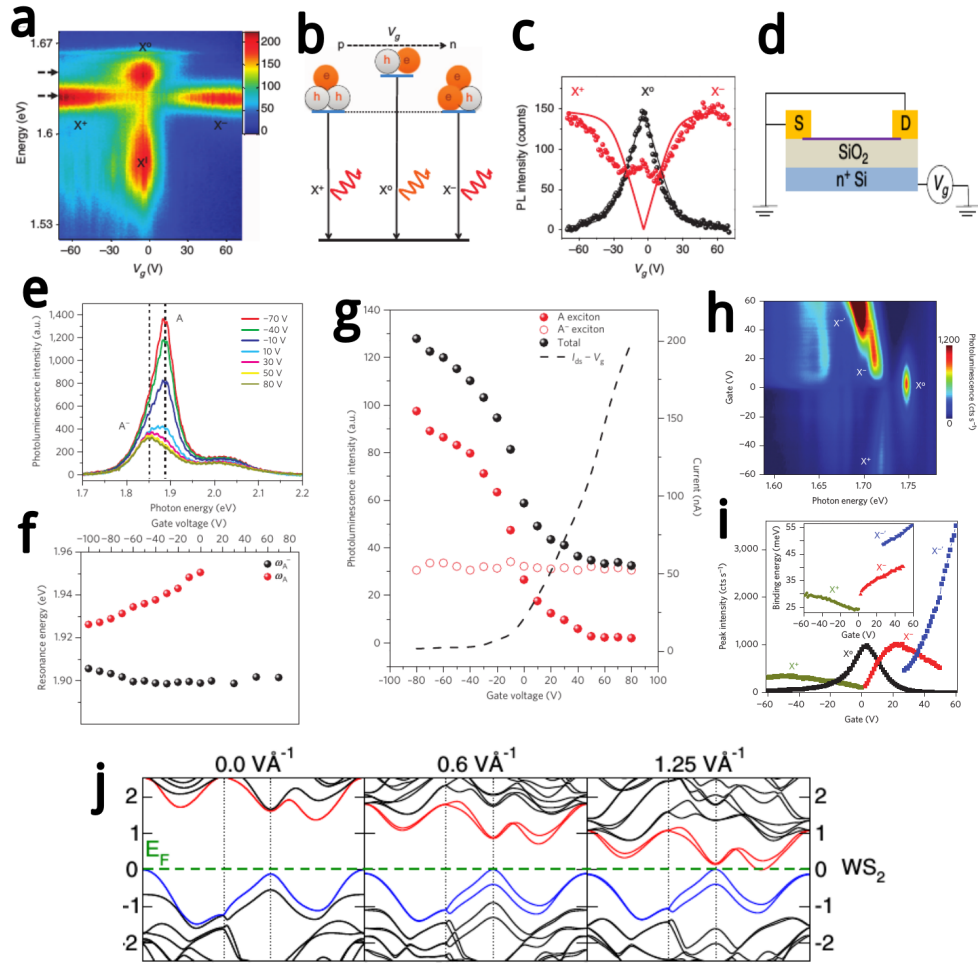


FIGURE 2.21: **a.** PL colour map as a function of back gate voltage of monolayer MoSe₂ at temperature of 20 K. **b.** Schematic diagram of negatively charged, neutral and positively charge exciton recombination. **c.** PL intensity of neutral and charged excitons of monolayer MoSe₂ as a function of back gate voltage. Spheres: raw data. Solid line: simulation result. **d.** Schematic diagram of an FET setup. **e.** PL spectra of monolayer MoS₂ as a function of back gate voltage. **f.** MoS₂ PL emission energy of excitons and negative trion as a function of gate voltage. **g.** MoS₂ PL intensity of exciton, trion and overall spectra as a function of back gate voltage. Dashed line: source-drain current. **h.** PL colour map of monolayer WSe₂ as a function of gate voltage. **i.** WSe₂ PL intensity of neutral and charged excitons as a function of gate voltage. Inset: corresponding peak energy variation with gate voltage. **j.** DFT calculated band structure of monolayer WS₂ as a function of vertical electric field strength. **a-d.** Reprinted with permission from ref. [143]. Copyright Macmillan Publishers Limited 2013. **e-g.** Reprinted with permission from ref. [172]. Copyright Macmillan Publishers Limited 2014. **h,i.** Reprinted with permission from ref. [207]. Copyright Macmillan Publishers Limited 2013. **j.** Reprinted with permission from ref. [203]. Copyright Royal Society of Chemistry 2013.

any spectral shape change (see figure 2.22b). The excitation power dependence of PL intensity is depicted in figure 2.22c, which demonstrates that power dependence deviates largely from the linearity regime under high excitation fluence. [208] Taking into consideration that the exciton density should have linear relationship with excitation power, the deviation from linear power dependence indicates that the increasing exciton density can influence the decay channels, which may originate from the exciton - exciton interactions. Time-resolved photoluminescence (TR-PL) can shed light on the decaying channel since the lifetime of excitons varies with the decay channels. Yuan *et al.*[162] performed TR-PL on monolayer WS₂ under different excitation power, as shown in figure 2.22d. With increasing incident power, another decay component with much shorter lifetime emerges, which is then attributed to exciton - exciton annihilation (EEA). EEA is the result of excitonic many-body effect in which energy emitted from the recombination of one exciton is transferred non-radiatively to another exciton. It can be understood as the excitonic analogy of the Auger recombination process.[209] The EEA process can be described by the following chemical reaction formula: $E + E \rightarrow EE \rightarrow E$ (higher energy) (E stands for exciton). According to chemical reaction rate, the EEA rate should have a quadratic relationship with exciton density. Therefore, the dynamics of exciton density at time t after excitation can be described as the following expression:[162]

$$\frac{dN}{dt} = -\frac{1}{\tau}N - \gamma N^2 \quad (2.14)$$

in which N is the the exciton density, τ is the exciton lifetime and γ is the EEA rate. With increasing exciton densities, EEA can gradually dominate and thus the first term in eq. 2.14 can be neglected. Therefore, the solution to eq. 2.14 is $N(t) = N_0/(1+\gamma N_0 t)$. By fitting the experimental results with the solution to eq. 2.14, it can be extracted that the EEA rates for monolayer TMDCs are $(4.3 \pm 1.1) \times 10^{-2} \text{cm}^2 \text{s}^{-1}$ for MoS₂, [209] $0.41 \pm 0.02 \text{cm}^2 \text{s}^{-1}$ for WS₂, [162] $0.33 \pm 0.06 \text{cm}^2 \text{s}^{-1}$ for MoSe₂ [210] and $0.35 \text{cm}^2 \text{s}^{-1}$ for WSe₂. [208] EEA rates of indirect excitons in bilayer and trilayer are reduced because EEA process must obey both momentum and energy conservation and therefore EEA

is an phonon assisted process for indirect excitons. It should also be noted that the threshold exciton densities for the observation of EEA is about 10^9 cm^{-2} and the average excitons separation distance is over 600 nm while the Bohr radius for excitons in TMDCs is only $\sim 4 \text{ nm}$,^[144] indicating very large exciton diffusion length, as show in figure 2.22e. ^[211] EEA defines the maximum bright excitons density that can be achieved in a semiconductor. In addition, EEA is the time reversed image of multiple exciton generation, a process which can greatly enhance the efficiency in light harvesting devices. The large EEA rate observed here indicates that TMDCs may be suitable for highly efficient photovoltaics. ^[209]

Further increase the incident power can shorten the average distance between two excitons. Therefore, the wave functions of the two excitons can overlap with each other and fuse together into a a four body, new excitonic species: biexcitons.^[212] This can lead to new luminescent feature in the PL spectra of TMDCs. The luminescence process of biexciton is shown in figure 2.22. With dense enough excitons in TMDCs, two excitons can interact with each other and fuse together, forming a four-body with higher energy (blue line). Then one of the exciton will decay radiatively and emit a photon with energy corresponds to the blue line with arrow, which is smaller than normal exciton due to the binding energy of the biexciton. The rest exciton will then go back to its original energy state and decay like a normal exciton. Shang *et al.*^[173] reported the first observation of bright biexcitons emission in monolayer WS_2 . Figure 2.22f shows the cryogenic PL spectra of monolayer WS_2 under three different excitation power. At low excitation power, there are two main features in which high energy peak is contributed by both exciton and trion while the low energy feature is believed to originate from localized states (LS) from surface adsorbates. Under high power excitation, the spectral weight of LS is reduced while a new peak between LS and trion in energy emerges. Figure 2.22g presents the power dependence of PL intensity of exciton, trion, the new peak and LS, with both excitons and trions showing linear dependence and the

sublinearity of LS power dependence. The new peak presents a quadratic power dependence, which is the characteristic feature for biexciton luminescence.[173] However, it should be pointed out that this rule cannot apply to all excitation power regime. A more general rule is quadratic relationship between the luminescence of biexciton and exciton.[213] and detailed analysis is presented in Chapter 6. The binding energy of biexciton is defined as $E_{b,X_A X_A} = 2E_{X_A} - E_{X_A X_A}$ and can be extracted from PL spectrum as the difference between the emission of biexciton and exciton. The binding energy of biexciton is 45 meV in monolayer WS₂ and 52 meV in monolayer WSe₂, which are almost two order of magnitude than those in quantum well, due to the exceptionally large exciton binding energy in atomically TMDCs.[214] The temperature stability of biexcitons in TMDCs has also been investigated, which shows drastic reduction in emission intensity after 40 K, indicating an increasing dissociation rate of biexciton with temperature. [214] However, Lee *et al.* [215] have reported the biexciton luminescence at room temperature with a preferential biexciton formation site at the edges due to the large population of excessive charge carriers caused by the excessive incorporation of growth promoters. This is contradictory to the conventional knowledge of biexciton formation process where only excitons participate. Another unexpected experimental result is that the gate dependent emission intensity of biexcitons in monolayer WS₂ where positive gate bias (more charge carriers and reduced number of neutral exciton) can greatly enhance the brightness of biexciton emission, as shown in figure 2.22j. Both the experimental findings raise the question about the biexciton formation process in monolayer TMDCs. Although Zhang *et al.* [156] proposed theoretically that the biexciton in monolayer TMDCs can be composed of a trion and a hole (figure 2.22k), more experiments should definitely be carried out to confirm this argument.

In addition, under high optical pump power, TMDC can also exhibit more optical non-linearity like second-harmonic generation which can emit photons with energy double that of the incident photons[216], or even the completely different optical response with

disappearance of the excitonic resonance[217], which will not be reviewed here as they go beyond the scope of this thesis.

Defects, edges and grain boundaries

Apart from external modulation method, PL emission of TMDCs also show strong dependence on the structural configurations. Van der Zande *et al.*[218] reported that the PL of two different kinds of grain boundaries (GBs) of monolayer MoS₂. Figure 2.23a shows PL mapping of GB across the middle of a mirror twin island. Dimmer PL emission intensity can be clearly observed at the GB region. On the contrary, the PL emission intensity is enhanced by 100 % at the tilt GB, as shown in figure 2.23b. The distinct behaviour between the PL response of two different kinds of GBs is attributed to the different local doping level induced by the different structural configurations. In mirror GB, the dominant structures are 8-4-4 defects (the number of atoms in a ring) and are metal atoms rich, leading to n type doping, thus to the PL quenching. In contrast, the tilt GB is p-type doped because the atomic structures are dominated by the sulphur-rich 5-7 defects. Gutierrez *et al.* [127] showed that edges of monolayer CVD grown WS₂ exhibit non-uniform PL even within the same single crystal domain, as shown in figure 2.23c. The PL mapping of a monolayer single-crystal WS₂ domain clearly shows the spatial dependence of PL emission, with dramatic enhancement at the edge region. The PL peak also experience great redshift from 1.95 eV in the centre to 1.99 eV along the edge region. Spatial variant strain is excluded according to the uniform $E'/E_g^1/E_{2g}^1$ Raman mapping, which will be discussed in section 2.3.3.5. Similar edge related PL enhancement has also been reported in a recent report, in which the authors claimed that the enhancement and spectral red shift were originated from the formation of biexciton[215] (see section 2.3.3.4). Heating induced crack can also lead to PL enhancement, as demonstrated by Nan *et al.*[219]. Figure 2.23d presents the PL mapping of a monolayer MoS₂ annealed at 500 °C, showing that PL from the crack region can be greatly enhanced. The enhancement is attributed not only to the p-type

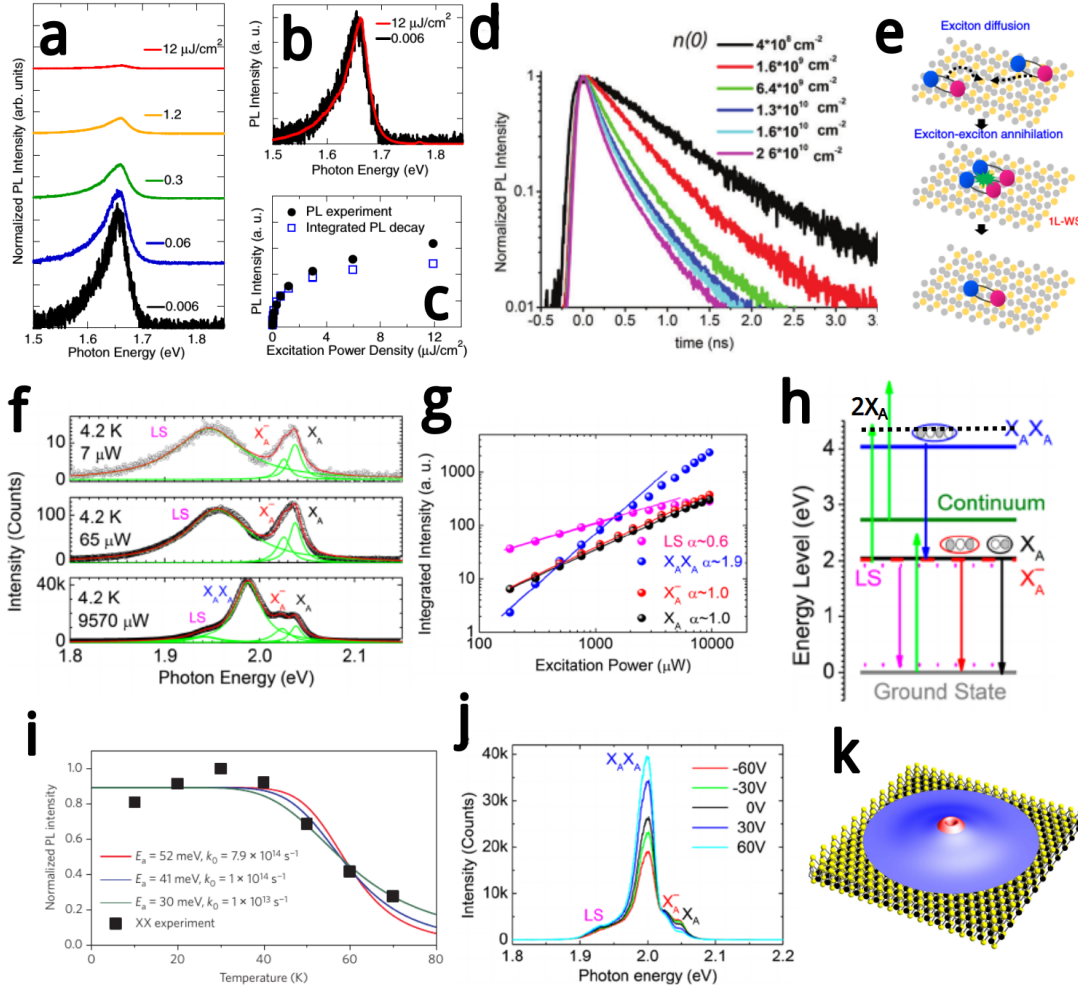


FIGURE 2.22: **a**. Normalized PL spectra of A exciton according to excitation power in monolayer WSe₂. **b**. Comparison between the PL spectra shape of monolayer WSe₂ under low and high optical pump. **c**. Power dependence of PL intensity of monolayer WSe₂. **d**. TR-PL of monolayer WS₂ under different excitation power. **e**. Schematic diagram of the physical process of EEA. **f**. Power dependent cryogenic PL of monolayer WS₂ with the biexciton emission in highest optical pump. **g**. Power dependence of cryogenic PL intensity of monolayer WS₂. **h**. Schematic diagram of the biexciton formation. **i**. Temperature dependence of biexciton emission in monolayer WSe₂. **j**. Gate voltage dependent PL of monolayer WS₂ under high optical pump with biexciton emission. **k**. Schematic diagram of the wave functions of biexciton composed of a trion (red) and hole (blue). **a-c,e**. Reprinted with permission from ref. [208]. Copyright American Physics Society 2014. **d**. Reprinted with permission from ref. [162]. Copyright Royal Society of Chemistry 2015. **f-h,j**. Reprinted with permission from ref. [173]. Copyright American Chemistry Society 2015. **k**. Reprinted with permission from ref. [156]. Copyright American Chemistry Society 2015.

doping of oxygen adsorbed on the cracked region, but also the reduced non-radiative decay rate, as demonstrated by the negligible temperature dependence of the PL from cracked region (figure 2.23e). However, the PL peak positions of crack regions show little temperature dependence while sizeable redshift is expected because of the negative temperature dependence of the band gap of a semiconductor (see section 2.3.3.4). This may suggest that different physical origin should account for the PL emission at different temperatures.

Other defects can also alter the emission properties of TMDCs. Chow *et al.* [179] manually introduced defects into monolayer WS₂ by oxygen plasma to investigate the PL variation with increasing defects densities. Figure 2.23f demonstrates that a new broad side band appears, and the energy separation against exciton reaches ~ 0.11 eV. The power dependence of spectral weight is also plotted, which shows that the spectral weight of defect related PL first reaches a maximum and then decrease with incident power. Based on that, the authors claimed the observation of saturation effect of defect related PL peak. However, this is the misunderstanding of the definition of saturation effect. The saturation effect is defined as the maximum intensity that can be achieved no matter the further increase of excitation power.[220] A proper way to claim the saturation effect is the observation of the decaying slope of the PL intensity as a function of incident power plotted in a double logarithmic scale.[221] In fact, the reduced spectral weight of the defect related PL peak in figure 2.23f is the result of the different exponents of the power dependence law ($I \propto P^\alpha$, I : PL integrated intensity, P : incident power) of between X^0 and X^D . Similar misleading claim has also been made by Tongay *et al.*[222] So far, the saturation of defect related PL has not been observed even at very high excitation power where biexcitons has been observed, as shown in figure 2.23g,h.[214, 176] Defects can also be created by exposure to water vapour. Kato *et al.* [223] reported the cryogenic PL under vacuum of monolayer WS₂ after being exposed to water vapour under vacuum, shown in figure 2.23i. Surprisingly, there only exhibits a single sharp peak originated from excitons and trions. However, the measurement

chamber is full of N_2 , several sharp low energy peaks appears, as shown in figure 2.23j. Similar phenomenon has also been observed in defective MoS_2 .^[222], indicating that the defects related PL is highly sensitive to the environment conditions.

2.3.3.5 Raman

Similar to graphene^[224], the Raman signatures of TMDCs can reveal many fundamental structural and vibrational properties of TMDCs, including layer staking order, number of layers, strain, doping level and so on. In some TMDCs, polarised sensitive Raman can reveal more information about the anisotropy of the target materials.^[225] Bulk TMDCs possess D_{6h}^4 point group symmetry and exhibit two principal first-order Raman peaks, $A_{1g}(\Gamma)$ and $E_{2g}^1(\Gamma)$, which can also be observed in atomically thin TMDCs.^[226] However, as the number of layers decreases, the point group symmetry changes as well and therefore the notation of Raman signatures should change accordingly. For odd layer number TMDCs which has D_{3h} symmetry, the $A_{1g}(\Gamma)$ and $E_{2g}^1(\Gamma)$ in bulk TMDCs should change to A_1' and E' while for even layer number, they should be $A_{1g}(\Gamma)$ and $E_g^1(\Gamma)$. In the following text, A_1'/A_{1g} and $E'/E_g^1/E_{2g}^1$ will be used to represent the two Raman signatures for clarity and simplicity. Both A_1'/A_{1g} and $E'/E_g^1/E_{2g}^1$ relate to intralayer (within the same layer) lattice vibration modes. A_1'/A_{1g} stands for the out-of-plane lattice vibration in which metal atoms stay still and two chalcogen atoms move perpendicularly against the atomic plane in opposite direction while $E'/E_g^1/E_{2g}^1$ represents in-plane vibration where two chalcogen atoms and metal atom move in the opposite direction within the atomic plane. Figure 2.24a shows typical Raman spectra of MoS_2 with different layer number. Detailed analysis of the peak positions reveals that with decreasing layer number, A_1'/A_{1g} experiences spectral redshift while $E'/E_g^1/E_{2g}^1$ goes through blueshift because the reduction in layer number leads to the decrease in van der Waals interaction and hence the restoring force of out-of-plane vibration mode A_1'/A_{1g} is reduced while that of $E'/E_g^1/E_{2g}^1$ is enhanced. Therefore, Lee *et al.*^[226] advanced that the peak position difference between $E'/E_g^1/E_{2g}^1$ and A_1'/A_{1g} can be an

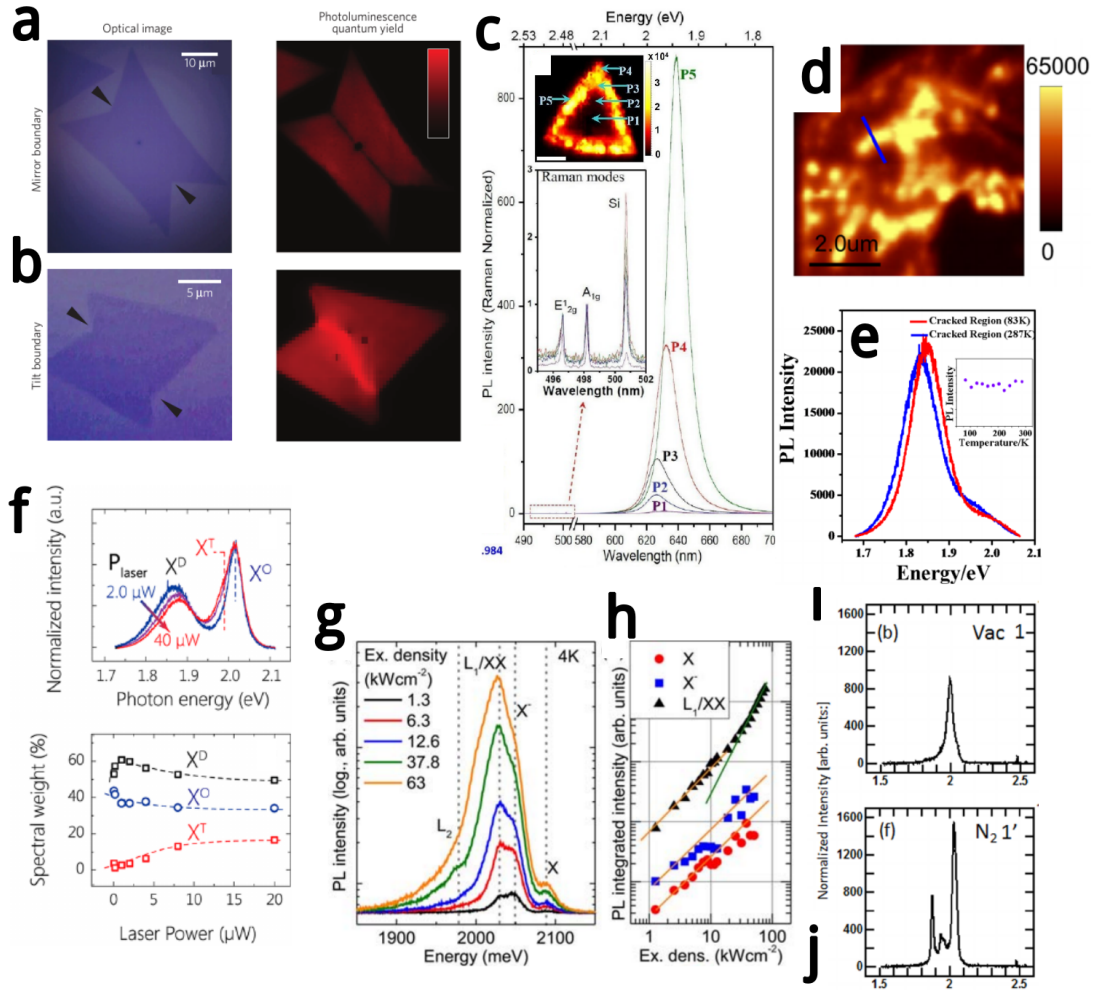


FIGURE 2.23: **a,b**. Optical image and PL quantum yield mapping of **a**) mirror twin island and **b**) tilt twin domain. **b**. PL spectra taken from different spatial point on the same single crystal domain. Upper inset: PL mapping. Scale bar: 5 μm. Lower inset: corresponding Raman spectra. **d**. PL mapping of annealed monolayer MoS₂ with cracked region. **e**. PL spectra of annealed monolayer MoS₂ at room temperature and 83 K. Inset: temperature dependence of PL intensity of cracked region. **f**. Power dependent room temperature PL of monolayer WS₂ after oxygen plasma and the corresponding power dependent PL spectral weight. **g**. PL spectra of exfoliated monolayer WS₂ under different excitation power, showing two defects related PL peak. **h**. Power dependence of the PL intensity corresponding to the different spectral components in **g**. **i,j**. cryogenic PL spectra of defective monolayer WS₂ in **i**) vacuum and **j**) N₂ environment. **a,b**. Reprinted with permission from ref. [218]. Copyright Macmillan Publishers Limited 2013. **c**. Reprinted with permission from ref. [127]. Copyright American Chemistry Society 2013. **d,e**. Reprinted with permission from ref. [219]. Copyright American Chemistry Society 2013. **f**. Reprinted with permission from ref. [179]. Copyright American Chemistry Society 2015. **g,h**. Reprinted with permission from ref. [176]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2015. **i,j**. Reprinted with permission from ref. [223]. Copyright American Chemistry Society 2014.

indicator to identify the layer number (figure 2.24b). Apart from layer number, A'_1/A_{1g} and $E'/E_g^1/E_{2g}^1$ can reveal other information of TMDCs, including strain[227, 193] and doping level[228, 229]. Figure 2.24e presents the Raman spectra of monolayer MoS₂ under different uniaxial strain. With increasing strain, the $E'/E_g^1/E_{2g}^1$ splits into two components and both peaks shift towards low-energy side with increasing strain while A'_1/A_{1g} remains unchanged. Based on these results, Grueneisen parameter γ and shear deformation potential, β can be derived. For monolayer MoS₂, γ is 1.1 which is half that of graphene (1.99) and β is 0.78.[193] A'_1/A_{1g} is sensitive to the doping level of TMDCs. Figure 2.24f shows the Raman spectra of monolayer MoS₂ in an FET setup under different gate voltage. It clearly shows that A'_1/A_{1g} experience redshift and peak broadening with increasing n-type doping level while $E'/E_g^1/E_{2g}^1$ changes little, as shown in figure 2.24h.[228] Oppositely, P-type doping can induce blueshift of the A'_1/A_{1g} and enhanced intensity.[229]

Resonant excitation can reveal more detailed second-order Raman signatures in TMDCs. Figure 2.24c presents the Raman spectrum of monolayer WS₂ under resonant excitation with incident laser wavelength of 514.5 nm. The most prominent peaks in the spectrum lies at $\sim 350 \text{ cm}^{-1}$, which is believed to be the second-order mode of longitudinal acoustic phonon at Brillouin edge LA(M). The strong 2LA(M) response is very likely to originate from the doubly resonant Raman process which involves resonant vertical electronic excitation and scattering with two phonon possessing opposite momentum in a conduction band with particular shape. Therefore, the intensity of 2LA(M) is closely associated with the band structure, which could be another indicator for layer number determination. Indeed, figure 2.24d shows that the intensity ratio of 2LA(M) over A'_1/A_{1g} strongly depends on the layer number, especially from monolayer to bilayer.

Although two different indicators have been investigated to determine the layer number, both have their drawbacks. For method associate with 2LA(M), its use can only be limited to WS₂ because to achieve double resonance in TMDCs other than monolayer

WS₂ requires laser with particular wavelength that is not readily available commercially. For method using the peak position difference between A'_1/A_{1g} and $E'/E_g^1/E_{2g}^1$, it can be affected by many other factors including doping and strain. Recently, the low-frequency interlayer Raman signatures starts to attract research interest and is believed to be a more efficient layer number indicator. Figure 2.24i shows the low-frequency Raman spectra of MoS₂ with different layer numbers. Two vibration modes, layer breathing mode (LBM) and shear mode (SM), which describe the perpendicular and in-plane movement of atomic plane with adjacent layer moving in opposite direction, show strong dependence towards layer number. [230]

2.3.4 Transport properties

The conductivity of a semiconductor is mainly determined by two factors, carrier mobility and carrier concentration. While carrier concentration can be modulated by many external methods, carrier mobility is more an intrinsic property. Here the discussion of transport properties focus mainly on the carrier mobility. In an ideal situation, the carrier mobility of a pristine semiconductor should only be determined by the phonon structure. Kaasbjerg *et al.* [233] performed first principal calculation to evaluate the intrinsic mobility of monolayer MoS₂ which is solely affected by phonon scattering, as shown in figure 2.25a,b. It shows that at low temperature, the mobility is mainly determined by acoustic phonons scattering while at elevated temperature, the optical phonons participate in the scattering process. Another important finding is that the mobility shows little dependence on the carrier concentration, until it arrives at 10^{13} cm⁻². At room temperature, the intrinsic mobility of monolayer MoS₂ should reach as high as 410 cm²V⁻¹s⁻¹. However, the mobilities extracted from FET transfer curve ranges from 0.1 - 10 cm²V⁻¹s⁻¹ [115]. Such big discrepancy between theoretical calculation and experimental results clearly points out that many extrinsic factors dominate the carrier scattering process other than phonons. In reality, charged impurities and

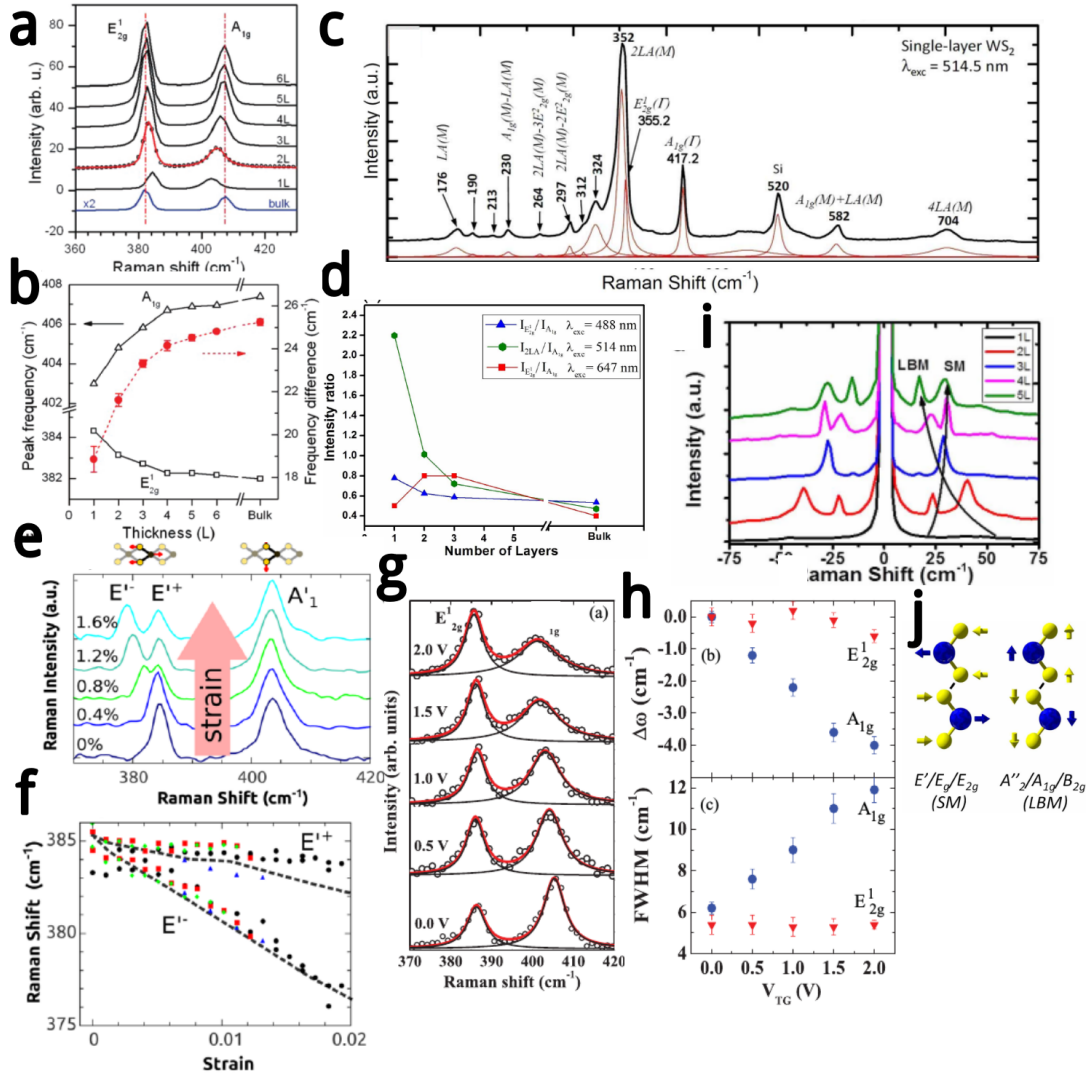


FIGURE 2.24: **a.** Raman spectrum of monolayer MoS₂. **b.** $E'_{2g}/E_{2g}^1/E_{2g}^1$ and A'_1/A_{1g} peaks positions and their difference of monolayer MoS₂ as a function of layer number. **c.** Raman spectrum of monolayer WS₂ under resonant excitation. **d.** Peak intensity ratio of maximum peak intensity over A_{1g} of WS₂ as a function of layer number. **e.** Raman spectra of monolayer MoS₂ under different strain. **f.** Two split E_{2g}^1 related peaks position as a function of strain. **g.** Raman spectra of monolayer MoS₂ under different gate voltage. **h.** Peak positions of monolayer MoS₂ as a function of gate voltage. **i.** Low-frequency Raman spectra of MoS₂ with different layer number. **j.** Schematic diagram of lattice vibration for LBM and SM vibration mode. **a,b.** Reprinted with permission from ref. [226]. Copyright American Chemistry Society 2010. **c,d.** Reprinted with permission from ref. [231]. Copyright Macmillan Publishers Limited 2013. **e,f.** Reprinted with permission from ref. [193]. Copyright American Chemistry Society 2013. **g,h.** Reprinted with permission from ref. [228]. Copyright American Physics Society 2014. **i,j.** Reprinted with permission from ref. [232]. Copyright Macmillan Publishers Limited 2013.

defects in TMDCs are inevitable and therefore Coulomb scattering must be taken into consideration when evaluating the mobilities of TMDCs. Engineering the dielectric environment can suppress the Coulomb interaction and therefore enhance the mobility. Indeed, by capping the monolayer MoS₂ with high k HfO₂, the mobility of monolayer MoS₂ increases to over 200 cm²V⁻¹s⁻¹. It seems that the Coulomb scattering should dominate the carrier scattering process at room temperature. However, Kim *et al.* [234] advanced that charged impurity scattering only dominates at low temperature, while the room temperature carrier mobility is determined by a combination effect of homopolar phonon and polar optical phonon, as shown in figure 2.25c. Therefore, it suggests that more investigations need to be performed to understand the main carrier scattering mechanism, especially at room temperature.

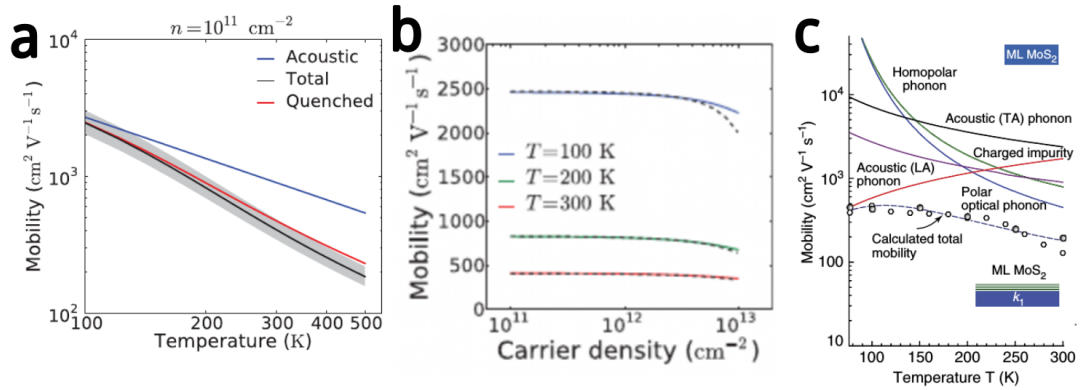


FIGURE 2.25: **a.** Carrier mobility in monolayer MoS₂ considering only phonon contribution. Shaded area: variation in the mobility associated with 10 % uncertainty in the calculated deformation potential. **b.** Theoretically derived carrier mobility as a function of carrier concentration at three different temperatures. **c.** Calculated carrier mobility considering different mechanism as a function of temperature. Dashed line: theoretical fitting result. Circles: experiment values. **a,b** Reprinted from [233] Copyright American Physics Society 2012. **c.** Reprinted with permission from ref. [234]. Copyright Macmillan Publishers Limited 2012.

2.3.5 Fabrication method

Since TMDCs are layered materials held together through Van der Waals force, scotch tape based mechanical cleavage method can be applied to isolate monolayer TMDCs, which was first demonstrated by Novoselov *et al.*[115] Careful selection of cleavage parameter can yield domain with both mono- and few- layer TMDCs, as shown in figure 2.26a.[125] This method produces TMDCs with best quality such as high crystallinity and clean surface[235] yet lowest yield[235, 123], and therefore lacks the ability for scalable production of TMDCs. In order to overcome this problem, chemical exfoliation method is proposed which has proven ability for mass production of graphene.[39] Two routes were proposed, which were electrochemical lithiation[236, 237] and liquid exfoliation[238]. Despite their amazing production yield, neither of the two methods can produce large area TMDCs film with high enough quality that can satisfies the entry criteria for electronics and optoelectronics industry.[239, 123, 235]

In order to reach a balance between production yield and film quality, CVD method was proposed, which can be realized through two routes: 1) direct sulphurization/selenization of pre-deposited transition metal precursor and 2) simultaneous sulphurization/selenization of transition metal precursor vapour and deposition. Zhan *et al.*[240] first proposed the preparation of continuous atomically thin MoS₂ film by routine 1 CVD method. In this work, a thin layer of Mo film was first pre-deposited onto SiO₂/Si wafer with a thickness of 1-5 nm, which then reacted with sulphur at 750 °C, yielding MoS₂ mono- and few-layer film. However, the resultant MoS₂ film based FET presented metallic behaviour and low on/off ratio, possibly due to the Mo residual.[235] In order to eliminate the effect of metal substrate, Lin *et al.*[241] reported that by employing MoO₃ instead of Mo as precursor, the produced MoS₂ exhibited much higher on/off ratio. Several other transition metal based precursors have also been investigated, including MoO₃[242], MoCl₅[243] and so on. Gaseous H₂S is also employed as sulphur precursor.[244] In addition to planar growth, vertically aligned MoS₂ and MoSe₂ has

been achieved *via* sulphurization of pre-deposited Mo film, which are ideal for energy applications.[245]

Although the sulphurization of transition metal or metal oxides can produce large area, continuous atomically thin TMDCs film, the layer number is non-uniform (see figure 2.26e) and grain size is typically very small, which is determined by the thickness of pre-deposited metal film. In order to solve this problem, Lee *et al.* [246] proposed that both the amount of the two precursors should be adjustable during the growth of TMDCs instead of being pre-determined. In this work, the target substrate was pre-treated by aromatic molecules as seeding promoters, which was believed to be essential for the lateral growth of MoS₂, [247] although the residual of these seed promoters can introduce the excessive charge carriers to the prepared TMDCs.[215] Later, it was demonstrated that nucleation for lateral TMDCs growth can happen on many non-catalytic dielectric surfaces such as SiO₂/Si, mica and so on if the synergy between sulphur concentration and reaction pressure is optimized.[218, 248] Indeed, by precise controlling the growth parameters (figure 2.26f), single crystal monolayer WS₂ with domain size over ~ 120 μm can be achieved, as shown in figure 2.26g.[218] In all the methods mentioned above, the target substrate is placed horizontally, leading to the spatial distribution of the concentrations of precursors across the substrate along gas flow which can result in the formation of isolated domains. Wang *et al.* [249] demonstrated that by placing the growth substrate vertically against the gas flow, monolayer TMDCs continuous film can be prepared (figure 2.26h).

Many other methods have been proposed to synthesize TMDCs films. For example, Wu *et al.*[250] introduced an physical vapour deposition method in which bulk MoS₂ was vapourized at 900 °C and the vapour was carried by Ar gas to the substrate, yielding triangular shape monolayer MoS₂ domain with area of about 400 μm^2 . Liu *et al.* [251] demonstrated the MoS₂ film can be prepared by thermolysis of (NH₄)₂MoS₄

which acted as precursor for both Mo and S. Kang *et al.*[252] presented a novel metal-organic CVD method (figure 2.26i,j) to produce wafer-scale monolayer MoS₂ and WS₂ by employing Mo(CO)₆ and W(CO)₆ as source of transition metal and (C₂H₅)₂S as sulphur precursor. The resultant TMDCs film shows very high FET electron mobility of up to 30 cm²V⁻¹s⁻¹. Although the continuous film of monolayer TMDCs have been achieved, there are still many challenges existing to prepare high quality, wafer scale monolayer TMDCs film, such as the preparation of single crystal monolayer wafer scale monolayer TMDCs since grain boundaries can degrade the electrical performance.[123]

2.3.6 Applications

2.3.6.1 Electronics

The Moore's Law has successfully described the development of modern digital electronics industry in the past decades. However, the deviation from the Moore's Law is emerging because channel length is approaching the limits set by the statistical and quantum effect, exceeding which can lead to ineffective electrostatic gate control, short-channel effect and difficulty in heat dissipation.[116] A simple mathematical description of the channel length limit can be given by $L_{ch} \approx 3\lambda$ in which L_{ch} is the channel length and $\lambda = \sqrt{t_{ox}t_{body}\epsilon_{body}/\epsilon_{ox}}$ is the geometric screening length where t_{ox} and t_{body} are the thickness and ϵ_{ox} and ϵ_{body} are the dielectric constants of gate oxide layer and channel. [254] Monolayer TMDCs are semiconducting materials with thickness of 0.7 nm, rendering themselves promising alternatives to silicon in digital electronics in order to overcome the challenges brought by the decreasing channel length for transistors miniaturization.[255, 256]

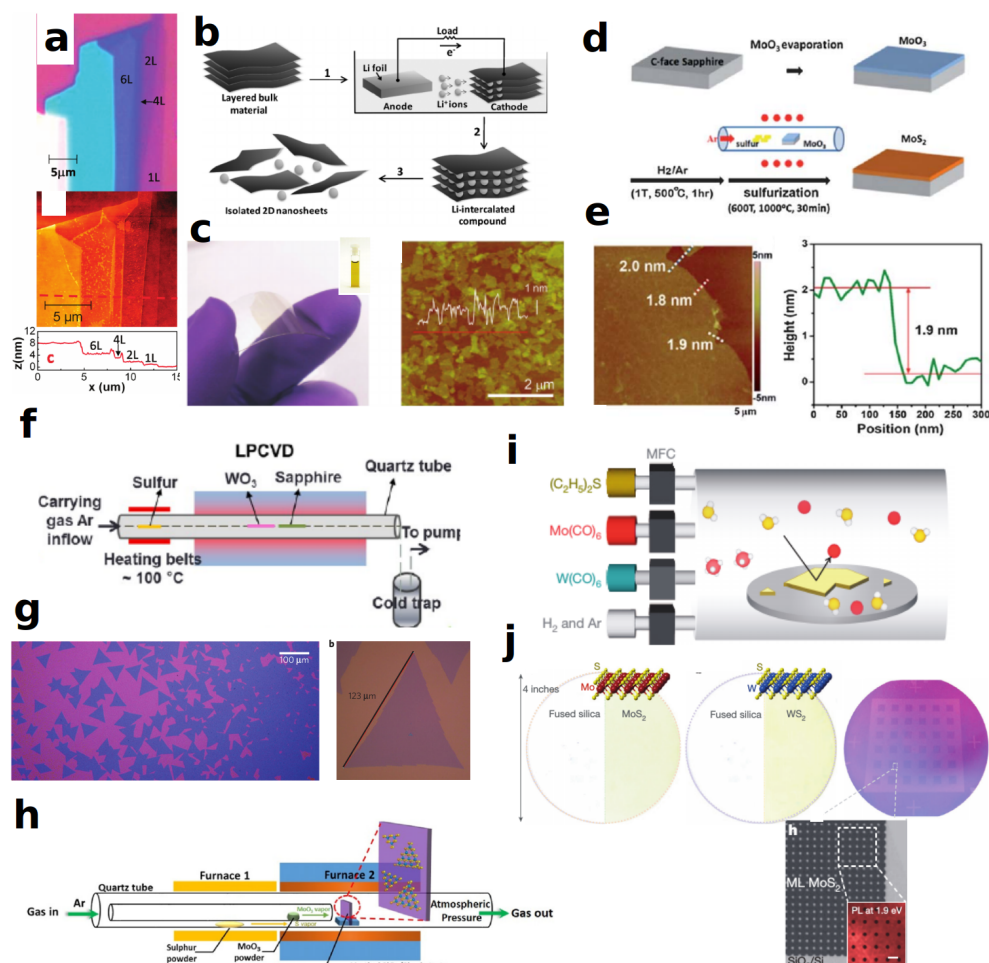


FIGURE 2.26: **a**. Optical image, AFM image and height profile of mechanical exfoliated MoS₂. **b**. Schematic diagram of electrochemical lithiation. **c**. Photograph of liquid exfoliated MoS₂ spin coated from water dispersion (shown in the inset) on flexible substrate and AFM characterization. **d**. Schematic diagram of sulphurization of thermally evaporated MoO₃. **e**. AFM characterization of MoS₂ film prepared by method in **d**. **f**. Schematic diagram of low pressure CVD growth of WS₂ on sapphire with double furnace for better temperature control. **g**. Optical image of CVD grown monolayer single crystal MoS₂ with lateral size of over 120 μm. **h**. Schematic diagram of CVD synthesis of MoS₂ with substrate placed vertically against the flow direction. **i**. Schematic diagram of MOCVD based synthesis method to prepare monolayer wafer scale MoS₂ and WS₂ film. **j**. Photograph of MoS₂ and WS₂ on sapphire and patterned MoS₂ on Si wafer. Inset: SEM image and PL mapping of the synthesized MoS₂. **a** Reprinted from [125] Copyright American Chemistry Society 2010. **b** Reprinted with permission from ref. [236]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2011. **c** Reprinted with permission from ref. [239]. Copyright American Chemistry Society 2011. **d** Reprinted from [241] Copyright from Royal Society of Chemistry 2012. **e** Reprinted with permission from ref. [253]. Copyright American Chemistry Society 2013. **f** Reprinted from ref. [218]. Copyright Nature Publishing Group 2013. **h** Reprinted with permission from [249]. Copyright IOP Publishing 2016. **i,j** Reprinted from ref. [252]. Copyright Nature Publishing Group 2015.

FETs are the basic building blocks for the digital electronics which can realize the output of two states, "1" and "0" (or ON and OFF states), in Boolean Logic. Extensive researches have been carried out on using TMDCs as channel materials for FETs. The performance of FETs is mainly characterized by three parameters: leakage current ("OFF" state current), on/off current ratio and mobilities. The leakage current determines the power consumption of a working transistor. Unlike gapless graphene,[20] TMDCs possess a sizeable bandgap of over 1 eV,[118] making them suitable materials to achieve desirably low leakage current. For example, the typical "OFF" state current of TMDCs based transistor can reach 10^{-9} A. [257] By employing annealing during FETs fabrication process to remove surface adsorbents on TMDCs [257] or encapsulation of TMDCs based FETs by oxide layer [258] or boron nitride (BN, an insulating 2D materials)[259], the "OFF" state current can reach as low as 10^{-13} A, as shown in figure 2.27b. The on/off current ratio describes how much difference between the working current during "1" state and leakage current during "0" state. Typically, this ratio should be in the range of 10^5 - 10^{10} . To achieve an optimized on/off current ratio, the ability to tune the carrier density in a broad range is required, which is mainly determined by the gate dielectric materials. The most commonly used gate structure is the back gate based on SiO_2/Si wafer with SiO_2 as dielectrics and heavily doped Si as gate electrode. For example, the on/off ratio of WS_2 FETs based on this structure can reach 10^5 . [257] The employment of top gated high k dielectric can greatly increase ratio to as high as 10^8 . [258] FET mobilities characterizes how fast the transistor can switch between "ON" and "OFF" states. In early reports, the measured FET mobilities of TMDCs were in the range of $0.1 - 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. [115] It is believed that the low mobility comes from the high density of midgap localized states,[260] caused by chalcogen vacancies, dislocations and surface adsorbents.[261, 262] In order to minimize the external effect on the mobility of TMDCs transistors, Radisavljevic *et al.* [258] reported their fabrication of top gated MoS_2 transistors by using HfO_2 (figure 2.27a) and the mobility was measured to be as high as $200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. For some TMDCs based FETs,

superconductivity can even be observed.[263]

The integration of multiple transistors leads to the realization of functional electronic circuits. Radisavljevic *et al.* [264] demonstrated a monolayer MoS₂ based inverter (figure 2.27c), which converts the logic "ON" state into logic "OFF" state (figure 2.27d) and a NOR gate based on which all other logic gate can be realized. More complex electronic circuits have been achieved on bilayer MoS₂, including static random-access memory (SRAM)(figure 2.27e) and oscillator ring (figure 2.27f).[13] Apart from digital electronic circuits, the TMDCs based FETs have also been utilized as bio-molecules and toxic gas sensors (figure 2.27g) [265, 266] because of the ultrahigh surface-to-volume ratio, rendering them sensitive enough to detect ultra-low dose of various target species.

2.3.6.2 Optoelectronics

Monolayer TMDCs possess direct optical band gap within the range of visible spectrum,[126] and therefore are suitable as functional materials in optoelectronics. [117] Generally, the optoelectronics can be classified into two categories: light harvesting devices which convert electromagnetic radiation into electrical signals and light generation devices which emit photons by converting the input of the external energy in the forms of either electricity or optical pump.

Photodetectors are one type of the light harvesting devices, which absorb photons with energy higher than the optical band gap and forms excitons. These generated excitons are then separated by various methods to generate electrical feedback. Two typical parameters are mostly used to characterize the performance of photodetectors, including photoresponsivity which is the ratio of current over total input light power and response time which describes how fast the photodetector can reach saturation current from dark current under fixed illumination. Phototransistors are one type of photodetectors in which excitons are separated by external bias. Limited by the large contact

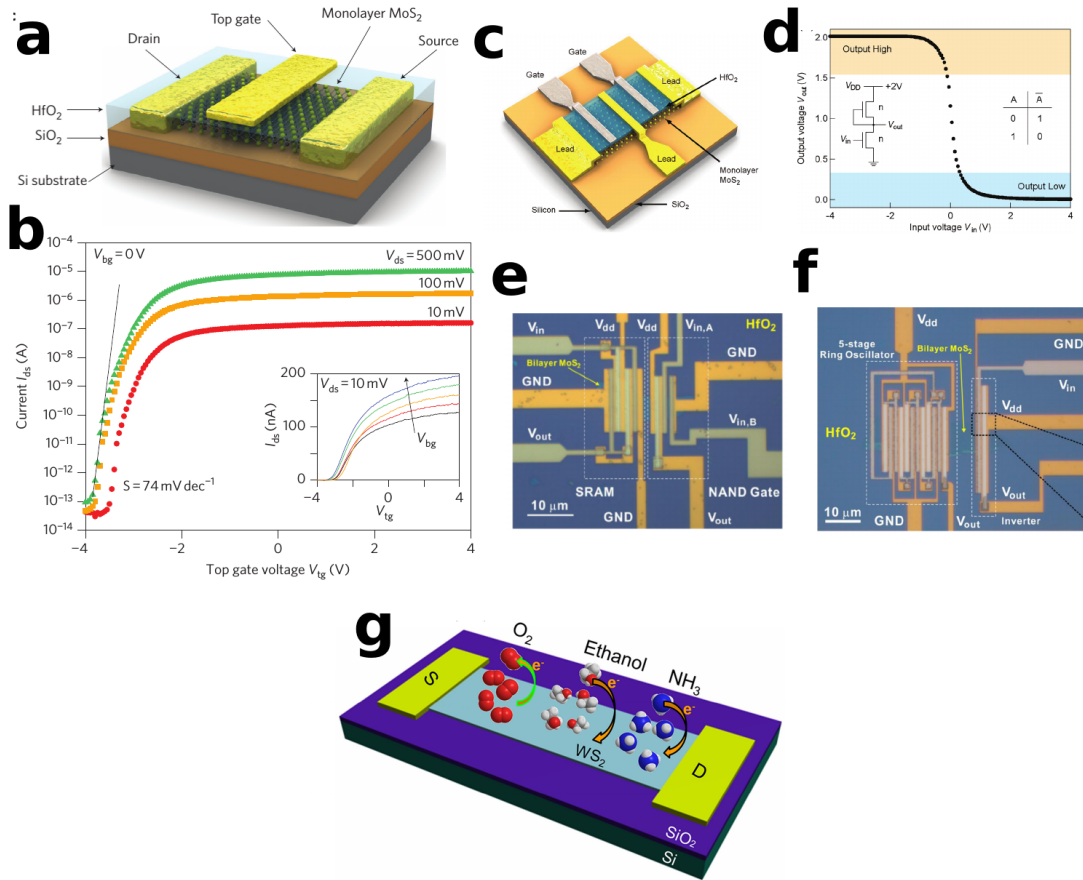


FIGURE 2.27: **a**. Schematic diagram of top-gated MoS₂ transistor with HfO₂ as dielectric layer. **b**. Transfer curves of MoS₂ transistor as illustrated in **a**. **c**. Schematic diagram of MoS₂ based inverter. **d**. Working curve of inverter in **b**. **e,f**. Optical images of integrated circuits based on bilayer MoS₂ with function as **e**) NAND gate and SRAM and **f**) oscillator ring. **g**. Schematic diagram of WS₂ FET based gas sensor. **a,b**. Reprinted with permission from ref. [258]. Copyright Macmillan Publishers Limited 2011. **c,d**. Reprinted with permission from ref. [264]. Copyright American Chemistry Society 2011. **e,f**. Reprinted with permission from ref. [13]. Copyright American Chemistry Society 2012. **j**. Reprinted with permission from ref. [265]. Copyright Macmillan Publishers Limited 2014.

resistance that decrease the photocurrent collection, the first MoS₂ based photodetector has photoresponsivity of about 7.5 mA/W, which is relatively low compared with Si based photodetector (about 100 mA/W) and response time of about 50 ms.[267] Lopez-Sanchez *et al.* [268] reported that the photoresponsivity of MoS₂ based phototransistor can reach as high as 880 A/W at incident wavelength of 510 nm, surpassing the firstly reported device by a factor of 10⁵, by simply replacing Ti/Au with Au as the electrodes to achieve lower contact resistance (figure 2.28a,b). Although the high gain can be achieved in the phototransistor which permits the detection of light with ultrahigh sensitivity, TMDCs based phototransistors suffers from their long response time,[117] while in many applications, high temporal resolution is highly desired. The excitons generated in semiconductors can also be separated by built-in electric field at interfaces of certain junctions and photodetectors based on this working principal always possess high time resolution. Tsai *et al.* [269] fabricated a few-layer MoS₂ based Schottky photodetectors, which can realize faster temporal response compared with phototransistors, with rise time of 70 μ s and fall time of 110 μ s (figure 2.28c,d). It also possesses high temperature stability which allow working in harsh environment. A even more faster photodetector is based on a p-n junction with response time of less than 15 μ s and photoresponsivity of 0.1 A/W, in which carbon nanotubes function as p-type material and MoS₂ is n-type semiconductor. [270]

Photovoltaic cell is another type of light harvesting devices. Different from photodetectors, photovoltaics must have the ability to separate excitons into free carriers without the help of external bias. Therefore, TMDCs must be incorporated into certain types of junctions to realize photovoltaic applications. Two parameters are usually adopted to evaluate the performance of TMDCs based photovoltaics, including power conversion efficiency which is the ratio of the generated electrical power over the input light power, and external quantum efficiency (EQE) which is the ratio of number of electrons generated over number of photons generated and is expressed as $EQE = (\frac{I_{sc}/e}{P_{inc}/E_{photon}})$ where I_{sc} is the short circuit current, e is the charge unit, P_{inc} is the power of incident

light and E_{photon} is the photon energy. The first TMDCs based photovoltaic device is based on MoS₂ - metal Schottky junctions in an FET setup with different metal for electrodes, leading to the separation of excitons and different carrier type collection preference. The power conversion efficiency for a single wavelength can reach 2.5 %, which is equivalent to or even higher than many other TMDCs based solar cell. However, this type of structure is suffered from the limited active area.[271] Lopez-sanchez *et al.*[178] advanced a MoS₂/Si p-n junction based solar cell (figure 2.28g) with working area only limited by the size of MoS₂. Despite the scalability, the EQE of this device is only 4.4% (figure 2.28h), which is much lower than the present commercial Si based solar cell with EQE as high as over 80 %. WSe₂ possess ambipolar transport nature and therefore is an ideal materials in p-n homojunction for photovoltaic application. Pospischil *et al.* reported that they fabricated WSe₂ homojunction solar cell by using split top gate, achieving an power conversion efficiency of about 0.5 %.

The excitonic photoluminescence and direct band gap of monolayer TMDCs also invigorate the exploration of their applications in light generation. LED is one of the light generation devices that attract much interest, which requires both electrons and holes to be injected into the TMDCs simultaneously. Sundaram *et al.* [273] first demonstrated the MoS₂ based electroluminescent device (figure 2.29a), with initial plan to create an homojunction by using split gate control. Yet due to the large band gap of MoS₂ and Fermi level pinning[260], negatively gated region fails to inject hole efficiently. However, electroluminescence (EL) is still observed, mainly near the metal-MoS₂ contact region (figure 2.29b), which is result of impact excitation, leading to very low EL efficiency of about 10^{-5} .[273] The idea of homojunction based LED is then realized in WSe₂ (figure 2.29c) [272, 174] with light emitting area in the centre of the device because it is relatively easy to achieve ambipolar transport in WSe₂. However, the power conversion efficiency is only 0.2 %, much lower than that of OLED (about 20 %). LED is basically the reverse operation of junction-based photovoltaics and therefore a working photovoltaics setup (figure 2.28g) can also be utilized to operate in an LED

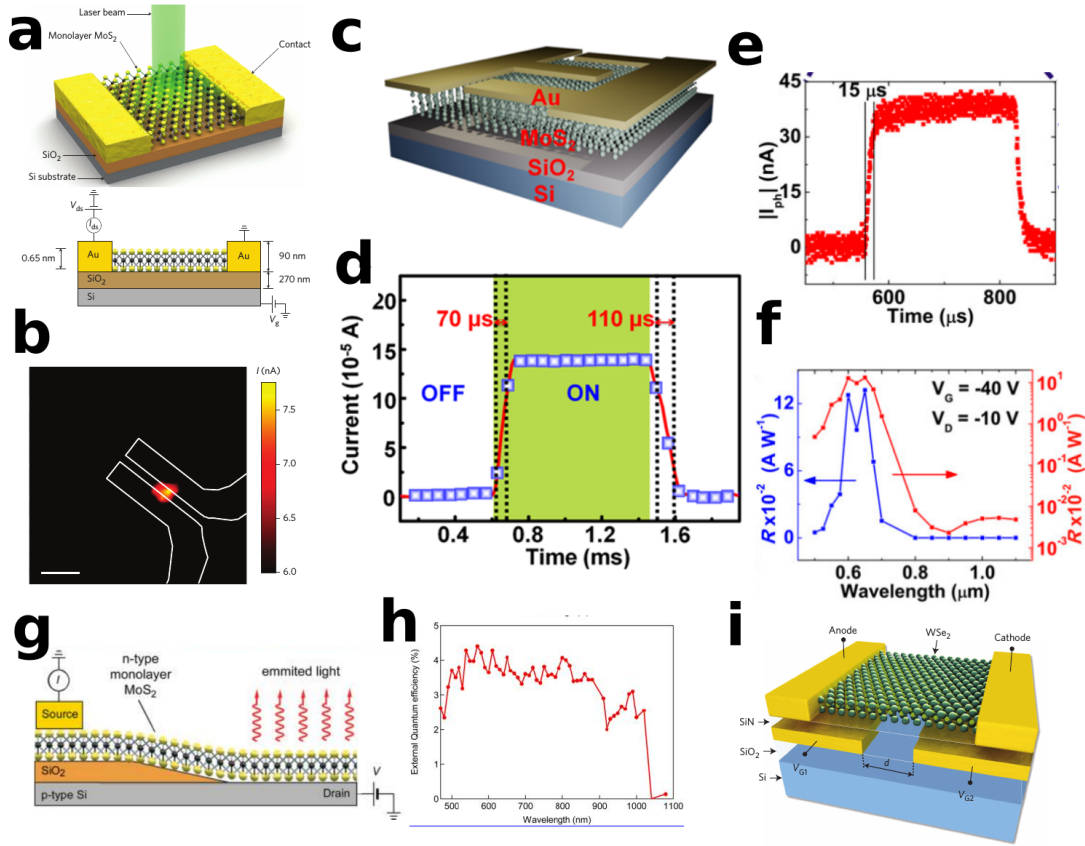


FIGURE 2.28: **a**. Schematic diagram of monolayer MoS₂ phototransistor with Au as electrodes to decrease contact resistance. **b**. Photocurrent mapping of MoS₂ phototransistor as illustrated in **a**. **c**. Schematic diagram of MoS₂ based Schottky photodiode. **d**. Time response of MoS₂ based Schottky photodetector in **c**. **e** Time response and **f** photoresponsivity of carbon nanotube - MoS₂ p-n junction photodetector. **g**. Schematic diagram of MoS₂ - Si heterojunction solar cell. **h**. EQE of solar cell in **g** as a function of the wavelength of incident light. **i**. Schematic diagram of WSe₂ based homojunction solar cell *via* split gate control. **a,b**. Reprinted with permission from ref. [268]. Copyright Macmillan Publishers Limited 2013. **c,d**. Reprinted with permission from ref. [269]. Copyright American Chemistry Society 2013. **e,f**. Reprinted with permission from ref. [270]. Copyright National Academy of Sciences 2013. **g,h**. Reprinted with permission from ref. [178]. Copyright American Chemistry Society 2014. **i**. Reprinted with permission from ref. [272]. Copyright Macmillan Publishers Limited 2014.

mode.[254] For example, the MoS₂ - Si p-n junction can also be used to emit light under forward bias.[178] In addition to LED, TMDCs can also be incorporated into optical cavities and other photonic architectures to realize other applications. Wu *et al.*[274] recently integrate WSe₂ with photonic crystal cavity (figure 2.29f,g) and realized lasing with ultralow optical pump threshold of about 27 nW.

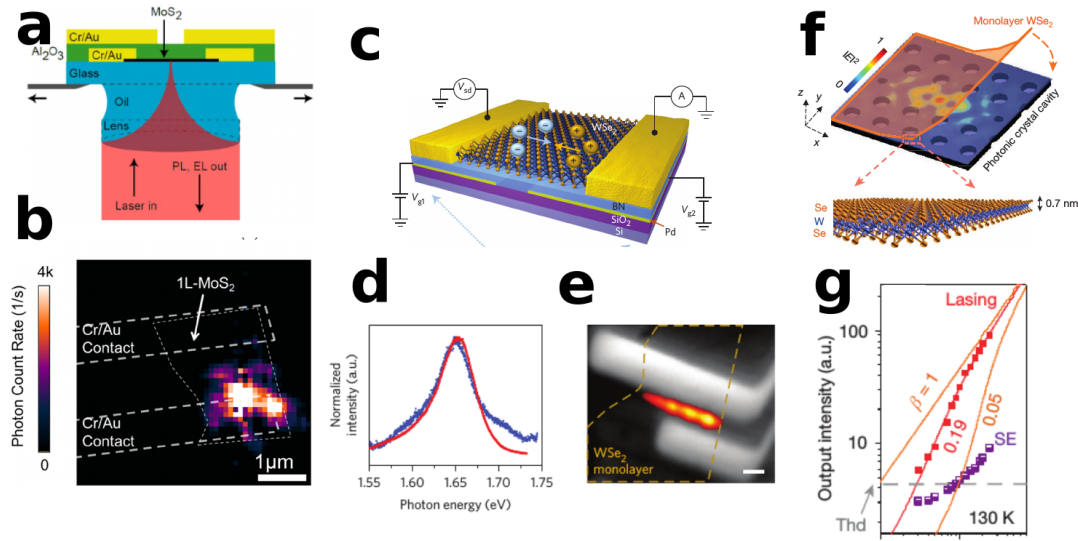


FIGURE 2.29: **a.** Schematic diagram of experimental setup for the characterization of monolayer MoS₂ with split top gate. **b.** EL mapping of devices in **a.** **c.** Schematic diagram of WSe₂ based LED based on split back gate. **d.** EL of the LED and PL of WSe₂ in the device in **c.** **e.** EL image superimposed on optical image of the device in grey scale. Scale bar: 2 μm. **f.** Schematic diagram of WSe₂ deposited on photonic crystal cavity. **g.** Light output intensity *versus* the optical pump power. Red squares: cavity emission. Violet half-filled square: stimulated emission at off cavity resonance. **a,b.** Reprinted with permission from ref. [273]. Copyright American Chemistry Society 2013. **c-e.** Reprinted with permission from ref. [174]. Copyright Macmillan Publishers Limited 2014. **f,g.** Reprinted with permission from ref. [274]. Copyright Macmillan Publishers Limited 2015. **g,h.** Reprinted with permission from ref. [178]. Copyright American Chemistry Society 2014. **i.** Reprinted with permission from ref. [272]. Copyright Macmillan Publishers Limited 2014.

2.3.6.3 All 2D applications

The previous review of the properties and applications of both graphene and TMDCs clearly shows that they are complementary in many aspects. For example, graphene is a

gapless material and manifest semi-metallic nature while TMDCs possess sizeable band gap that is close to the band gap of silicon. TMDCs have the difficulty in outputting electrical signal through conventional metal electrodes because of the Fermi energy pinning and the existence of mid-gap states[260] while Fermi level of graphene can be tuned in a wide range through different methods to form ohmic contact with other materials. Therefore, it is believed that bringing both graphene and TMDCs together into devices should have much better performance than those only utilizing one type of 2D materials.

Chuang *et al.* [275] demonstrated a WSe₂ FET with graphene as source-drain electrodes whose Fermi level can be tuned by the ionic liquid top gate to form ohmic contact with WSe₂, as shown in figure 2.30a,b. The resultant mobility of WSe₂ FET can reach as high as 300 cm²V⁻¹s⁻¹, which is close to the intrinsic, phonon limited mobilities. The ability to observe the intrinsic mobilities limit is due to the absence of Schottky barrier at contact region by using graphene as electrodes. TMDCs based phototransistors suffer from low photoresponsivity because of the poor photo-generated charge carriers collection due to the high Schottky barrier at metal electrodes - TMDCs interfaces. This problem can be solved by introducing graphene into the system. For example, the photoresponsivity of graphene-MoS₂ based phototransistor [276] can reach as high as 5×10⁸ A/W at room temperature, with theoretical power conversion efficiency of about 1 %, [277] as shown in figure 2.30c,d. Compared with other devices using metal as electrodes, the utilization of graphene dramatically improves the photoresponsivity by at least 1000 times. [278] The performance of junction based photodetector can also be greatly improved if graphene is introduced into the system. Yu *et al.* [279] reported that a vertically stacked graphene - MoS₂ - Ti photodetector (figure 2.30e) possessed peak EQE of as high as 55 % (figure 2.30f) and response time of as low as 50 μs.

The atomic thickness, high optical transparency and mechanical flexibility of 2D materials can also pave the way for another important application, flexible thin film transistor

(TFT), which will be the backbone of the next generation flexible display electronics. [280] Das *et al.* [281] demonstrated an all-2D flexible thin film transistor using monolayer graphene as source, drain and top gate electrodes, BN as gate dielectric and bilayer WSe₂ as channel material (figure 2.30g,h). This all 2D flexible TFT possess a carrier mobility of $45 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is 100 times higher than that of amorphous silicon based TFT, and on/off ratio of 10^7 . This 10 atomic layer thick device permits more than 88% of incident light within the whole visible spectrum to pass through. Its excellent optical and electrical performance can sustain even under the in-plane strain of as high as 2 % (figure 2.30h,i). The integration of 2D materials can also stimulate new concepts of devices. For example, tunnelling field effect transistors (TFETs) based on graphene, BN and WS₂ has been demonstrated (figure 2.30j), achieving unprecedented current modulation and high "ON" state current (figure 2.30k). [232]

2.4 Conclusion

Despite the booming researches on graphene and TMDCs, it is still difficult to evaluate their impact on the world beyond academia. Historically, the commercialization of a novel materials can take more than 2 decades. For example, Dupont costed 20 years to gain profit from Kevlar (polymer fibre) [282] while carbon fibres took even longer. [283] Therefore, in the most optimistic view, graphene is on the half way of commercialization while there are still 15 years ahead for TMDCs. Despite many inspiring applications that have been proposed for graphene and TMDCs, or even achieved like the first graphene based touch screen in China, the importance of understanding the fundamental properties of materials and exploiting possible routes to manipulate them can never be omitted, which can provide continuous power to drive the performance of 2D materials based devices to their limit.

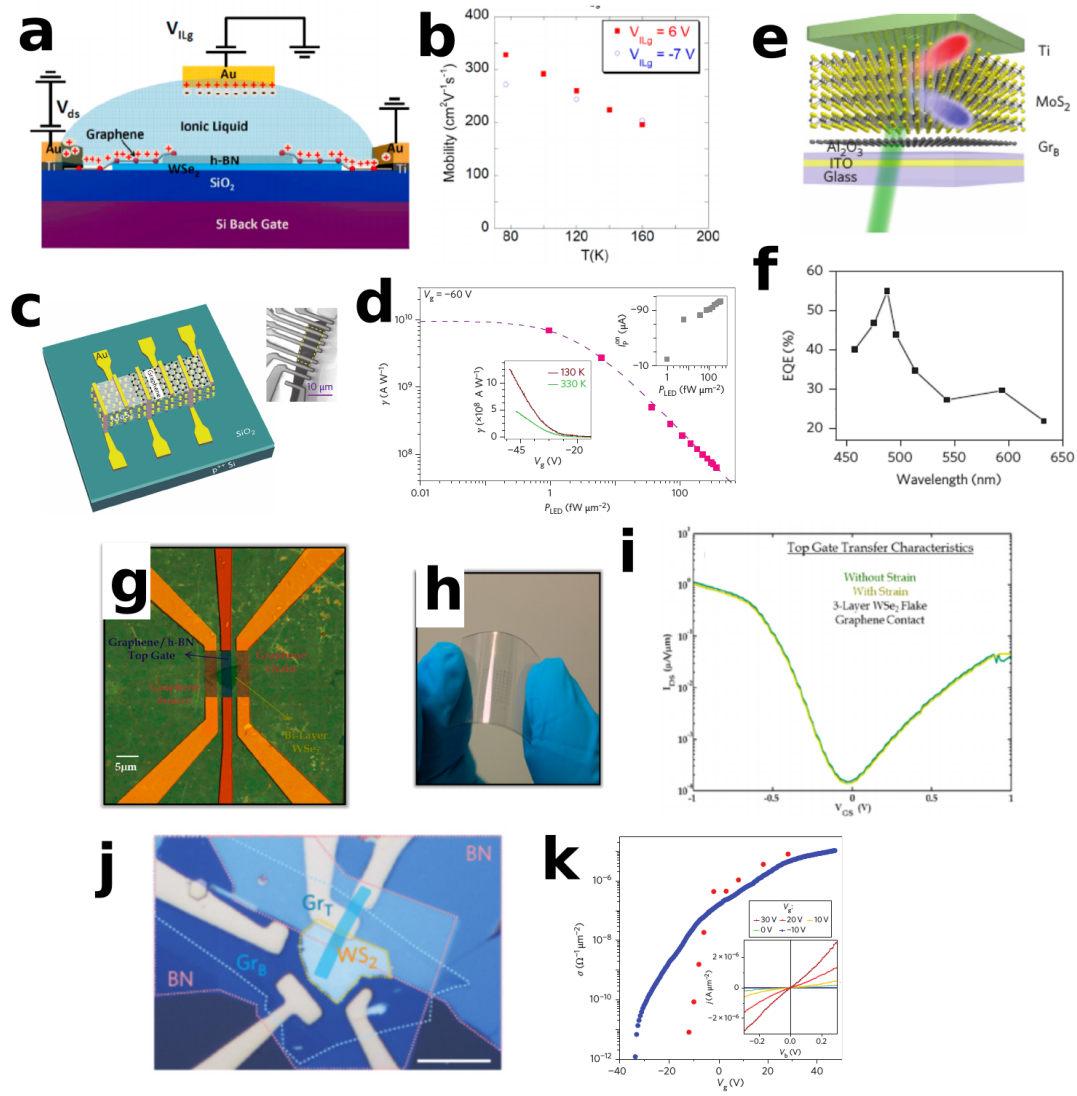


FIGURE 2.30: **a**. Schematic diagram of WSe₂ FET with graphene as source and drain electrodes. **b**. Mobility of FET in **a** as a function of temperature. **c**. Schematic diagram of MoS₂ - graphene heterostructure as phototransistor. Inset: SEM picture of MoS₂ - graphene heterostructure. **d**. Photoresponsivity of phototransistor in **c** as a function of incident power. Inset left: photoresponsivity as a function of gate voltage at two different temperatures. Inset right: photo-current as a function of incident light power. **e**. Schematic diagram of graphene - MoS₂ - Ti photodetector. **f**. EQE of device in **e** as a function of wavelength of incident light. **g**. SEM image of all 2D materials based TFT. **h**. Photograph of all 2D TFT on flexible substrate. **i**. Electrical characteristics of flexible all 2D TFT with and without strain. **j**. Optical image of all 2D materials based TFET. **k**. Transfer curve of TFET in **j**. Inset: I-V curves at different gate voltage. **a,b**. Reprinted with permission from ref. [275]. Copyright American Chemistry Society 2014. **c,d**. Reprinted with permission from ref. [276]. Copyright Macmillan Publishers Limited 2013. **e,f**. Reprinted with permission from ref. [279]. Copyright Macmillan Publishers Limited 2013. **g-i**. Reprinted with permission from ref. [281]. Copyright American Chemistry Society 2014. **j,k**. Reprinted with permission from ref. [232]. Copyright Macmillan Publishers Limited 2013.

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Chapter 3

Methods

3.1 Introduction

This chapter introduces the various experimental and theoretical techniques employed in this research project. Instead of looking into details of the working principals of these techniques, this chapter mainly focus on introducing the experiment details such as the instrument models and their specifications as well as particular experimental nuances. Based on the information provided in this chapter, it is expected that all experiments and simulations in the following chapters can be replicated.

3.2 Graphene growth and transfer

3.2.1 CVD synthesis of graphene

Graphene samples used in Chapter 4 are synthesized using atmospheric pressure CVD. Experimental set-up is illustrated in figure 3.1. A $1 \times 1 \text{ cm}^2$ piece of copper foil (Alfa Aesar, Puratronic 99.8%, 25 μm thick) is first immersed in 1% HCl (Alfa Aesar) to

remove oxide layer, followed by the ultrasonication in acetone and IPA for 10 minutes, respectively. Pretreated copper foil is loaded into a ceramic boat which is then inserted into the middle of an 1-inch in diameter and 1 m in length quartz tube within a split-tube furnace (Carbolite). Three pipelines are connected to the quartz tube, which supplied argon, hydrogen (25% hydrogen, 75 % argon, BOC) and methane (1% methane, 99% argon, BOC) with flow rate controlled by digital mass flow controller (Alicat MCR). There are three steps involved in the growth stage. In the first step, copper foil is annealed at temperature 1060 °C for 1 hour with 200 sccm argon and 100 sccm hydrogen flowing. In the next step, methane flow is set at 10 sccm and hydrogen flow rate is reduced to 30 sccm lasting for 1 hour. Following this, methane is disabled and the copper is immediately removed from the furnace hot zone for rapid cooling in the last stage. Sample is then taken out of the quartz tube when copper is cooled to room temperature.

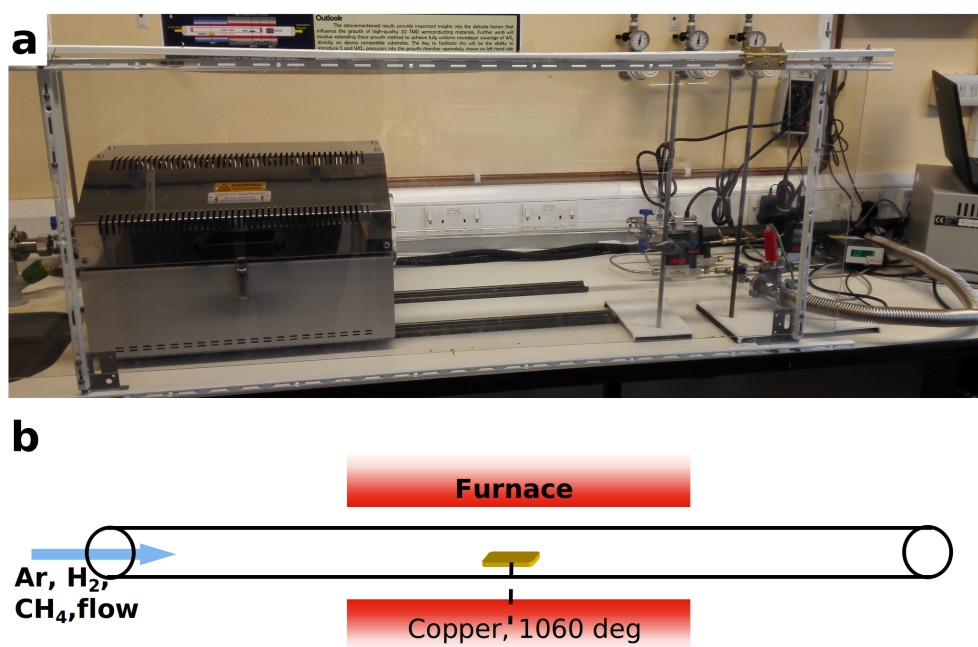


FIGURE 3.1: **a.** Picture of CVD system for graphene synthesis. **b.** Schematic diagram of CVD system in **a.**

3.2.2 Graphene transfer

A layer of poly-methyl-methacrylate (PMMA) scaffold (MicroChem , 8% wt. in anisole, 495k molecular weight) is spin-casted on the graphene side of the copper at 4500 rpm for 60 seconds and cured at 180 °C for 90 seconds. The underlying copper is then etched away by floating the sample on iron chloride (III) aqueous solution for several hours until only transparent PMMA+graphene film is left. The film is then cleaned by floating on DI water for several times and then on diluted HCl solution to remove residual FeCl_3 , followed by being rinsed again in DI water for another 30 minutes to eliminate any other contaminants. Finally, the film is transferred onto a target substrate, for example, Si wafer with 300 nm oxide layer on top (University Wafer), quartz plate or silicon nitride TEM grid (Agar Scientific Y5385). The as-transferred sample is left in fume hood overnight for completely drying, which is then heated at 150 °C for 15 minutes if transferred to flat substrate like clean Si wafer and quartz substrate or at 180 °C for at least 12 hours if it is transferred to TEM grid or pre-patterned Si wafer for better adhesion with substrates. PMMA layer is removed by immersing sample in acetone placed in 45 °C water bath or heated in furnace at 300 °C overnight if transferred to TEM grid.

3.3 WS_2 growth and transfer

3.3.1 CVD synthesis of WS_2

Monolayer and bilayer WS_2 crystals are synthesized *via* CVD with elemental sulphur and tungsten trioxide as precursors. The picture and schematic diagram are shown in figure 3.2. Two furnaces are involved in order to increase the adjustability and are placed end-to-end. 300 mg sulphur is loaded into a 1 inch quartz tube and is located in the middle of furnace 1 while 200 mg tungsten trioxide is placed in a 0.5 inch quartz

tube and located in the middle of furnace 2. The employment of double-walled-tube setup is to prevent earlier sulphurization of tungsten trioxide before it reaches target substrate and leads to formation of bulk tungsten disulphide. The whole system is then purged by Ar with flow rate of 500 sccm. Following the purging process, furnace 2 is set to 1170 °C. When the temperature of furnace 2 reaches 500 °C, furnace 1 is set to reach 180 °C. This ensures the proper sulphur introduction time. After being heated up, vaporized sulphur and tungsten trioxide are carried by pure argon gas with flow rate of 250 sccm to the surface of target substrate, where tungsten trioxide undergoes sulphurization if furnace 2 reaches target temperature, lasting for ~ 3 minutes. After that, the heating unit of furnace 2 is disabled and the temperature of furnace 1 is elevated to 400 °C to remove the excessive sulphur. Then furnace 1 is switched off. Sample is then taken out until both furnace reach room temperature.

3.3.2 WS₂ transfer

A thin layer of PMMA (MicroChem, 8% wt. in anisole, 495k molecular weight) is spin casted onto the as-grown WS₂ on Si wafer at spinning speed of 4500 rpm and cured at 180 °C for 90 seconds. Excessive PMMA at side faces of Si wafer, which may block the contact between etching solution and substrate, is scratched off by diamond blade in order to accelerate the etching process. The as-grown sample is then floated onto 1 mol/L potassium hydroxide (KOH) aqueous solution immersed in 45°C water bath. PMMA/WS₂ film was detached from substrate after about 1 hour, which is then rinsed in DI water for several times to remove excessive KOH. The transparent film is transferred to a target substrate, by adopting the procedures similar to those used for transferring graphene, as described in section 3.2.

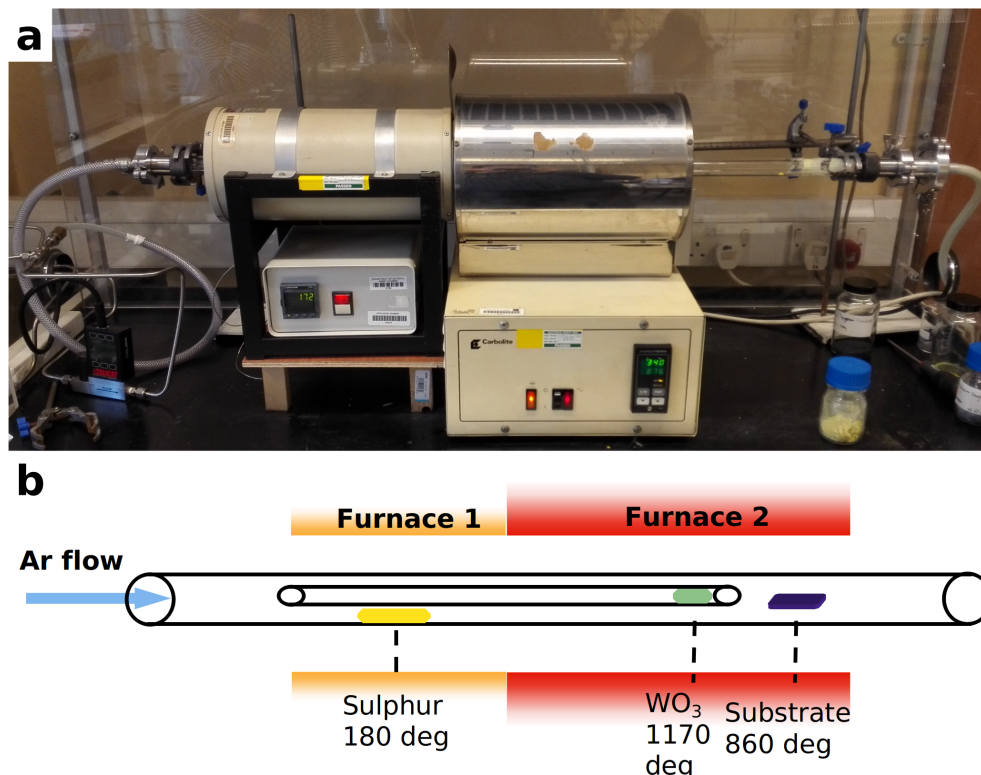


FIGURE 3.2: **a).** Picture of CVD system for WS_2 synthesis. **b.** Schematic diagram of CVD system for WS_2 synthesis.

3.4 Scanning electron microscopy

Scanning electron microscopy provides a simple and quick way to characterize the morphology of 2D crystals. The instrument used in this project is Hitachi S-4300 field emission scanning electron microscope. The acceleration voltage is 3 kV if target sample is graphene or 2 kV if WS_2 is in interest. With optimized focusing and astigmatism corrector values, the best spatial resolution can reach 500 nm. SEM samples are prepared by grounding the graphene/Si wafer, graphene/copper or WS_2 /Si wafer with SEM stub through sticky carbon tape to avoid charging effect to the largest extent.

3.5 Sheet resistance measurement

Sheet resistance measurement in Chapter 4 are performed in a home-built instrument designed and built by myself under the supervision of Professor Jamie Warner, as shown in figure 3.3c based on van der Pauw method. Basically, point spring loaded tips (RS electronics, 521-611) are fixed on the hand-made plastic cantilever. Probe tips can be moved freely by simply unscrewing the screws on the cantilever, which allow measurement to be taken on samples with size of ranging from 0.5 cm by 0.5 cm to 5 cm by 5 cm, as shown in figure 3.3d. After the probe tips are at right position, samples could be fixed on the plastic bread board by tightening the screws. Due to the fact that only two ports of the source meter (Keithley 2400) can output electrical signals, two mechanical switches are employed to avoid swapping the position of banana plugs, which greatly improve the measurement efficiency. Metal contacts are made either by putting silver paste or by thermal evaporation of Cr/Au contact with the help of home built shadow mask as shown in figure 3.3a,b.

3.6 Optical transmission measurement

The measurement of optical transmittance of graphene provides an quick way to determine the layer numbers of graphene within 10 layers. The instrument employed in the measurement is JASCO V-570 along with measurement software. The transmittance of a bare substrate is first taken to serve as a base line. The transmittance of graphene transferred to transparent substrate is then measured in the range of 400 nm to 700 nm with a spectral resolution of 0.2 nm.

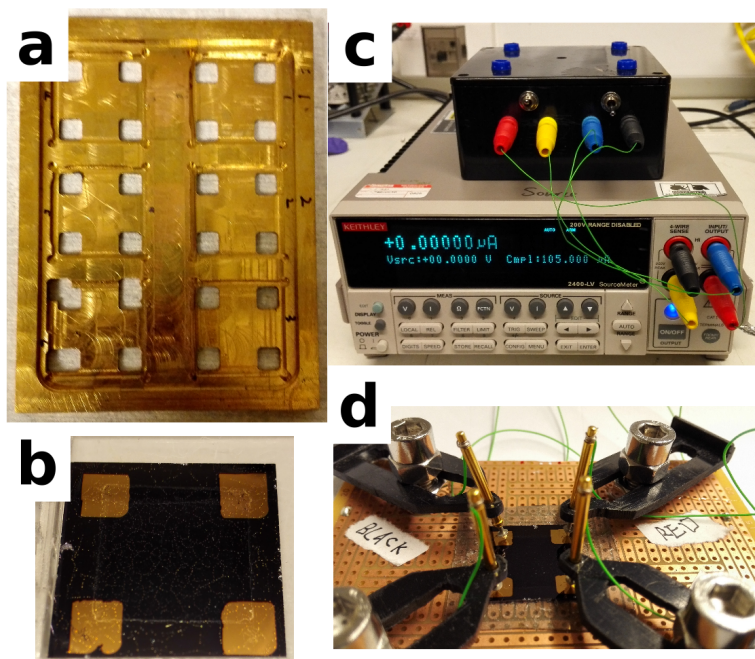


FIGURE 3.3: **a.** Shadow mask for metal contact evaporation. **b.** Graphene on SiO_2 with thermally evaporated Cr(10 nm)/Au(90 nm) metal contacts. **c.** Picture of typical experimental setup for sheet resistance measurement. **d.** Picture of home-built sheet resistance measurement box.

3.7 Transmission electron microscopy

AC-TEM images of FeCl_3 doped graphene in Chapter 4 were captured with the help of JEOL JEM-2200MCO operating at an acceleration voltage of 80 kV. It is equipped with a CEOS image aberration corrector which has the ability to correct third order spherical aberration coefficients. A partially automated software is provided to facilitate the aberration correction process after initial beam alignment and astigmatism correction.

3.8 TEM image analysis

3.8.1 TEM image processing

Raw AC-TEM images are full of noise which makes them harder to figure out the actual atomic structures directly by eyes. Therefore, appropriate image post-processing are necessary. In this project, AC-TEM images are treated by different filters to reduce the noise level and enhance the contrast in ImageJ [1, 2] for easier structures identification. Bandpass filter with large filtering structures down to 100 pixels and small filtering structure up to 1 pixel is first applied to images to remove the shading effect caused by the inhomogeneous illumination during image capturing. Following this, a moving average smoothing filter with 3×3 kernel is employed to reduce the noise. The brightness and contrast are then optimized which can further facilitate the structures identification.

3.8.2 TEM image simulation

TEM image simulation plays a important role in TEM image analysis because it provides an way to determine the validity of the atomic structure directly inferred from raw TEM data. All simulations shown in chapter 4 are performed in JEMS (programmed by Dr. P. A. Stadelmann). Atomic structures are plotted in Accelrys Discovery Studio 4.0, optimized by using the built-in Dreiding force field model and output into co-ordinates list file. The output files are converted into JEMS readable input file with the help of a Python script written by Dr. C. S. Allen. Parameters of the microscope are required to generate accurate simulation results. The simulation conditions of the microscope OJ2200 were list as follows: accelerating voltage: 80 kV; C_c : 0.591; C_s : -0.005; defocus: 0; energy spread: -0.32; lens instability: 0. Simulation results can be generated by JEMS based on multislice algorithms. [3, 4]

3.9 Atomic force microscopy

Atomic force microscopy was used to determine the number of layers of WS₂ accurately in chapter 6 as well as to characterize the morphology of monolayer crystals in chapter 7. All measurements are performed on Asylum Research MFP-3D atomic force microscope in Professor Harish Bhaskaran's group with the help of Mr. Xiaochen Wang in non-contact mode. Samples in interest were either transferred or directly grown on Si wafers which were sufficiently flat. Parameters like scanning area, scanning speed, tip vibration amplitude and so on were optimized to yield morphology images with highest resolution and least artifacts.

3.10 Raman and Photoluminescence microscopy

Raman and, especially PL microscopy constituted the majority of the research on WS₂ in this project. Raman microscopy and part of the PL measurements are conducted on JY Horiba LabRAM ARAMIS confocal Raman microscope. A frequency-doubled Nd:YAG laser with output wavelength of 532 nm is focused by a 50× long-working distance objective. Two gratings with groove density of either 600 or 1800 slits/mm are available. When taking photoluminescence of WS₂ and Raman of graphene, 600 slit/mm grating is used to include broad enough spectral range while 1800 slits/mm is employed to reach high enough spectral resolution when measuring the Raman spectra of WS₂. However, due to the lack of capability to integrate other measurement units into the system, *e.g.*, electrical unit used in chapter 5 or cryogenic chamber employed in Chapter 6 and 7, most of the PL measurements were performed on a home-built system, shown in figure 3.4. 532 nm from a diode-pumped-solid-state laser (Thorlabs, DJ532-40) is reflected by a dichroic mirror (Semrock, LPD01-532RU-25) and focused by 50× ultra-long working distance (Nikon) onto a target sample after beam expansion and collimation. The reflected inelastic scattered light along with laser beam is collected

by the objective, which then enters the spectrometer (Princeton Instruments, Acton SP-2300) with 600 slits/mm grating after laser beam was filtered by a laser line filter (Thorlabs, FL532-3). The incident Light with different wavelength is separated spatially in the spectrometer and detected by a air-cooling CCD (Princeton Instruments, Pixis 100). A LabVIEW based software is designed for better controlling, the interface of which is presented in figure 3.4d. In Chapter 5, electrical signals were generated by Keithley SourceMeter[®] 2400. The model of the cryostat used in chapter 6 and 7 is Janis ST-500 which is shown in figure 3.5.

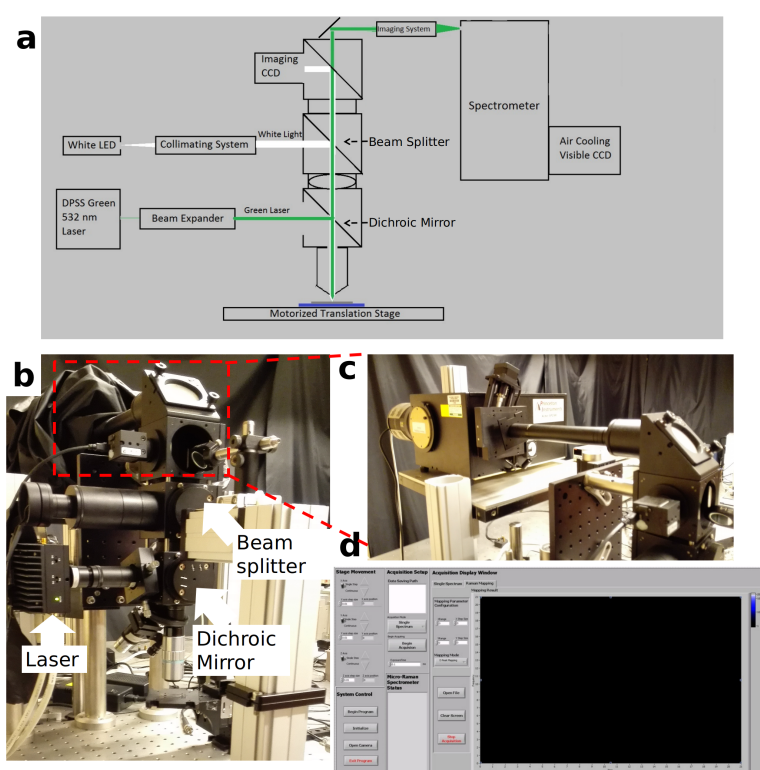


FIGURE 3.4: **a.** Schematic diagram of PL and Raman microscope. **b.** Picture of excitation and collection part of PL and Raman microscope. **c.** Picture of detection part of PL and Raman microscope. **d.** LabVIEW based controlling software.

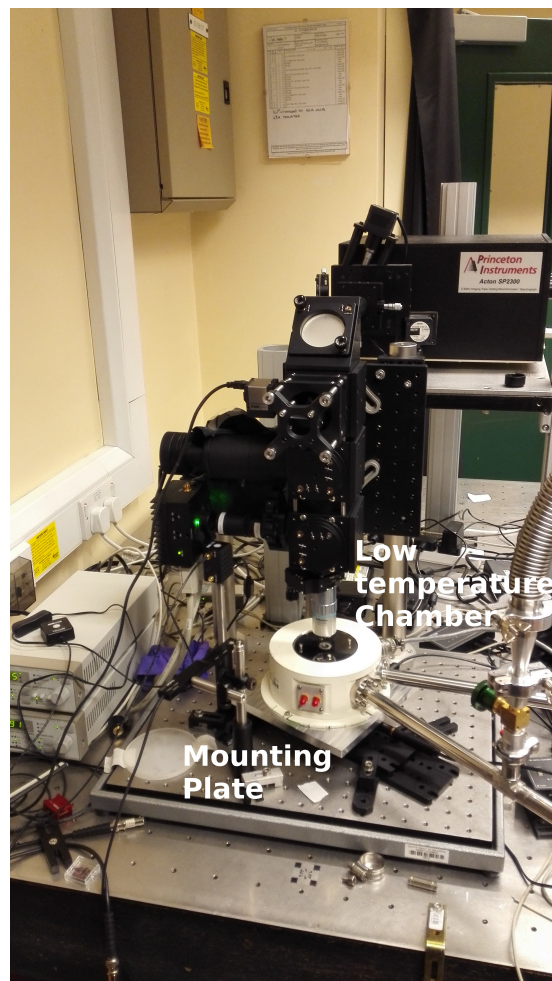


FIGURE 3.5: Picture of PL and Raman microscope with low-temperature chamber mounted on a home-made mounting plate.

Chapter 3 References

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Chapter 4

Metal Chlorides Doped Graphene

4.1 Introduction

Doping is one of the most important techniques in semiconductor industry because it provides an effective way to manipulate the properties of semiconductors. Similar argument can be applied to graphene. Although pristine graphene possesses a lot of exotic properties, it still cannot satisfy the demand of practical applications. For example, although graphene has been predicted to replace ITO as TCEs for touch screens,^[1] there is still no commercialized products until now, mainly due to its high resistivity apart from economic factors. Therefore, doping is an essential step before graphene can walk out of labs and serve the society.

Among all the available doping techniques, spin coating dopant dissolved in certain solvent to target materials is one of the cheapest technique and is suitable for large scale processing. This is especially attractive to consumer electronics industry. Therefore, in the first section of this chapter, I will investigate the behaviour of graphene before and after spin-coating metal chloride solutions, especially the improvement of sheet resistance, which is an important electrical property for TCEs materials. With

the development of microelectronics and nanoelectronics, doping techniques with higher spatial precision is requested. In the second section, another important doping technique is introduced which can reach nanoscale spatial precision.

The outline of this chapter is as follows. In the section 4.1, I briefly introduce the background and motivation of this project. The results section can be separated into two parts. In the first part, I demonstrate the doping effect on graphene after spin-coating metal chloride solutions. The second part introduce a novel doping technique with ultra-high spatial precision. The atomic structures of doped graphene and their dynamic are presented, along with their unique magnetic properties derived from DFT calculations. The last section gives an brief conclusion to this chapter.

4.2 Results and Discussion

4.2.1 Electrical and Optical Properties of FeCl_3 Doped Graphene

In figure 4.1, I present the effect on the electrical and optical properties of graphene after spin-coating FeCl_3 dissolved in ethanol solution. The graphene used here possess an average sheet resistance of $\sim 500 \Omega/\square$. Figure 4.1a shows that with increasing doping solution concentration, the sheet resistance drops dramatically up to over 70 % if the concentration reaches slightly above 10 mg/ml. However, further increasing in the concentration cannot decrease the sheet resistance any more, indicating an saturation effect. In figure 4.1b, optical transmission of graphene doped with different concentrations of dopant solution is presented. The more concentrated the dopant solution is, the less transparent the graphene film will be. The transmittance @ 500 nm of an ideal material for TCEs should be higher than 85 %. Thus the concentration should not exceed 15 mg/ml. In order to figure out the optimal doping concentration, the conductance ratios are calculated, in which the highest ratio of 4.6 correspond to the

solution concentration of 7 mg/ml. Therefore, an optimal solution concentration is 7 mg/ml FeCl_3 /ethanol solution.

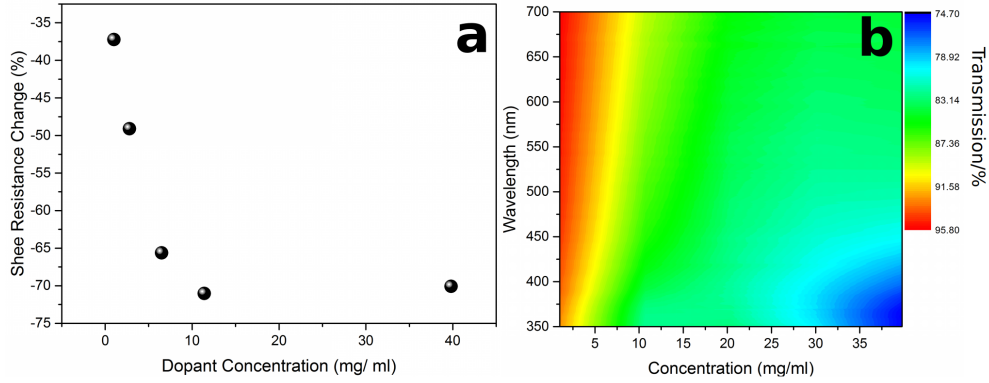


FIGURE 4.1: **a.** Sheet resistance change percentage *versus* concentration of doping solution. **b.** Optical transmission after doping.

Stability is another important parameter needs special attention. In figure 4.2, the sheet resistance change of graphene doped with 7 mg/ml FeCl_3 as a function of ageing time relative to as-doped value is presented, where zero day means as-doped. If the doped sample is left in air, the sheet resistance increases by 55% in 4 days. The de-doping rate gradually decreases as time goes on and the sheet resistance of the graphene film will eventually approach a value which is sample dependent. A possible explanation is that FeCl_3 can absorb water from humid air and form hexahydrate FeCl_3 and therefore the doping effect deteriorates. In order to justify this statement, a comparison experiment is carried out where the stability of doped graphene stored in desiccator is investigated and the result is presented in figure 4.2. Clearly, the de-doping rate is greatly suppressed by about 45%. This indicates that an insulation layer must be considered to prevent water invasion if this type of dopants is employed.

In figure 4.3, I present the source-drain current passing through graphene based FET (the schematic diagram is shown in the inset of figure 4.3) as a function of gate voltage before and after doping. Before the sample is doped by FeCl_3 ethanol solution, the

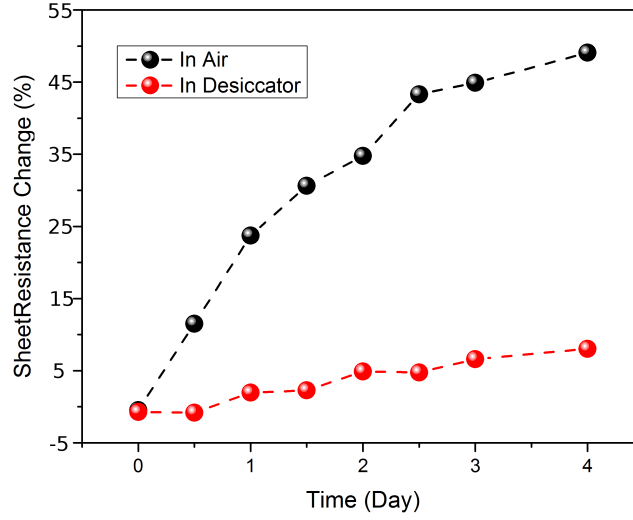


FIGURE 4.2: Sheet resistance change as a function of time. Black spheres: doped graphene sample stored in air. Red spheres: doped graphene sample stored in desiccator.

source drain current has strong dependence on gate voltage. With increasing gate voltage, source drain current decreases continuously towards the highest bias, indicating that the as-prepared graphene is already heavily p-doped. After doping, the conductivity is improved and source drain current still decreases with increasing gate bias, indicating that graphene becomes more p-doped. However, the gate dependence curve possesses more gentle slope, inferring that gate bias dependence become much weaker, which is possibly due to the increasing electron scattering centres and high carriers concentration.

Figure 4.4 depicts the Raman mapping of graphene before and after doping and their statistics of peak positions of two characteristic vibration modes, G mode and 2D mode. The G mode and 2D mode of pristine graphene are $1588.4 \pm 2.7 \text{ cm}^{-1}$ and $2677.4 \pm 4.2 \text{ cm}^{-1}$ while those of doped sample are $1587 \pm 1.7 \text{ cm}^{-1}$ and $2677.4 \pm 2.8 \text{ cm}^{-1}$, respectively. G band is believed to be an indicator which can reveal the doping level of graphene.[2, 3] However, in this case, no obvious G peak shift is observed, which is probably due to the weak doping effect. Similar effect has been observed on AuCl_3

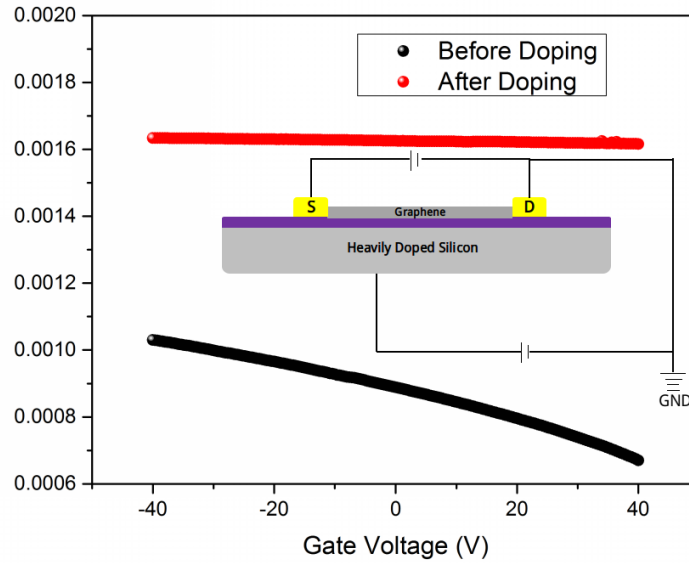


FIGURE 4.3: Gate dependent source-drain current before (black spheres) and after (red spheres) doping. Source-drain bias: 1 V. Inset: schematic diagram of graphene based FET used to measure the transport properties.

doped graphene sample, where G band shift can only be noticeable after concentrated dopant solution was introduced to graphene.^[4]

Morphology is another important parameter that needs careful characterization. Typical optical images before and after doping are shown in figure 4.5. Figure 4.5a presents the typical optical image of as-transferred graphene, which shows very high uniformity, indicating that the graphene in interest here possess good continuity and uniform thickness. After the FeCl_3 dopant solution is spun coated on top of the graphene film (figure 4.5b), a lot of bumps turn up which are possibly the excessive FeCl_3 . This indicates an non-uniform flatness of the doped sample, which could lead to electrical short if it is applied in the devices.

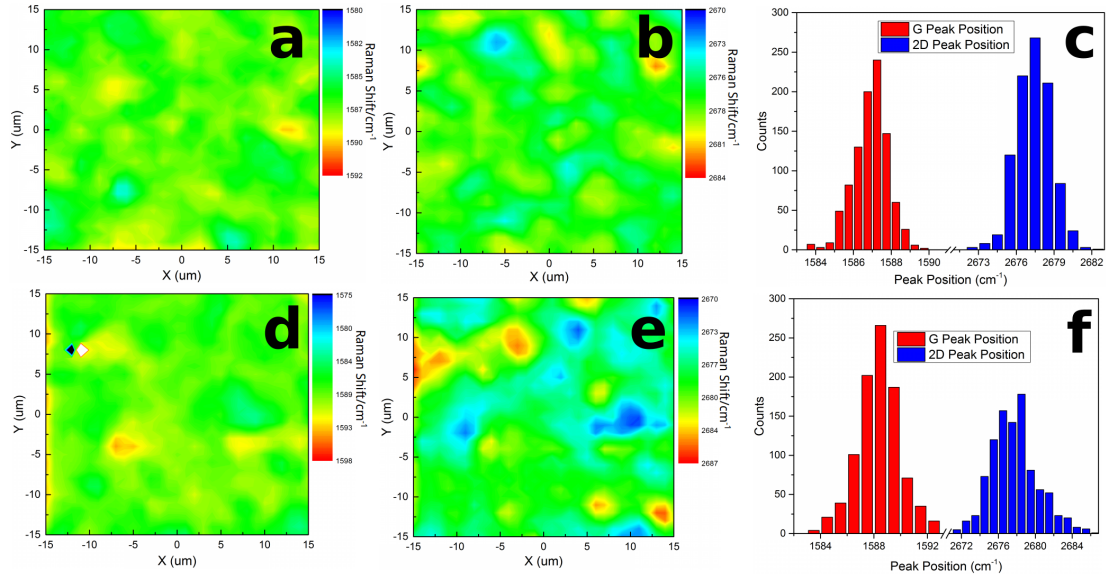


FIGURE 4.4: **a,b.** Raman **a)** G mode **b)** $2D$ mode mapping of pristine graphene. **c.** Statistics of Raman positions in **a)** and **b)**. **d,e.** Raman **d)** G mode **e)** $2D$ mode mapping of 7 mg/ml FeCl_3 /ethanol solution doped graphene. **e).** Statistics of Raman positions in **d)** and **e)**.

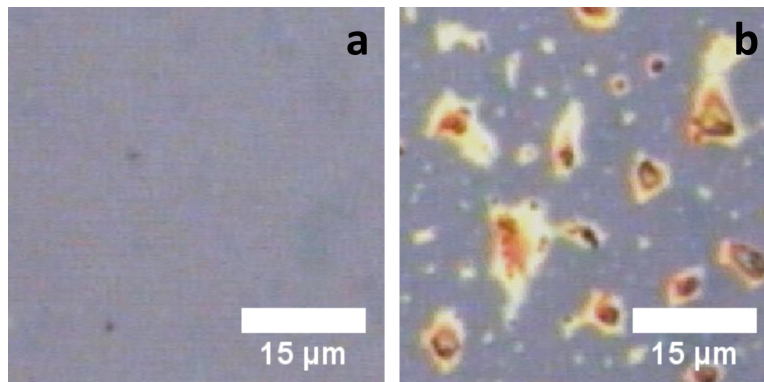


FIGURE 4.5: Optical images of graphene **a)** before and **b)** after doped by 7 mg/ml FeCl_3 solution through spin coating.

4.2.2 Atomic structure of FeCl₃ doped Graphene

In previous section, I mainly focus on investigating the properties of FeCl₃ doped graphene through spin coating dopant solution, which is a doping technique in macroscopic scale. Apart from spin coating, previous literatures reported several other techniques to realize doping in graphene, including synthesizing hybridized graphene,[5, 6] intercalation,[7, 8], chemical modification,[9, 10] low energy ion implantation,[11] and defect-assisted doping.[12] Among these techniques, defect-assisted doping demonstrated highest spatial resolution, with nanoscale spatial manipulation of single dopant atom placement. This technique is realized with the help of AC-TEM operating at 80 kV, in which a vacancy is first created in graphene within a typical area 10×10 nm² by focusing electron beam.[13] These vacancies possess enhanced reactivity and therefore can act as trap centre for dopant atoms.

AC-TEM can also facilitate the *in-situ* structural characterization of the dopants on graphene. Cretu *et al.*[14] reported W atom on graphene can oscillate spatially between two reconstructive defects or vibrate locally around one trapping centre, revealing that strain can facilitate atom adsorption on graphene. Robertson *et al.*[12] reported their observation of the dynamics of single Fe atom embedded in graphene lattice, which can induce pronounced displacement of the adjacent carbon atoms.[12] Aberration-corrected scanning electron microscope (AC-STEM) and electron energy loss spectroscopy demonstrated that single Fe atom embedded in graphene presents resistance to oxidation.[15]

In this section, I will mainly discuss the atomic structure of FeCl₃ doped graphene. Here only Fe atoms were found in the AC-TEM images. Unlike in the previous reports which used residual surface contamination during transfer process that can limit the variety of structural configurations of Fe-graphene vacancy complexes, I intentionally

introduced external Fe source to the surface of graphene by drop casting FeCl_3 aqueous solution to as-prepared graphene transferred to TEM grid, resulting in plenty of mobile Fe atoms on graphene surface and facile filling into vacancies. Four stable Fe atoms pair-graphene vacancies complexes were observed. Spin-sensitive DFT calculation also reveals unique magnetic properties of each structures. Time-sequence TEM images show mutual transformations among these complexes. Along with the binding energies of Fe obtained from DFT calculations, possible mechanisms for the structural transformations are proposed.

In order to introduce Fe atom into graphene lattice and form stable bonding, mono- and di- vacancies are first created by using the focused electron beam with appropriate parameters.[13] Similar to previous report, these vacancies can be trap centres for individual Fe atoms and lead to the formation of two different Fe-vacancy complexes, as shown in figure 4.6.[12] In figure 4.6a, I present the AC-TEM image of single Fe atom in a monovacancy in which one carbon atom is replaced by one Fe atom. Figure 4.6b demonstrates single Fe atom embedded in divacancy where two neighbouring carbon atoms are replaced by one Fe atom. The atomic structures of these two configurations are presented in figure 4.6c,d, with insets showing the side views of these two complexes. Increasing dopant concentration can result in the formation of Fe dimer-vacancy complexes. Before further discussion is presented, I will first make a definition to Fe dimer-vacancy complexes. In many cases, two Fe atoms can be trapped by graphene vacancies separated with distance of more than one lattice constant, which are regarded as two isolated single Fe-graphene vacancy complexes. However, if two Fe atoms are trapped in graphene vacancies that are adjacent with each other, those structures can be viewed as Fe dimer-graphene vacancy complexes. According to our observation, the formation of Fe dimer always occurs sequentially with the initial single Fe dopant trapped in the pre-defined vacancy shown in figure 4.6, which can again be a trapping center to attract an additional Fe atom to form Fe dimer complexes.

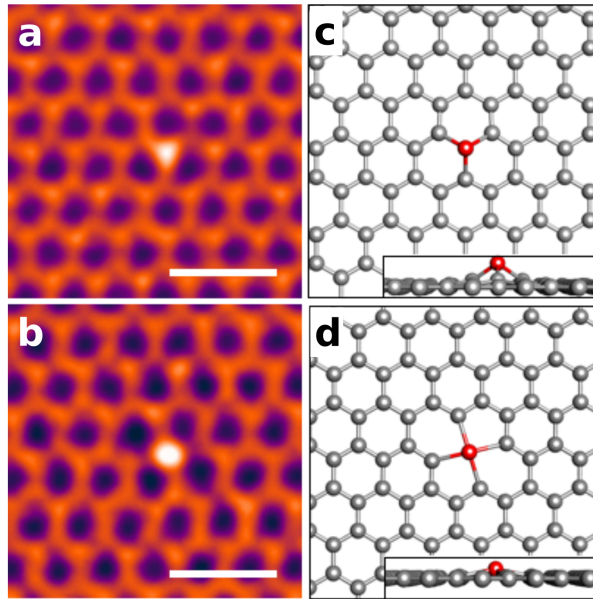


FIGURE 4.6: Single Fe atom dopant in graphene vacancies. **a,b.** Smoothed AC-TEM images of single Fe atom in **a)** monovacancy (Scale bar: 1.2 nm) and **b)** divacancy (Scale bar: 1.5 nm). **c,d.** DFT optimized atomic models corresponding to AC-TEM images in **a)** and **b)**. Inset: side view of the optimized atomic structures.

Figure 4.7a-d present smoothed AC-TEM images of four different Fe dimer (DiFe) along with multislice image simulation [16, 17] results in figure 4.7e-h based on the relaxed atomic structures presented in figure 4.7i-l. In figure 4.7a, the AC-TEM image shows a pair of Fe atoms trapped by a graphene trivacancy which is denoted as DiFe@TV_1. An Fe atom marked by a black circle in figure 4.7i replaces carbon pairs interstitially and forming 4 covalent bonds with nearest atoms while the black arrow marked Fe atom in figure 4.7i substitutionally take the place of only one carbon atom and bond with three neighbouring atoms. Another Fe dimer trapped in graphene trivacancy is presented in figure 4.7b, which is denoted as DiFe@TV_2. Different from DiFe@TV_1 where both Fe atoms are at the same side of graphene sheet, in DiFe@TV_2, two Fe atoms are at different sides of graphene plane. This results in differences in bonding coordination number as well as atom positions of Fe dimer. Figure 4.8 demonstrates that the such differences can lead to unequal distance between the Fe atom marked by black circle and carbon atoms marked by red circle in figure 4.7i,j. Figure 4.8c,d present the gray

value profile marked by the yellow box in figure 4.8a,b which are AC-TEM image and multislice image simulation[16, 17] based on the DFT optimized atomic structure in the inset, respectively. It shows that the marked Fe atoms are almost in the middle point of the line connecting two marked carbon atoms. On the contrary, the distance difference in DiFe@TV_2 is *ca.* 82 pm and the distance ratio is about 1.27, which are much larger than those in DiFe@TV_1, as presented in figure 4.8e-h. This clearly shows that there are two distinct configurations in Fe dimer-graphene trivacancy complexes. DiFe@TV_1 appears more frequently than DiFe@TV_2 despite that DiFe@TV_2 are 1.03 eV energetically favoured compared with DiFe@TV_1 according to DFT calculations. This can be explained by the fact that more mobile Fe atoms from drop-casted FeCl_3 solution are on the same side of graphene sheet and therefore can facilitate the formation of DiFe@TV_1 whereas additional energy is required for an Fe atom to diffuse through the vacancy to the other side of graphene sheet to form DiFe@TV_2 .

Fe dimer can also be embedded in graphene tetravacancy, forming another new type of dimer complex and subsequently denoted DiFe@QV. (Here I refer tetravacancy (TV) as quadvacancy (QV) to avoid confusion with trivacancy (TV)) In this complex, two Fe atoms substitute for two adjacent pairs of carbon atoms interstitially in tetravalent bonding configuration. In the last structure of dimer complex, two Fe atoms replace two carbon atoms adjacent to each other and both form bondings with three neighbouring carbon atoms, as shown in figure 4.7d. It is the only case in which there is no direct bonding between two Fe atoms.

In some cases, single Fe atom is likely to switch from one place to another, resulting in two bright spot in the AC-TEM images which may resemble those of Fe dimer complexes within the acquisition time. In order to confirm that the two bright spots in figure 4.7a-d come from two Fe atoms instead of single atom switching, I measured the intensity profile across two regions highlighted by two yellow boxes in a typical image of Fe doped graphene shown in figure 4.9a. Region 2 shows the AC-TEM image of a single

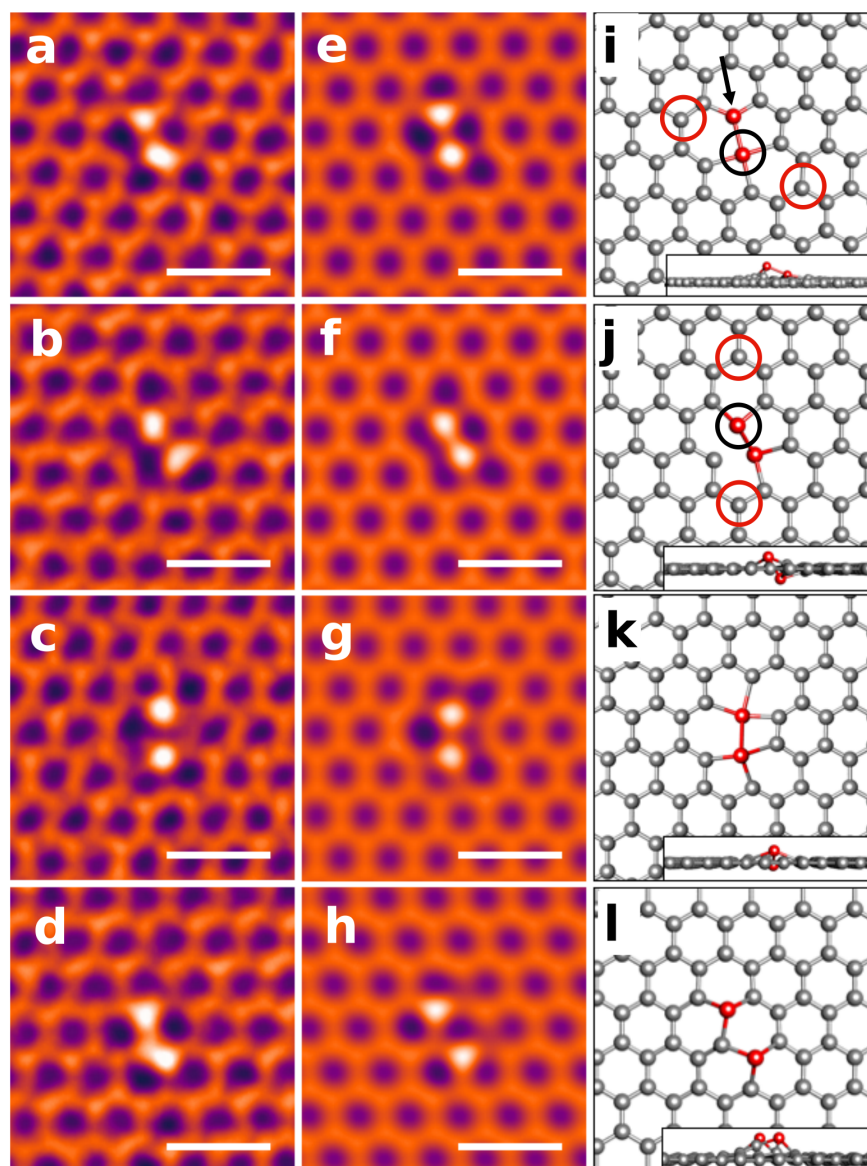


FIGURE 4.7: Four different structures of Fe dimer trapped in graphene vacancies. **a-d.** Smoothed AC-TEM images of Fe dimer in **a)** trivacancy_1 (DiFe@TV_1) (Scale bar: 1.2 nm), **b)** trivacancy_2 (DiFe@TV_2) (Scale bar: 1.3 nm), **c)** quadvacancy (DiFe@QV) (Scale bar: 1.4 nm) and **d)** two adjacent monovacancy (Fe@2MV) (Scale bar: 1.2 nm). **e-h.** Image simulations based on multislice algorithms according to the DFT optimized atomic models in panel **i-l** which corresponds to panel **a-d**. Inset: side view of the optimized atomic structures. Scale bar in **e-h**: 1.2 nm.

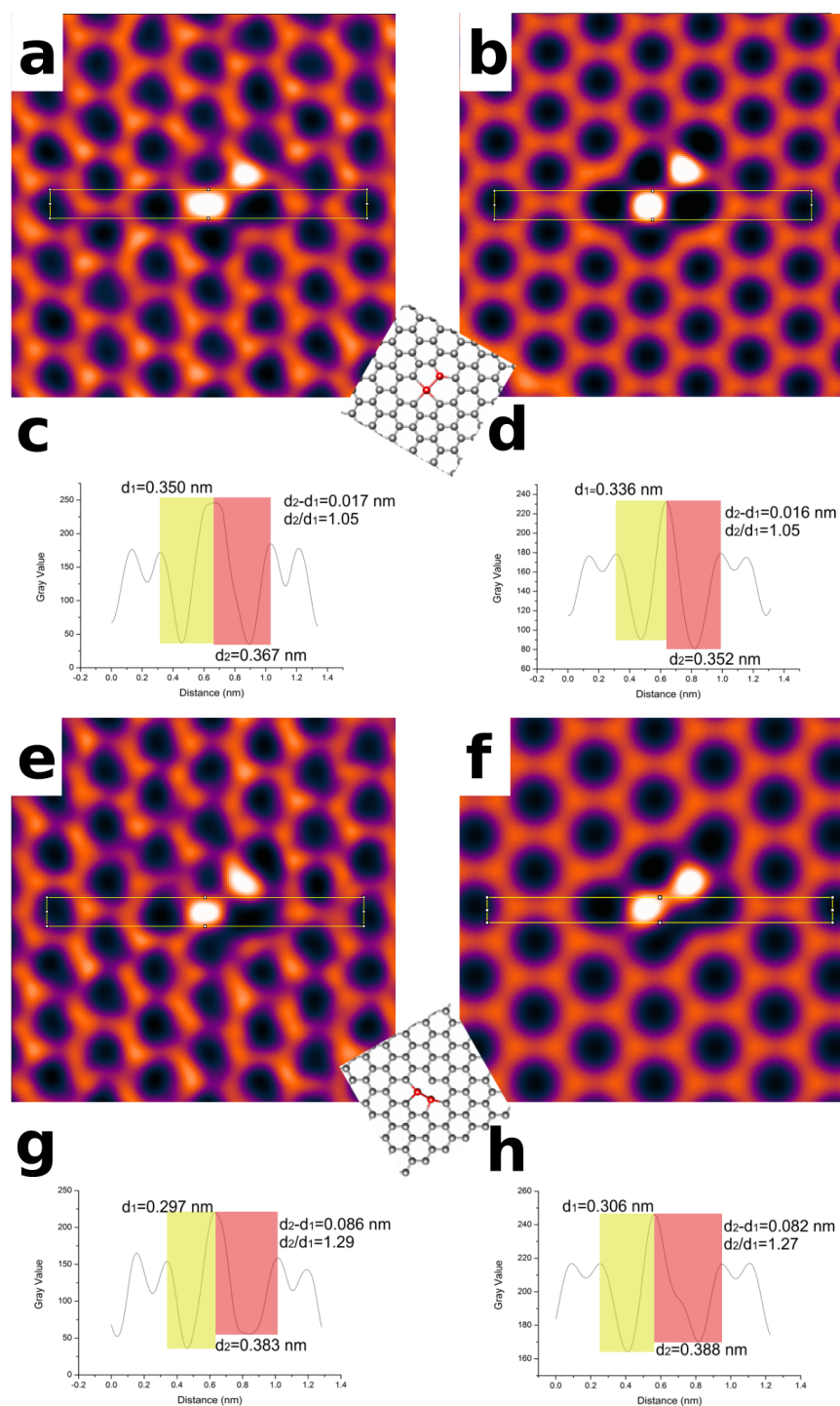


FIGURE 4.8: **a.** AC-TEM image of DiFe@TV_1, **b.** multislice image simulation of DiFe@TV_1. **c,d.** Gray value profile of regions marked by yellow box in **c)** AC-TEM image and **d)** simulation image. Inset: DFT optimized atomic structure. **e-h.** Distance analysis of DiFe@TV_2.

Fe atom in graphene monovacancy which can serve as a reference value for measurement from Fe pairs in region 1. Figure 4.9b presents the AC-TEM image in figure 4.9a which is plotted in "Spectrum" color-look-up-table (CLUT) for better visualization. Clearly, there is little difference in the contrast of all three sites corresponding to Fe atoms. Figure 4.9c,d present the intensity box profile highlighted by yellow boxes in figure 4.9a. The CCD counts differences between dark spot in both regions and their surrounding carbon atoms are close to each other, indicating that the two dark spots observed are the result of two heavy Fe atoms instead of the switching of single Fe atom.

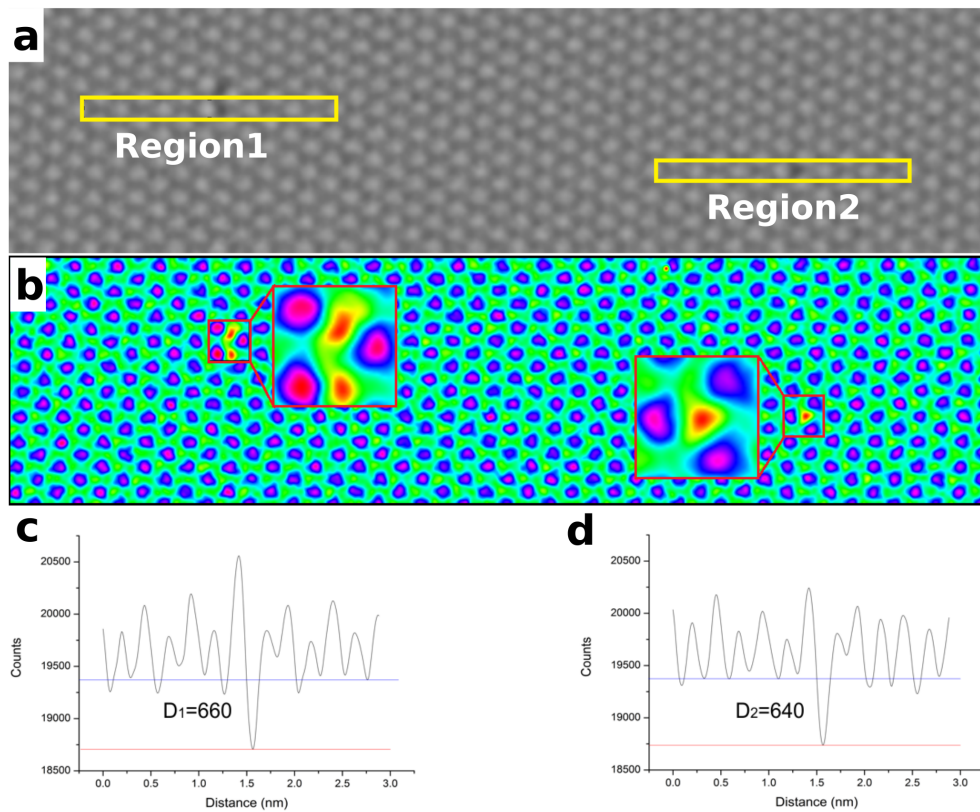


FIGURE 4.9: **a,b.** AC-TEM images of Fe doped graphene in **a)** gray scale and **b)** "spectrum" colour scale. **c,d.** CCD intensity box profiles across two regions marked by yellow boxes in **a)**.

Given the observations of four stable Fe dimer complexes, spin-sensitive DFT calculations are performed to derive the magnetic moments for each of these structures which are concluded in figure 4.10. In order to understand the effect of the additional Fe on

the magnetic properties of graphene, the magnetic moments of single Fe atom complexes as well as the corresponding vacancies are also included. Fe@MV possesses zero magnetic moment while the magnetic moment of monovacancy structure is $\sim 1.50 \mu_B$. Graphene with divacancy is non-magnetic while Fe@DV complex has a magnetic moment of as large as $3.55 \mu_B$. These values are close to what have been reported in other literatures,[18, 19, 20] indicating that the DFT calculation results used here are reliable. The magnetic moment of a graphene trivacancy is $1.05 \mu_B$ [21] and the addition of two Fe atoms at the same side of graphene (DiFe@TV_1) increases this value to $2.00 \mu_B$ while Fe atoms at different side of graphene (DiFe@TV_2) can induce a magnetic moment of $4.00 \mu_B$. Tetravacancy in graphene lattice has a magnetic moment of $2.00 \mu_B$. After two Fe atoms are incorporated into the vacancy site, the magnetic moment of the complex rises to $4.00 \mu_B$. DiFe@2MV is the combination of two Fe@MV and therefore is expected to be non-magnetic. However, surprisingly, it possesses a non-zero magnetic moment of about $2.00 \mu_B$. This indicates that the magnetization originates from a non-covalent interaction between two Fe atoms. In order to figure out the distance dependence of this interaction, magnetic moments of two Fe@MVs with varying separation distance are investigated, which shows that longer spatial separation leads to demagnetization, suggesting that such interaction is very localized.

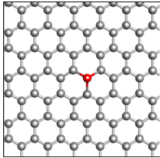
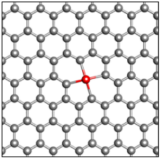
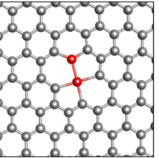
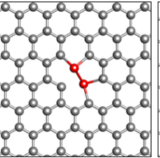
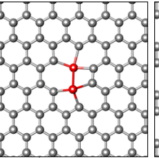
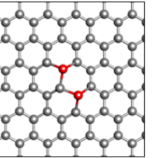
	Fe@MV	Fe@DV	DiFe@TV_1	DiFe@TV_2	DiFe@QV	DiFe@2MVs
Structure						
Magnetic Moment	$0.00 \mu_B$	$3.55 \mu_B$	$2.00 \mu_B$	$4.00 \mu_B$	$4.00 \mu_B$	$2.00 \mu_B$

FIGURE 4.10: Spin sensitive DFT calculated magnetic moments of Fe atoms embedded in graphene vacancies with different configurations.

In order to observe the structural dynamics of these dimer complexes, time sequential

imaging was performed, which revealed that all dimer structures started from single Fe atom-divacancy structures. Figure 4.11 presents two sets of TEM images in time sequence where in both cases a second Fe atoms joins an Fe@DV structure. In figure 4.11a,b, I present the AC-TEM images which demonstrate the transition from Fe@DV to DiFe@TV_1 after 11 seconds of observation. In this case, an additional Fe atom replaces the carbon atom labelled by a red circle in figure 4.11c. Figure 4.11e,f depict the transition from initial state, Fe@DV to DiFe@QV after 19 seconds under imaging electron beam irradiation. In this case, the second Fe atoms take the place of a pair of carbon atoms marked by red ellipse in figure 4.11g.

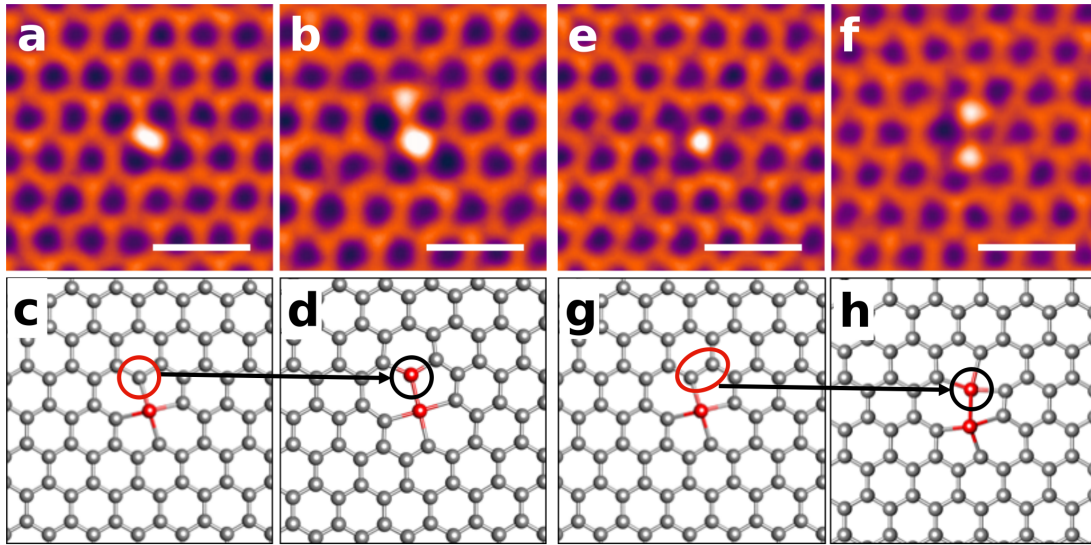


FIGURE 4.11: Transition from single Fe-divacancy complex into an Fe dimer structure. **a-d.** Transition from Fe@DV to DiFe@TV_1. **a,b)** Smoothed AC-TEM images of **a)** Fe@DV (Scale bar: 1.3 nm) and **b)** DiFe@TV_1 (Scale bar: 1.1 nm). **c,d.** DFT optimized atomic structure. Time difference between **a)** and **b)**: 11 seconds. **e-h.** Transition from Fe@DV to DiFe@QV. Scale bar in **e,f**: 1.3 nm. Time difference between **e)** and **f)**: 19 seconds. Red spheres: Fe atoms. Black spheres: carbon atoms.

The transition demonstrated in figure 4.11 is reversible rather than single directional. There are chances that dimer structure can return to single dopant complexes under electron beam irradiation. Figure 4.12a-d present a typical transition from DiFe@TV_2 back to Fe@DV, where Fe atom labelled by red circle in figure 4.12c is replaced by

a carbon atom highlighted by a black circle in figure 4.12d. DiFe@QV is also found to revert to Fe@DV, presented in figure 4.12e-h, in which an Fe atom highlighted in black circle is replaced by a pair of carbon atoms labelled by a red circle. Robertson *et al.* [12] proposed that single Fe atom embedded in graphene vacancy could hardly be sputtered away by electron beam with 80 kV acceleration voltage due to the high mass and high binding energy (> 6 eV) while the maximum energy transferred from collision between electrons and Fe atoms is only 3.4 eV. Therefore, the mechanism behind this type of transitions needs to be investigated.

In order to clarify the mechanism behind, the binding energies (E_b) and sputtering (E_s) of DiFe@TV_1, DiFe@TV_2 and DiFe@QV are calculated, shown in figure 4.13. Here the binding energy is defined as the energy required to remove one atom from the lattice which then mobilizes on the surface of graphene while the sputtering energy describes the minimum energy required to sputter an atom away from graphene lattice into vacuum and therefore should be higher than binding energy. Calculation results show that the sputtering energies for three structures are much higher than the maximum energy transferred to Fe atom through collision with electrons, which rules out the possibility of direct sputtering. The binding energies of the Fe atoms in DiFe@TV_1 is smaller than $E_{m,Fe}$ and therefore it is likely that Fe atom can be displaced from the lattice under electron beam irradiation and move freely on the graphene surface due to the low migration barrier on perfect graphene sheet, leaving a single Fe atom dopant in the lattice. However, the binding energies of Fe atom in the other two structures are still higher than $E_{m,Fe}$ and therefore prevent direct ejection of Fe atoms to the graphene surface. One possible explanation is that such transition is facilitated by an intermediate state between the initial and final configurations. Indeed, real time monitoring reveals that dimer structures are able to switch back and forth between different configurations which is illustrated in figure 4.14. It is likely that both DiFe@TV_2 and DiFe@QV can first transform to DiFe@TV_1 which possesses lower Fe binding energy with the help of electron beam irradiation, followed by the ejection of Fe atom onto graphene surface.

However, the due to limitation of temporal resolution of the microscope, intermediate states were hardly resolved.

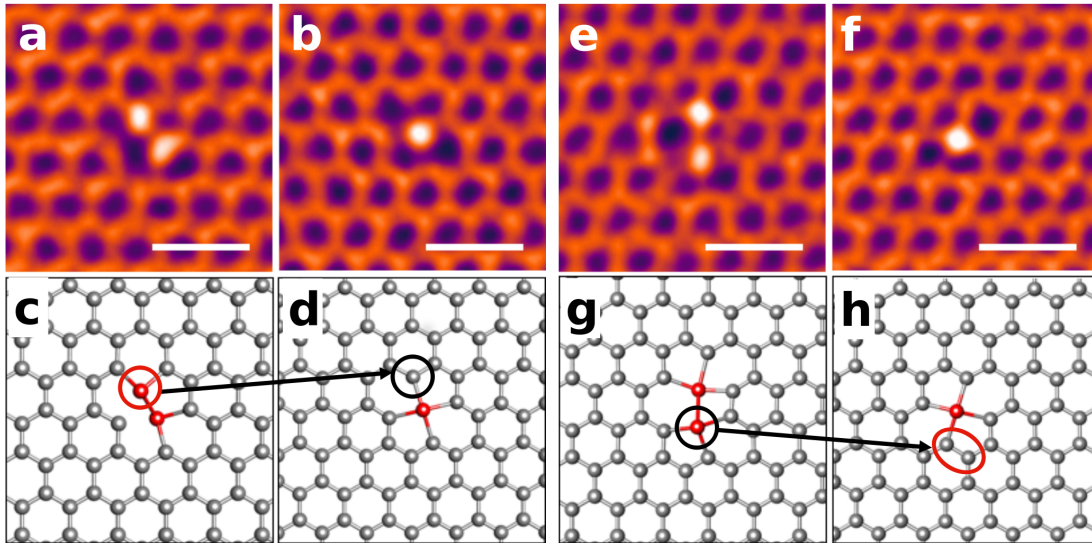


FIGURE 4.12: Transition from Fe dimer structure to single Fe-divacancy complex. **a-d.** Transition from DiFe@TV_2 to Fe@DV. **a,b.** Smoothed AC-TEM images of **a)** DiFe@TV_2 and **b)** Fe@DV. **c,d.** DFT optimized atomic structure. Time difference between **a)** and **b)**: 22 seconds. **e-h.** Transition from DiFe@QV to Fe@DV. Time difference between **e)** and **f)**: 23 seconds. Red spheres: Fe atoms. Black spheres: carbon atoms. Scale bar: 1.3 nm.

Figure 4.14 present the mutual transitions between dimer structures and in particular, between DiFe@2MV and DiFe@TV_1. Figure 4.14a-d demonstrate a transition from DiFe@2MV to DiFe@TV_1. Possible process is that a carbon atom is first trapped by a defect and rest on top of the DiFe@TV_1. Subsequently, it can migrate to an in-plane position and as a result separate the two Fe atoms apart and weaken the bonding. The addition of carbon atoms that mediate the mutual dimer structures transformation arises from the residual carbon atoms mobilizing on the graphene surface. A reverse transition is also observed and presented in figure 4.14e-h.

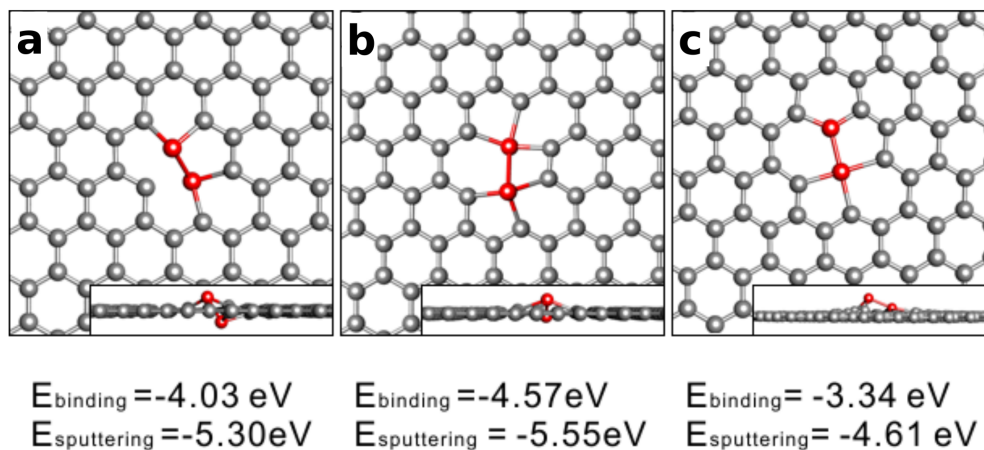


FIGURE 4.13: Binding and sputtering energies of Fe atom in dimer structures. a). DiFe@TV_2. b). DiFe@QV. c). DiFe@TV_1.

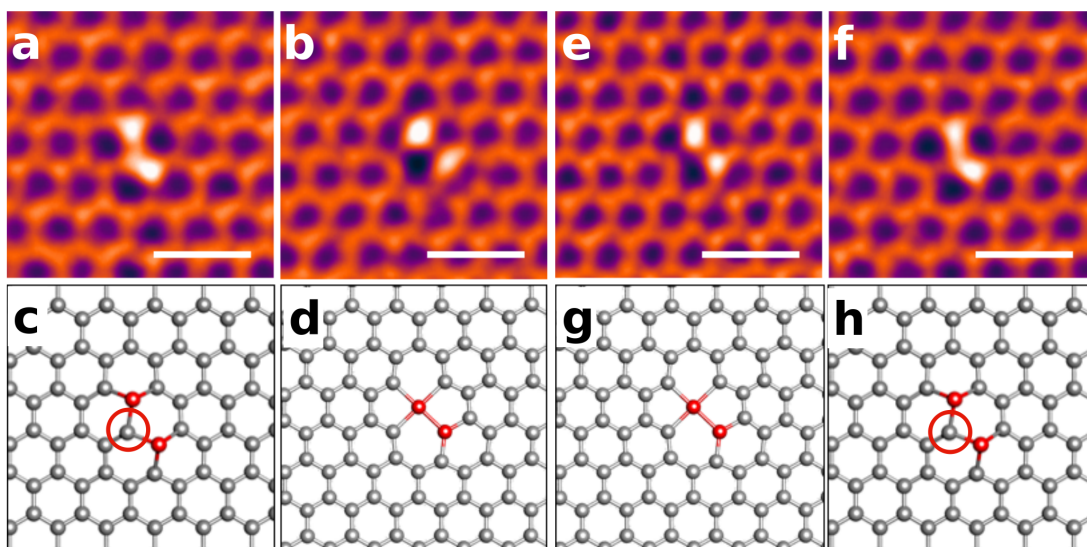


FIGURE 4.14: Mutual transformation between two dimer structures. a-d. Transition from DiFe@TV_1 to DiFe@2MV. a,b. Smoothed AC-TEM images of a) DiFe@TV_1 and b) DiFe@2MV. Scale bar in a, b: 1.3 nm. c,d. DFT optimized atomic structures. Time difference between a) and b): 7 seconds. e-h. Transition from DiFe@2MV to DiFe@TV_1. Scale bar in e: 1.4 nm. Scale bar in f: 1.2 nm. Time difference between e) and f): 9 seconds. Red spheres: Fe atoms. Black spheres: carbon atoms.

4.3 Conclusion

In conclusion, doping provides an effective way to control the electrical, optical and magnetic properties of graphene. Spin coating metal chloride solutions on graphene can greatly improve its conductivity. The more concentrated the solution is, the lower the resistivity of graphene is, until it reaches a threshold after which the trend stops. Therefore, it is important to find an optimal doping concentration, which is determined to be 7 mg/ml in this thesis. The resultant sheet resistance and optical transmission of doped graphene are $175.8 \Omega/\square$ and 89.7%, corresponding to a conductance ratio of 4.6.

This chapter also introduces another novel doping technique with nanoscale spatial resolution. Spatially predefined vacancy is created within an area of $10 \times 10 \text{ nm}^2$ region *via* focused electron beam.^[13] The introduction of additional Fe source by drop casting concentrated FeCl_3 solution leads to the formation of Fe dimer-graphene vacancies complexes with four different structures observed. All dimer complexes start from the single Fe atom-divacancy complex. Dimer complexes are relatively stable but mutual structural transformation between single complexes and dimer complexes or two different dimer structures are also observed. Spin-sensitive DFT calculations show that each of these structures possess different magnetic moments varying from $2.00 \mu_B$ to $4.00 \mu_B$. These dimer complexes can provide new pathway to manipulate carrier states and therefore have the potential to be incorporated into applications including spintronics.^[22]

Chapter 4 References

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Chapter 5

Modulation of WS₂ Photoluminescence by Lateral Electric Field

5.1 Introduction

In this chapter, I investigate the PL response of WS₂ towards lateral electric field. WS₂ belongs to TMDCs family, which are another class of 2D materials other than graphene. Atomically thin TMDCs consist of three atomic layers with two hexagonal planes of chalcogen atom X (S, Se) bonded to one layer of transition metal atoms M (Mo, W) arranged in hexagonal lattice. These 2D TMDCs possess unique electrical[1, 2, 3] and optical properties[4, 5, 6, 7, 8] and therefore are promising for applications in varieties of optoelectronics such as photo-detectors,[9, 10, 11] solar cells,[12, 13, 14, 15], LEDs[14, 16, 17] and photo-transistors.[18, 19]

For many applications, it is essential that the optical properties of active materials needs to be properly engineered *via* external modulation. The same argument can be applied

to atomically thin TMDCs. Tongay *et al.*[6] reported their observation of thermally driven indirect-to-direct bandgap crossover in multilayer MoSe₂, possibly due to the larger inter-layer spacing induced by heating. Strain has also been utilized to alter the luminescent emission of WSe₂ because of the changes in lattice parameters.[20] Compatible with modern electronic industry, electrical methods are more desired to control the luminescence of semiconductors. Different PL emission spectra can be achieved through electrostatic charging TMDCs in an FET configuration.[21, 22] Sufficiently high vertical electric field can even close the bandgap of TMDCs, as predicted by the DFT calculations.[23] However, few reports have explored the luminescence response towards lateral electric field, which has been proved to be an efficient tools to manipulate the luminescent properties of many other materials. Bludau *et al.*[24] and Skromme *et al.*[25] observed PL quenching from bulk GaAs and InP and advanced that impact ionization should be the mechanism. The luminescence of low-dimension materials can also be manipulated by lateral electric field. Al_{0.3}Ga_{0.7}As/GaAs/Al_{0.3}Ga_{0.7}As single quantum well presented electric field induced PL quenching with ultra-high time response, which opened up an pathway to quantum well based high speed optical modulator.[26] Field induced PL switching from single colloidal quantum dots has also been reported, explained by direct exciton ionization.[27] Rothenberg *et al.*[28] reported PL quenching of quantum nanorods under electric field because of the diminishing transition matrix element.

This chapter mainly focuses on the investigation of PL response of monolayer and bilayer WS₂ under lateral electric field. The outline of this chapter is as follows: in section 5.1, I briefly introduce the motivation of investigating the PL response of WS₂ towards electrical method. In section 5.2, results of lateral electric field dependent PL of both monolayer and bilayer WS₂ are presented, followed by discussion of possible mechanisms. Section 5.3 gives short summary to this work.

5.2 Results and Discussion

Large 2D single crystals of WS₂ were grown by CVD on Si substrate with a 300 nm oxide layer using previously reported method[29], yielding primarily monolayer domains, but some bilayer and few-layer domains can also be found. Figure 5.1a presents a scanning electron microscopy (SEM) image of the monolayer triangular shape WS₂ domain with an average size of about 100 μm . By optimizing the RGB colour channel of the microscope imaging CCD, monolayer and bilayer WS₂ crystals can be distinguished by optical contrast.[16] In figure 5.1b,c, the optical microscopy images of monolayer (triangle) and bilayer (hexagonal) isolated domains are presented. PL spectroscopy is employed to further confirm the difference between monolayer and bilayer, shown in figure 5.1d. Under the same excitation and acquisition conditions, the integrated PL intensity of monolayer is about 200 times stronger than that of bilayer crystal, owing to the direct to indirect band gap crossover from monolayer to bilayer WS₂. [8] Raman spectroscopy can also give insights to the number of layers of WS₂, which is shown in figure 5.1e. The black curve represents the Raman spectrum of monolayer WS₂, and the two characteristic vibration modes, $E'/E_g^1/E_{2g}^1$ and A'_1/A_{1g} phonon modes at ~ 356 and 418.9 cm^{-1} . With additional one atomic layer, these two vibration modes change correspondingly. $E'/E_g^1/E_{2g}^1$ mode experiences softening and peak position shift to 354.9 cm^{-1} while A'_1/A_{1g} goes through red shifting to 419.8 cm^{-1} , which are consistent with previous reports.[8, 30] A weak peak is found around 380 cm^{-1} , which is reported to originate from the symmetry assignment $2\text{LA}(M)+2E_{2g}^2(M)$. [31] (LA is the longitudinal acoustic phonons; M refers to the specific direction and magnitude of the momentum q of the phonon and in the phonon dispersion; they appear at the M point of the Brillouin zone.) In figure 5.1f, I present the schematic diagram of the experimental setup employed here. In-plane electric field is created by applying a source-drain bias across the WS₂ crystal. Lithography process to make electrodes to the WS₂ is intentionally avoided because defects and contaminations are very likely to be introduced

during the process, which could affect the intrinsic PL of WS_2 . [22] Instead, I directly positioned two ultrafine tungsten tips using micro-manipulators to the surface of WS_2 as stable source-drain electrodes. The tungsten tips were typically separated by $20\ \mu\text{m}$ underneath a long working distance objective lens in a PL confocal micro-spectrometer. PL was excited by a 532 nm laser focused into a $\sim 2\ \mu\text{m}$ in diameter spot and incident in the middle of the two electrodes. Although a Schottky barrier is expected due to the misalignment between the WS_2 conduction band and the work function of the tungsten tips, it won't affect the qualitative observation of the effects of biasing in WS_2 .

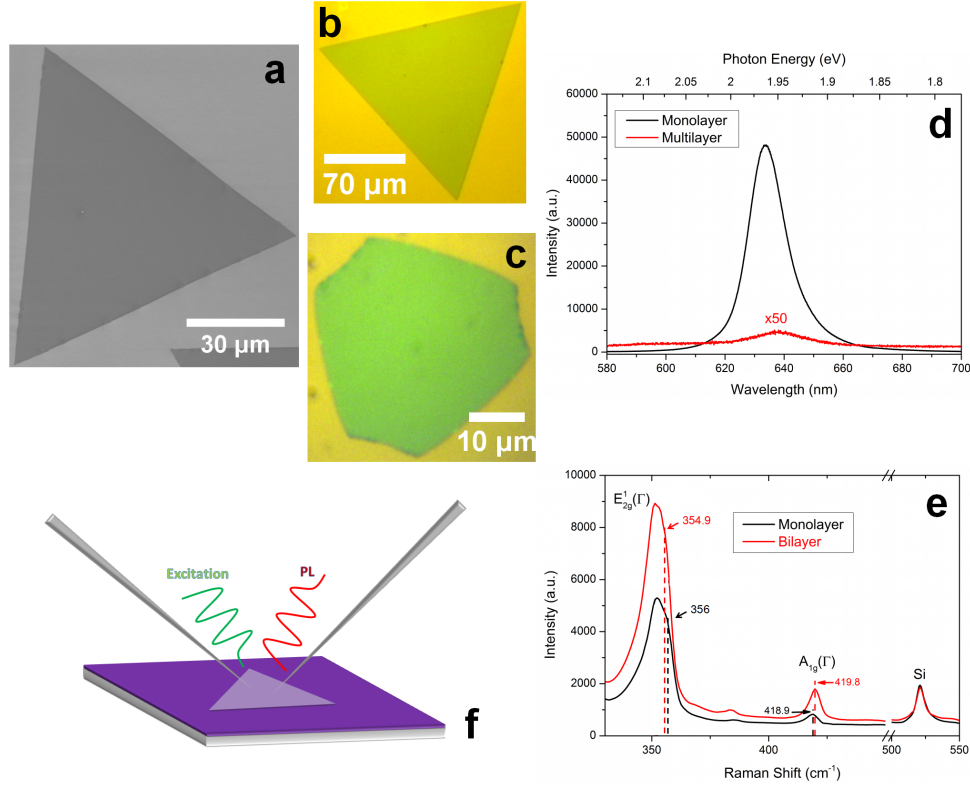


FIGURE 5.1: **a**. SEM image of monolayer single-crystal WS_2 domain with triangular shape. **b,c**. Optical image of **b**) monolayer and **c**) bilayer. **d**. PL spectra of both monolayer (black) and bilayer (red). **e**. Raman spectra of monolayer and bilayer WS_2 . **f**. Schematic diagram of the experimental set-up used to measure PL response under lateral electric field.

5.2.1 Monolayer

Figure 5.2a,b shows the an typical example of PL behaviour of monolayer WS₂ under an external lateral electric field. Under low electric field, minimal current flows in the crystal and PL remains almost unchanged. However, when the electric field exceeds a certain value, such as 1 kV/cm in this case, the intensity of PL starts to decrease. A maximum drop up to 50% of the original value is observed in figure 5.2 as the electric field continues to increase. It also presents reversible behaviour where the PL intensity returns to the original value as the electric field goes back to zero. This indicates that the bias induced PL quenching is not caused by permanent structural changes or chemical reactions with species in the air. There is a small difference in the rate of PL change with forward and reverse sweeps of the electric field, probably due to the charging effect, but the main purpose of figure 5.2c is to show the reversibility of this phenomenon. In addition to the PL quenching effect, another feature shown in figure 5.2a,b is the small red shift of PL spectra under high bias, which will be discussed in detail in the following section. Applying a higher electric field can lead to further quenching of the PL intensity up to 83 % compared with the zero-bias value, shown in figure 5.3. However, this can also result in a larger spectral red shift, or even damage to the WS₂ crystal due to the joule heating. Figure 5.2c,d shows both traces of PL integrated intensity and source-drain current *versus* a lateral electric field. The nonlinearity of the I - V curve arises from the Schottky barrier, because of the misalignment between the work functions of the source-drain electrodes and the WS₂ conduction band.[32] In figure 5.2e, I depict the integrated PL intensity as a function of source-drain current to figure out the correlation between current and PL intensity. With minimal current flow, PL intensity shows fluctuations in a small range, which is then followed by a quenching process. With current increasing continuously, the quenching rate decreases gradually. Similar measurements and analysis have been repeated on numerous monolayer crystals, which all present similar qualitative behaviour.

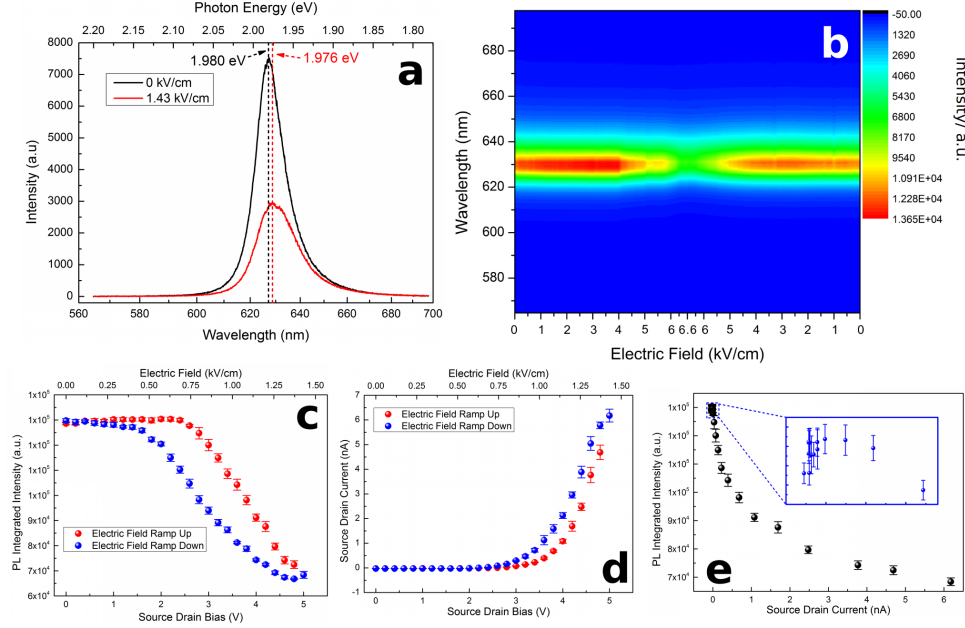


FIGURE 5.2: **a.** Typical PL spectra under two different electric field, 0 and 1.43 kV/cm. Quenching effect can be clearly observed. **b.** Colour contour map of PL spectra under a lateral electric field. **c.** PL integrated intensity *versus* electric field. **d.** I - V trace with laser illumination. Red spheres: electric field ramps up. Blue spheres: electric field ramps down. **e.** Correlation between the integrated PL intensity and the source-drain current. Inset: magnified image of the area labelled by a blue rectangle.

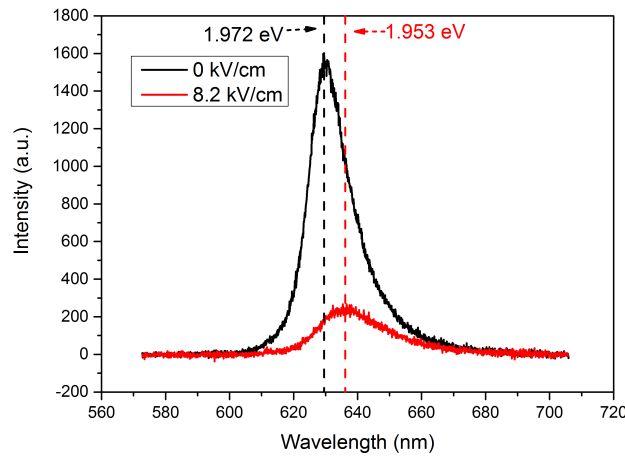


FIGURE 5.3: PL quenching under large electric field (8.2 kV/cm). Obvious redshift is observed from 1.972 eV (under 0 kV/cm) to 1.953 eV (8.2 kV/cm)

In some other cases, two different quenching rates are observed, presented in figure 5.4. Figure 5.4a,b depict the typical PL spectra under two different electric field as well the colour contour map of PL spectra as a function of electric field, again showing the quenching effect as well as the reversibility of the phenomenon. In figure 5.4c, I show the PL integrated intensity *versus* electric field. Since charging effect cannot be omitted during electric field ramping back to zero, discussion only limit to data points acquired during electric field ramping up. Clearly, we can divide it into three category: 1) No intensity change (before 0.8 kV/cm); 2) slow quenching (from 0.8 kV/cm to 2.0 kV/cm) and fast quenching (from 2.0 kV/cm to 2.56 kV/cm). In category 1), electric field is too small to induce any changes in PL. Once the electric field exceeds threshold yet still with minimal current flowing, PL starts quenching with relative slow rate, as shown in category 2). Category 3) demonstrates that further increasing the electric field led to the onset of current flowing (figure 5.4d), coinciding with faster PL quenching. This indicates that the PL quenching process is related not only to the electric field but also to the current flowing in the material. The different behaviour between figure 5.2 and figure 5.4 may come from the different Schottky barrier heights in the two cases.

5.2.2 Bilayer

The PL response of bilayer WS₂ towards source-drain biasing shows distinct behaviour from that of monolayer WS₂ with PL being enhanced, as illustrated in figure 5.5a and contour colour map in 5.5b. The PL intensity does not change much under a weak electric field with little current flowing. As the field strengthens to a certain threshold value (2.0 kV/cm in this case), the PL emission intensity starts to increase and reach up to 150 % of the original value in this case. This behaviour also presents reversibility, which eliminates the possibility of permanent structural change or chemical reaction caused by the electric field and joule heating. In addition to the intensity change, the electric field also leads to slight spectral red shift and broadening. Figure

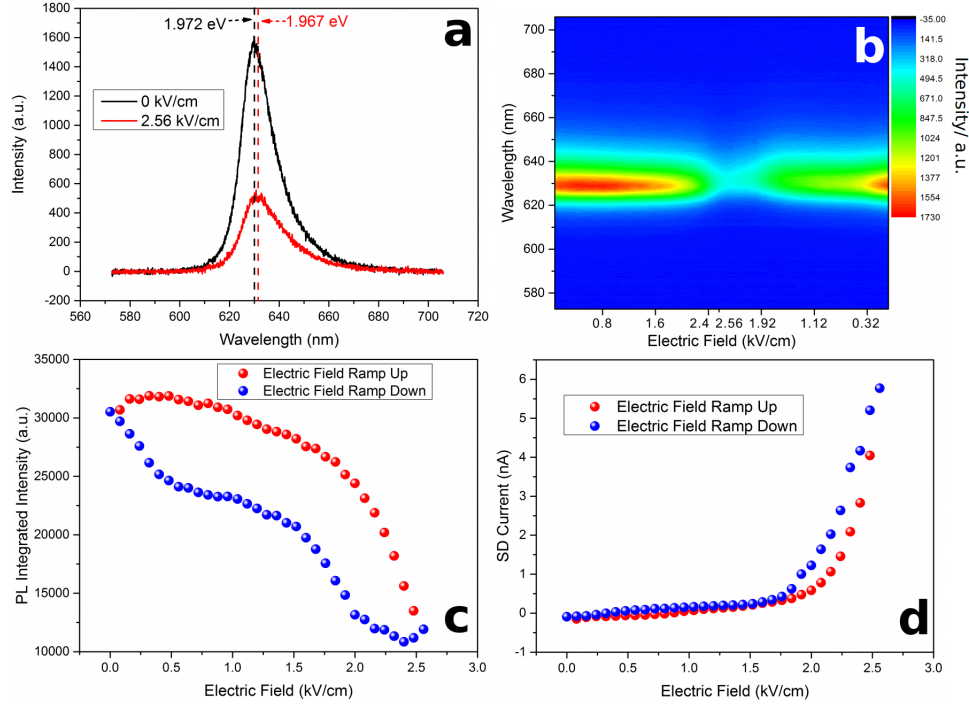


FIGURE 5.4: PL quenching with two different quenching rate. **a.** Typical PL spectra under two different electric field, 0 and 2.56 kV/cm. **b.** PL colour contour map of monolayer WS_2 under a lateral electric field. **c.** PL integrated intensity *versus* electric field. **d.** I - V trace with laser illumination. Red spheres: electric field ramps up. Blue spheres: electric field ramps down.

5.5c plots the integrated PL intensity as a function of electric field, which enables the exploration of the PL intensity change in details. A noteworthy phenomenon is that the PL intensity first undergoes quenching if the electric field reaches a lower threshold value (1.25 kV/cm in this case) prior to the enhancement. The coexistence of both quenching and enhancement indicates two competing mechanisms behind the PL change. The I - V relationship is plotted in figure 5.5d, where the nonlinearity is attributed to the Schottky barrier between the W electrode and the conduction band of bilayer WS_2 . Figure 5.5e shows the correlation between PL intensity and source-drain current. It starts with fluctuations within a limited range under a very small current flow. The increase in current first concurs with PL quenching, which is then followed by enhancement. The enhancement rate slows and stabilizes at a constant value with further increasing current. We have repeated these measurements on more than 10

different bilayer crystals to verify the consistency of the behaviour. Another example can be found in figure 5.6.

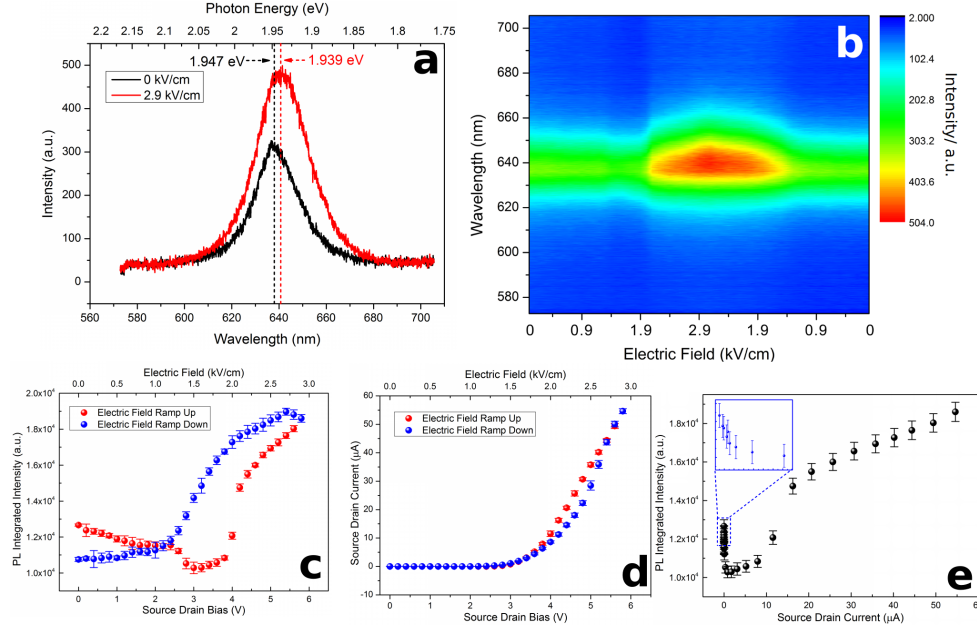


FIGURE 5.5: PL of bilayer WS_2 under lateral electric field. **a.** Typical PL spectra under two different electric field, 0 and 2.9 kV/cm. PL enhancement can be clearly observed. Small red shift of PL peak position from 1.947 eV to 1.939 eV is labelled. **b.** Colour contour map of bilayer PL spectra under different lateral electric fields. **c.** PL integrated intensity *versus* lateral electric field. **d.** I - V trace with laser illumination during PL measurement. Red spheres: source-drain bias ramps up. Blue spheres: source-drain bias ramps down. **e.** Correlation between the integrated PL intensity and the source-drain current. Inset: magnified image of the area highlighted by a blue dashed rectangle.

5.2.3 Possible mechanism

Tongay *et al.*[6] reported that elevated temperature can induce similar layer dependent PL variation in $MoSe_2$. In order to explore whether joule heating mainly contributes to the phenomenon observed, PL variations of both monolayer and bilayer WS_2 with lattice temperature are monitored. Figure 5.7a,b present the temperature dependence of PL intensity and the emitted photon energy of monolayer WS_2 . Figure 5.7a shows that rising temperature can lead to obvious PL quenching. In this case, PL intensity at

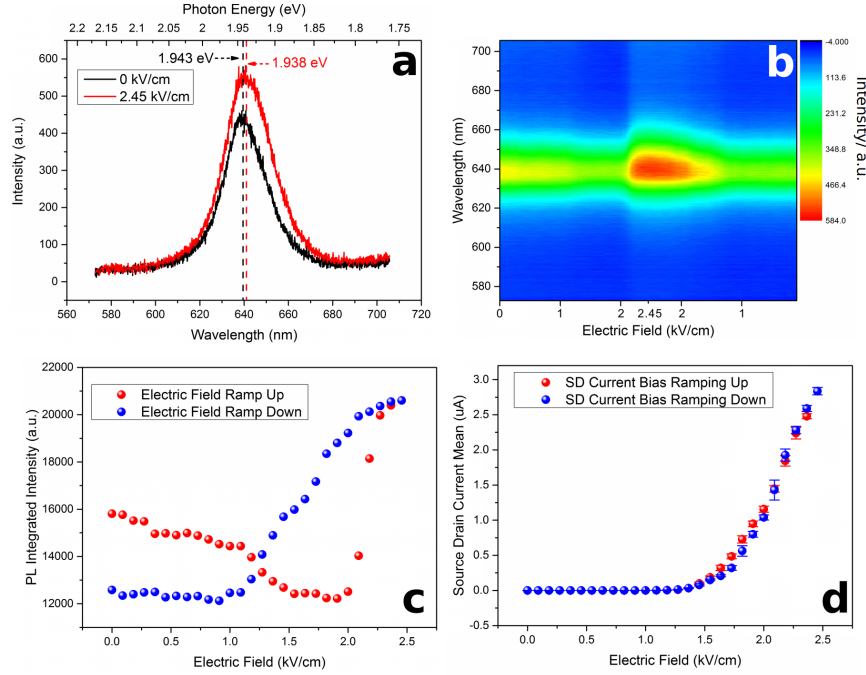


FIGURE 5.6: Another example of bilayer WS_2 PL behaviour under lateral electric field. **a**). Typical PL spectra under two different electric field, 0 and 2.9 kV/cm. Enhancement effect can be clearly observed. Small red shift from 1.947 eV to 1.939 eV is labelled. **b**). Colour contour map of bilayer PL spectra variation with different lateral electric fields. **c**. PL integrated intensity *versus* lateral electric field. **d**). I - V trace with laser illumination during PL measurement. Red spheres: electric field ramps up. Blue spheres: electric field ramps down.

415 K is reduced by up to 40 % of the room temperature intensity, which is the result of exponentially increasing non-radiative electron-hole recombination rate at higher lattice temperature.[33] In figure 5.7c,d, I present the temperature dependent PL of bilayer WS_2 . The increasing temperature results in the PL intensity decrease by about 48% of the original value at lattice temperature of 415 K, showing opposite behaviour induced by electric field in figure 5.5. Similar experiments were repeated on more than 10 samples to ensure the consistency. Therefore, joule heating cannot explain the PL enhancement induced by electric field in bilayer WS_2 . Apart from intensity change, large spectral red shifts are observed in both cases, as shown in figure 5.7b,d. Similar behaviour has also been observed in conventional semiconductors, as a result of the increased electron-phonon interaction and slight changes in bonding lengths. Such

temperature dependence of PL peak position offers a non-invasive way to evaluate the lattice temperature of a semiconductor.[34] By employing a standard expression to correlate the semiconductor band gap with the lattice temperature, it is possible to derive the expression for the temperature dependence of PL emission photons energy:[35]

$$E(T) = E_0 - S \langle \hbar\omega \rangle [\coth(\frac{\langle \hbar\omega \rangle}{2k_B T})] \quad (5.1)$$

where the E_0 is the emission energy at 0 K, S is a dimensionless coupling constant and $\langle \hbar\omega \rangle$ is the average phonon energy. For monolayer WS₂, the best fitting yields $E_0 = 2.08$ eV, $S = 2.47$, and $\langle \hbar\omega \rangle = 13$ meV while for bilayer, the parameters are $E_0 = 1.97$ eV, $S = 2.70$, and $\langle \hbar\omega \rangle = 10.8$ meV. The expressions derived here enable the determination of temperature changes of a semiconductor under biasing condition.[34] In figures 5.2a and 5.5a, the PL emission energy has a red shift of 4 meV for monolayer and 8 meV for bilayer, which correspond to temperature increases of about 15 K and 29 K for monolayer and bilayer WS₂, respectively. Such small temperature changes can only induce PL quenching by about 6.0 % for monolayer and 6.5 % for bilayer which are much smaller than the PL intensity changes observed in figure 5.3 and figure 5.5. Therefore, it is reasonable to rule out that temperature effect is the dominant factor to the field dependent PL changes.

Apart from joule heating, several physical processes have been advanced to explain the field induce PL quenching in semiconductors which include: a) Auger decay,[36] b) direct exciton ionization[27], c) impact ionization[24, 25] and d) field induced bandgap modification.[23] Because the electric field can lead to the brightening of bilayer WS₂ PL, the phenomena in both monolayer and bilayer WS₂ cannot be solely explained by mechanisms like Auger decay, direct exciton ionization and impact ionization. Iveland *et al.*[36] showed that Auger process can limit the electroluminescence of LED, but it became dominant only under very high carrier densities,[36, 37] especially for wide band gap semiconductors[38] while CVD grown monolayer and bilayer WS₂ are only slightly

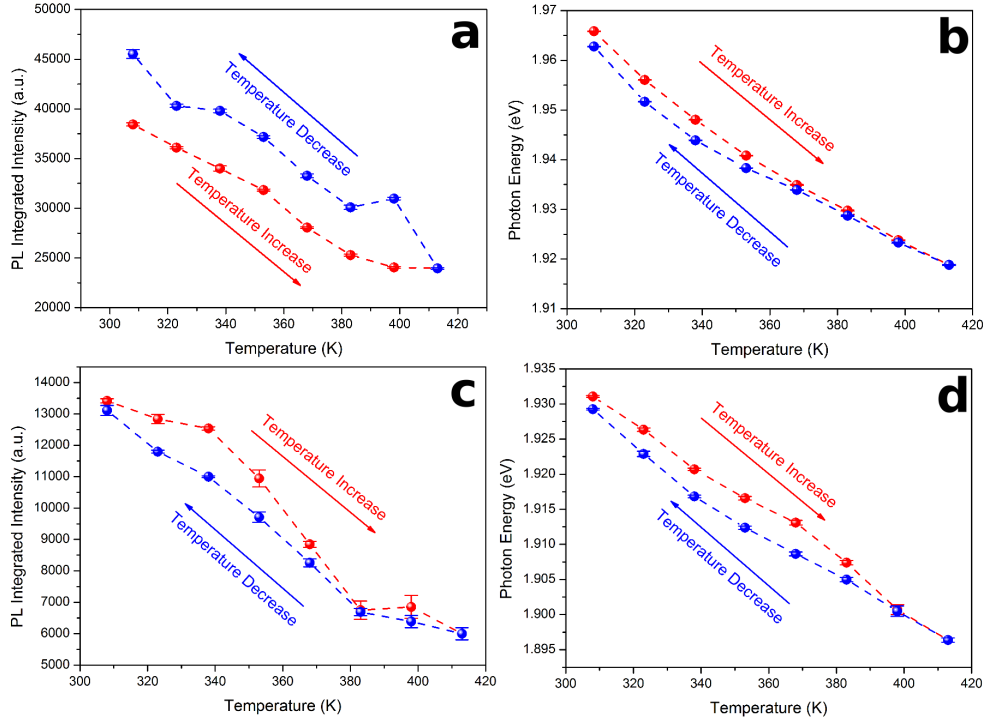


FIGURE 5.7: Temperature dependent PL measurement. **a,b.** Monolayer. **c,d.** Bilayer. **a,c.** Integrated PL intensity *versus* temperature. **b,d.** PL photons emission energy *versus* temperature. Red sphere: Temperature ramps up. Blue sphere: Temperature ramps down.

n-doped.[39] As for direct exciton ionization, The calculation of the threshold electric field strength of direct exciton ionization can determine its validity. The threshold value is approximately expressed by $E_{ex}/(e \times a_{ex})$, in which E_{ex} is the binding energy of excitons, e is the charge unit and $a_{ex} = (m/\mu_0)\epsilon_r a_B$ is the exciton radius where m_0 is the electron rest mass, μ is the reduced effective mass of exciton, ϵ_r is the relative dielectric constant, and a_B is the Bohr radius.[40] Since the electric field applied here is along the in-plane direction, I only consider the in-plane components of the dielectric constant. For monolayer WS₂, $E_{ex} = 0.28$ eV, $\mu = 0.16 m_0$ and $\epsilon_{r,xy} = 13$. [41] The corresponding threshold electric field is about 6×10^5 V/cm, 2 orders of magnitude higher than the field applied in the experiment (about 10^3 V/cm, shown in figure 5.2b,c). The binding energy of direct band gap excitons of bilayer WS₂ is about one-half of that of monolayer counterpart while the reduced mass and dielectric constants are very

close to those of monolayer.[3, 16] Hence the threshold value of direct exciton ionization in bilayer is about 10^5 V/cm, which is still too high compared with the experimental value (1.25×10^3 V/cm, figure 5.5b,c). Therefore, direct exciton ionization cannot mainly account for the field induced quenching observed in monolayer and bilayer WS₂.

The conduction charge carriers in WS₂ can be accelerated by the applied electric field. If the kinetic energy reaches certain value, these conduction carriers can ionize the excitons through collision. However, the exceptionally large exciton binding energies of both monolayer and bilayer WS₂ indicate that such impact ionization is also unlikely to be the dominant contributor in field induced PL quenching within the experimental parameters since the maximum kinetic energy of photo-excited electrons can reach 44 meV (71 meV) in monolayer (bilayer) under the maximum electric field employed here. (Detailed calculations can be found in Appendix C) Although chances are that the energy of very small amount of carriers may exceed the binding energy due to the energy distribution, it cannot be the dominant factor to PL quenching in monolayer WS₂.

Electric field induced modification to the band structure of atomically thin WS₂ requires much higher electric field[23] than those we applied in our measurement. Typically fields are perpendicular to the plane of WS₂ and large electric field can be therefore generated owing to the ultra-thin nature of the WS₂ and hence the tiny separation between electrodes. In the experimental configuration I used (figure 5.1f), electrodes were separated by about 20 μ m, a limiting factor to reaching the expected electric field.

Apart from the mechanisms discussed above, modification to the excitons recombination pathways associated with photo-excited carriers population changes in the conduction band minima can also result in the change of PL of monolayer WS₂. A change in the level occupancy factors of the K-K direct recombination pathway are likely to be the main contributor to the PL quenching in monolayer WS₂. Electrons in an n-type semiconductor with multiple conduction band extrema can transfer from conduction band

minimum to a secondary band extremum under an electric field.[42, 43] Here I propose that quenching in figure 5.2 can possibly be attributed to the transfer of photo-excited electrons from conduction band minima at the K point to the secondary conduction band extremum at T point which is the middle point between K and Γ (step II in figure 5.8) after the electrons are excited by the incident photon to the first conduction band valley (step I in figure 5.8), considering that the energy difference between the first and second CB extrema is about 70 meV, as derived by DFT calculations.[44] As a result, the level occupancy factors of K-K direct recombination is decreased. An accompanied phenomenon when the inter-valley electron transfer occurs is negative differential resistance in I - V traces, which is not observed here. This could possibly due to the very close electron effective mass between two conduction band extrema.[42] The inter-valley photo-excited electrons transfer can also help to explain the PL enhancement in bilayer WS₂ with the energy difference between the first and second CB extrema about 85 meV,[45] where some of the photo-excited electrons from the conduction band minimum at T point can be transferred to the secondary conduction band extremum at K point and therefore increase the level of occupancy factors of the K-K direct recombination pathway. A schematic diagram of inter-valley electron transfer process is shown in figure 5.8.

The transfer of photo-excited electrons between two conduction band extrema requires both energy and momentum changes. Two physical processes could cause the acceleration of electrons includes 1) drifting in electric field and 2) scattering by another energetic conduction charge carriers which gain kinetic energy from electric field. Considering that the change of PL quenching rate coincides with the onset of source-drain current observed in monolayer WS₂ (figure 5.4), I believe that physical process 2) is the dominant contributor to the inter-valley electron transfer.

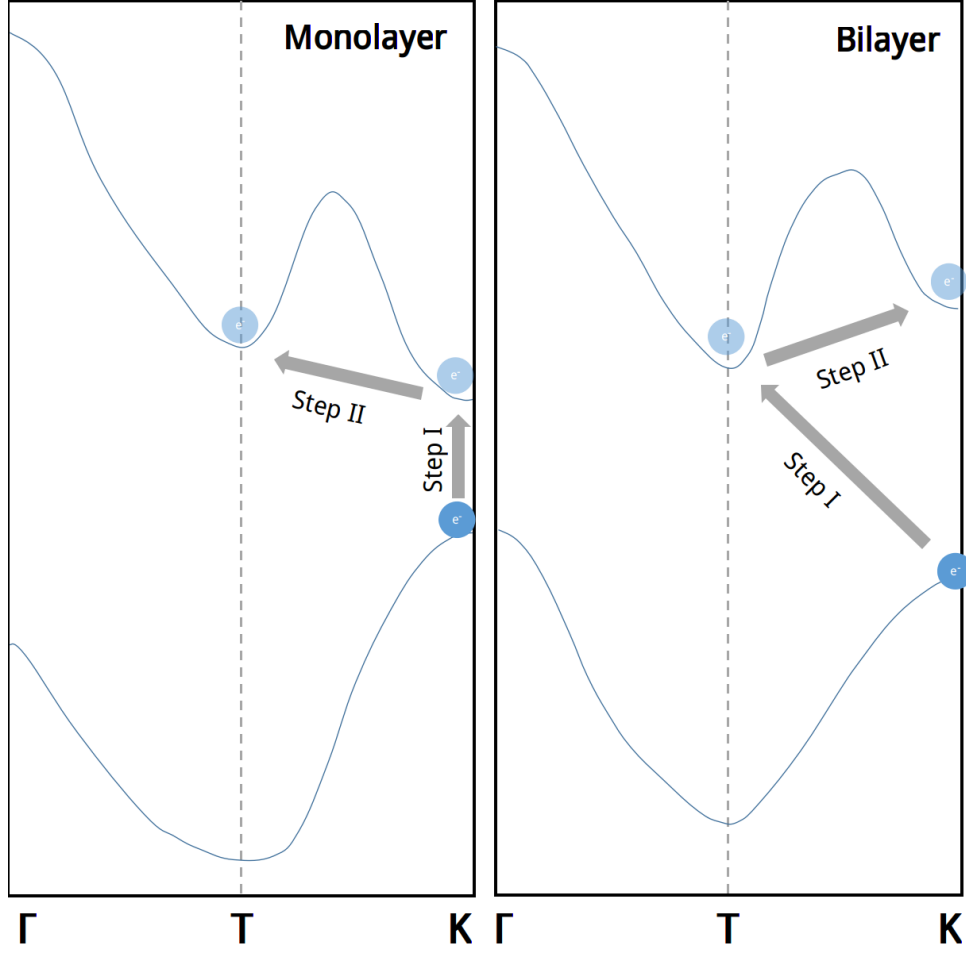


FIGURE 5.8: Schematic diagram for the transfer of photo-excited electrons under lateral electric field in both mono- and bi- layer WS_2 .

5.3 Conclusion

In conclusion, applying a lateral electric field to atomically thin WS_2 crystals leads to the modulation of their PL. PL of monolayer WS_2 can be suppressed while the emission intensity of bilayer WS_2 can be enhanced. Temperature dependent PL was performed, based on which the joule heating effect was ruled out. I propose that intervalley electrons transfer between the first and the second CB extrema be the possible mechanism to the field dependent PL changes. This is due to the very unique band structure (small energy difference between conduction band extrema) and exceptionally

large exciton binding energy in atomically thin WS₂. On the contrary, it is very hard to observe the effect of this physical process on the PL of bulk semiconductor because the energy difference between the first two conduction band extrema is much greater than exciton binding energy.^[46] This work can not only shed light on better understanding of the fundamental optoelectronic properties in 2D WS₂, but also may provide insights into the fabrication of high performance optoelectronic devices based on 2D TMDCs.

Chapter 5 References

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Chapter 6

Observation of High-Order Excitonic Species in WS₂

6.1 Introduction

The previous chapter focuses on the investigation of the response of ground state excitons within WS₂ towards external electrical modulation. Apart from excitonic ground state, the emergence of atomically thin TMDCs offers an ideal platform to investigate the higher-order excitonic species,[1] such as biexcitons which are very hard to probe in bulk materials due to the low excitons and biexciton binding energies. For instance, Sie *et al.*[2] reported that they have probed both homo- and hetero-biexcitons states by using the transient absorption spectroscopy technique in monolayer MoS₂. Bright biexciton states have been observed in both monolayer WS₂ and WSe₂ by creating dense excitons gas.[3, 4] The ability to probe a biexciton or even higher-order excitonic molecules can help to understand the exceptional many-body effect within TMDCs. Apart from fundamental physics interests, the understanding of high-order excitonic

behaviour can facilitate the development of practical applications such as single photon sources[5, 6] and lasers.[7, 8]

The up-to-date researches of biexcitons within TMDCs limited their focus on monolayer crystals.[2, 3, 4] Combining two monolayers through van der Waals forces into bilayer TMDCs leads to properties with stark contrast compared to its monolayer counterpart, including the opposite PL responses towards lateral electric field,[9] electrically controllable inversion symmetry[10] and even more pronounced valley polarization and coherence[11]. Additionally, the crossover of direct-to-indirect gap induced by inter-layer coupling resulted in great reduction to the quantum yield of direct gap excitons. As a result, the luminescence of biexciton comprised of two direct excitons is expected to fade away.

In this chapter, I will mainly emphasize on probing the bright biexciton states within WS₂, especially in bilayer WS₂. Section 6.1 introduces recent progress on the investigation of high-order excitonic molecules within TMDCs as well as the motivation of exploring the biexcitons in bilayer WS₂. Section 6.2 presents the observation of bright biexciton states in as-grown bilayer sample which is absent after transfer process, followed by the discussion of possible mechanism. Biexcitons formation in transferred monolayer WS₂ is also investigated. Section 6.3 gives a brief summary to this chapter.

6.2 Results and discussion

6.2.1 Bilayer

Figure 6.1a presents an optical image of a typical WS₂ domain with both monolayer and bilayer coexisting grown by CVD method with carefully selected parameters.[12] Difference in optical contrast can help to distinguish monolayer and multilayer.[13] PL spectra in figure 6.1b provides further proof where region with darker optical contrast

(marked by red cross in the inset of figure 6.1b) is much less luminescent than region with lighter optical contrast (marked by black cross in the inset of figure 6.1b).[14, 15] In order to obtain the exact number of layers of areas with darker optical contrast in the inset of figure 6.1b, atomic force microscopy (AFM) was performed in the region highlighted by red dotted box in the inset of figure 6.1b, the result of which is presented in figure 6.1c. Clearly, it shows a step at the boundary of regions with different optical contrast in the inset of figure 6.1b. The height difference across the boundary is about 0.7 nm, presented in the inset of figure 6.1c, which indicates that the darker region is comprised of two WS₂ layers. The increasing in layer number also lead to the characteristic Raman vibration modes, $E'/E_g^1/E_{2g}^1$ and A'_1/A_{1g} going through softening and stiffening, respectively,[16, 17] shown in figure 6.1d,e. Atomic resolution aberration-corrected transmission electron microscopy (AC-TEM) can also provide evidence of bilayer WS₂. Step edges at the boundary of monolayer and bilayer can be found in figure 6.1f, where the bilayer region (left) shows darker contrast compared with monolayer region (right). The inset in figure 6.1f presents the FFT and the corresponding zig-zag direction is indicated by the yellow arrow. The magnified image of step edge highlighted by red dotted rectangle is shown in figure 6.1g. An TEM image of monolayer WS₂ with atomic resolution as well as its FFT are presented in figure 6.1h,i, respectively.

Excitation power dependent PL spectroscopy can provide insights into the physical origins of each PL components.[18] Under high power excitation, high-order excitonic states can be probed, which can provide insights into the many-body effect within the materials.[3, 4] In figure 6.2a-c, I present PL spectra of bilayer WS₂ taken at liquid nitrogen (LN) temperature under three different excitation power. The PL spectrum under low excitation power ($\sim 10^2 \text{ W/cm}^2$) in figure 6.2a is mainly contributed by three components: excitons (X, red curve), trions (X^- , green curve), localized states (LS, blue curve) and indirect transition (I, light blue curve). LS related emission is likely to originate from adsorbents.[3, 19, 20] Increasing excitation power leads to new luminescent feature emerging (figure 6.2b,c, dark yellow curves). Laser power dependences of

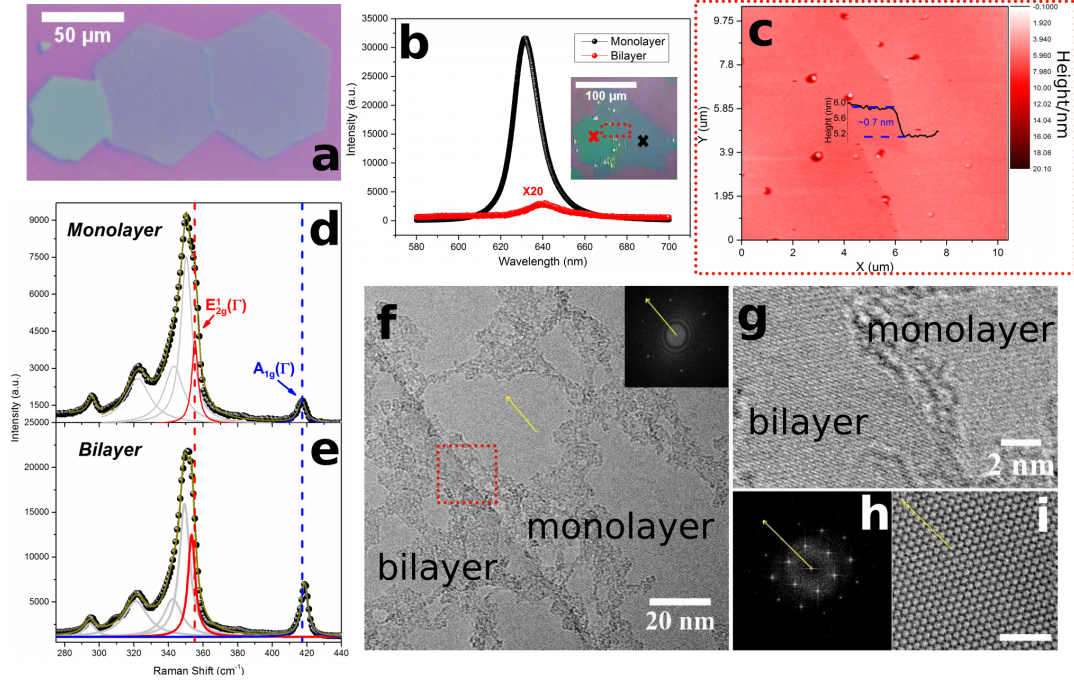


FIGURE 6.1: **a.** Optical images of monolayer and bilayer WS_2 coexisting on one domain. **b.** Photoluminescence spectra of monolayer (black curve) and bilayer (red curve) from region marked by black cross and red cross in the inset. **c.** AFM image of WS_2 highlighted by red rectangle in the inset of **b.** **d,e.** Raman spectra of **d)** monolayer and **e)** bilayer. Red curves: Lorentzian fitting results of E'_g/E_{2g}^1 . Blue curves: Lorentzian fitting results of A'_1/A_{1g} . Light grey curves: Lorentzian fitting results of other Raman vibration modes. **f.** TEM image of a monolayer-bilayer step edge. Inset: FFT of the image with the zig-zag lattice direction highlighted by yellow arrow. **g.** Higher magnification of TEM image from monolayer-bilayer step edge region highlighted by red dotted rectangle in panel **f.** **h.** FFT of AC-TEM image of **i).** AC-TEM image of the monolayer WS_2 showing lattice structure. Yellow arrow indicates zig-zag lattice direction.

PL integrated intensity of X , X^- and the new emission peak are extracted and plotted in figure 6.2d. The power dependence of X emission presents near-linearity while the PL integrated intensity of X^- increases in slightly super-linear trend which has been previously observed on monolayer WSe_2 and was believed to be related to the loss of trions population to LS at low excitation density.[4] The high excitation power related new PL feature exhibits super-linearity with a power law exponent of about 1.6. Figure 6.2e presents that the emission intensity of the new luminescent peak grows nearly

quadratic with that of X emission with a power law exponent of 1.9, which provides strong evidence that the new luminescent feature originates from emission from bright biexciton states. Another example of biexciton formation in the bilayer system is shown in figure 6.3. One point needs to be clarified is that the quadratic power dependence of biexciton is not always satisfied. More general criteria is the quadratic relationship between biexcitons and excitons emission intensity.[4, 21] Simple derivation is given as follows. The excitons and biexcitons densities should follow the coupled rate equations:

$$\frac{dn_X}{dt} = G - \frac{n_X}{\tau_X} + \frac{n_{XX}}{\tau_{XX}} - \alpha n_X^2 \quad (6.1)$$

$$\frac{dn_{XX}}{dt} = \frac{1}{2}\alpha n_X^2 - \frac{n_{XX}}{\tau_{XX}}$$

in which n_X is the excitons density, n_{XX} is the biexcitons density, G is the laser pumping rate, τ_X is the lifetime of excitons, τ_{XX} is the lifetime of biexcitons and α is the formation rate of biexcitons from excitons. Under steady state conditions where $\frac{dn_X}{dt} = \frac{dn_{XX}}{dt} = 0$, the solutions to the coupled equations are,

$$n_X \propto \left(1 + \frac{G}{G_0}\right)^{0.5} - 1 \quad (6.2)$$

$$n_{XX} \propto \left[\left(1 + \frac{G}{G_0}\right)^{0.5} - 1\right]^2$$

where $G_0 = 1/2\alpha\tau_X^2$. Under low excitation power where $G \ll G_0$, excitons density grows linearly with laser power while biexcitons populate quadratically. Under high excitation power ($G \gg G_0$), n_X grows as a square root function of the excitation power while n_{XX} possesses linear power dependence. Yet the relationship $n_{XX} \propto n_X^2$ should always be followed.[21] In figure 6.2f, the peak positions of X, X⁻ and XX are provided from which the binding energy of X⁻ and XX can be extracted. The binding energy of X⁻ is about 20 meV, smaller than what has been reported[11]. Discrepancy between

the binding energy differences of trions of CVD as-grown and mechanically exfoliated monolayer TMDCs have been reported, which is believed to originate from the different doping level as well as strain.[3] The measured binding energy of biexcitons is 36 ± 4 meV. This value is smaller than what has been measured from monolayer TMDCs due to the reduced X binding energy in bilayer WS₂. X binding energy in monolayer WS₂ is reported to be in the range of 0.36 eV - 0.7 eV.[22, 23, 24] Meanwhile, the binding energy of excitons in the bilayer materials is one-half of that in monolayer.[25] The ratio of binding energies of biexcitons over those of excitons is called the Haynes factor[26], within the range of 0.09 - 0.2, similar to the ratio extracted in monolayer TMDCs.[3, 4]

In many applications, transferring CVD as-grown WS₂ to target substrate is inevitable. Therefore, examining the properties of transferred sample is beneficial to practical applications. In figure 6.4a-c, I present the power dependent PL measurement on as-transferred bilayer WS₂ sample. Unlike in the case of as-grown sample, only three luminescent features are observed in the spectra taken under both low ($\sim 10^2$ W/cm²) and high excitation power ($\sim 10^2$ kW/cm²) which are excitons, trions and LS. Figure 6.4d,e show the Raman spectra of both as-grown and as-transferred bilayer WS₂, which are deconvoluted into different vibration modes including two characteristic features, A'_1/A_{1g} and $E'/E_g^1/E_{2g}^1$ highlighted in coloured curves in figure 6.4d,e. A'_1/A_{1g} is associated with the out-of-plane vibration of sulphur atoms, which can be affected by doping level.[27] Here the peak positions of A'_1/A_{1g} mode before and after transferring process changed little, indicating that the doping level remained almost unchanged. $E'/E_g^1/E_{2g}^1$ mode is related to the in-plane vibration of tungsten and sulphur atoms and therefore is sensitive to the change of lattice strain.[28] The transferring process led to a red shift of ~ 1.3 cm⁻¹ to $E'/E_g^1/E_{2g}^1$ vibration mode, indicating a change in the lattice strain. The $E'/E_g^1/E_{2g}^1$ mode and lattice strain can be linked quantitatively through Gruneisen parameter and the relation is given as $\gamma_G = -\Delta\omega_G/2\omega_G^0$, [29] where γ_G is the Gruneisen parameter for vibration mode G, $\Delta\omega_G$ is the peak shift after strain is applied, ω_G^0 is the

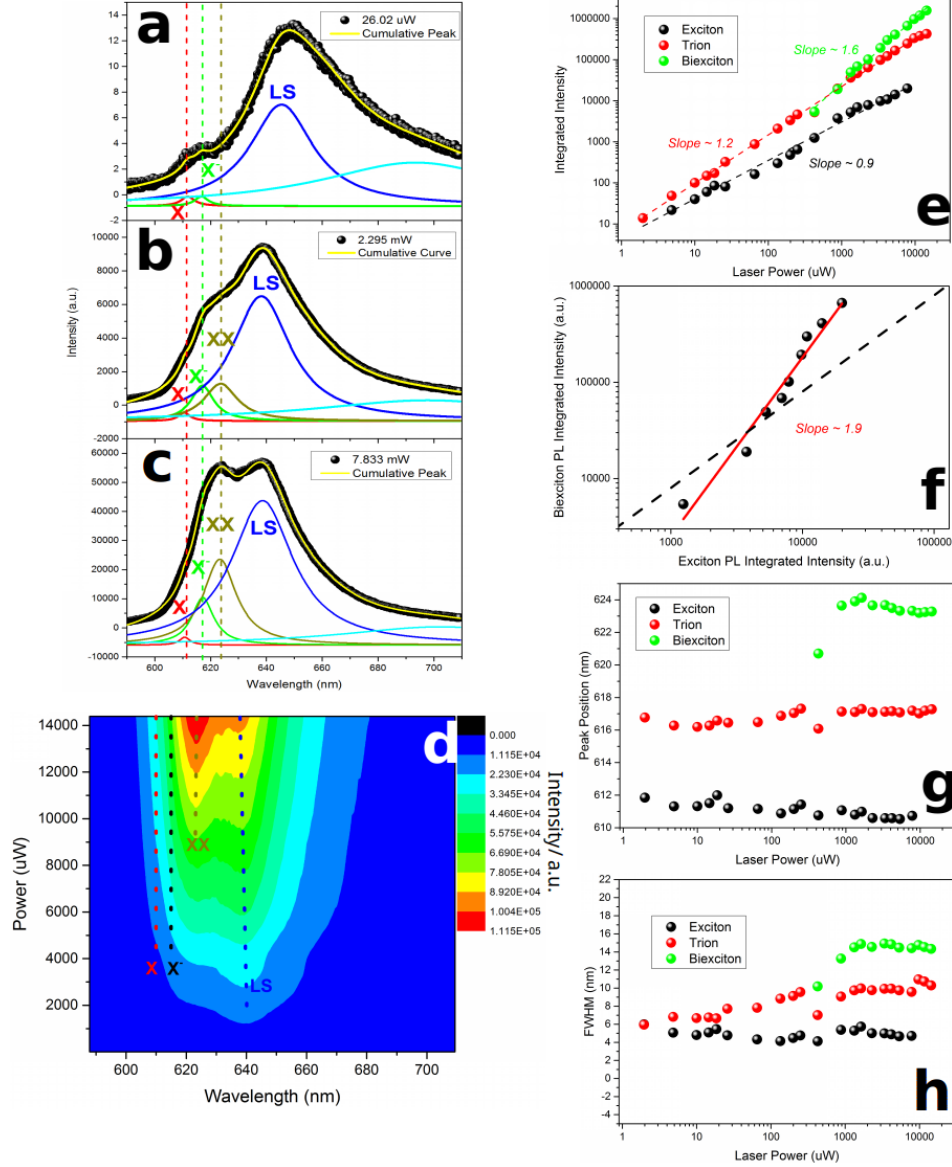


FIGURE 6.2: Power dependent PL of CVD as-grown bilayer WS_2 at 77 K. **a-c.** PL spectra of bilayer WS_2 under three different excitation power. Dashed curves in **a)-c)** are guide lines to show peak positions of excitons, trions, biexcitons. **d).** Power dependent PL colour contour of as-grown bilayer WS_2 . **e.** PL integrated intensity of the excitons, trions and biexcitons emission spectra *versus* laser power in double logarithmic scale. **f.** Logarithmic plot of the integrated intensity of PL spectra of biexcitons *versus* that of excitons. **g.** Semilogarithmic plot of PL peak positions of excitons, trions and biexcitons peaks *versus* input laser power. **h.** Semilogarithmic plot of FWHM of excitons, trions and biexcitons *versus* excitation power.

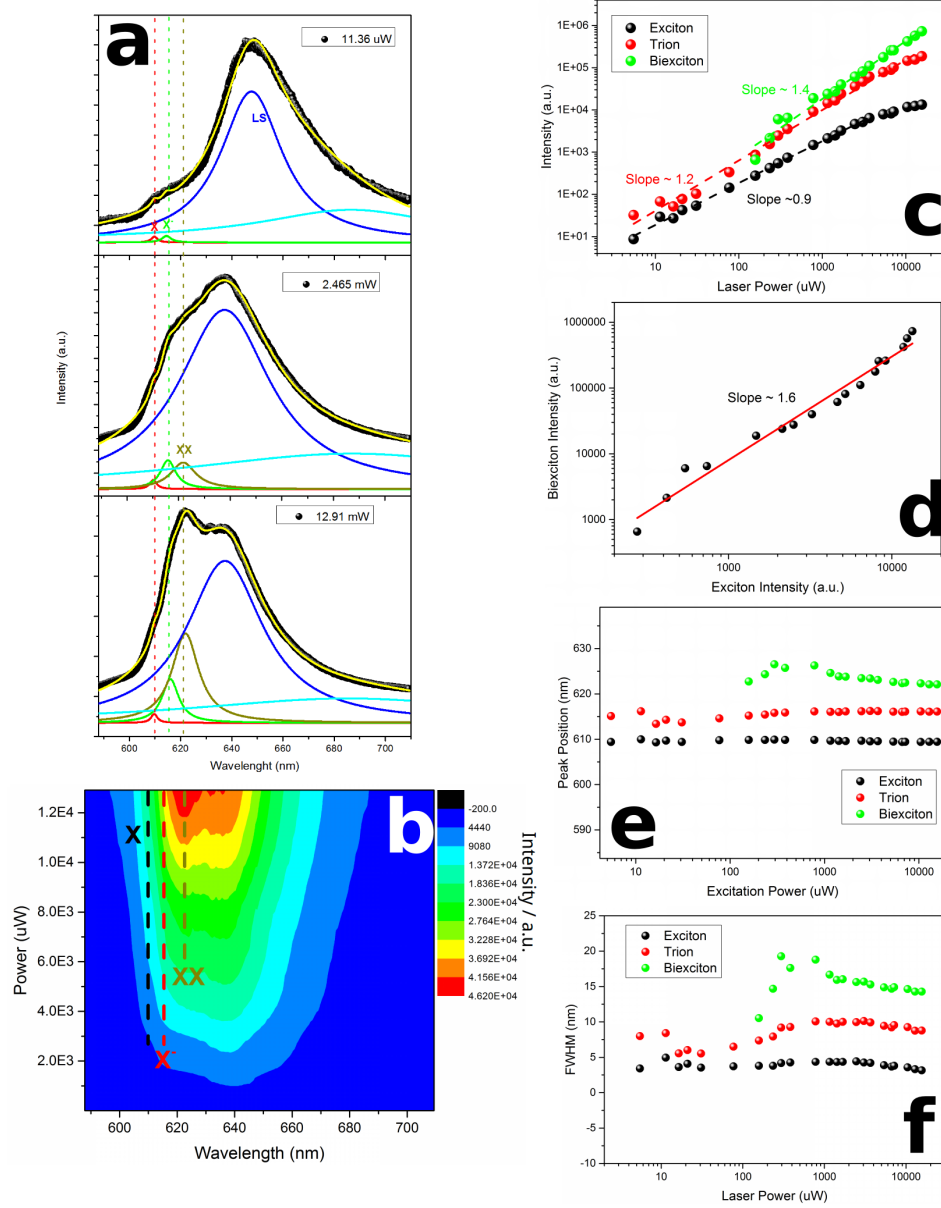


FIGURE 6.3: Another example of biexcitons formation in CVD as-grown bilayer WS_2 at 77 K. **a.** PL spectra of bilayer WS_2 under three different excitation power. Dashed curves are guidelines to show peak positions of excitons, trions, biexcitons. **b.** Power dependent PL colour contour. **c.** PL integrated intensity of the excitons, trions and biexcitons emission spectra versus laser power in logarithmic scale. **d.** Logarithmic plot of the integrated intensity of PL spectra of biexcitons versus that of excitons. **e.** Semilogarithmic plot of PL peak positions of excitons, trions and biexcitons peaks versus input laser power. **f.** Semilogarithmic plot of FWHM of excitons, trions and biexcitons versus excitation power.

peak position of vibration mode G with no strain and ϵ is the strain applied. In monolayer WS₂, the Gruneisen parameter is 0.54[29] while this value changes little within bilayer crystals.[30] Combining the Raman peak position extracted from 6.4d,e with Gruneisen parameter yields that the as-grown bilayer possessing a biaxial tensile strain of $\sim 0.4\%$ which is likely to come from the difference in thermal expansion coefficient between WS₂ and growth substrate (SiO₂ in this case). This value is very close to that in CVD as-grown monolayer MoS₂. [31] Given that strain has been reported to induce the indirect-to-direct gap crossover in multilayer WSe₂, [32] one possible explanation to the absence of biexcitons after transferring process is that the release of strain can result in the decrease of the quantum yield of direct gap excitons in bilayer WS₂. To prove this argument, DFT calculated band structures of both 0.4% biaxially strained (red curve) and strain-free (black curve) bilayer WS₂ are presented in figure 6.4g. It clearly shows that 0.4% biaxial strain could induce an observable downshift of the conduction band valley at the K point (highlighted by blue dotted circle in figure 6.4f) while other parts of the band structure change little. In figure 6.4g, I extract both the direct (K-K) and indirect (T- Γ) gap values with (red circles) and without (black squares) strain, showing that the direct band gap is reduced by 55 meV whereas the indirect band gap changes little. The strain induced reduction in the energy difference between direct and indirect bandgap can result in an increase of QY of direct band gap excitons in as grown bilayer WS₂, [32] therefore the probability to observe bright biexciton states.

It is highly desired that materials have the ability to remain functional under room temperature. In figure 6.5a, I present the power dependence of PL of as-grown bilayer WS₂ at room temperature. There are two main features in the spectra, which are attributed to direct gap excitons (X) and indirect gap excitons (I). No obvious peak shape change was observed with increasing excitation, which indicates that no new excitonic states were created. Figure 6.5b depicts the integrated intensity of X as a function of excitation power showing linear power dependence, which is typical for luminescent emission from excitonic ground state. Although the peak shape remains unchanged, the

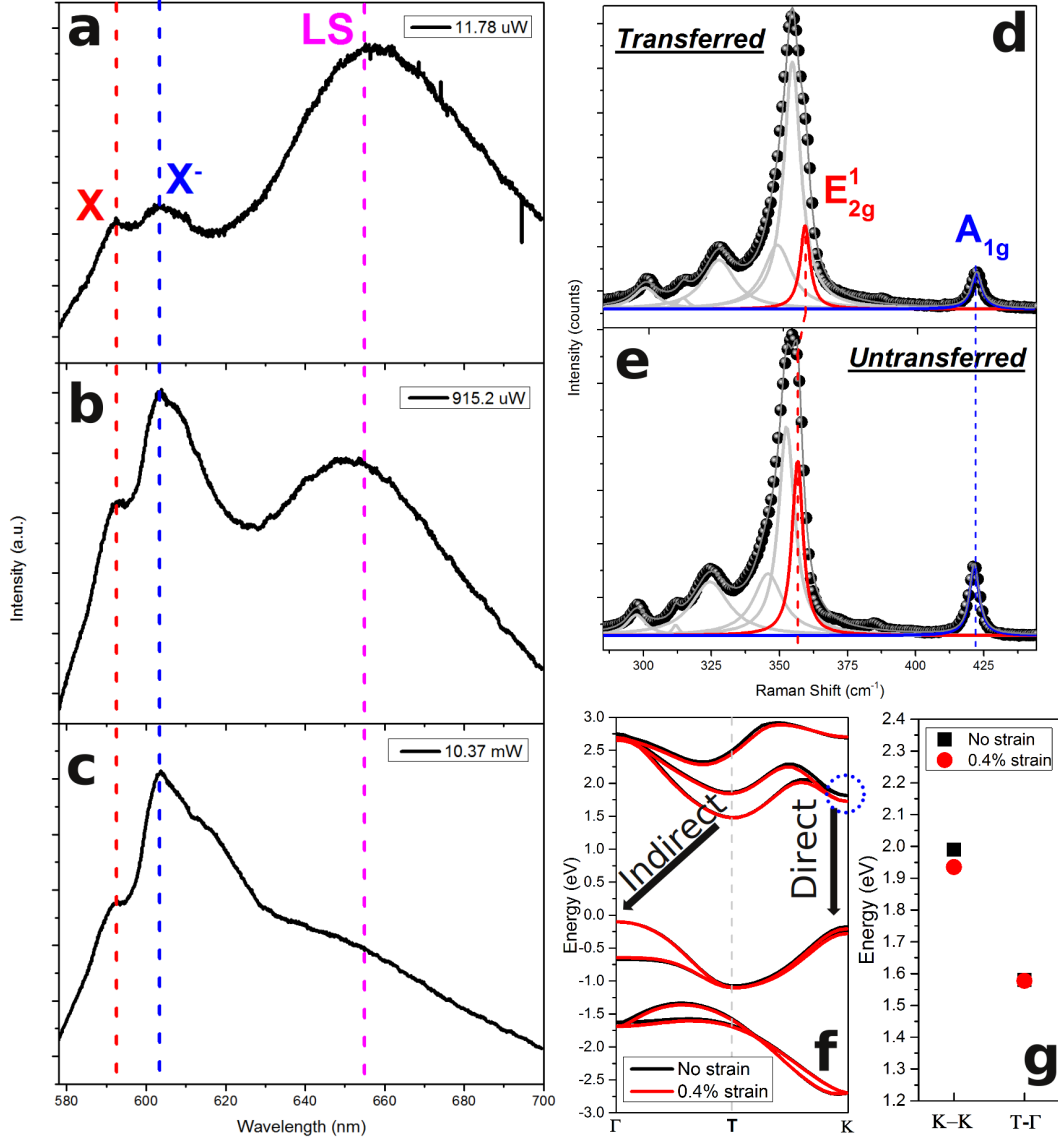


FIGURE 6.4: Power dependent PL of as-transferred bilayer WS_2 at 77 K. **a-c.** PL spectra of as-transferred bilayer WS_2 under three different excitation power. Dashed curves in **a)-c)** are guide lines to show peak positions of excitons, trions and LS. **d,e.** Raman spectra of **d)** as-transferred and **e)** as-grown bilayer WS_2 . **f.** DFT calculated band structures of strain-free (black curve) and 0.4 % biaxially strained (red curve) bilayer WS_2 . **g.** Band gap of direct K-K transition and T- Γ indirect transition of bilayer WS_2 with (red circles) and without (black squares) strain.

direct excitons related PL peak experiences both spectral red shift as well as broadening with increasing excitation power, presented in figure 6.5c, which is probably the result of laser induced heating.[17] The absence of biexcitons at room temperature indicates that the population of biexcitons decays with temperature. In figure 6.5d, I depict the biexcitons emission integrated intensity as a function of temperature under fixed excitation power in order to investigate the thermal stability of biexcitons. The increasing temperature leads to the decrease in the emission intensity of biexcitons and becomes hardly resolved if the temperature exceeds 150 K. Such temperature dependence can be described by a thermal dissociation model where the formation rate of biexciton remains unchanged whereas the dissociation rate is thermally activated.[4] The population decay rate as a function of temperature is given as $\gamma(T) = \tau_{XX}^{-1} + k_0 \exp(E_a/k_B T)$, in which τ_{XX} is the life time of the biexcitons, k_0 is a prefactor and E_a is the thermal dissociation energy.[4] The biexciton emission intensity is proportional to the inverse of decay rate, $\gamma^{-1}(T)$. The best fitting result according to this model is shown in figure 6.5d as red curve which yield a dissociation energy of about 26 ± 5 meV. The dissociation energy is smaller than the binding energy of biexcitons, indicating that the biexcitons should be thermally dissociated into excitonic species other than two bright excitons.

6.2.2 Monolayer

Differently, bright biexcitons can still be observed in transferred monolayer WS₂, as shown in figure 6.6. Figure 6.6a presents the PL spectra under 3 excitation powers with light grey curves representing the contributions of excitons and trions and blue curves standing for biexcitons. Figure 6.6b shows the power dependent PL colour contour. Power dependences are shown in figure 6.6c,d. The quadratic relationship in figure 6.6d between the emerging peaks and excitons peak confirms that the emerging peak is originated from biexcitons radiative decay. In figure 6.6e, I present the peak positions of excitons (~ 590 nm), trions (~ 602 nm) and biexcitons (~ 607 nm) *versus*

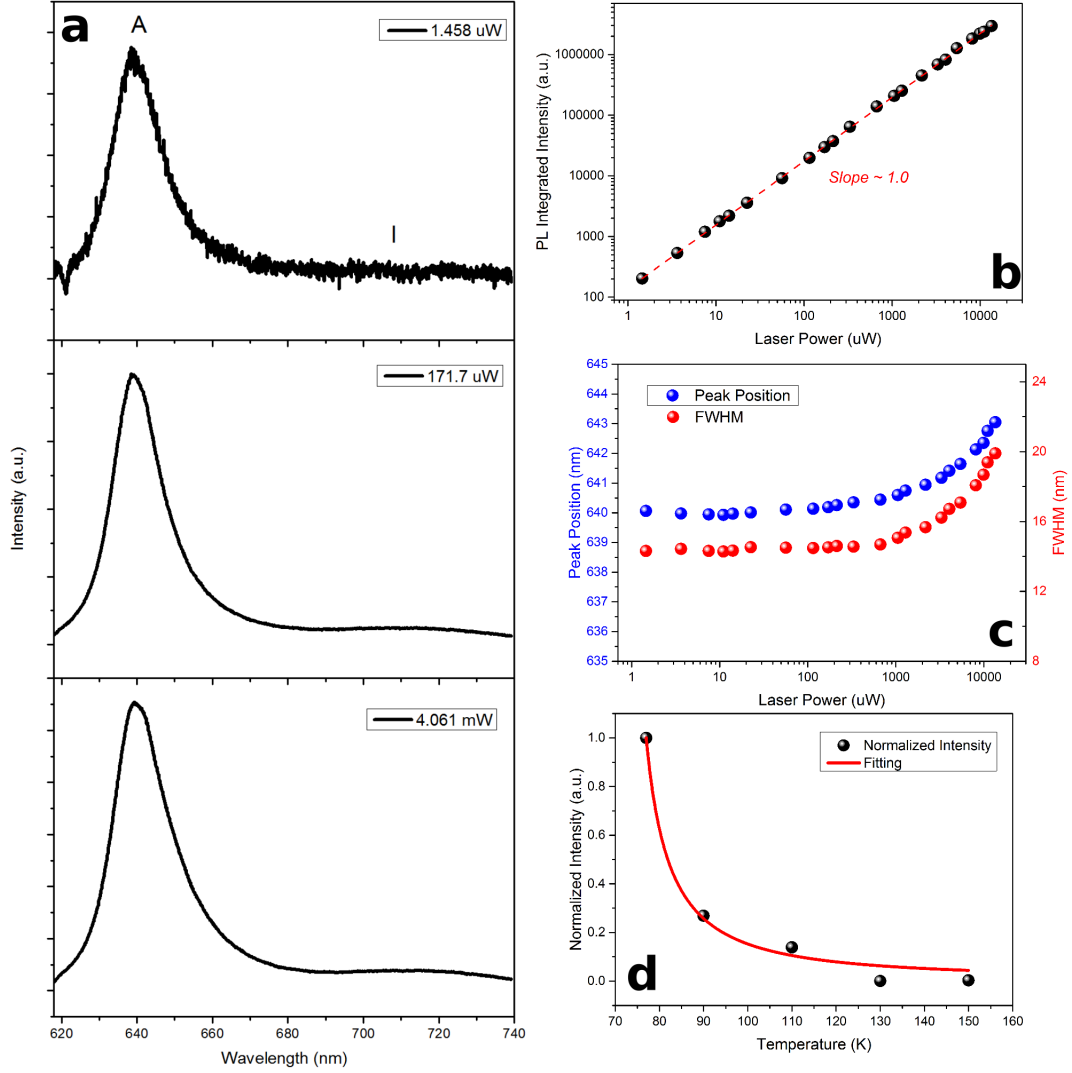


FIGURE 6.5: **a.** PL spectra of as-grown bilayer WS_2 under three different excitation powers. **b.** PL integrated intensity of direct gap excitons *versus* laser excitation power in logarithmic scale. Red dashed line: linear fitting result, with slope of about 1.0. **c.** Semi-logarithmic plot of peak position and FWHM of direct exciton PL peak *versus* excitation power. **d.** Temperature dependent integrated intensity of biexciton emission. Red curve: fitting result according to the temperature dependent biexcitons population formula described in the main text.

excitation power, from which the binding energy of trions and biexcitons can be derived with $E_{b,trion} = 42 \text{ meV}$ and $E_{b,biexcitons} = 60 \text{ meV}$, with corresponding Haynes of 0.08 $\sim$ 0.16. These values are consistent with what have been reported in the previous reports.[4, 3]

6.3 Conclusion

In this chapter, I mainly focus on characterizing biexcitons luminescence in both as-grown and transferred CVD bilayer WS₂ by using excitation power dependent cryogenic PL technique. Biexcitons luminescence can be detected in as-grown bilayer system with a binding energy of 36 meV, corresponding to a Haynes factor within the range of 0.09 - 0.20. However, such high-order excitonic molecules related emission cannot be observed in transferred bilayer WS₂ crystals. Raman spectra reveal that a biaxial tensile strain of about 0.4 % in as-grown samples is released during transfer process. DFT calculations are then performed, which shows that a 0.4 % biaxial tensile strain can decrease the energy difference between direct and indirect band gap. As a result, the quantum yield of direct excitons in strained samples should be higher than that in zero-strain bilayer WS₂, which facilitates the formation of biexcitons. The biexcitons emission is greatly suppressed under higher temperature owing to the increasing thermal dissociation with a dissociation energy of 26 meV. I have also investigated the biexcitons formation in transferred monolayer WS₂, which shows a binding energy of $\sim$ 60 meV, almost twice as large as that in bilayer WS₂.

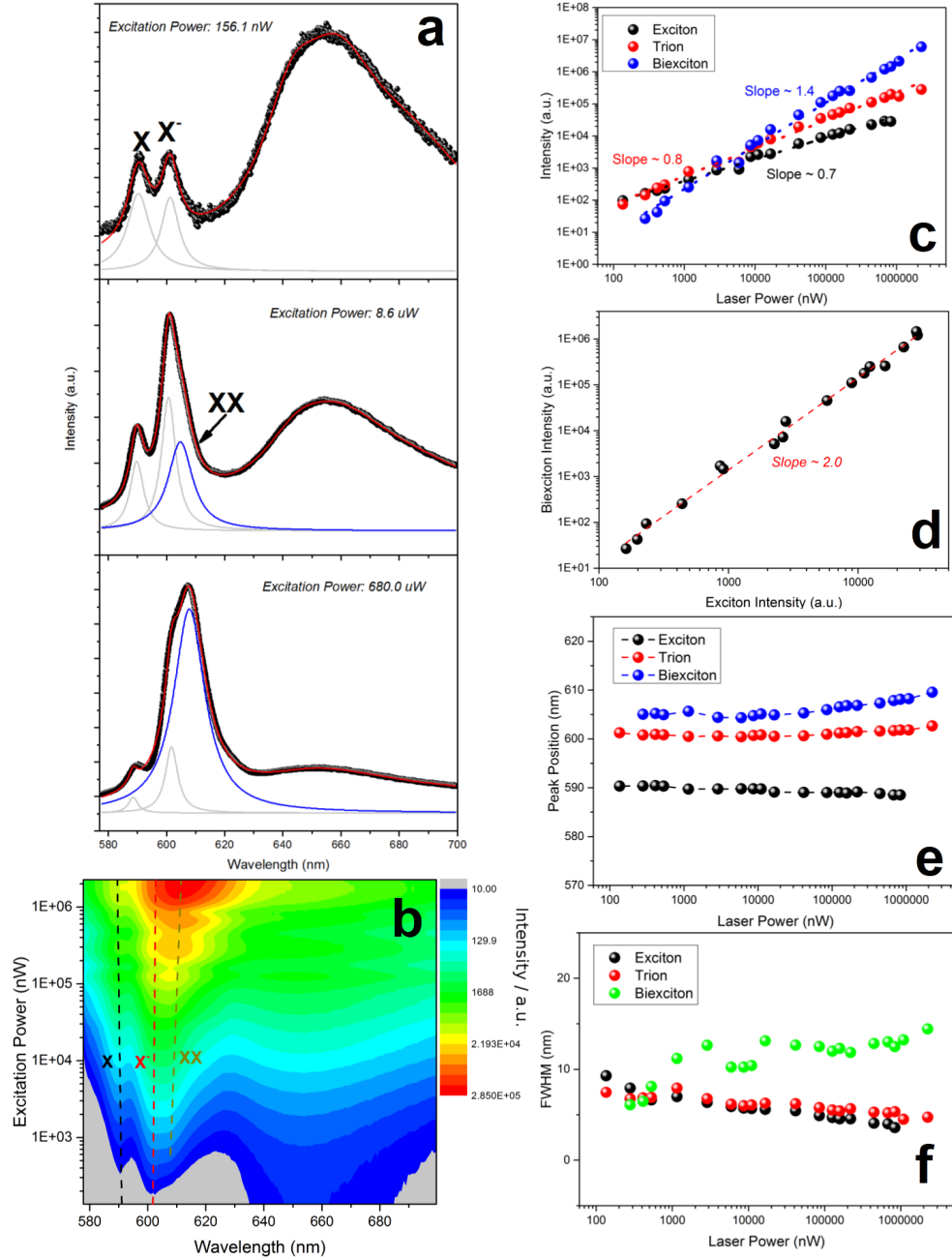


FIGURE 6.6: Example of biexcitons formation in CVD transferred monolayer WS_2 at 77 K. **a.** PL spectra of monolayer WS_2 under three different excitation power. **b.** Power dependent PL colour contour. Dashed curves are guide lines for peak positions of different components. **c.** The PL integrated intensity of the excitons, trions and biexcitons emission spectra *versus* laser power in logarithmic scale. **d.** Logarithmic plot of the integrated intensity of PL spectra of biexcitons *versus* that of excitons. **e.** Semilogarithmic plot of PL peak positions of excitons, trions and biexcitons peaks *versus* input laser power. **f.** Semilogarithmic plot of FWHM of excitons, trions and biexcitons *versus* excitation power.

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Chapter 7

Revealing Defect-State Photoluminescence in Monolayer WS₂ by Cryogenic Laser Processing

7.1 Introduction

In the previous two chapters, measurements were performed on as-grown WS₂. However, in order to effectively implement the monolayer TMDCs into applications, their stabilities in ambient conditions worth thorough investigations, due to the fact that the instability of the material in air can pose great challenges in device fabrication and handling because the properties of the materials can be modified which can greatly influence the device performance. This argument especially applies to two-dimensional materials owing to their ultrahigh surface-area-to-volume ratios. For example, as-prepared multi-layer graphene oxides were metastable, which experience one-month relaxation process

before reaching final structural and chemical state.[1] Few-layer black phosphorus (BP) also suffered greatly from degradation in ambient conditions. It has been observed a mobility reduction ratio of as-prepared over degraded BP, which can reach as high as 10^4 . [2, 3] The properties of topological insulator [4] or even graphene [5] can be influenced if they were stored in ambient condition, the latter of which was once believed to be highly chemically inert. [6] In recent reports, Zhang *et al.* [7] showed that WS₂ can be oxidized if it was exposed to UV light in a high-humidity environment. Elevated temperature has been demonstrated to accelerate the oxidation process, preferentially starting from grain boundaries. [8] Recently, Gao *et al.* [9] reported that they have observed the severe degradation of WS₂ and MoS₂ caused by the ageing effect during the storage in ambient conditions for several months. X-ray photoemission spectroscopy and Auger electron spectroscopy revealed that the degradation was the result of oxidation and organics adsorption. Therefore, the understanding of the optical properties variations with degradation is essential, which, in return, can serve as an indicator which enables non-invasive detection of these changes before the degradation area becomes optically visible.

In this chapter, I mainly examine the time-evolution of optical and morphological properties of monolayer WS₂ stored in ambient conditions. Degradation can also occur on monolayer WS₂, but with much longer time scale than BP. Starting at nanoscale, the degradation regions gradually expand and become optically visible with increasing ageing time. However, no obvious changes are observed spectroscopically at either room temperature or at LN temperature. I propose that adsorbents related excitons could influence the formation of defects related excitons emission. Here adsorbents mean that chemicals physisorbed on the surface of the WS₂ which do not change the lattice structure and chemical composition while defects mean those can change the chemical composition of WS₂ which includes vacancies, impurities and so on. A laser exposure methods is adopted to revive the defects related excitons emission.

7.2 Results and discussion

CVD synthesized monolayer WS₂ crystals were left in ambient conditions to age with different time span. Figure 7.1a-c present optical images of typical monolayer WS₂ samples that are as-grown, 2-month aged and 8-month aged in ambient conditions. Both as-grown and 2-month aged samples show very uniform optical contrast. However, there are a lot of granular structures appearing on 8-month aged samples, which have not been observed on the other two samples. SEM images of monolayer WS₂ with different ageing time are presented in figure 7.1d-f. Similar to optical image, SEM image of as-grown sample in figure 7.1d also shows very high contrast uniformity. Differently, in figure 7.1e, 2-month aged sample presents a few particles and rough edges along with uniform contrast in other regions of the crystal. Figure 7.1f shows that 8-month aged sample possesses grains with lighter contrast, the density of which decreases from crystal edges to central area. In order to study the surface morphology quantitatively, I have also presented AFM images in figure 7.1g-i. Similar to what has been observed in optical and SEM images, both as-prepared and 2-month aged samples in figure 7.1g,h present flat surfaces in spite of scattered particles on the 2-month aged sample, which may come from unintentional contaminant when being stored in ambient condition. On the contrary, large height variations were observed on 8-month aged crystals, shown in figure 7.1i. The inset presents a height profile along the blue dashed line across one of the granules with light contrast, indicating that the granular structure is 3.5 nm higher than the surrounding WS₂ surface. Typical values are in the range of 1.5 nm to 4.5 nm.

The observation of degradation *via* optical microscopy, SEM and AFM leads to another important question: is it possible to detect the defects before it become optically visible? Spectroscopic methods have been proved to be an effect tool to probe defects states.[10, 11] In figure 7.2, integrated intensity maps of both PL and two characteristic Raman features, A'_1/A_{1g} and $E'/E_g^1/E_{2g}^1$ of as-grown, 2-month and 8-month aged WS₂

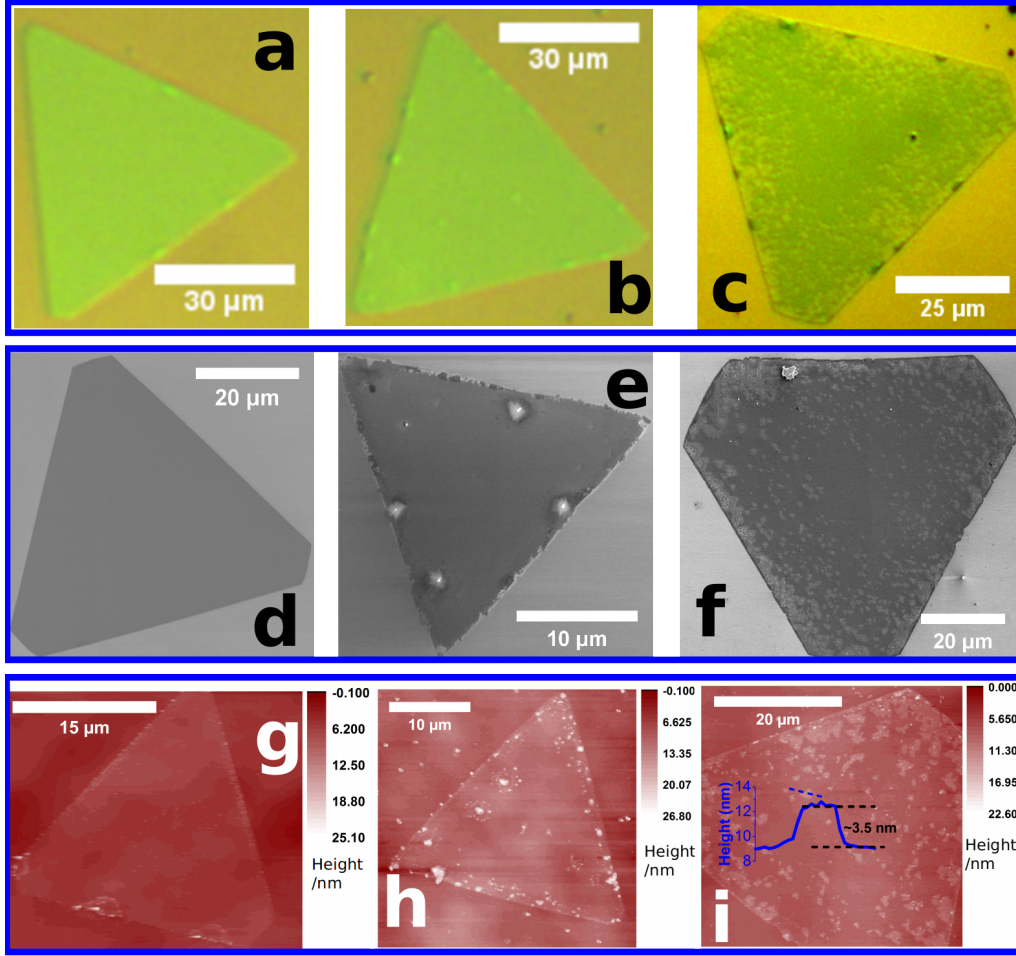


FIGURE 7.1: **a-c.** Optical images of **a)** as-grown, **b)** 2-month aged and **c)** 8-month aged monolayer WS₂. **d-f.** SEM images of **d)** as-grown, **e)** 2-month aged and **f)** 8-month aged monolayer WS₂. **g-i.** AFM surface morphology images of **g)** as-grown, **h)** 2-month aged and **i)** 8-month aged WS₂. Inset in **i**: height line profile across the blue dashed line in the area with light contrast. The average height across the region is about 3.5 nm.

monolayer domains are presented. Both as-grown and 2-month aged samples presents uniform intensity map for both PL and Raman, while noticeable intensity variations were observed in 8-month aged sample, with weaker intensity areas corresponding to regions with lighter optical contrast in figure 7.2i. Such correspondence suggests that monolayer WS₂ can be degraded if being left in ambient for certain period of time,

which is caused by either oxidation[12, 13] or water vapour induced etching[14] followed by contamination filling in. Considering that the granular structures are at least 1.5 nm higher than the WS₂ surface, it is less likely that water vapour induced etching is the main contributor. The degradation process starts preferentially from crystal edges, which may probably due to the richness of dangling bonds at the edges.

In some materials, degradation can introduce new Raman features even at room temperature. For example, an additional Raman D peak can arise from defective regions compared with pristine graphene.[15] In figure 7.3a,b, normalized Raman spectra of as-grown as well as 8-month aged monolayer WS₂ are presented. No noticeable variation can be distinguished for the overall spectra. The spectra were then deconvolved into separate Lorentzian peaks in order to understand the contributions of different vibration modes, especially the two characteristic modes for TMDCs, $E'/E_g^1/E_{2g}^1$ and A'_1/A_{1g} , which show no obvious spectral shifts. PL can also act as a powerful tool to characterize the existence of defects. A new PL emission peak with much broader spectral width and lower emission energy than excitons and trions related peaks emerged from monolayer TMDCs after ion bombardment[11] or argon plasma treatment[10]. Figure 7.3c,d show the PL spectra of monolayer WS₂ before and after ageing. Yet no obvious PL shape change is observed apart from slight blueshift of aged sample, which, however, cannot serve as an indicator for the existence of defects due to the previously reported spectral positions variations from different regions in the same as-grown monolayer single crystal domain.[16]

PL at cryogenic environment can exclude the thermal interference and therefore give more intrinsic properties of target materials that cannot be detected at room temperature.[17, 18] Figure 7.4a,c present the PL spectra of both as-grown and 8-month aged monolayer WS₂ acquired at liquid nitrogen (LN) temperature. It should be noted here that the regions of the two samples that the excitation laser spot focused on possess similar optical contrast. Two main features can be resolved in the spectra, which are consistent with

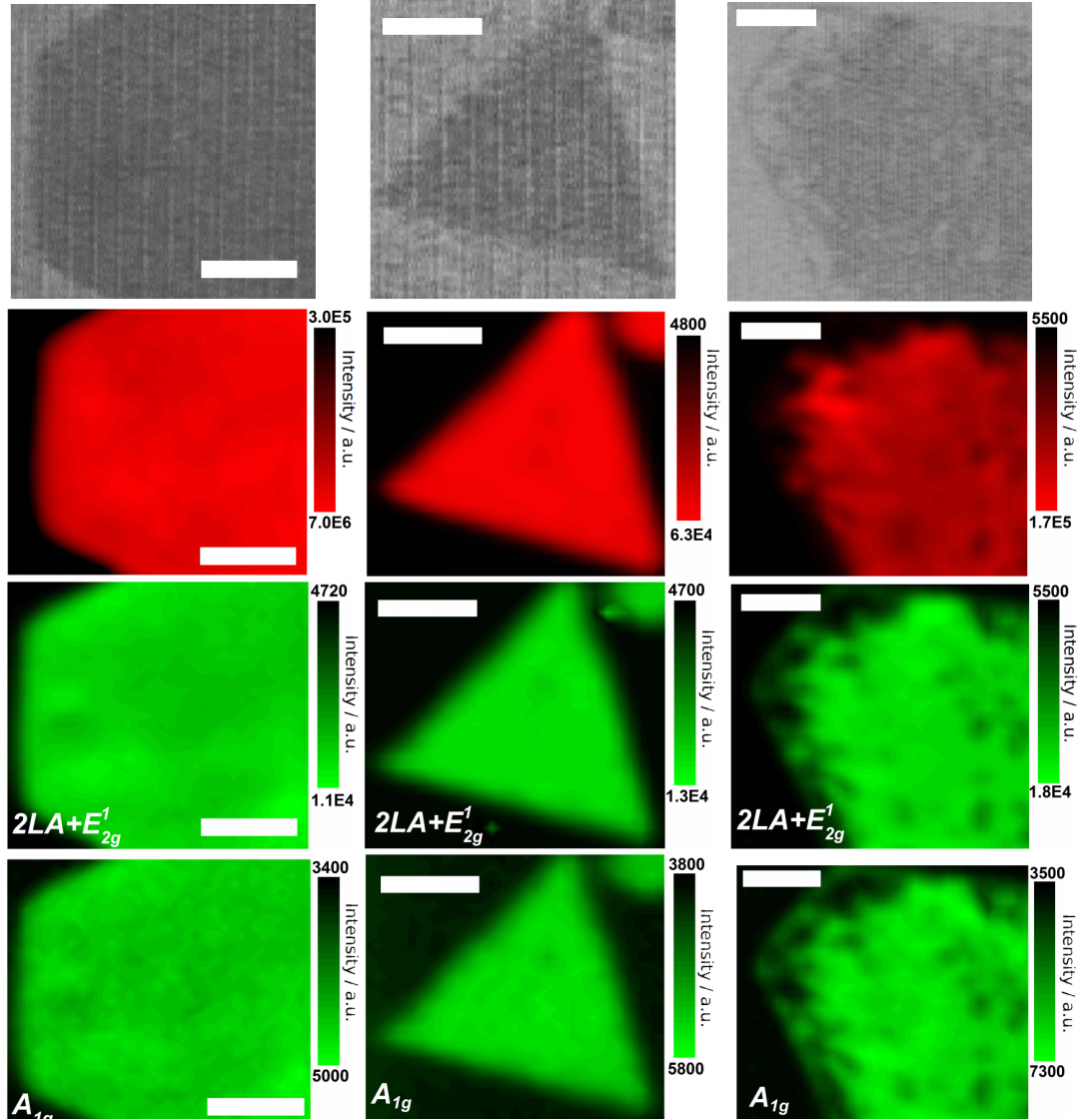


FIGURE 7.2: **a-d.** **a)** Optical image, **b)** PL integrated intensity mapping, **c)** $2LA+E_{2g}^1$ Raman peak intensity mapping and **d)** A_{1g} intensity mapping of as-grown monolayer WS₂. **e-h).** Optical image and spectroscopic mapping of 2-month aged monolayer WS₂. Panels are arranged in the same order as that in **a-d.** **i-l).** Optical image and spectroscopic mapping of 8-month aged sample. Panels are arranged in the same order as that in **a-d.** Scale bar: 20 μm

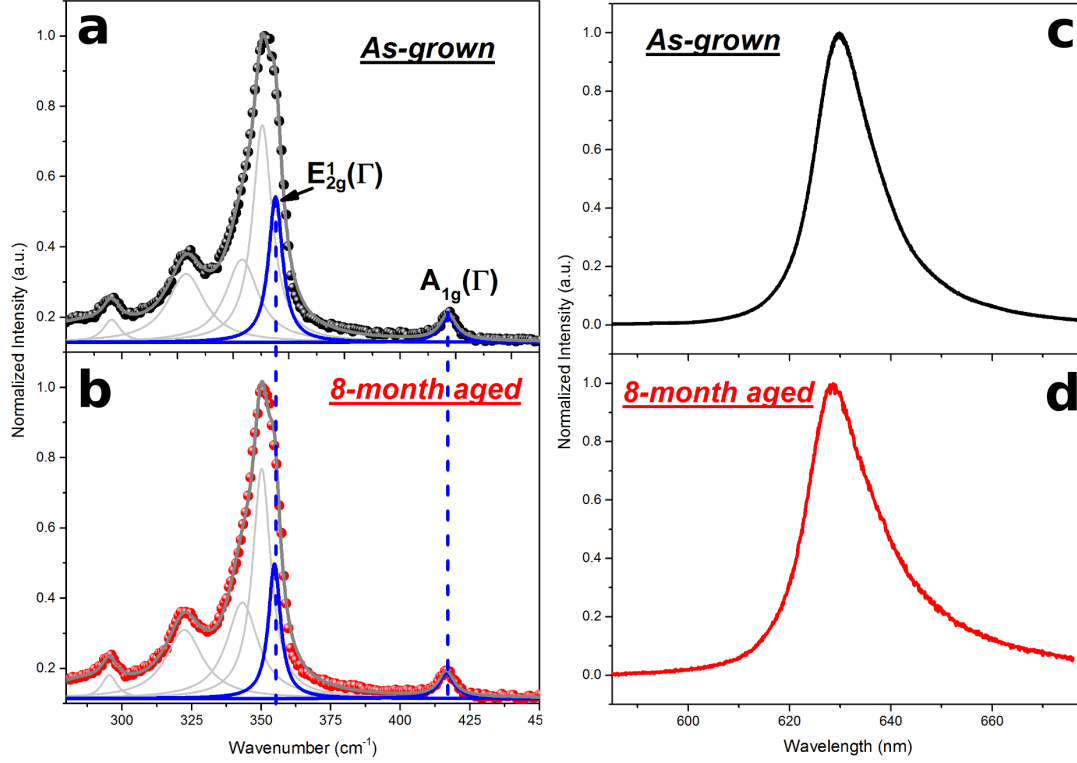


FIGURE 7.3: Room temperature normalized PL and Raman spectra. **a,c.** **a)** Raman and **c)** PL spectra of as-grown sample. **b,d.** **b)** Raman and **d)** PL spectra of 8-month aged sample. In **a,b**, black spheres are experimental data. Light grey and blue curves are multiple-Lorentzian fitting results. Dark grey curves are cumulative fitting results.

previous literature.[18] The shoulder at high energy side originates from the combination of excitons (~ 610 nm) and trions (~ 615 nm) while the broad peak locating at low energy side is attributed to localized states (LS) induced by impurities adsorption.[18, 19] However, until now, there is no noticeable difference between as-grown and aged samples. Previous report showed that mid-gap states induced by defects can be passivated by oxygen or other adsorbents.[20] The dominance of LS in the spectra indicates that most of the photo-excited excitons are bounded to adsorbents, which can reduce their diffusion length drastically. Adsorbents are likely to come from air when the sample is exposed to ambient condition. Therefore, a plausible derivation is that impurities can completely cover the whole monolayer WS₂ domain whereas defects are scattered in the regions with normal optical contrast compared with adsorbents. Most of the

defects can therefore be passivated by the adsorbents. As a result, the possibility of the formation of defects bounded excitons can be greatly reduced. Previous literature demonstrated that laser irradiation can facilitate the desorption process of molecules once physisorbed on dielectric surfaces.[21] In figure 7.4b,d, I presented the PL spectra of as-grown and aged samples after being irradiated by focused laser beam with power of ~ 5 mW (~ 40 kW/cm²) for 30 seconds. Indeed, emission from LS of both samples were suppressed greatly after irradiation, indicating that most of the adsorbents once laying on the laser irradiated area has been removed from the WS₂ surface. This leads to stronger emission from excitons and trions in as-grown monolayer WS₂, shown in figure 7.4b. In stark contrast, PL shape of 8-month aged sample changed totally, with a new luminescence feature dominating the whole spectrum, presented in figure 7.4d. Here this new peak is denoted as peak U. Similar measurements have been carried out on 20 8-month aged domains, which all presented same behaviour. This peak can be still observed under excitation power as low as ~ 17 nW (0.1 W/cm²), as shown in figure 7.5. Positions of peak U range from 622 nm to 628 nm, which are similar to values reported in previous literature in which defect were created intentionally by exposing WS₂ to water vapour.[14] Many applications require the transfer of WS₂ from growth substrate to other substrates, during which polymer scaffold is inevitable. Considering that peak U can be hidden by adsorbents from air, polymer residual can also have the similar effect, which may be even harder to be removed by laser exposure. Therefore, it is essential to prove if this method can be utilized to evaluate the quality of transferred sample. Figure 7.4e,f present the PL spectra of transferred WS₂ crystal before and after laser treatment. In figure 7.4e, there are three main features in the untreated sample, which originate from excitons (~ 591 nm), trions (~ 602 nm)[22] and LS emission. Compared with non-transferred sample, excitons and trions related PL peaks blueshift, which is probably due to the strain releasing after transfer process.[23] After laser irradiation with power of ~ 5 mW for 10 seconds, LS related emission intensity is reduced and peak U emerges which possess similar emission energy as the values

reported in other literature. [22] Another example of the PL response of both 8-month aged non-transferred and transferred monolayer after laser exposure are presented in figure 7.6. In order to confirm that the processing laser power will not induce any damage, room temperature Raman and optical microscopy before and after laser exposure are presented, as shown in figure 7.7. In this case, laser processing is performed in ambient condition, which is believed to be easier to introduced damage because of the existence of oxygen and water. However, no obvious Raman peaks intensity variation or morphology change can be observed, indicating that the laser processing technique with parameters employed in this case won't introduce any damage to monolayer WS₂. In spite of the resemblance of peak positions with values reported in previous literatures and the different behaviour between as-grown and 8-month aged samples, it is still too early to correlate peak U with defects before several other possible explanations are ruled out. It should be noted here that peak U in non-transferred WS₂ possesses similar emission energy as bright biexcitons in monolayer WS₂. [18] Power dependent measurements were performed, which is depicted in figure 7.4g,h. Peak U of both non-transferred and transferred 8-month aged sample possess linear power dependence, referring that peak U is not related to higher-order excitonic species.

Exposing monolayer WS₂ to irradiation with lower laser processing power such as 1 mW ($\sim 8 \text{ kW/cm}^2$) in figure 7.8 can also lead to such transition. In addition, figure 7.8 also demonstrate that PL shape evolves with exposure time, indicating that such PL change is a gradual process instead of an abrupt transition. Figure 7.8a presents typical PL spectra of 8-month aged monolayer WS₂ after laser irradiation treatment under fixed laser power with varying exposure time. Black curve represents the PL spectrum of untreated sample. After 1 second irradiation, a noticeable reduction in LS emission intensity can be observed, accompanying by the emergence of peak U. Similar irradiation treatments were performed at the same region with increasing exposure time. Clearly, peak U becomes more dominant in the spectrum whereas LS emission was suppressed continuously, depicted by blue and pink curves in figure 7.8a. With exposure

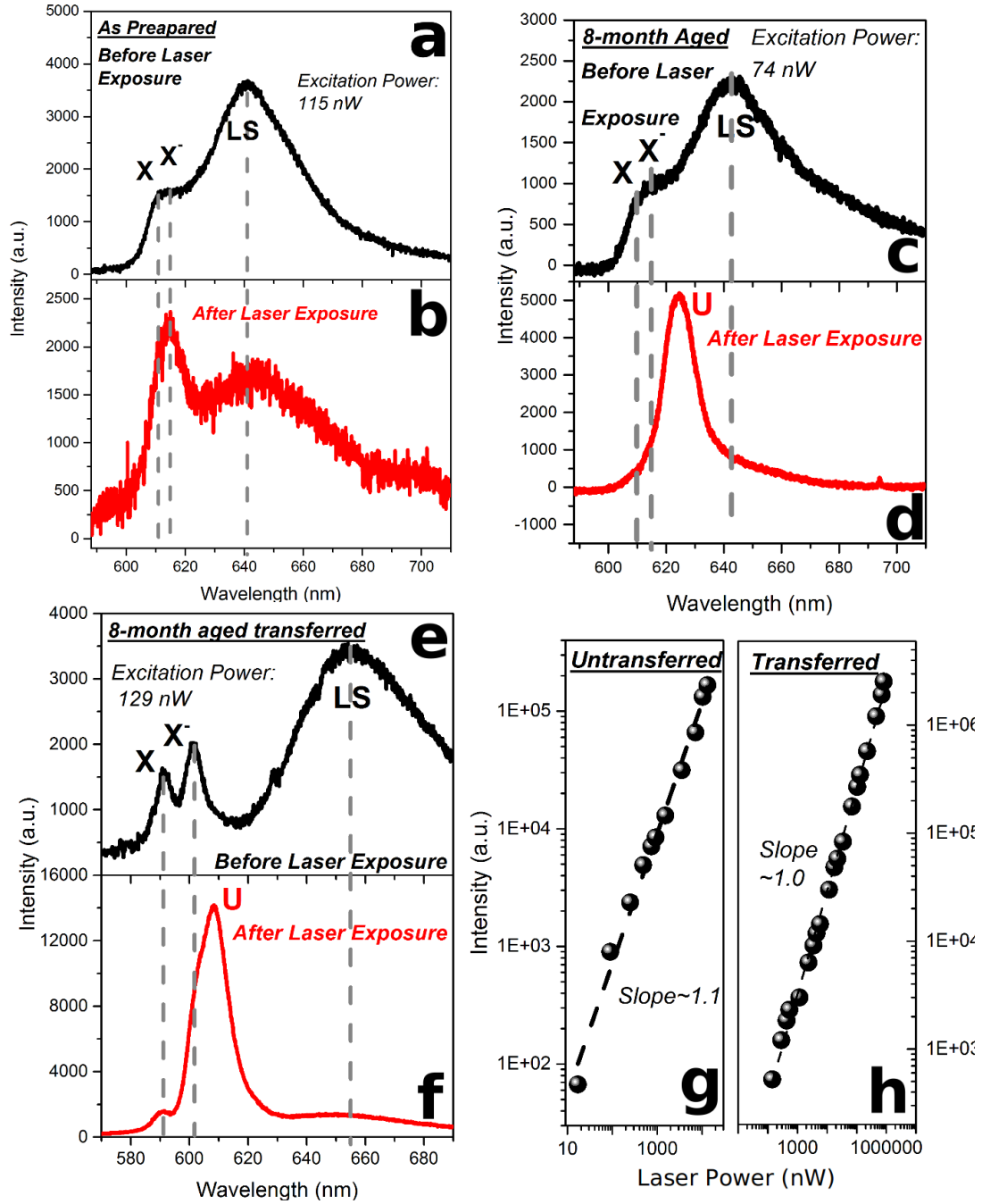


FIGURE 7.4: PL spectra taken under cryogenic environment. **a,b.** PL spectra of as-grown monolayer WS₂ **a)** before and **b)** after laser exposure. **c,d.** PL spectra of 8-month aged non-transferred sample **c)** before and **d)** after laser exposure. **e,f.** PL spectra of 8-month aged as-transferred monolayer WS₂ **e)** before and **f)** after laser treatment. **g,h.** Power dependence of peak U from 8-month aged **g)** non-transferred and **h)** transferred samples.

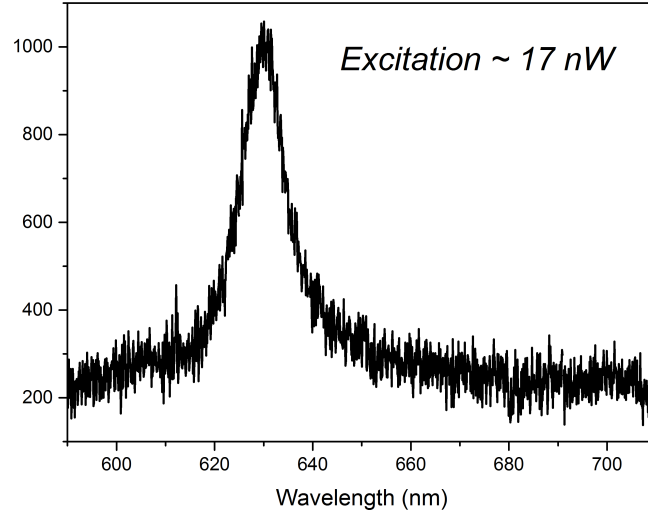


FIGURE 7.5: PL spectra of 8-month aged monolayer WS₂ after laser processing with excitation power of 17 nW (0.1 W/cm²)

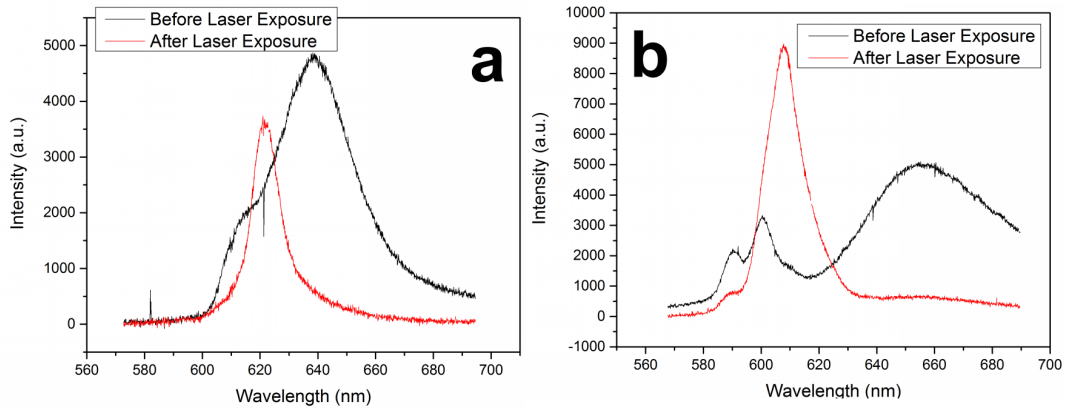


FIGURE 7.6: Another example of PL of aged WS₂ before and after laser exposure. **a.** PL spectra of 8-month aged non-transferred monolayer WS₂ before and after laser exposure. **b.** PL spectra of 8-month aged transferred sample before and after laser exposure.

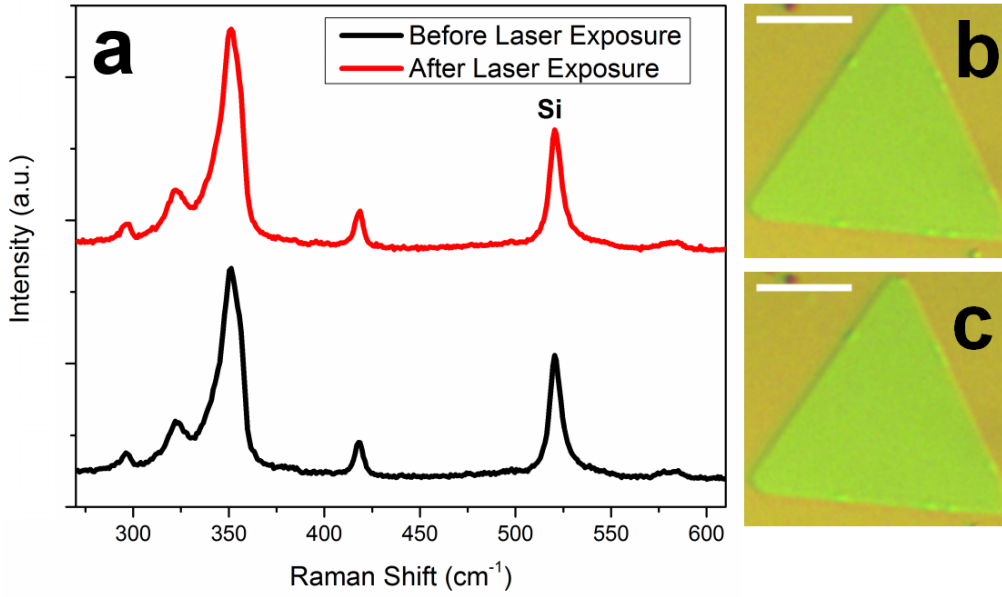


FIGURE 7.7: **a.** Raman spectra of as-grown monolayer WS₂ before and after laser exposure. **b,c.** Optical images of monolayer WS₂ **b)** before and **c)** after laser exposure.

time longer than 10 minutes, no further obvious changes happened to the spectrum. Figure 7.8b presents the PL evolution of transferred sample with varying irradiation time, which shows similar progressional behaviour. The exposure time dependence of PL evolution suggests a lower possibility that the laser irradiation induced PL change was caused by phase change, where an abrupt transition is expected. In addition, the most common phase transition for monolayer 2H-TMDCs is 2H-to-1T transition. 1T-TMDCs exhibit metallic behaviour, the PL of which can be neglected compared with 2H phase.^[24] Therefore, the laser induced phase transition can be ruled out.

I have also tested the life time span of peak U, which tends to be over 12 hours if the sample was kept in vacuum chamber under cryogenic environment. This can possibly be explained by the fact that the impurities at WS₂ surface are frozen and immobilized at low temperature. Therefore, very few impurities can diffuse to the laser treated "clean" area from its surrounding "dirty area". However, at room temperature, impurities become mobilized and therefore can diffuse back to laser irradiated "clean" area, leading

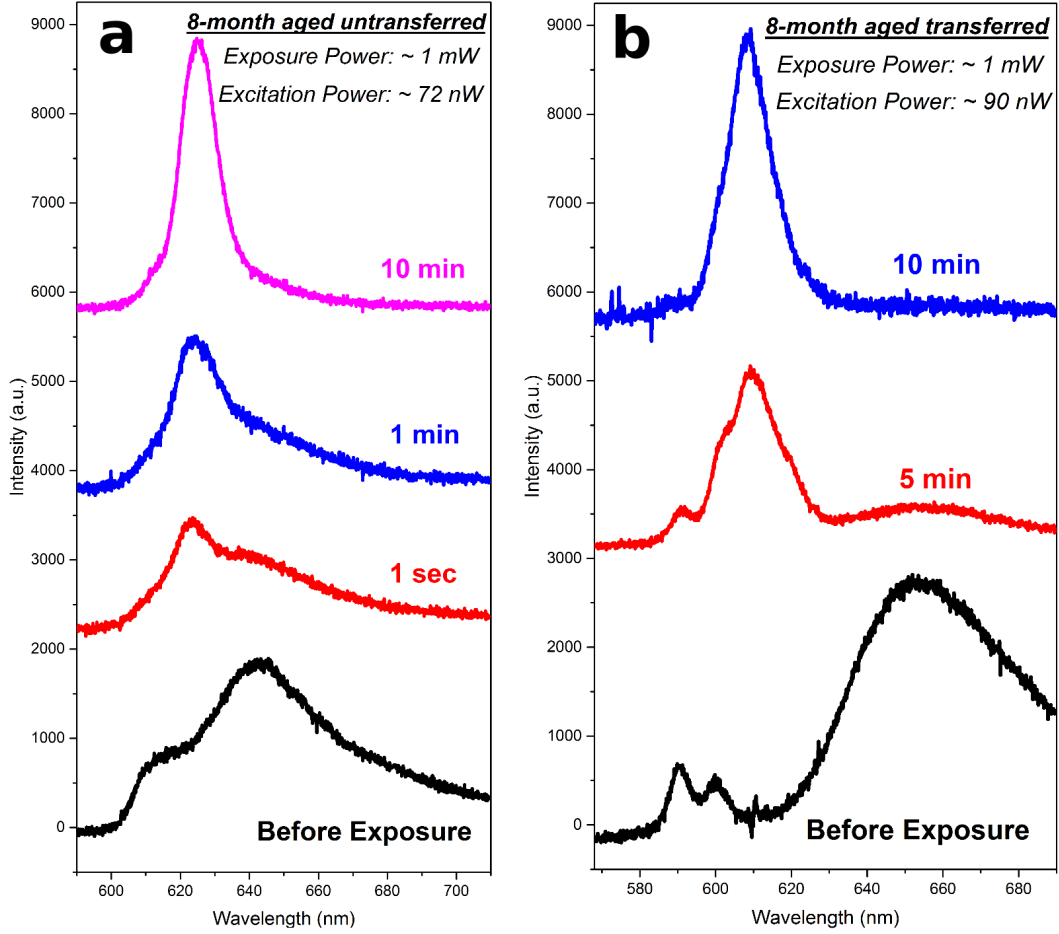


FIGURE 7.8: PL shape evolution with laser exposure time under fixed incident power. **a.** 8-month aged non-transferred WS₂. Black curve: before laser exposure. Red curve: 1 second exposure. Blue curve: 1 minute exposure. Pink curve: 10 minutes exposure. **b.** 8-month aged transferred sample. Black curve: before laser exposure. Red curve: 5 minutes exposure. Blue curve: 10 minutes exposure.

to the diminishing of peak U and reviving of LS emission if the PL is measured at 77 K again. Figure 7.9 demonstrates that PL changes before and after the temperature cycle, where temperature of laser treated sample is increased to room temperature and then is cooled down back to 77 K. Figure 7.9a presents the peak U dominated PL spectrum of non-transferred 8-month aged WS₂. Temperature cycle is then applied and the corresponding PL spectrum is plotted in figure 7.9b. As expected, peak U disappears and LS revives. I have also included the spectrum of PL (orange dotted

curve) before laser treatment for comparison, which clearly shows that PL changes back to its original shape after temperature cycle. The reviving of LS indicates that the laser cleaned areas are refilled by adsorbents coming from the surrounding dirty area. Similar phenomenon can also occurs to transferred monolayer WS₂, as shown in figure 7.9c,d. Based on the foregoing discussion, it is now can be concluded that peak U can be assigned to defect related feature.

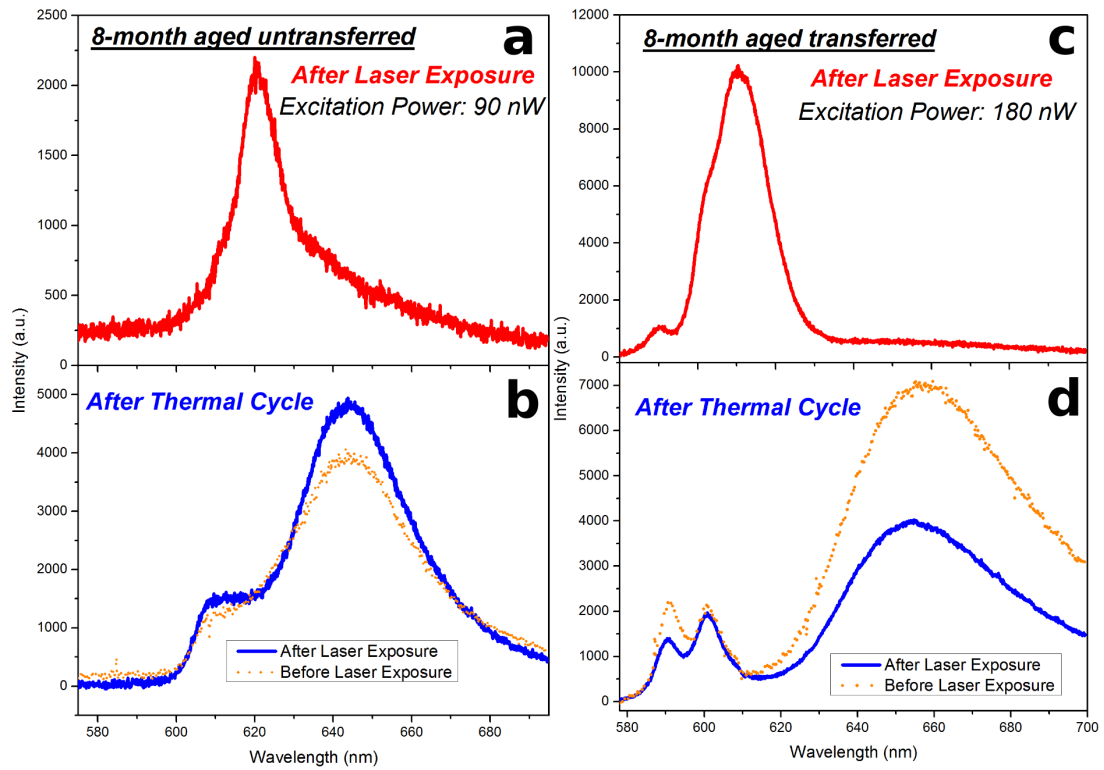


FIGURE 7.9: Thermal cycle effect. **a.** PL spectrum of aged non-transferred sample after laser exposure. **b.** PL spectra of laser treated non-transferred sample after temperature cycle. Orange dotted line: PL spectrum before laser treatment. **c.** PL spectrum of laser treated 8-month aged transferred monolayer WS₂. **d.** PL spectrum after temperature cycle. Orange dotted line: PL spectrum before laser treatment.

In order to figure out its origin, degradation is intentionally introduced into WS₂. It has been demonstrated that heating in ambient condition can accelerate the degradation of WS₂.^[8] Figure 7.10a-c present the cryogenic PL spectra before and after laser exposure of WS₂ with different heating time in ambient conditions at temperature of

150 °C. Figure 7.10a shows that the PL spectrum remains its original shape after laser processing (power density $\sim 8 \text{ kW/cm}^2$), with a great reduction of LS emission intensity. In figure 7.10b, the PL response of WS₂ after 30 minutes heating in air at 150 °C is presented, which exhibits no new luminescence feature. In figure 7.10c, the heating time is extended to 90 minutes, which leads to the emergence of peak U but no morphology change is observed, as shown in figure 7.11. In order to exclude the effect of thermal decomposition, a control experiment is performed in which WS₂ is heated at 150 °C for 90 minutes with argon flowing, which shows no peak U after laser processing, as shown in figure 7.10d. This indicates that degradation here is more likely related to oxidation. It should be pointed out here that the PL spectrum also experience redshift with increasing heating time, which is very likely the result of increased strain after heating.[\[23\]](#)

Figure 7.12 demonstrates the PL spectra of monolayer WS₂ as a function of ageing time. There is no additional peak emerging in the post laser processing ($\sim 8 \text{ kW/cm}^2$) PL spectra until 3 weeks later, in which a clear shoulder emerges, locating at around 625 nm. With longer ageing time, the emission intensity of peak U increases gradually and become dominant over the whole spectrum in the 7th week. In figure 7.13, the integrated intensities weights of peak U extracted by peaks fitting shown in figure 7.12 over the whole spectra were presented. It clearly shows that the peak U is gradually dominate the PL emission from WS₂. At this stage, no obvious optical contrast can be observed, indicating that this laser processing technique proposed here possesses high sensitivity towards defects in WS₂. It may also have the potential to be extended to the quality characterization of other TMDCs.

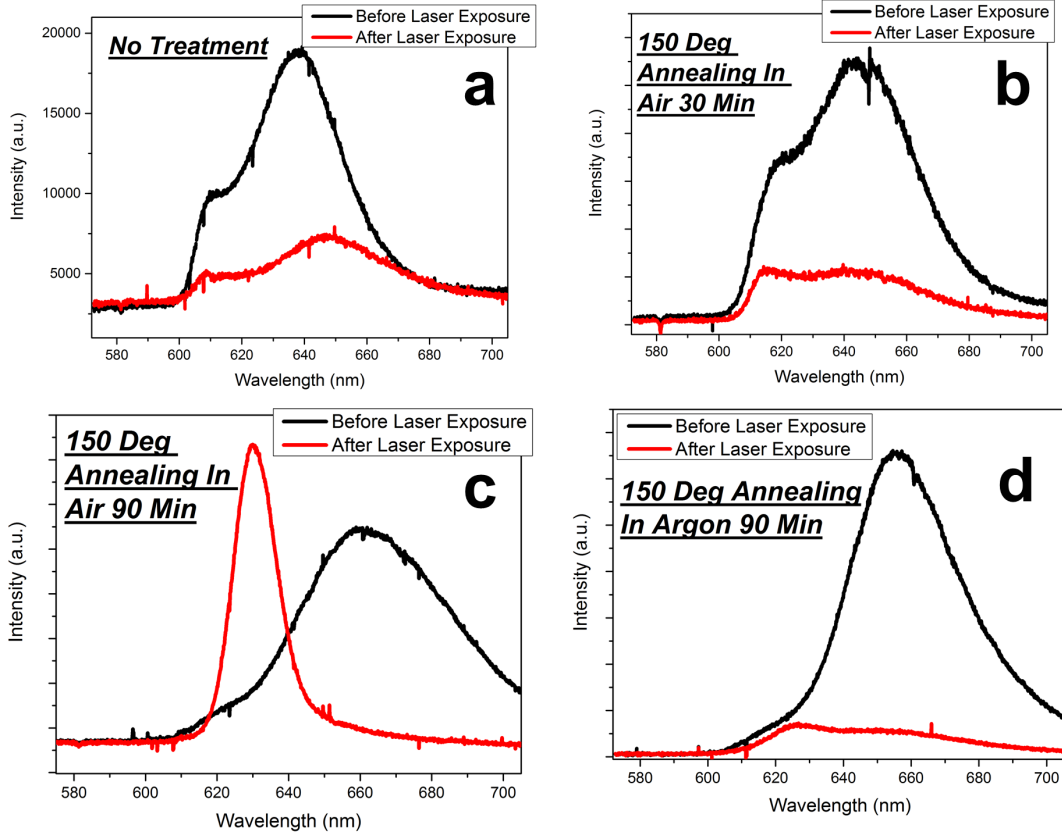


FIGURE 7.10: Controlled degradation of WS₂ through heating. **a-d.** PL spectra at 77 K of **a)** as grown WS₂, **b)** WS₂ after annealing in air at 150 °C for 30 minutes, **c)** WS₂ after annealing in air at 150 °C for 90 minutes and **d)** WS₂ after annealing in argon at 150 °C for 90 minutes.

7.3 Conclusion

In this chapter, I monitor the degradation process of monolayer WS₂ in air and the effect of degradation on the optical properties of monolayer WS₂. A novel laser processing technique is developed which allows the direct probe of defects state *via* cryogenic PL microscopy and has the potential to be used as an effective and fast characterization tool to characterize the 2D TMDCs' quality. The benefits of this research can be three-fold. Firstly, it advances the ageing process of WS₂ and the characterization technique, suggesting that corresponding research on the air insulation technique must

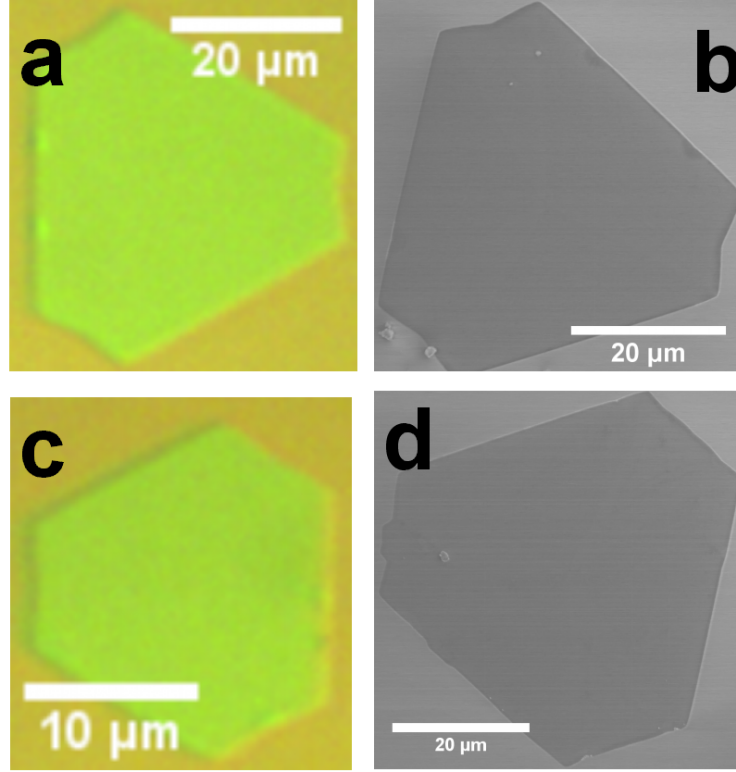


FIGURE 7.11: Optical and SEM images of controlled degradation of WS₂ through heating. **a,b.** **a)** Optical image and **b)** SEM image of as grown WS₂. **c,d.** **a)** Optical image and **b)** SEM image of WS₂ after annealing in air at 150 °C for 90 minutes.

be developed, which could be invaluable to the industrialization of TMDCs. Secondly, it could lead to a WS₂ based single photon source if proper ageing time and laser processing parameters are chosen.[25, 26, 27, 28] Thirdly, the results also demonstrate a controllable method to manipulate the PL emission spectra of aged monolayer WS₂, which can be applied into ultra-thin optical memory devices.[29]

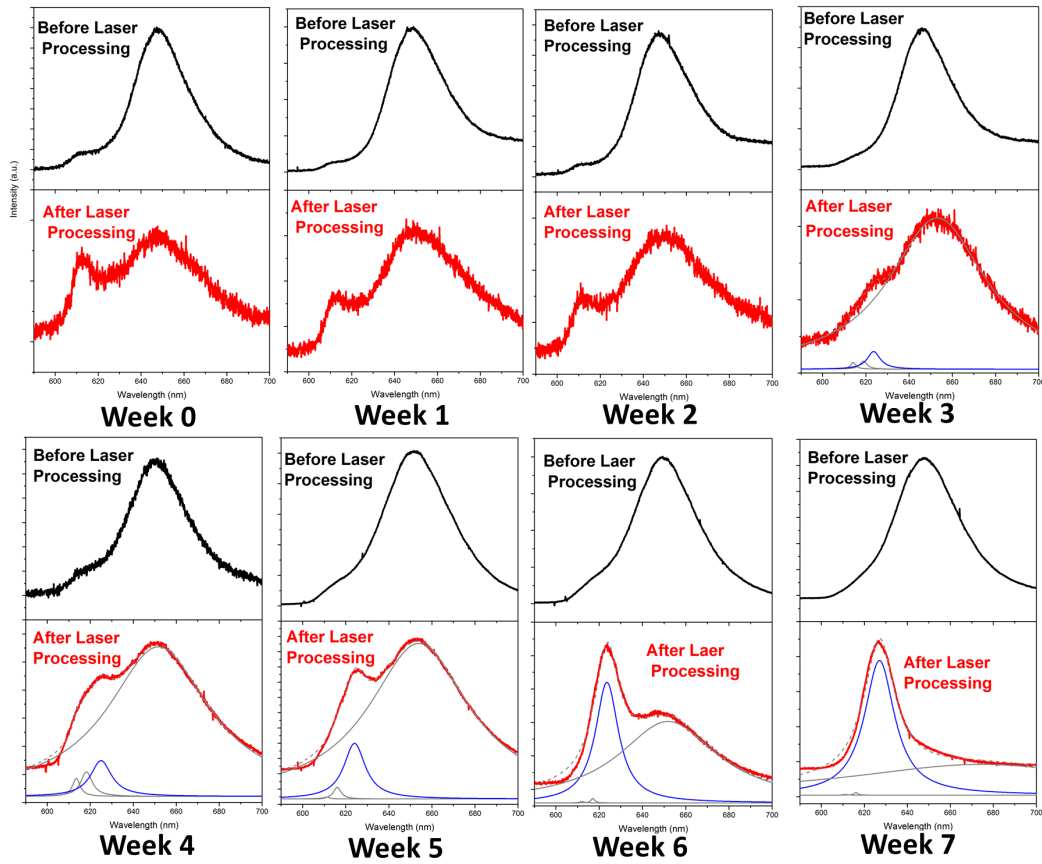


FIGURE 7.12: PL spectra of WS₂ as a function of ageing time from as-grown to 7 weeks.

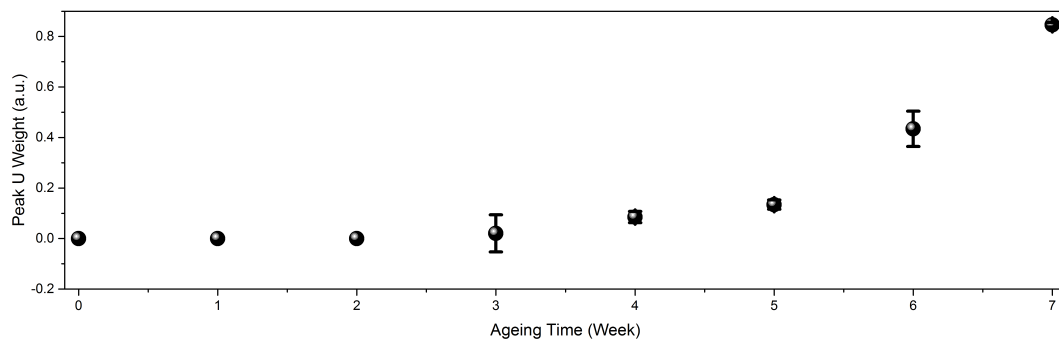


FIGURE 7.13: PL weights of peak U over that of the whole spectra as a function of ageing time.

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Chapter 8

Conclusion and Future Outlook

8.1 Thesis summary

The realization of the all-2D-materials based electronics and optoelectronics requires the deep understanding of the properties of the materials themselves, which serves as the motivation of this research project. This doctorate thesis focus on the characterization and modulation of the electrical and optical properties of two different types of 2D materials, graphene and WS₂. In Chapter 4, I demonstrate that the electrical performance of graphene can be improved by chemical doping with iron (III) chloride and the atomic structures of doped sample monitored by AC-TEM is also presented. The next three chapters mainly focus on the modulation of optical properties of TMDCs *via* three different methods. Chapter 5 presents that the layer dependent PL response towards lateral electric field, with PL quenching in monolayer WS₂ and PL enhancement in bilayer WS₂. Chapter 6 shows the formation of bright higher order excitonic species, biexcitons, in CVD as-grown bilayer WS₂ under high excitation power, which is absent in transferred bilayer region due to the strain release. Chapter 7 investigates the PL behaviour of aged monolayer WS₂, in which a novel laser processing technique is

proposed to eliminate the influence of adsorbents on WS₂ which allows the observation of the defect related PL under cryogenic environment.

8.2 Conclusion

Graphene is predicted to be a competitive candidate to replace ITO as the next generation TCEs in electronics and optoelectronics. However, such application can be hindered by the relatively high sheet resistance of as-grown CVD graphene. In this thesis, it is demonstrated that chemical doping with iron (III) chloride through spin coating provides a pathway for improving the sheet resistance while maintaining the optical transmittance at high level with macroscopic doping spatial resolution. In some applications, doping resolution within nanoscale is required. This thesis shows that such high-spatial-resolution doping can be achieved with the help of AC-TEM. The atomic resolving power of AC-TEM also provides an opportunity for *in-situ* monitoring the atomic structures of doped graphene and their dynamics, which clearly shows four different Fe dimer - graphene vacancy complexes and their formation process and mutual transformations. Theoretical calculations also reveal that the implementation of Fe atoms in graphene lattice can induce local magnetic moment, apart from electrical conductance improvement.

The focus of this thesis then shifts to TMDCs, which can act as the active materials in optoelectronics. Due to the high speed and booming development of electronics industry, altering the optical properties of TMDCs through electrical method is more desired than through many other techniques. Based on this motivation, the PL behaviours of both monolayer and bilayer WS₂ are investigated, which presents the electric field induced PL quenching in monolayer WS₂ and enhancement in bilayer WS₂. The layer dependence of the PL variation caused by electric field inspires the possible mechanism where the applied electric field can induce the transfer of photoexcited electrons from

conduction band minima to secondary extrema and therefore modify the resultant recombination pathways. This is the result of the unique band structures (small energy difference between conduction band minima and secondary extrema) and exceptionally large exciton binding energy.

Understanding the PL behaviour of TMDCs under high optical excitation condition can unveil the magnitude of many-body interactions. This thesis demonstrates that the bright biexcitons states can be observed in CVD as-grown bilayer WS₂ under high optical pump. However, once the bilayer is transferred to another substrate, biexcitons related luminescence is absent even under the highest excitation power that can be achieved in the experimental setup. This is the result of increased energy difference between conduction band minima and secondary extrema caused by the strain release during transfer process. Differently, biexcitons can still be probed even in transferred monolayer WS₂, inferring the strong thickness dependence of the magnitude of many-body interaction in TMDCs.

The utilization of TMDCs in industrialized optoelectronics requires the knowledge of the ageing effect on them. The last part of thesis monitors the morphology change of monolayer WS₂ stored in ambient conditions, which suggests that monolayer WS₂ can suffer greatly from degradation after left in air for 8 months. More importantly, a non-invasive laser processing technique with high sensitivity is proposed to revive the degradation-related PL which is buried by the adsorbents physisorbed on monolayer WS₂ during the storage in air before laser processing.

8.3 Future outlook

Further research based on this thesis can be carried out from two aspects. Firstly, investigations into the electrical and optical properties of 2D materials and the ability to manipulate them *via* novel techniques are always required, which can be shed light on

the fabrication of 2D materials based conventional electronics and optoelectronics with better performance. Meanwhile, the scope of the research should not be limited and more properties other than electrical and optical properties should be taken into consideration, which can stimulate the invention of novel types of working devices. Secondly, it is also important to understand the fundamental properties of graphene/TMDCs heterostructures. Short-term emphasis should be laid on the Schottky barrier height at the interface and the ability to tune the barrier height in a scalable, stable and low-cost method. Ultimately, all of the research results can give insights into the fabrication of effective all-2D materials based next generation electronics and optoelectronics.

Appendix A

Image Filter Algorithms

A.1 Smoothing filter

The smoothing filter used in ImageJ is a 3×3 moving average filter with a kernel of

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

, which then convoluted with original images. Assume that the pixel value of the original image (n by n) is f_{ij} , for $i, j = 1, \dots, n$, and the elements in kernel are w_{kl} , for $k, l = -1, 0, 1$ and the elements in smoothed image are h_{ij} , which follows a relation that $h_{ij} = \sum_{k=-1}^1 \sum_{l=-1}^1 w_{kl} f_{i+k, j+l}$ for $i, j = 2, \dots, n-1$. The calculation omits the pixels at the boundary, which is obtained by either using the original value or by image expansion. This smoothing method is simple and fast, but suffers two main drawbacks. It is not isotropic (i.e. circularly symmetric), but smooths further along diagonals than along rows and columns. The second one is that the weights have an abrupt cut-off instead of gradually decaying to zero, leaving discontinuity in the smoothed image.

A.2 Band-pass filter

The band pass filter effect is shown in figure A.1. Figure A.1(a) shows the original AC-TEM image, where shading effect is obvious. By applying band-pass filter in ImageJ where the large filter structure is down to 100 pixels which determine the black area in A.1(b) and small filter structure is up to 1 pixel which determine the diameter of white circular area in figure A.1(b). It should also be noted here that the central pixel in the band pass filter should 1.0 which is used to maintain the average brightness, as shown in figure A.1(c). The resultant image is shown in figure A.1(d), which clearly shows that shading has been filtered.

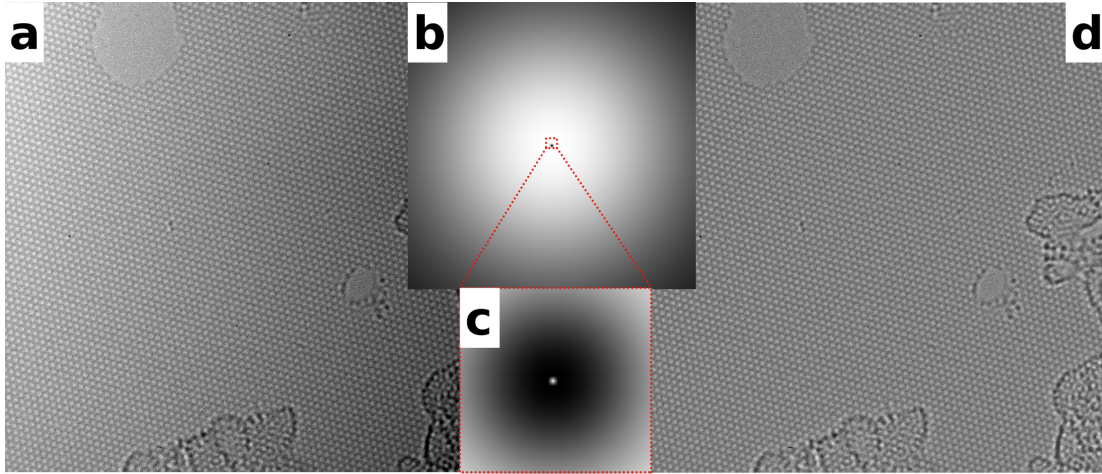


FIGURE A.1: Band pass filter effect. **(a)**. Original AC-TEM image. **(b)**. Band pass filter. **(c)**. Magnified image of region labeled by red dotted rectangle. **(d)**. AC-TEM image after band pass filtering.

Appendix B

Van der Pauw Method

B.1 Background

Before the van der Pauw method was invented, semiconductor needs to be first cut into a special shape (for example, a bridge shape) before specific resistivity and Hall effect can be measured. However, the cutting process is of great technical difficulties. Therefore, a method that can be applied to samples with arbitrary shape is highly desired. Van der Pauw method was first proposed by Dr. L. J. van der Pauw^[1] in 1958 in order to solve the problem.

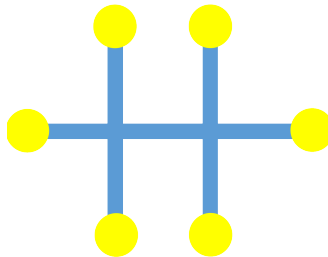


FIGURE B.1: Bridge shape for measuring resistivity and Hall effect of semiconductors.

B.2 Van der Pauw Method

The van der Pauw method considers semiconductors with arbitrary shape, as shown in figure B.2. The first step is to force current flowing between terminal A,B (i_{AB}) and measure the voltage drop at DC ($V_{DC} = V_D - V_C$), yielding $R_{AB,CD}$. The next step is to force current to flow between B,C (i_{BC}) and measure the voltage drop at DA ($V_{DA} = V_A - V_D$), yielding $R_{BC,DA}$. These two values follow the formula:

$$\exp(-\pi R_{AB,CD}d/\rho) + \exp(-\pi R_{BC,DA}d/\rho) = 1 \quad (\text{B.1})$$

where d is the thickness of the sample and ρ is the resistivity and $\rho/d = R_s$ is sheet

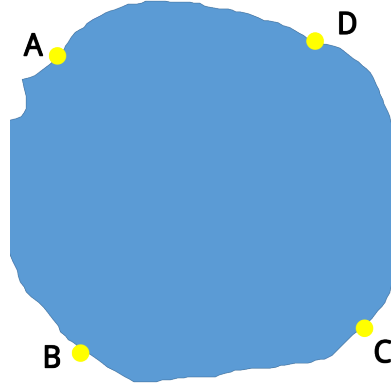


FIGURE B.2: Arbitrary shaped semiconductor with 4 contacts.

resistance. To prove equation B.1, a special case is first considered where the semiconductor interested is a semi-infinite plane with thickness of d and has 4 electrodes. Current i is passing through terminal A and collecting at terminal B. Voltage drop is then measured between terminals C and D. According to superposition theory, the bias between C and D can be viewed as superposition of the effect of current source A and B. Let's first do not consider the effect of terminal B. Once the current i has entered the semiconductor, it will flow away from point A with radial symmetry. Therefore,

the current density of a certain point P is

$$\vec{J} = \frac{i}{\pi r d} \hat{r} \quad (\text{B.2})$$

According to Ohm's law, the current density can be written in the form of $\vec{J}_A = \sigma \vec{E}_A$.

Therefore, the electric field can be expressed as

$$\vec{E}_A = \frac{i}{\sigma \pi r d} \hat{r} \quad (\text{B.3})$$

According to the definition of electrical potential, $V_{DC,A} = -\int_C^D \vec{E}_A d\vec{r} = \frac{i}{\sigma \pi d} \ln \frac{a+b}{a+b+c}$.

Similarly, if only the current at point B is considered, $E_B = -\frac{i}{\sigma \pi r d}$ and therefore

$V_{DC,B} = -\int_C^D \vec{E}_B d\vec{r} = \frac{i}{\sigma \pi d} \ln \frac{b+c}{b}$. Hence, the bias between point C and D is

$$V_{D,C} = \frac{i}{\sigma \pi r d} \ln \frac{(a+b)(b+c)}{(a+b+c)b} \quad (\text{B.4})$$

and the resistance is $R_{AB,DC} = \frac{1}{\sigma \pi d} \ln \frac{(a+b)(b+c)}{(a+b+c)b}$. Similarly, if current is forced between terminals B and C and measure the bias between A and D, which is $V_{AD} = \frac{i}{\sigma \pi d} \ln \frac{(a+b)(b+c)}{ac}$ and the resistance $R_{BC,AD} = \frac{1}{\sigma \pi d} \ln \frac{(a+b)(b+c)}{ac}$. $\exp(-d\pi R_{AB,CD}) + \exp(-d\pi R_{BC,DA}) = \frac{b(a+b+c)}{(a+b)(b+c)} + \frac{ac}{(a+b)(b+c)} = 1$ A more generalized derivation requires

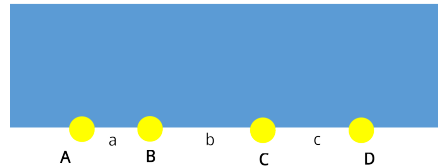


FIGURE B.3: A semi-infinite semiconductor with 4 metal contacts at the periphery.

many advanced mathematics. We can consider the semi-infinite plane in figure B.3 as the upper plane of a complex plane z , and actual semiconductor plane with arbitrary shape is defined in another complex plane, t . According to conformational mapping theorem, it is always possible to find a mapping function so that the arbitrary shape in

plane t can be mapped to complex z as the upper plane. Therefore, the above derivation can be applied here. However, in order to apply the conformational mapping, 4 prerequisites must first be fulfilled.

Appendix B References

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Appendix C

Kinetic Energy of Electrons Gained From Electric Field in WS₂

The kinetic energy that charge carriers in a semiconductors gain from electric field can be described by the effective electron temperature given by:[1]

$$T_e = \frac{T}{2} \left\{ 1 + \left[1 + \frac{3\pi}{8} \left(\frac{\mu_0 E}{u_s} \right)^2 \right]^{1/2} \right\}$$

in which T_e is the effective electron temperature, $u_s \sim 1000\text{m/s}$ is the sound velocity in WS₂, [2] $\mu_0 = 200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ is the electron mobility, [3] T is the lattice temperature. The minimal PL peak shift observed indicates that the lattice temperature is close to room temperature (300 K). Therefore, the kinetic energy of electrons in monolayer under the electric field of 1 kV/cm (threshold electric field to observe PL quenching in monolayer WS₂) is $E_{elec,ml} = k_B T_e \approx 44\text{meV}$. For bilayer WS₂, the threshold electric field to observe PL enhancement is 2 kV/cm and therefore the average kinetic energy of electrons is $E_{elec,bl} = k_B T_e \approx 71\text{meV}$.

Appendix C References

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