

**OPTICAL PROPERTIES OF 2D TRANSITION METAL
DICHALCOGENIDES ENHANCED BY PLASMONIC
NANOSTRUCTURES**

WANG ZHUO

(B.Sc. SICHUAN UNIV, M.Eng. SICHUAN UNIV)

**A THESIS SUBMITTED
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY**

**NUS GRADUATE SCHOOL FOR INTEGRATIVE
SCIENCES AND ENGINEERING
NATIONAL UNIVERSITY OF SINGAPORE
&
PHYSICS DEPARTMENT
IMPERIAL COLLEGE LONDON**

SUPERVISORS:

PROFESSOR ANDREW T. S. WEE (MAIN SUPERVISOR)
ASSOCIATE PROFESSOR QIU CHENG-WEI
PROFESSOR STEFAN A. MAIER (IMPERIAL COLLEGE LONDON)
ASSOCIATE PROFESSOR JOEL K. W. YANG (IMRE AND SUTD)

EXAMINERS:

PROFESSOR WU YI-HONG
DR. RUPERT OULTON (IMPERIAL COLLEGE LONDON)
ASSOCIATE PROFESSOR XIAODONG-XU (UNIVERSITY OF
WASHINGTON)

2017

DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis. This thesis has also not been submitted for any degree in any university previously.

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives license. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the license terms of this work.



WANG ZHUO
30 November, 2017

ACKNOWLEDGEMENTS

I sincerely appreciate my supervisors Profs. Andrew Wee, Cheng-Wei Qiu, Stefan Maier and Joel Yang for their insightful guidance in my PhD study. I would like to especially express my gratitude to Prof. Wee who has always shown his confidence and belief in my research work, and Prof. Qiu for standing by my side whenever I needed his help and for training me as a qualified researcher. I would also like to express my appreciation to Prof. Maier whose highly efficient and conscientious working style has inspired me a lot as a researcher, and to Prof. Yang whose devotion to scientific research has impacted me in a positive manner. Besides, I am also grateful to my thesis advisory members Prof. Wei Chen and Prof. Yihong Wu for making sure that my research and thesis have progressed reasonably well.

I am in debt to Dr. Zhaogang Dong for patiently guiding me in terms of designing experiments and writing manuscripts, and Dr. Lei Wang for measuring transient absorption spectra. My thanks also go to my important collaborators Prof. Goki Eda, Prof. Lain-Jong Li, Prof. Qinghua Xu, Prof. Huiying Yang, Dr. Yinghong Gu, Mr. Hai Zhu, Miss. Lei Jin Dr. Yung-Huang Chang and Mr. Junyong Wang who have provided research facilities or practical assistance in the experimental/simulation part of my thesis. I should never forget to thank my seniors Prof. Dacheng Wei, Prof. Wenjing Zhang, Prof. Yumeng Shi, Dr. Gustavo Grinblat and Prof. Lei Zhang who taught me through all the required experimental and simulation techniques, as well as to my friends Mr. Junyou Tan, Dr. Yuli Huang, Mr. Shengtao Mei, Mr. Zhibo Song, Mr. Yujie Zheng, Dr. Cheng Han, Dr. Shunfeng Wang, Dr. Shisheng Li, Mr. Qi Zhang and Dr. Ivan Verzhbitskiy with whom I often discussed physics problems.

On a personal note, I am grateful to my parents and grandparents for their selfless love, strict requirements and high expectations on me. After all these years, these have driven me to become a responsible and valuable person. Last but not the least, I acknowledge NGS for offering me a decent scholarship via which I have the privilege to have enjoyed this wonderful PhD program jointly hosted by two prestigious universities, and Center for Advanced 2D materials for providing many excellent experimental facilities.

LIST OF PUBLICATIONS

1. **Z. Wang**, Z.G. Dong, Y.H. Gu, Y. H. Chang, L. Zhang, L.J. Li, W.J. Zhao, G. Eda, W.J. Zhang, S. A. Maier, J. K. W. Yang, C.W. Qiu and A.T. S. Wee. Giant Photoluminescence Enhancement in WSe₂-Gold Plasmonic Hybrid Structures. *Nat. Commun.* 7, 11283 (2016). (IF:11.3).
 2. L. Wang, **Z. Wang**, H.Y. Wang, Y.L. Huang, D. Wang, X.H. Ye, X.B. Li, A.T.S. Wee, S.A. Maier, Q.D. Chen, M.L. Zhong, C.W. Qiu, and H.B. Sun. Slow C-exciton Relaxation and Effective Hot-Carrier Extraction in Molybdenum Disulphide Monolayers. *Nat. Commun.* 8, 13906 (2017) (IF:11.3, **Author with equal contribution**).
 3. We.J. Zhang, Q.X. Wang, Y. Chen, **Z. Wang**, A.T. S. Wee. Van der Waals Stacked 2D Layered Materials for Optoelectronics. *2D Mater.* 3, 022001 (2016). (IF: 9.61)
 4. **Z. Wang**, Z.G. Dong, H. Zhu, L. Jin, M.H. Chiu, L.J. Li, Q.H. Xu. G. Eda, S.A. Maier, J.K.W. Yang, C.Q. Qiu, A.T.S. Wee. WSe₂-Mediated Gap-Plasmon Nonlinear Mirror. (In submission)
- During my master
5. **Z. Wang**, D.Q. Xiao, J.G. Wu, M. Xiao, F.X. Li and J.G. Zhu. New Lead-Free (1-x)(K_{0.5}Na_{0.5})NbO₃-x(Bi_{0.5}Na_{0.5})ZrO₃ Ceramics with High Piezoelectricity. *J. Am. Ceram. Soc.* 97 (3), 688-690, (2014). (IF: 2.79, Top journal in ceramics)
 6. **Z. Wang**, J.G. Wu, M. Xiao, D.Q. Xiao, T. Huang, B. Wu. Phase Transition and Electrical Properties of (1-x)K_{0.5}Na_{0.5}NbO₃-xBi_{0.5}Na_{0.5}ZrO₃ Lead-Free Piezoceramics. *Ceram. Int.* 40 (7), 9165-9169, (2014).
 7. **Z. Wang**, Y.Q. Zhuo, D.Q. Xiao, W.J. Wu, C. Zhang, X.L. Huang and J.G. Zhu. Ferroelectric Properties of Rare-Earth Oxides Doped (K_{0.4}Na_{0.6})_{0.95}Li_{0.05}(Nb_{0.95}Sb_{0.05})O₃ Lead-Free Piezoceramics. *Curr. Appl. Phys.* 11, S143-S148, (2011).
 8. **Z. Wang**, D.Q. Xiao, J.G. Wu, W.F. Liang, W.J. Wu, T. Huang and J.G. Zhu. Enhanced Electrical Properties of Bi₄Ti₃O₁₂-Modified (K_{0.5}Na_{0.5})NbO₃ Lead-free Piezoceramics. *Ferroelectr.* 458 (1), 188-193 (2014)
- Chinese Patents
9. D.Q. Xiao, **Z. Wang**, F.X. Li, J.G. Wu, J.G. Zhu and P. Yu, (K,Na)NbO₃-(Bi,Na)(Zr,Ti)O₃ Lead-Free Piezoelectric Ceramics. (ZL 2013 1 0200214.9)
 10. D.Q. Xiao, **Z. Wang**, M. Xiao, J.G. Wu, J.G. Zhu and P. Yu, (K,Na)NbO₃-(Bi,K,Li)(Zr,Ti)O₃ Lead-Free Piezoelectric Ceramics. (ZL 2013 1 0198923.8)

TABLE OF CONTENTS

DECLARATION.....	ii
ACKNOWLEDGEMENTS	iii
LIST OF PUBLICATIONS	v
TABLE OF CONTENTS	vi
ABSTRACT.....	ix
LIST OF FIGURES	xi
LIST OF TABLES	xxi
LIST OF ABBREVIATIONS	xxii
Chapter 1 Introduction and literature review.....	1
1.1 Background of 2D TMDCs	2
1.1.1 Crystal structure.....	2
1.1.2 Electronic band structure	3
1.2 Light-matter interactions in 2D TMDCs	4
1.3 PL of 2D TMDCs.....	8
1.3.1 Physics of PL	8
1.3.2 PL enhancement methods	10
1.3.3 Interaction between light, plasmonic nanostructures and TMDCs..	14
1.3.4 Other factors influencing PL	17
1.4 SHG of 2D TMDCs.....	20
1.4.1 Basic concept of SHG.....	21
1.4.2 Motivation for SHG spectroscopy	25
1.4.3 Methods to improve SHG	30
1.5 Photocarriers of TMDCs	33
1.5.1 Physics and applications of photocarriers	34
1.5.2 Ultrafast spectroscopy	36
1.5.3 Pump-probe studies of TMDCs	38
1.6 Objective and scope of this thesis	40
1.7 References	42
Chapter 2 Fabrication and characterization techniques.....	45
2.1 Preparation of 2D materials.....	45
2.1.1 Growth of TMDCs.....	45
2.1.2 Growth of graphene	47
2.2 Transfer techniques	48
2.3 Fabrication of metal nanostructures	49

2.4 Optical characterization.....	51
2.4.1 PL and Raman	51
2.4.2 SHG spectroscopy	53
2.4.3 Reflectance spectroscopy	54
2.4.4 Transient absorption spectroscopy	56
2.5 Characterization of morphology.....	61
2.5.1 AFM.....	61
2.5.2 SEM.....	62
2.6 Scanning tunneling macroscopy.....	62
2.7 References	62
Chapter 3 Giant PL Enhancement in WSe₂-Gold Plasmonic Hybrid Structures.....	64
3.1 Introduction	64
3.2 Experimental and simulation methodology.....	65
3.2.1 Growth and transfer of WSe ₂	65
3.2.2 Characterizations	67
3.2.3 Numerical simulation method	68
3.3 WSe ₂ -plasmonic hybrid nanostructures.	69
3.4 Observation of PL enhancement in WSe ₂	70
3.5 PL enhancement mechanism.....	73
3.6 Polarization dependence of PL emission	80
3.7 Discussion	82
3.7 Summary	83
3.8 References	84
Chapter 4 Enhanced Second Harmonic Generation	87
of WSe₂ by Metasurfaces.....	87
4.1 Introduction	87
4.2 Methods.....	89
4.2.1 Material growth and quality of WSe ₂	89
4.2.2 Fabrication of gold substrate and transferring of WSe ₂	90
4.2.3 Characterization.....	90
4.2.4 Numerical simulations	90
4.3 Results and discussion.....	92
4.3.1 Hybrid structure and characterization facility	92
4.3.2 Giant SHG enhancement	94
4.3.3 SHG enhancement mechanism and position	99
4.4.4 Influence of crystal and trench orientation	102

4.5 Summary	106
4.6 References	107
Chapter 5 Slow Cooling and Efficient Extraction of.....	109
C-Exciton Hot Carriers in MoS₂ Monolayer.....	109
5.1 Introduction	109
5.2 Preparation of 2D materials.....	112
5.2.1 Growth and transfer of graphene film	112
5.2.2 Growth and transfer of MoS ₂ film.....	114
5.2.3 Characterization setup	115
5.3 Theoretical calculations.....	116
5.4 Steady-state optical characterization.....	117
5.5 Electronic bandgap measurement and transient experiment.....	118
5.6 Free-carrier relaxation feature for C-exciton hot carriers	126
5.7 Initial extraction process for C-exciton hot carriers.....	128
5.8 Discussion	130
5.9 Summary	131
5.10 References	132
Chapter 6 Summary and outlook	135
6.1 Summary	135
6.2 Outlook.....	137
6.3 References	139
Appendices.....	140
Copyright Permission.....	140
Figures in Chapter 1 and 2.....	140
Figures and contents in Chapter 3	181
Figures and contents in Chapter 5	181

ABSTRACT

As a typical two dimensional (2D) materials system, transition metal dichalcogenides (TMDCs) such as tungsten diselenide (WSe_2) and molybdenum disulfide (MoS_2) have been demonstrated to be potentially useful building blocks for optoelectronic integrated circuits. However, being atomically thin limits light-matter interaction, resulting in low light-to-light or light-to-electron conversion efficiency. Hence, enhancing their light emission or photoelectron extraction efficiency are critical for integrating these materials in devices.

The first part of this thesis focuses on enhancing the linear light absorption and emission of WSe_2 by placement on sub-20-nm-wide gold trenches. We report a giant photoluminescence (PL) with an enhancement factor of 20,000 from monolayer WSe_2 over the trenches, due to enhanced absorption and Purcell factor by lateral gap plasmons confined in the trenches. This work paves a way towards plasmon-enhanced nonlinear optical properties, photodetectors and sensors of TMDCs.

The second part reports enhanced second harmonic generation (SHG) at 400 nm from monolayer WSe_2 over the trenches, owing to the intensification of local fields at the excitation wavelength induced by gap plasmons in the trenches. Furthermore, the trenches aligned in a single direction allows for dynamic tuning of the SHG amplitude from WSe_2 by selective excitation of the gap plasmon. This work demonstrates a practical approach for optimizing the nonlinear optical properties of TMDCs, which can be utilized to configure a tunable nonlinear light emitter.

Chapter 5 investigates the hot-carrier relaxation and extraction mechanisms in MoS₂, revealing the photo-electron conversion processes. We report a slower hot-carrier cooling for C-excitons in MoS₂ owing to favorable band alignment and transient excited-state Coulomb environment and demonstrate a high hot-carrier extraction efficiency (80%) in MoS₂ monolayer/graphene heterostructures. This work provides experimental and theoretical physics insights for the photo-electron conversion process in TMDCs.

LIST OF FIGURES

Figure 1.1 Structure of TMDC materials ⁵ . (a) Three-dimensional schematic representation of a typical MX_2 structure, with the chalcogen atoms (X) in yellow and the metal atoms (M) in grey. (b) Schematics of the structural polytypes: 2H (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination), 3R (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination) and 1T (tetragonal symmetry, one layer per repeat unit, octahedral coordination). The lattice constants a are in the range 3.1 to 3.7 Å for different materials. The stacking index c indicates the number of layers in each stacking order, and the interlayer spacing is ~ 6.5 Å. Figures reproduced with permission from: (a-b), ref. 5, © 2012 Nature Publishing Group.	3
Figure 1.2 Electronic band structure of TMDCs ⁶ . Top panel shows calculated band structure of bulk WSe_2 (a) and bulk MoS_2 (b). Bottom panel show band structure of monolayer WSe_2 (c) and monolayer MoS_2 (d). The arrows indicate the lowest energy transitions. Figures reproduced with permission from: (a-d), ref. 6, © 2012, EDP Sciences, SIF, Springer-Verlag Berlin Heidelberg.	4
Figure 1.3 Effects resulting from light-matter interactions in 2D TMDCs. Light-matter interactions lead to PL, SHG, photocarriers, thermal effects and so on.	4
Figure 1.4 Band structures and DOS of a TMDCs ⁸ . The arrows indicate the transitions corresponding to the first prominent peaks in the optical conductivity. Figure reproduced with permission from: ref. 8, ©2013 American Physical Society.	6
Figure 1.5 Optical response of 2D TMDCs. (a) Absorption (gray lines) and PL (color lines) spectra of single-layer semiconducting transition metal dichalcogenide crystals (MoS_2 , MoSe_2 , WS_2 , WSe_2) ⁹ . (b) SHG from WSe_2 ¹⁰ . (c) Schematic view of a photodetector ¹¹ and a photovoltaic cell. Figures reproduced with permission from: (a), ref. 9, © 2013, American Chemistry Society; (b), ref. 10. © 2015, Nature Publishing Group; (c), ref. 11, © 2013, Nature Publishing Group.	7
Figure 1.6 Coupled TMDCs–GaP cavity photonic devices ¹⁷ . (a) SEM image of the GP nanocavity before the transfer of MoS_2 monolayer. (b) Enhanced PL of monolayer MoS_2 at two cavity modes due to the Purcell effect. ϕ , polarization analyser angle with respect to the long edge of the cavity. Figures reproduced with permission from: (a-b), ref. 17, © 2013, American Institute of Physics Publishing LLC.	11
Figure 1.7 Coupled TMDCs–plasmonic nanostructures. (a,b) PL intensity of heterostructure of MoS_2 /silver discs ¹⁸ , and PL intensity of bare MoS_2 , bowtie array and bowtie- MoS_2 ¹⁹ , respectively. (c) Reflection curves of a representative silver discs plasmonic nanostructure that is used in (a). (d) Experimental $\Delta R/R$ spectra of bare MoS_2 , bowtie, and bowtie- MoS_2 system for three different samples ¹⁹ that are used in (b). Figures reproduced with permission from: (a,c), ref. 18, © 2015, American Chemical Society; (b, d), ref. 19, © 2015, American Chemical Society.	12
Figure 1.8 Coupled TMDCs–plasmonic nanostructure consisting of a silver nanocube over a gold substrate ²⁰ . (a) 3D illustration of the nanostructure, consisting of a silver nanocube over a gold substrate, separated by a monolayer of MoS_2 , HfO_2 and polymer layers. (b) PL spectra from a MoS_2 monolayer on	

a SiO ₂ /Si substrate (blue) and in the nanocavity (red) obtained using a diffraction-limited excitation spot. Figures reproduced with permission from: (a-b), ref. 20, © 2015, American Chemical Society.	13
Figure 1.9 Illustration of the localized surface plasmon effect on plasmonic nanostructures ²¹ . Gold nanoparticles are taken as an example. Figure reproduced with permission from: (a), ref. 21, © 2014, The Royal Society of Chemistry.	14
Figure 1.10 MoSe ₂ -spacer-antenna and the related optical properties ²² . (a) Schematic view of the system. (b) The excitation rate of the electric field of a plane wave in the characteristic points of the antenna (center with dark blue and a top-end corner with green), normalized to the intensity of a plane wave in a setup without the antenna. The illumination plane wave is polarized along the short axis of the antenna as indicated by the inset arrow. Quantum yield (c), PL enhancement (d) and radiative decay rate (e) enhancement for a dipole emitter placed above the center of the antenna and polarized parallel to its long (dark blue) or short (red) axis; the quantities were calculated also for the case where the dipole emitter was placed above the top-end corner of the antenna and parallel to its long (green) or short (light blue) axis. Figure reproduced with permission from: (a-e), ref. 22, © 2016, Nature Publishing Group.	16
Figure 1.11 PL is influenced by charge transfer, strain and suspension. (a) PL spectra of bilayer MoS ₂ flake as exfoliated (red) and after 2.0 nm Au deposition (black) ²³ . (b) The energy band diagram for MoS ₂ and Au ²³ . The direction of the arrow represents the transfer of electrons from MoS ₂ to Au after the contact is established ²⁴ . (c) Evolution of the Raman spectrum as monolayer MoS ₂ is strained from 0 to 1.6%. (d) PL spectra of monolayer MoS ₂ as it is strained from 0 to 1.8% ²⁴ . (e) Optical image of mono- and few-layer MoS ₂ crystals on a silicon substrate with etched holes ²⁵ . (f) PL image of the same samples in (e) ²⁵ . Figure reproduced with permission from: (a-b), ref. 20, © 2016, Nature Publishing Group; (c-d), ref. 24, © 2013, American Chemistry Society; (e-f), ref. 25, © 2010, The American Physical Society.	18
Figure 1.12 Summary of the factors influencing the PL of TMDCs integrated with metallic nanostructures and non-metallic nanocavities.	20
Figure 1.13 Effects of wavevector mismatch on the efficiency of SHG or SFG ³²	24
Figure 1.14 SHG intensity and SHG polarization of 2H and 3R-MoS ₂ ³¹ . (a) SHG intensity of 2H and 3R-MoS ₂ as a function of layer number. (b) Schematic of the crystal structure of 2H-MoS ₂ (two layer unit cell outlined in red) with the side projection showing the flipped orientation of each layer and the anti-parallel orientation of the SH dipoles. (c) Crystal structure of 3R-MoS ₂ (three layer unit cell outlined in red) with parallel SH polarization in each layer. Individual layers are identical to the 2H structure, however the unit cell and bulk crystal are noncentrosymmetric. Figures reproduced with permission from: (a-c), ref. 31, © 2016, Nature Publishing Group.	25
Figure 1.15 Crystal structure determined by SHG spectroscopy. (a) OM of the exfoliated MoS ₂ sample. A, B and C are folded bilayers ³⁶ . Scale bar: 2 μm. (b) SHG microscope images ³⁶ of the same region in (a). (c) Top views of atomic structures of the 2H, 2H-like (Mo), 2H-like (S), 3R-like and 3R bilayers, respectively ³⁶ . (d) SHG image of a polycrystalline monolayer of MoS ₂ ³⁷ . (e) The direct crystal orientation image shows the crystal orientations of the irregular-shaped polycrystalline aggregates ³⁷ . (f) Schematics show the flakes I	

and II are two crystals with opposite orientations, and flakes II and III have an orientation mismatch of $\sim 12^\circ$ ³⁷ . Figure reproduced with permission from: (a-c), ref. 36, © 2014, Nature Publishing Group; (d-f), ref. 37, © 2014, American Association for the Advancement of Science.	27
Figure 1.16 Schematic for SHG, 2-photon PL and 1-photon PL processes, and the related emission intensity as a function of pump or emission energy ³⁸ . (a) Schematic for SHG when 2 incident photons are resonant with the 2p state of the A exciton. (b) Results of SHG spectroscopy as a function of $2\hbar\omega$. (c) Schematic for 2-photon PLE. (d) 2-photon PLE intensity (left axis, black squares), and linear polarization (right axis, blue circles) as a function of $2\hbar\omega$. (e) Schematic for 1-photon PLE. (f) 1-photon PLE intensity (left axis, black squares), and linear polarization (right axis, blue circles) as a function of $\hbar\omega$. Figures reproduced with permission from: (a-f), ref. 38, © 2015 American Physical Society.	28
Figure 1.17 SHG enhancement in 2D TMDCs by nanostructures. (a) Schematic of WSe ₂ transferred on silicon photonic crystal ⁴³ . (b) Reflectivity of the higher order cavity modes before and after monolayer WSe ₂ transfer ⁴³ . (c) PL from WSe ₂ (black), SHG spectra from mode α (blue) and mode β (red) ⁴³ . (d) Schematic of the device structure formed by the dielectric mirror on a glass substrate and a silver mirror on a suspended membrane ⁴⁴ . (e) The measured voltage dependence of the total output SHG power enhancement factor normalized to a monolayer on glass substrate ⁴⁴ . (f) SHG signal generated from the MoS ₂ flake inside the cavity (red solid line) and on a glass substrate (blue solid line) ⁴⁴ . Figures reproduced with permission from: (a-c), ref. 43, © 2016 IOP Publishing Ltd; (d-f), ref. 44, © 2016 American Chemical Society.	31
Figure 1.18 Schematic view and band diagram of optoelectronic devices based on 2D TMDCs. (a) Schematic diagram of few-layer WS ₂ vertical photoconductor with graphene as top and back electrodes ² . (b) Schematic band diagram for the heterostructure as shown in (a) with a built-in electric field to separate the generated electron-hole pair ² . (c) Schematic illustration of the photodetector based on graphene/MoS ₂ stacked layers ⁴⁷ . (d) Schematic illustration of the photoelectron transfer process in as shown in (c) ⁴⁷ . Figures reproduced with permission: (a-b), ref. 2, © 2013, American Association for the Advancement of Science; (c-d), ref. 47, © 2014, Nature Publishing Group. ...	35
Figure 1.19 Carrier dynamics and transport properties revealed by pump-probe technique ⁷ . (a) Schematic view of the pump-probe technique applied on monolayer WSe ₂ . (b) The exciton lifetime (red squares, left axis) as a function of the pump fluence. (c) Differential reflection signal as a function of both the probe delay and the probe position measured from the monolayer WSe ₂ sample. Figures reproduced with permission from: (a-c), ref. 7, American Chemistry Society.	38
Figure 1.20 Energy and electron transfer verified by pump-probe technique ⁵¹ . (a) Schematic view of a hybrid composed of monolayer WS ₂ and Al disks. (b) Spectral cut at 500 fs from part (symbols) fit to a multiple-Gaussian function (solid line). (c) Schematic of the mechanism of energy transfer at the studied hybrid system. (d) Schematic of the proposed mechanism of charge transfer at the studied hybrid system. Figures reproduced with permission from: (a-d), ref. 51, © 2016, American Chemistry Society.	39

Figure 2.1 Schematic illustration for the growth of TMDCs by CVD method. (a-b) Schematic of the synthesis process of MoS ₂ by using precursors of MoO ₃ and S powers. The temperature control of S power is achieved by heating tape (a) or by putting it at an appropriate place nearby the furnace (b). (c) Schematic illustration for the synthesis of MoS ₂ layers by sulfurization of MoO ₃ film on c-face sapphire ⁴ . Figure reproduced with permission from: (c), ref. 4, © 2012, the Royal Society of Chemistry.	47
Figure 2.2 Photos of the furnaces (MTI Corporation) that were used to grow 2D materials. (a) The furnace was used to grow monolayer MoS ₂ . (b) The furnace was used to grow monolayer graphene.	48
Figure 2.3 Processes to transfer TMDCs or graphene on desired substrates. (a) Pictures showing the procedure to transfer as-synthesized MoS ₂ layer from a sapphire to a SiO ₂ /Si wafer ⁴ . (b) Schematic view of the transfer process of graphene ⁷ . Figure reproduced with permission from: (a), ref. 4, © 2012, the Royal Society of Chemistry.	48
Figure 2.4 Detailed illustration on the fabrication process of template-stripped gold substrates used in Chapter 3 (Left Panel) and Chapter 4 (Right Panel). (a, a') Spin coating of hydrogen silsesquioxane (HSQ) resist onto the silicon substrate. (b, b') Electron beam exposure of HSQ resist with the design pattern and NaOH/NaCl salty development of HSQ resist. (c, c') Silicon etching by inductively coupled plasma (ICP). (d, d') Residue HSQ resist mask sputtered away by reactive-ion etching (RIE) oxygen plasma. (e, e') Deposition of 150-nm-thick gold film by using e-beam evaporator. (f, f') Drop casting of optical adhesive (OA) glue onto the gold film and followed by a glass coverslip. OA glue is then cured by UV irradiation. (g, g')-(h, h') Template stripping process to fabricate the patterned gold nanostructures.	49
Figure 2.5 Optical setup of PL and Raman, and the related physics process. (a) Photo of a typical PL and Raman setup (WITec). (b) Light absorption and emission process. $\hbar\omega_0$ is the energy of the incident light, $\hbar\omega$ is the energy of the emitted light in the PL process. (c) Raman scattering process. $\hbar\omega_q$ is the energy of the emitted phonon.	52
Figure 2.6 Raman spectra of TMDCs. (a) Raman spectra of monolayer WSe ₂ taken with a laser under conventional geometry (VV) and cross polarization (VH) ¹⁰ . (b) Raman spectra of MoS ₂ with various thickness ¹¹ . Figure reproduced with permission from: (a), ref. 10, © 2014, Nature Publishing Group; (b), ref. 11, © 2015, American Chemical Society.	53
Figure 2.7 Comparison of SHG and PL processes. (a) Demonstration of the process related with SHG. (b) Demonstration of the process related with PL.	54
Figure 2.8 Photo of the CRAIC UV-VIS-NIR micro-spectrophotometer (model QDI 2010) used to measure reflectance spectra.	55
Figure 2.9 Pump-probe setup. A schematic view of a typical two colour pump-probe setup. Pump (red) comes from the Ti: sapphire oscillator. The continuum white light (silver) generated from the sapphire crystal (blue) is used as the probe.	56
Figure 2.10 Contributions in TA spectra. (a) Physics process of signal contributions in transient absorption spectroscopy ¹³ . Both the ground state bleaching (GSB) and the stimulated emission (SE) result in a negative change in absorbance $\Delta A < 0$. The excited-state absorption (ESA) and the absorption of a photoproduct (PA) give a positive signal $\Delta A > 0$. (b) Components comprising transient absorption spectrum: ground-state bleaching (dashed line), stimulated	

emission (dotted line), excited-state absorption (gray line), sum of these contributions (thick solid line)¹⁴. Figure reproduced with permission from: (b), ref. 13, © 2009, Photosynthesis Research, Springer.....57

Figure 2.11 | TA spectra¹⁵. (a) Decay-associated spectra (DAS) of the two lifetime τ_1 and τ_2 , and time course of absorption intensity for two detection wavelength λ_1 and λ_2 . (b) States-associated absorption (SAAS) and states-associated emission spectra (SAES) of the two-component system.....59

Figure 2.12 | Setup for morphology characterization. (a) Atomic Force Microscopy (FastScan, Bruker). (b) Field Emission Scanning Electron Microscopy (FEI Verios 460). 61

Figure 3.1 | Characterization results of WSe₂ on as-grown sapphire. (a) Optical microscope image of WSe₂ grown on sapphire. The scale bar is 10 μm . The black dots are nucleation points of WSe₂ in the growth process. (b) Raman and PL spectra of WSe₂ on sapphire as measured by 532-nm pump laser. The laser powers for measuring PL and Raman spectra were 110 μW and 450 μW respectively, and the corresponding integration times were 0.5 s and 15 s, respectively. 66

Figure 3.2 | PL signal of unpattern gold film and gold nanostructure without WSe₂. The pitches range from 60 to 200 nm. The PL signal measured by 532-nm (a) and 633-nm pump laser (b), respectively. 67

Figure 3.3 | Schematic of WSe₂-gold plasmonic hybrid structure with strong optical absorption. (a) Schematic of PL emission from a single crystal monolayer of WSe₂ flake on a gold substrate. Part of the triangular flake rests on the patterned region of the substrate consisting of sub-20 nm wide trenches. (b) Representative simulation of the electric field distribution of the lateral gap plasmons with a WSe₂ monolayer flake suspended over a single trench. The polarization of the incident laser field is across the gap. The dashed yellow line denotes the boundary between air and gold. The scale bar is 20 nm. (c) Representative Scanning electron micrograph (SEM) image of WSe₂ on square arrays with a trench width of 12 nm (Patterned) and unpatterned gold film (Unpatterned). The scale bars in the main figure and the inset are 1 μm and 100 nm, respectively. 69

Figure 3.4 | Characterization results of WSe₂-gold plasmonic hybrid structure. (a) SEM image of a WSe₂ flake on a patterned nanostructure with a pitch of 760 nm. “A” points to a portion of WSe₂ suspended above an intersection of two underlying trenches, while “B” corresponds to WSe₂ on unpatterned gold film. “C” points to a tear defect. The scale bar is 1 μm . (b) PL intensity (I) mapping of the WSe₂-gold plasmonic hybrid structure. A 532-nm pump laser was chosen for a fine PL mapping resolution. (c) PL spectra from A, B and as-grown WSe₂ on sapphire. The 532-nm laser power is 30 μW and integration time is 0.5 s. (d) Comparison of Raman spectra from WSe₂ on patterned and unpatterned gold film, and on sapphire. The pump laser is 532 nm with the power of 450 μW . The integration time was 15 s. 71

Figure 3.5 | Comparison of Lorentz-fitted PL spectra of WSe₂ on unpatterned gold (a) and on as-grown sapphire (b), respectively. PL spectra of monolayer WSe₂ (red curve) are fitted (black curve) with Lorentz functions and decomposed into exciton (blue curve) and trion (green curve) peaks. 72

Figure 3.6 | Optical characteristics of patterned gold nanostructures with different pitch sizes. (a) Relative reflectance spectra of patterned gold nanostructures with pitch sizes of 60 – 200 nm with respect to the unpatterned gold film. The solid and dashed curves present the experimental and simulated spectra, respectively. The dash dot line indicates the position of the pump laser of 633 nm. (b) Experimental (Exp.) and simulated (Sim.) resonance wavelength of the patterned gold nanostructures as a function of pitch size. (c) SEM images of the template-stripped gold nanostructures with respective pitch sizes. The inset numbers denote the pitch sizes in the unit of nm. The scale bars in the SEM images are 100 nm. 73

Figure 3.7 | Comparison of gold patterned nanostructure with pitches of 200 and 220 nm. Atomic force microscope (AFM) measurement results of nanostructured silicon templates with the pitch sizes of 200 nm (a) and 220 nm (b), and the corresponding height profile along the white dashed lines (c) and (d). (e) Experimentally measured relative reflectance spectrum with respect to unpatterned gold film for gold nanostructure substrates with the pitch sizes of 220 nm and 200 nm. (f) Simulated relative reflectance spectrum of gold patterned nanostructure with different trench depths (the pitch size is 220 nm). 74

Figure 3.8 | Photoluminescence spectra, near-field intensity enhancement, Purcell factor enhancement and PL enhancement of WSe₂ on patterned gold nanostructures with different pitch sizes. (a, b) PL spectra measured by 532-nm and 633-nm pump laser, respectively. (c, d) Simulated enhancement factor of the near-field intensity for the WSe₂ monolayer flake as placed on the trench region of the gold substrate compared to that on unpatterned gold film at the pump laser wavelength of 532 nm and 633 nm, respectively. This enhancement factor for the near-field intensity is denoted as “EF_{NF}”, which accounts for the excitation process. (e) Simulated enhancement factor for the Purcell factor at the PL emission wavelength of WSe₂ (750 nm) denoted as “EF_{PF}”, accounting for the emission process. 75

Figure 3.9 | Experimental PL enhancement factor (EF) (after correcting for the trench area fraction) and the simulated product of near-field enhancement factor (EF_{NF}) at the related excitation wavelength and Purcell factor enhancement factor (EF_{PF}) at the emission wavelength (750 nm). The excitation pump is 532-nm laser (a) and 633-nm laser (b), respectively. The data points and corresponding error bars are obtained, respectively, by calculating the mean value and standard error of PL EF based on ten experimental PL spectra for each nanostructure. The inset in (b) shows the PL mapping of a WSe₂ monolayer flake sited on patterned gold nanostructure with a pitch of 200 nm (on the left of the dashed line) and unpatterned gold film (on the right of the dashed line) under the illumination of 633-nm pump laser. The intensity value at each pixel was obtained by integrating the PL spectrum across the spectrum window of 700 – 820 nm. The solid line presents the shape of the flake and the dashed line presents the boundary of the patterned and unpatterned substrate. The laser power was 30 μW and integration time was 0.5 s. 77

Figure 3.10 | The method to calculate the PL enhancement factor of WSe₂ over the trench. (a, b) Comparison of PL spectrum of WSe₂ on pitch 200 nm and on unpatterned gold measured by 633-nm laser. The PL peak energy and full-width at half-maximum (FWHM) in (a) are 1.64 eV and 65 meV respectively, while the corresponding values in (b) are 1.62 eV and 101 meV. The pump laser power

was 30 μW and integration time was 0.5 s. (c) Diagram showing the area of multiple trenches perpendicular to the polarization direction of the laser within a laser spot. The trench parallel to the polarization direction of the laser is not shown for simplicity. The white arrow denotes the polarization direction of the laser and the red circle represents the laser spot. A denotes the pitch size and W denotes the trench width. The dashed lines illustrate how Pythagorean theorem was used to calculate the length of the trenches. 78

Figure 3.11 | Polarization-dependent characteristics of PL emission from WSe_2 flake on gold nanostructures with a pitch size of 920 nm and a pump laser of 532 nm. (a) SEM image of WSe_2 flake on the gold nanostructures. The white dashed circles denote the region, where the trenches in the gold film intersect and the dashed square denotes the center of the square region. (b, c) Simulated electric field distribution at a plane 1 nm above the surface of patterned gold nanostructures with 0-degree and 45-degree polarizations, respectively. (d, e, f) Corresponding PL intensity mappings with polarization angles of 0, 45 and 90 degrees, respectively. The intensity value at each pixel was obtained by integrating the PL spectrum across the spectrum window of 700 – 820 nm. The white arrows show the polarization directions of the pump laser. (g, h) PL and Raman spectra of WSe_2 taken at the intersection of gold trenches and square center, respectively. All the scale bars are 1 μm . The laser power and integration time for measuring PL (Raman) is 30 μW and 0.5 s (450 μW and 15 s). 80

Figure 3.12 | Power dependence of monolayer WSe_2 PL spectra from patterned gold nanostructures. (a) and unpatterned gold film (b), by varying pumping power of 532-nm laser. The integration time in PL measurements was 0.1 s. PL FWHM and peak energy of WSe_2 on the patterned gold substrates (c) and on the unpatterned gold film (d), as a function of laser power. PL peak intensity and integrated intensity of WSe_2 on the patterned gold nanostructures (e) and on the unpatterned gold film (f), as a function of laser power. 83

Figure 4.1 | Characterization results of WSe_2 on sapphire, flat gold and the metasurface. (a) Optical microscope image of WSe_2 grown on sapphire. (b-c) Raman, PL and SHG mappings of a triangular-shape WSe_2 on sapphire. The intensity value at each pixel for PL mapping was obtained by integrating the PL spectrum across the spectrum window of 700 – 820 nm, for Raman is the spectrum window of 245 – 265 cm^{-1} and for SHG is the peak intensity at 400 nm. The PL and Raman were measured by 532-nm CW laser, and SHG was measured by 800-nm fs laser. (e-g) Comparison of PL, Raman and SHG spectra from WSe_2 on different substrates. 89

Figure 4.2 | Height of the ridges on silicon template. AFM measurements of patterned silicon template with pitch sizes of 170 nm (a) and 910 nm (b), and the associated height profile along the white dashed lines (c) and (d). 91

Figure 4.3 | Schematic of second-harmonic generation (SHG) from monolayer WSe_2 flake on a gold substrate. Part of the flake was on the metasurface consisting of sub-20-nm-wide trenches and the rest on flat gold film. (b) Representative scanning electron micrograph (SEM) image of WSe_2 on metasurface with a trench width of 16 nm (Metasurface) and flat gold film (Flat gold). (c) Optical setup for measuring SHG mappings and SHG spectra. This fundamental-wave (FW) laser was linearly polarized via a polarizer. Then it was reflected by a dichroic mirror (Semrock, FF750-SDiO2-25 $\times$ 36) and focused on

the sample through a 100 $\times$ air objective with a numerical aperture (NA) of 0.90 (Nikon, Ti-U inverted microscope, TU Plan Fluor). The sample was mounted on a piezo-actuated 3D nanopositioning stage (Physik Instrumente, P545.2R7). The generated second-harmonic wave (SHW) was then back collected by the same objective and passed through the dichroic mirror. Next, the SHW went through a short pass filter (Laser 2000, FF01-750/SP-25) that was used to completely filter out the FW laser. Finally, a flip mirror was used to redirect the SHW to either a photomultiplier tube (PicoQuant, PMA 182) for SHG mapping or a spectrometer (Princeton Instruments, 2300i) for spectrum measurement.⁹²

Figure 4.4 | Large SHG enhancement observed in WSe₂ on metasurface. (a) SEM image of WSe₂ flakes on gold metasurface (dark grey) and on flat gold film (grey). The white dashed square shows the region of metasurface. The colour of gold substrate without WSe₂ is light grey. (b) Reflectance spectra of gold metasurface (M) and flat gold film (F) under the illumination of white light polarized parallel (x) and perpendicular (y) to the trenches orientation. (c-d) SHG peak intensity mapping of WSe₂ on gold metasurface (A/A') and flat gold film (B and B') under resonant excitation and non-resonant excitation, respectively. The pump laser is 800 nm with power on the sample of 0.5 μ W. (e-f) SEM image (e) of metasurface with and without WSe₂, and the related SHG mapping (f).....96

Figure 4.5 | Quantitative comparison of SHG intensity. (a) Representative SHG spectra of Points A, A', B and B' as shown in SHG mappings. (b) SHG intensity with an error bar of WSe₂ on metasurface and on flat gold film. 98

Figure 4.6 | SHG enhancement mechanism. (a) Lattice structure of single crystalline monolayer WSe₂ with triangular shape. a and b are principle axes in the monolayer plane in the crystal coordinates (a , b , c), where a corresponds to a zigzag direction, b corresponds to an armchair direction that has a mirror plane symmetry and c is the out-of-plane 3-fold rotation axis. (b) Simulation of the electric field distribution of the lateral gap plasmons with a WSe₂ monolayer flake being suspended over a single trench with a width of 18 nm and a pitch of 170 nm. The polarization of the incident laser field is across the gap. The dashed yellow line denotes the boundary between air and gold. 100

Figure 4.7 | SHG enhancement positions. (a) SEM image of single-crystalline monolayer WSe₂ flake on metasurface with a pitch size of 910 nm. We purposely chose the large pitch size here so that the SHG emission from the neighbouring trenches could be spatially resolved. (b) Simulated electric field distribution at a plane 1 nm above the surface of metasurface with pump polarization perpendicular (left panel) and parallel (right panel) to the trench. The short dot line denote the geometry of the trench. (c-d) SHG mappings of WSe₂ flake on metasurface as shown in the SEM image under resonant excitation and non-resonant excitation, respectively. The white dashed lines outline the borders of the WSe₂ flake. The white arrows show the polarization directions of the pump laser. 102

Figure 4.8 | Influence of crystal and trench orientation (a) SEM image of WSe₂ flake on flat gold film (I) and metasurface (II). White dashed line denotes the region of the investigated WSe₂ flake with the armchair directions denoted by blue dashed arrow. a and b are principle axes in the monolayer plane in the crystal coordinates. x and y are from laboratory coordinates (x , y , z), where x is perpendicular to y , y corresponds to the polarization of pump laser. The SHG components detected parallel to the polarization of pump laser, *i.e.*, $\mathbf{E}_\omega // \mathbf{E}_{2\omega}$.

θ is the rotate angle of the sample. θ_0 is the initial angle between the b and $\mathbf{E}_\omega$. The yellow bar denotes the orientation of the trench. (b-c) Polar plot of the normalized SHG intensity from I and II, respectively. The black squares are experimental data which are fitted by red curve according to the symmetry analysis in the text. The blue triangle with white dashed arrow are used to denote the crystal orientation. (d-e) Normalized SHG intensity from I and II as a function of laser power in log-log scale plot, respectively. (f) Normalized SHG intensity from I and II as a function of laser wavelength, respectively. The data points and corresponding error bars are obtained, respectively, by calculating the mean value and standard deviation of the SHG peak amplitude based on 10 spectra for each regions. 104

Figure 5.1 Properties of graphene grown on copper. (a) OM of graphene grown on copper. (b) Raman spectrum of graphene grown on copper.	112
Figure 5.2 Properties of graphene transferred onto quartz. (a) Optical microscope image of graphene on quartz under 100 $\times$ objective. (b) Raman spectrum of graphene on quartz. (c) G peak (1562–1640 cm^{-1}) mapping of graphene on quartz. (d) 2D peak (2638–2739 cm^{-1}) mapping of graphene on quartz.	113
Figure 5.3 Characterization of MoS ₂ on Si wafer. (a) Optical microscope image of MoS ₂ on quartz under 100 $\times$ objective. (b, c) PL and Raman of MoS ₂ on Si wafer.	115
Figure 5.4 Characterization of MoS ₂ transferred onto quartz. (a) Optical microscope image of MoS ₂ on quartz under 100 $\times$ objective. (b) AFM height profile of MoS ₂ on quartz. (c) Cross-sectional profile along the red line in (b).	115
Figure 5.5 Influence of graphene on the electronic bandgap of MoS ₂ monolayer. (a) Optical microscope and AFM images of MoS ₂ monolayer/graphene heterostructure. The scale bar is 2 μm . (b) Theoretically predicted energy band structure corresponding to the direct transitions in the momentum space of MoS ₂ monolayers considering the spin-orbit coupling. E_g , energy gap; E_b , exciton binding energy. The green area is the band nesting region. The vertical brown, pink, and purple arrows in b represent the optical transitions of A/B/C-exciton, respectively. (c) Steady-state absorption spectra of graphene, MoS ₂ monolayer, and MoS ₂ monolayer/graphene heterostructure. The orange solid line is the PL spectrum of MoS ₂ monolayer under 532 nm excitation. (d) STS spectra for MoS ₂ monolayer and MoS ₂ monolayer/graphene heterostructure. (e) Sketch of electronic and optical bandgaps for MoS ₂ monolayer (bottom figure). The top image illustrates the MoS ₂ monolayer (sky blue solid sphere represents the Mo atom, and yellow solid sphere represents the S atom); brown, pink, and purple spheres represent the A/B/C-exciton, respectively; the orange curves represent the hot-carrier cooling and diffusion processes. (f) Sketch of electronic and optical bandgaps for MoS ₂ monolayer/graphene heterostructure (bottom figure). The top illustration schematizes the MoS ₂ monolayer/graphene heterostructure (black solid sphere represents the C atom); the red arrows indicate the vertical electron extraction processes. E_{opt} , optical bandgap.	117

Figure 5.6 DFT calculation of the projected band structure (left) and density of states (right) of MoS ₂ -graphene heterostructure. The blue dots (left figure) represent the contribution of carbon atoms in graphene.	120
Figure 5.7 Global fitting for transient absorption spectra of MoS ₂ monolayers. (a) Transient absorption spectra of MoS ₂ monolayers probed at different delay times under 400 nm excitation (pump density of 5 $\mu\text{J cm}^{-2}$, initial exciton density of $1.28 \times 10^{12} \text{ cm}^{-2}$). (b) Global analysis for the transient absorption data in a. The vertical dashed line indicates the position of the C-exciton state, while the horizontal dashed line indicates $\Delta O.D. = 0$. (c) Normalized decay dynamics of A-, B-, and C-exciton states under the pump condition in (a). The red solid lines are the global fitting results. (d) Normalized decay dynamics of the C-exciton state under 400 nm, 600 nm and 650 nm excitation with similar initial exciton density. The solid lines are the global fitting results.	122
Figure 5.8 Transient absorption of bilayer graphene. (a) Photography of the twisted bilayer graphene on Si/SiO ₂ studied here. (b) Transient absorption spectra of the twisted bilayer graphene (blue line), and pure Si/SiO ₂ substrate (magenta line) probed at 0.2 ps under 400 nm excitation (300 $\mu\text{J cm}^{-2}$). The dot line indicates the spectrum probed at 0 ps. (c) The dynamics probed at 580 nm for the twisted bilayer graphene, and Si/SiO ₂ substrate.	123
Figure 5.9 Transient absorption spectra of MoS ₂ monolayer measured by 600 nm and 650 nm pump laser, respectively as well as their global analysis (a) Transient absorption spectra of MoS ₂ monolayers probed at different delay times under 600 nm excitation (initial exciton density of $1.27 \times 10^{12} \text{ cm}^{-2}$). (b) Transient absorption spectra of MoS ₂ monolayers probed at different delay times under 650 nm excitation (initial exciton density of $1.13 \times 10^{12} \text{ cm}^{-2}$). (c) Global analysis for the transient absorption data in panel (a). (d) Global analysis for the transient absorption data in panel (b).	124
Figure 5.10 Excitation-density dependent transient behaviours on MoS ₂ monolayers. (a) Transient absorption spectra of MoS ₂ monolayers probed at 0.36 ps under 400 nm excitation with different excitation power densities. (b) Reciprocal of decay traces of the C-exciton state (430 nm) under different excitation power densities, normalized at the minimum $\Delta O.D.$. ⁻¹ . Inset shows the traces in the main panel within the first 10 ps.	126
Figure 5.11 Initial carrier extraction in MoS ₂ monolayer/graphene heterostructure. (a) Transient absorption spectra of MoS ₂ monolayer/graphene heterostructures probed at different delay times under 400 nm excitation (initial exciton density of $1.73 \times 10^{12} \text{ cm}^{-2}$). (b) Global analysis for the transient absorption data in (a). The vertical dashed line indicates the position of the C-exciton state, while the horizontal dashed line indicates $\Delta O.D. = 0$. (c) Illustration of the photophysical processes in the MoS ₂ monolayer and initial charge transfer in the MoS ₂ monolayer/graphene heterostructure.	128
Figure 5.12 Decay dynamics of A-, B- and C-exciton state. (a), Normalized decay dynamics of A-, B-, and C-exciton state for MoS ₂ monolayer/graphene heterostructures under the pump condition in Fig. 5.11, panel a. A direct comparison for the exciton dynamics in the TA experiments of MoS ₂ with and without graphene substrate under 400 nm excitation. (b), (c) and (d) show, respectively, the normalized dynamics of A-, B- and C-exciton state. The red solid lines are the global fitting results.	130

LIST OF TABLES

Table 5.1 Femtosecond time-resolved TA dynamics parameters obtained by global fitting under 400 nm excitation.....	129
---	-----

LIST OF ABBREVIATIONS

2D	Two dimensional
TMDCs	Transition metal dichalcogenides
WSe ₂	Tungsten diselenide
MoS ₂	Molybdenum disulfide
MoSe ₂	Molybdenum diselenide
WS ₂	Tungsten disulfide
MX ₂	Stoichiometric formula of TMDCs
2H	Hexagonal symmetry, two layers per repeat unit
3R	Rhombohedral symmetry, three layers per repeat
1T	Tetragonal symmetry, one layer per repeat unit
Å	Angstrom
DFT	Density functional theory
PL	Photoluminescence
SHG	Second harmonic generation
GaP	Gallium phosphide
PPC	Planar photonic crystal
Eq.	Equation
TRPL	Time-resolved photoluminescence
TA	Transient absorption
CVD	Chemical vapor deposition
PMMA	Polymethyl methacrylate
HAuCl ₄	Chloroauric acid
VBM	Valence bands maximum
CBM	Conduction bands minimum

AFM	Atomic force microscopy
SEM	Scanning electron microscopy
LSPs	Localizes surface plasmons
SPPs	Surface plasmon polaritons
EF	Enhancement factor
WO ₃	Molybdenum oxide
HSQ	Hydrogen silsesquioxane
MIBK	Methyl isobutyl ketone
IPA	Isopropyl alcohol
NaOH	Sodium hydroxide
OA	Optical adhesive
EBL	Electron beam lithography
NaCl	Sodium chloride
HBr	Hydrogen bromide
RIE	Reactive-ion-etching
ICP	Inductively-coupled plasma
FDTD	Finite-difference time-domain
DI	Deionized
DOS	Density of state
OD	Optical density

Chapter 1 Introduction and literature review

Two-dimensional (2D) materials have impressive electrical, optical, thermal and mechanical properties originating from the atomically-thin nature thus attracting tremendous interest since the discovery of graphene. Among them, 2D semiconducting transition metal dichalcogenides (TMDCs) such as tungsten diselenide (WSe_2) and molybdenum disulfide (MoS_2) have been extensively studied owing to their relatively strong interaction with light in the visible spectral range as compared with graphene¹. The light-matter interaction in 2D TMDCs gives rise to intriguing optical and optoelectronic properties that can be utilized in ultrathin light-emitting devices or photodetectors². However, in absolute terms, the light-matter interaction is still weak, resulting in low light-to-light or light-to-electron conversion efficiency³. Fortunately, an integration of photonic nanostructures or other 2D materials provides a possible solution to this problem⁴. Hence, a comprehensive understanding of the physics of light-matter interactions and developing approaches to enhance light emission or photoelectron extraction efficiency are critical for applications in photonic or optoelectronic devices.

This chapter first provides a background on 2D TMDCs and a brief review of the physics of light-matter interactions, with elaboration on absorption, photoluminescence (PL), second harmonic generation (SHG) and photocarriers. Methods of improving optical properties by integration of photonic nanostructures or other 2D materials as well as a review of previous work are also discussed. At the end of the chapter, the objective and scope of the thesis are highlighted.

1.1 Background of 2D TMDCs

When TMDCs are one monolayer thick, their unique crystal symmetry and electronic band structure give rise to novel optical and optoelectronic properties that are absent in their bulk counterparts. In this section, we present the crystal and electronic band structure of 2D TMDCs, and their related physical properties.

1.1.1 Crystal structure

Monolayer TMDCs with MX_2 stoichiometry, where M is defined as a transition metal element (M= Mo, W, etc.) and X is defined as a chalcogen (X = S, Se, etc.), are composed of a layer of M atoms sandwiched by two layers of X atoms, as shown in Fig. 1.1a⁵. The monolayer is only several Ångströms thick resulting in quantum confinement in the out-of-plane direction. The quantum confinement leads to novel optical and electronic properties that are tunable by electric field, doping, strain and environment effects. Furthermore, the flexibility and lack of surface dangling bonds enable the 2D materials to be integrated with photonic structures or stacked with other 2D materials with different lattice constants. The stacking of monolayers forms the bulk crystal with polytypes of 2H, 3R or 1T that vary in stacking order and metal atom coordination, as shown in Fig. 1.1b. The phase determines the electronic and optical properties of TMDCs. For instance, the 2H-phase TMDCs are generally semiconducting, while 1T-phase TMDCs are generally metallic. The 2H monolayer phase has broken in-plane inversion symmetry, allowing second-harmonic emission, while SHG does not exist in the 1T phase with inversion center. In this thesis, we used the commonly available 2H-structure TMDCs,

since they are direct-bandgap semiconductors and have no inversion symmetry in the monolayer.

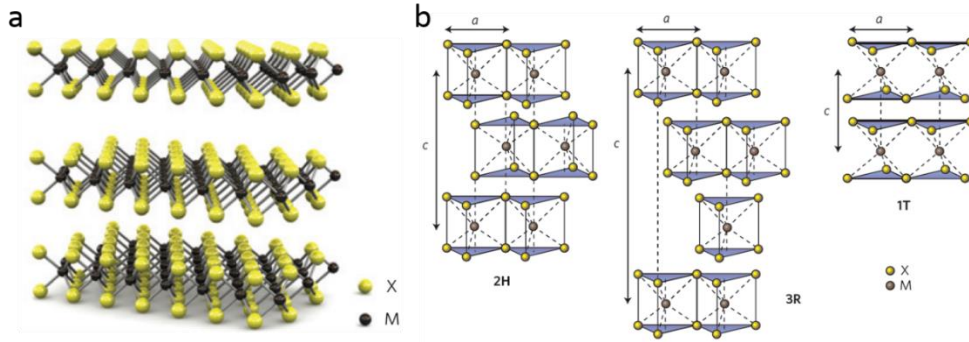


Figure 1.1 | Structure of TMDC materials⁵. (a) Three-dimensional schematic representation of a typical MX₂ structure, with the chalcogen atoms (X) in yellow and the metal atoms (M) in grey. (b) Schematics of the structural polytypes: 2H (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination), 3R (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination) and 1T (tetragonal symmetry, one layer per repeat unit, octahedral coordination). The lattice constants *a* are in the range 3.1 to 3.7 Å for different materials. The stacking index *c* indicates the number of layers in each stacking order, and the interlayer spacing is ~ 6.5 Å. Figures reproduced with permission from: (a-b), ref. 5, © 2012 Nature Publishing Group.

1.1.2 Electronic band structure

The applications of TMDCs in optical and optoelectronic devices rely on their electronic properties, such as band structure and density of states. TMDCs have sizable bandgaps that change from indirect in bulk to direct in monolayers, allowing applications such as light-emitters, transistors, photodetectors and electroluminescent devices. The bulk TMDCs such as WSe₂ and MoS₂ are indirect-bandgap semiconductors with conduction-band minimum at the *Q* point and valence-band maximum at the *Γ* point in reciprocal space (Fig. 1.2a-b). In the monolayer, they cross over to become direct-bandgap semiconductors with gaps located at the *K* and the degenerate *K'* points (Fig. 1.2c-d)⁶. All MX₂ compounds undergo a similar transition from indirect to direct bandgap with decreasing layer numbers, covering the bandgap energy

range of 1.1–1.9 eV. The discovery of direct bandgaps in TMDCs opens up the possibility of developing light-emitting devices and photodetectors.

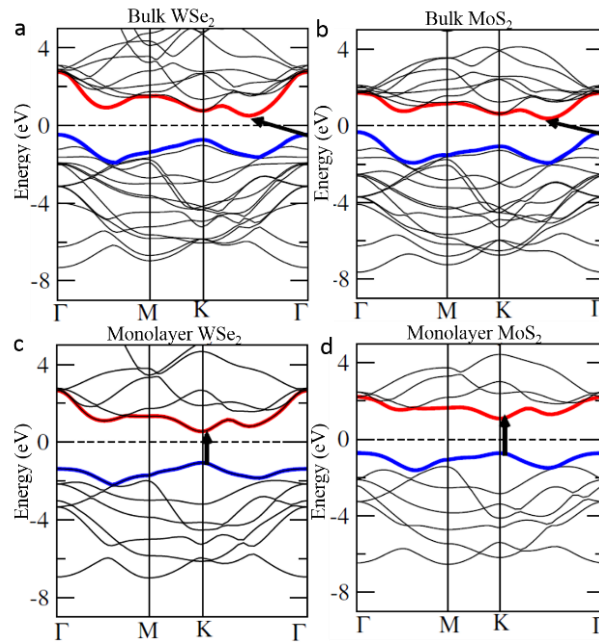


Figure 1.2 | Electronic band structure of TMDCs⁶. Top panel shows calculated band structure of bulk WSe₂ (a) and bulk MoS₂ (b). Bottom panel show band structure of monolayer WSe₂ (c) and monolayer MoS₂ (d). The arrows indicate the lowest energy transitions. Figures reproduced with permission from: (a-d), ref. 6, © 2012, EDP Sciences, SIF, Springer-Verlag Berlin Heidelberg.

1.2 Light-matter interactions in 2D TMDCs

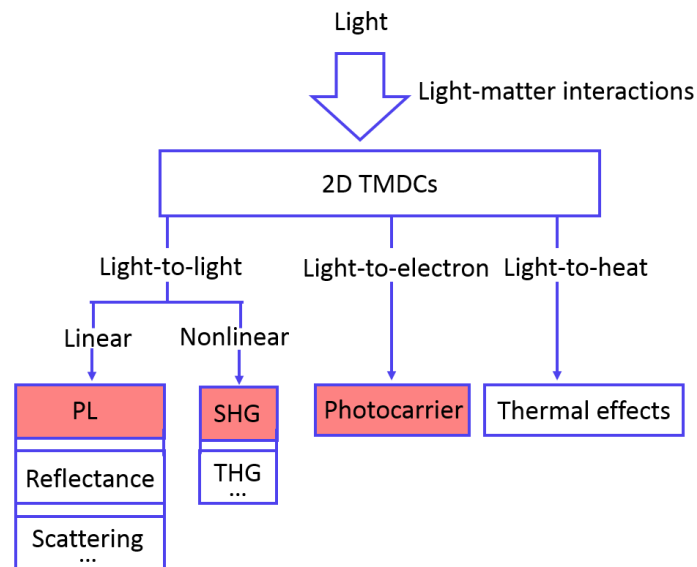


Figure 1.3 | Effects resulting from light-matter interactions in 2D TMDCs. Light-matter interactions lead to PL, SHG, photocarriers, thermal effects and so on.

The unique crystal symmetry and electronic band structure introduced above bring in novel optical and optoelectronic properties. These properties arise from light-matter interaction in TMDCs, i.e., when light is absorbed by 2D TMDCs, it undergoes light-to-light, light-to-electron and light-to-heat conversion processes, resulting in PL, Raman, SHG, photocarriers, thermal effects and so on (Fig. 1.3). This section will present physics process involved in light absorption, PL, Raman, SHG and photocarriers.

Monolayer TMDCs have absorption coefficients of more than $5 \times 10^7 \text{ m}^{-1}$ in the visible range after normalization to the corresponding atomic thickness, which is an order of magnitude larger than the absorption coefficients of GaAs and Si⁷. The enhanced light-matter interactions arises from the phenomenon of ‘band nesting’ in TMDCs which leads to enhanced photon absorption, according to A. H. Castro Neto’s DFT calculations⁸. As shown in the band structure of a TMDC (left panel of Fig. 1.4), band nesting refers to regions with conduction band and valence band parallel to each other. When the materials absorb a photon, the generated electrons and holes propagate with the same velocities but in opposite directions. As shown in the right panel of Fig. 1.4, these regions have van Hove singularities (VHS), leading to high electronic density of states, *i.e.*, the number of electrons per volume participating in the absorption process at a given energy is high.

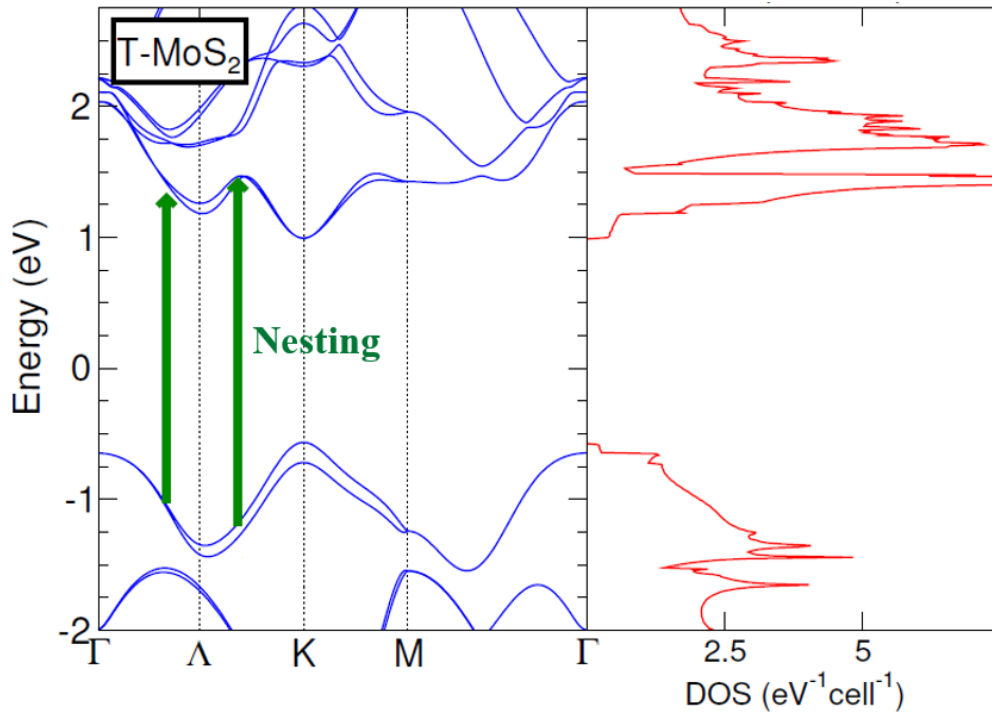


Figure 1.4 | Band structures and DOS of a TMDCs⁸. The arrows indicate the transitions corresponding to the first prominent peaks in the optical conductivity. Figure reproduced with permission from: ref. 8, ©2013 American Physical Society.

In the light absorption process, the band-to-exciton mechanism, *i.e.*, electrons in the valence band absorb sufficient energy to be excited to the conduction band, and the electrons and holes they leave behind remain electrically ‘bound’ together by binding energy, plays an important role in the absorption spectra of TMDCs. The binding energy accounts for the difference between electronic band gap and optical band gap. As shown in Fig. 1.5a⁹, the optical absorption spectra of monolayer TMDCs is dominated by direct transitions of electrons from the valence to conduction band near the K and K' points. Monolayer WSe₂ (MoS₂) can absorb nearly 10% of incident light at the exciton resonance wavelength 750 nm (650 nm) and even more strongly at shorter wavelengths where there are band nesting regions. Other TMDCs have similar spectral trends except that the resonances lie in different spectral regions.

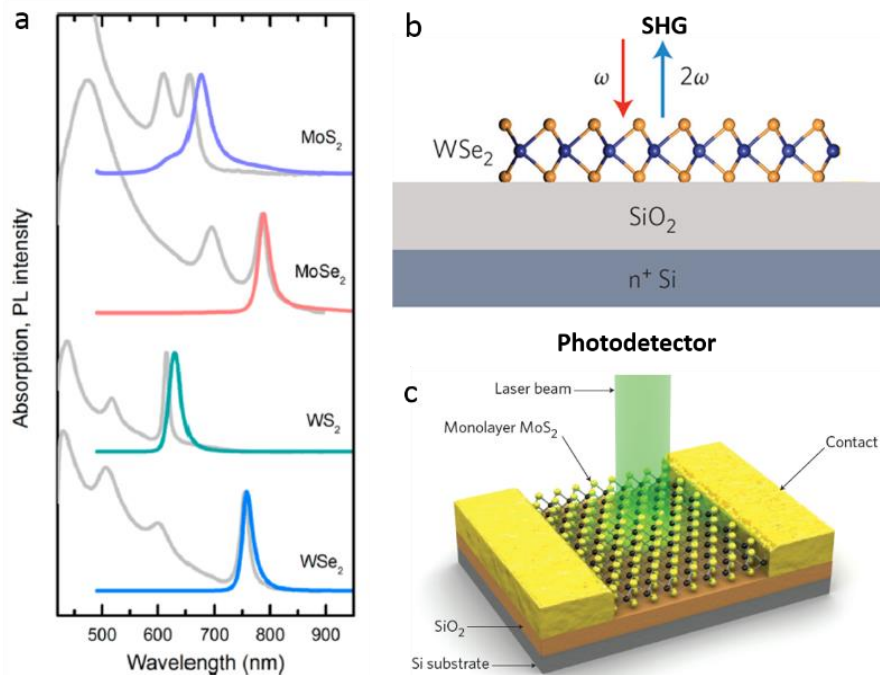


Figure 1.5 | Optical response of 2D TMDCs. (a) Absorption (gray lines) and PL (color lines) spectra of single-layer semiconducting transition metal dichalcogenide crystals (MoS₂, MoSe₂, WS₂, WSe₂)⁹. (b) SHG from WSe₂¹⁰. (c) Schematic view of a photodetector¹¹ and a photovoltaic cell. Figures reproduced with permission from: (a), ref. 9, © 2013, American Chemistry Society; (b), ref. 10. © 2015, Nature Publishing Group; (c), ref. 11, © 2013, Nature Publishing Group.

The electron-hole pairs bonded by the Coulomb force are called excitons. In addition to excitons, high-order excitonic quasiparticles such as trions (bound states of two holes and one electron or two electrons and one hole) have also been reported in TMDCs. The trion in 2D TMDCs has binding energy roughly an order of magnitude larger than those in conventional quasi-2D semiconductors, thus allowing them to be observed in the absorption spectrum even at room temperature. The behavior of excitons and trions has a strong influence on the optical properties in 2D TMDCs, including light absorption and emission.

The absorbed light in 2D TMDCs can be converted to optical and optoelectronic properties that are superior or complementary to those observed in the first discovered 2D material graphene. Graphene, a monolayer of carbon

atoms arranged in a honeycomb structure, is a gapless semimetal with excellent electron conductivity, making it a promising electrode material to collect electrons in electronic devices. However, the lack of bandgap in graphene and existence of inversion symmetry limit its application in light-emitting devices in the visible light range based on linear and nonlinear optical processes. In contrast, 2D TMDCs are direct-bandgap semiconductors and have inversion symmetry breaking when thinned down to a monolayer, thus possessing intriguing PL⁹ and SHG¹⁰ properties in the visible wavelength range, as shown in Fig. 1.5a-b. Furthermore, unlike graphene which interacts weakly with light in the visible light range, photon-sensitive TMDCs can convert visible light into hot carriers, facilitating its application as ultrathin photodetectors¹¹ and photovoltaic cells (Fig. 1.5c).

Although light-matter interactions in TMDCs are strong as compared with graphene, it is inherently weak in absolute terms because the optical absorption length is extremely short (<1 nm for monolayer). For practical optical and optoelectronic devices based on 2D materials, a key challenge is to maximize light-matter interactions in the materials and enhance the resulting properties of PL, SHG or photoelectron extraction efficiency. In order to optimize these properties, the related physics and progress in this field are reviewed in the following sections.

1.3 PL of 2D TMDCs

1.3.1 Physics of PL

Upon light illumination, electrons in the materials can be excited from the valence band to the conduction band. In the relaxation process, the excited electrons will decay to the ground states by two pathways: radiative (in the form

of photon emission) and nonradiative (*e.g.* in the form of phonon emission) processes. The radiative decay process involving absorption of light and subsequent emission of light with lower energy is defined as photoluminescence (PL). As shown in Fig. 1.5a, the absorption spectra and PL are correlated. For WSe₂ (MoSe₂), the absorption peak at wavelength of 750 nm (800 nm) corresponds well with the PL peak at this wavelength. In contrast, for MoS₂ (WS₂), the two peaks are shifted. The Stokes shift of peak position is attributed to the inhomogeneity of dielectric environment, which affects the surface interaction of monolayer MoS₂ (WS₂) and changes the binding energy of the excitons, *i.e.*, the electron-hole pair bounded by Coulomb force.

In TMDCs, the PL intensity is influenced by many factors including layer number, strain, and interfacial interactions such as charge transfer, photonic nanostructures, and so on. First, we discuss how the layer number of the material influences the electronic structure and optical properties. As WSe₂ has a higher quantum yield at room temperature than TMDCs such as MoSe₂, MoS₂, WS₂, we use it as the model system in this thesis. A systematic study of WSe₂ with different layer numbers was reported by Zeng et al¹². As WSe₂ thins to a few layers, the PL intensity from the direct interband transition drops and reaches a maximum at one monolayer, over 3 orders of magnitude higher than that from the bulk and nearly one order of magnitude stronger than the bilayer. This light emission behavior is fully consistent with the calculated band structure. In addition, an interesting ‘valley optical selection rule’ for PL of monolayer TMDCs is obeyed such that the circularly polarized component of PL signal has the same helicity as the excitation laser¹³⁻¹⁵. This can be used as a tool to identify the optical transition in the degenerate *K* and *K'* valleys. Details

about this valley selection rule is beyond the scope of the thesis, so it will not be discussed in detail.

1.3.2 PL enhancement methods

The direct bandgap in monolayer TMDCs leads to much stronger PL as compared with their few-layer and bulk counterparts, opening up the possibility of developing ultrathin light-emitting devices. However, the low light absorption of monolayer TMDCs in absolute terms and large nonradiative recombination rate of excitons that far exceeds the radiative recombination rate result in low PL efficiency (less than 10^{-2}), limiting their application in practical devices¹⁶. Fortunately, the integration of TMDCs with external photonic structures such as optical cavities and plasmonic nanostructures offers possible solutions. Particularly, integration with plasmonic nanostructures enables the significant manipulation of the near-field incident light and local optical density of states surrounding the 2D TMDCs, thus resulting in modified absorption/emission properties. Furthermore, this integration procedure is easily achieved, either by transferring 2D TMDCs on plasmonic or photonic nanostructures or patterning nanostructures on TMDCs, which will be discussed further in Chapter 2. The transfer method will not sacrifice their physical and chemical stabilities as the 2D membrane is flexible and has no dangling bonds.

Tuning the emission process

The coupling of 2D TMDs with optical cavities has been demonstrated to significantly enhance the PL of TMDCs. The first example was shown by Xuetao Gan and colleagues¹⁷. In their experiment, monolayer MoS₂ was transferred onto a planar photonic crystal (PPC) nanocavity made by semiconducting gallium phosphide (GaP) membrane with a cavity resonance

overlapping with the broad exciton resonance of monolayer MoS₂ (Fig. 1.6a). As shown in Fig. 1.6b, a PL enhancement of 5-fold in MoS₂ at the cavity with resonance mode (green) is obtained due to Purcell effect.

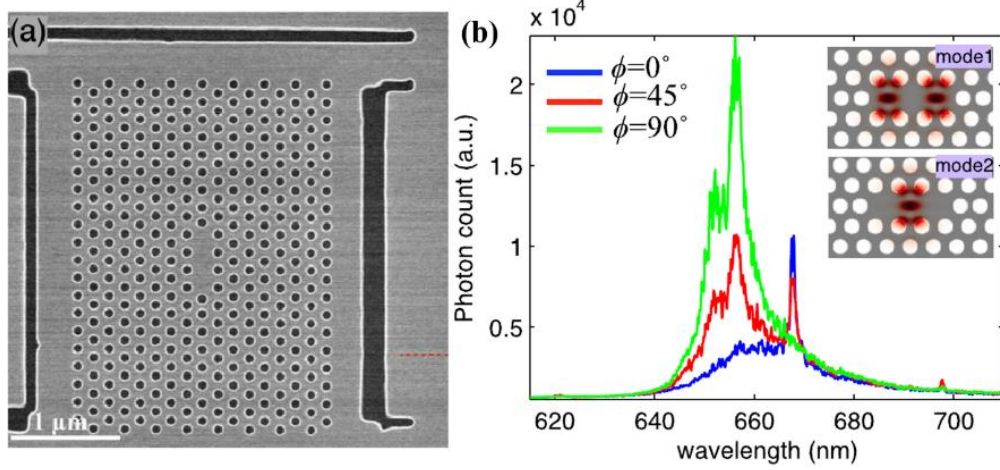


Figure 1.6 | Coupled TMDCs–GaP cavity photonic devices¹⁷. (a) SEM image of the GP nanocavity before the transfer of MoS₂ monolayer. (b) Enhanced PL of monolayer MoS₂ at two cavity modes due to the Purcell effect. ϕ , polarization analyser angle with respect to the long edge of the cavity. Figures reproduced with permission from: (a-b), ref. 17, © 2013, American Institute of Physics Publishing LLC.

The Purcell effect is the enhancement of spontaneous emission rate of a fluorescent molecule inside a cavity or resonator. Fermi's golden rule dictates that the emission rate is proportional to the density of final states, thus the enhancement originates from a larger density of final states of the nanocavity than that of free space (albeit the number of final states may be not). The enhancement magnitude is determined by the Purcell factor. One method to measure the Purcell factor is using the equation, $(3/4\pi^2)(Q/V_m)(\lambda_0/n)^3$, where Q , V_m , λ_0 and n denote the cavity quality factor, mode volume, resonance wavelength and refractive index of the substrate, respectively¹⁷. These high Q value and subwavelength V_m of a cavity or resonator, lead to enhancement in the emission rate. In numerical simulation, however, this method is not preferred as the definition of V_m depends on the structure, and the calculation

method is complex. Another equivalent but easier method is treating the fluorescent molecule as a dipole source and dividing the power emitted by the dipole source in the cavity or resonator by the power emitted by the dipole in free space since the emission rate is proportional to density of final states, and the density of final states is proportional to the power emitted by the source. In Chapter 3, we used the second method to simulate the Purcell factor with consideration of loss caused by gold absorption.

Combined excitation and emission enhancement

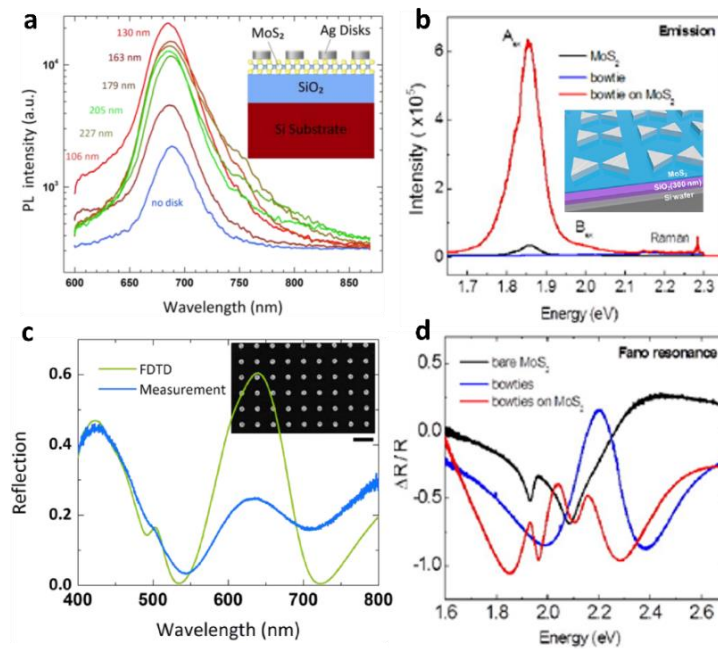


Figure 1.7 | Coupled TMDCs-plasmonic nanostructures. (a,b) PL intensity of heterostructure of MoS₂/silver discs¹⁸, and PL intensity of bare MoS₂, bowtie array and bowtie-MoS₂¹⁹, respectively. (c) Reflection curves of a representative silver discs plasmonic nanostructure that is used in (a). (d) Experimental $\Delta R/R$ spectra of bare MoS₂, bowtie, and bowtie-MoS₂ system for three different samples¹⁹ that are used in (b). Figures reproduced with permission from: (a,c), ref. 18, © 2015, American Chemical Society; (b, d), ref. 19, © 2015, American Chemical Society.

Further PL enhancement of 2D TMDCs has been obtained by designing metallic plasmonic nanostructures with multiple resonances. These resonances simultaneously couple to excitation and emission wavelengths, increasing the

light absorption owing to the excitation field localization and strengthening the light emission owing to increased scattering cross-section of the plasmonic nanostructures. As a result, PL is enhanced. Butun *et al.* demonstrated enhanced PL with an enhancement factor of 12 from monolayer MoS₂ by plasmonic silver nanodisc arrays (Fig. 1.7a) is achieved¹⁸. Lee *et al.* also demonstrated PL enhancement (over 15-fold) in MoS₂ using silver bowtie nanoantenna arrays (Fig. 1.7b)¹⁹. The plasmon resonances of these nanostructures can be identified from the reflectance spectra (Fig. 1.7 c and d).

Optimizing excitation, emission and collection efficiency

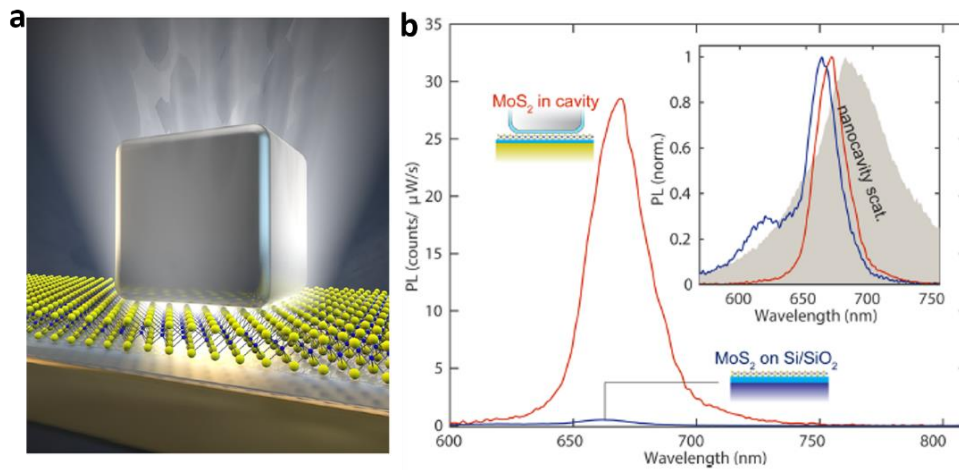


Figure 1.8 | Coupled TMDCs–plasmonic nanostructure consisting of a silver nanocube over a gold substrate²⁰. (a) 3D illustration of the nanostructure, consisting of a silver nanocube over a gold substrate, separated by a monolayer of MoS₂, HfO₂ and polymer layers. (b) PL spectra from a MoS₂ monolayer on a SiO₂/Si substrate (blue) and in the nanocavity (red) obtained using a diffraction-limited excitation spot. Figures reproduced with permission from: (a-b), ref. 20, © 2015, American Chemical Society.

The PL enhancement has been improved from several-fold to ~ 2000-fold by simultaneously optimizing light absorption, emission and collection efficiency²⁰. This large enhancement was obtained by integrating MoS₂ into a plasmonic nanostructure consisting of a silver nanocube over a gold film separated by a nanoscale dielectric spacer (<10 nm), as demonstrated in Fig.

1.8a and b. The resonance modes in the nanostructures aligned with quasi-particle gap and excitons, respectively, enable simultaneous enhancement of the absorption and the PL quantum yield. Furthermore, as the light emission from the nanostructures is directional with a single radiation lobe normal to the substrate, the light collection efficiency from MoS₂ with nanostructures is optimized thus increasing the total detected PL.

Interestingly, metallic plasmonic nanostructures have also been reported to quench the PL of TMDCs. To take full advantage of the metallic nanostructures in enhancing PL, we need to have an in-depth comprehension of the interaction between light, metallic plasmonic nanostructures and TMDCs so as to avoid or reduce possible quenching effects.

1.3.3 Interaction between light, plasmonic nanostructures and TMDCs

Excitation process

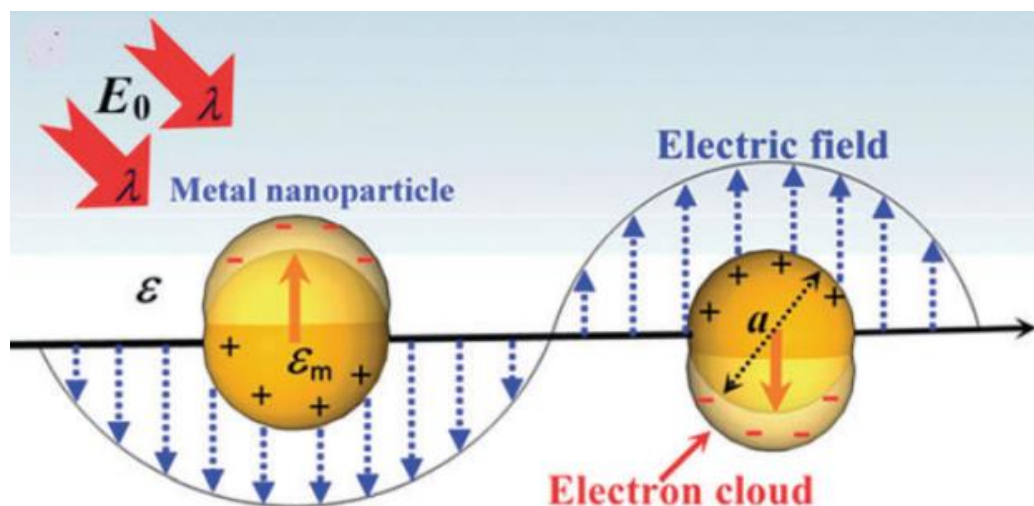


Figure 1.9 | Illustration of the localized surface plasmon effect on plasmonic nanostructures²¹. Gold nanoparticles are taken as an example. Figure reproduced with permission from: (a), ref. 21, © 2014, The Royal Society of Chemistry.

Light coupling with metallic plasmonic nanostructures can generate localized surface plasmons, collective oscillations of free electrons, resulting in

confined and enhanced fields at the edges or gaps of the nanostructures as compared to the excitation field (Fig. 1.9)²¹. This enhanced field works on TMDCs by enhancing the excitation rate of electron-hole pairs, so metallic plasmonic nanostructures always make a positive contribution on final PL emission in the excitation process.

Radiative emission

However, in the emission process, plasmonic nanostructures can cause not only PL enhancement but also quenching in TMDCs. We can understand the enhancement mechanism from two different but equally valid perspectives. The existence of plasmonic nanostructures near TMDCs increases the optical density of states, owing to the confinement of the emission field in the vicinity of the plasmonic nanostructures. This increases the radiative decay rate of the TMDCs due to the decrease in the modal volume, namely, the effective cavity where the mode is confined within, according to Purcell effect. The increase in radiative decay rate leads to a net increase in the emission intensity as shown previously. Another way to look at the enhanced emission is to treat plasmonic nanostructures as efficient antennas that radiate the emission in the far field in a more efficient way compared to the normal substrate, thus increasing the probability of far field emission for the TMDCs.

Nonradiative emission

Both PL enhancement and PL quenching are competing effects in plasmonic nanostructures. PL quenching occurs when nonradiative energy transfers from the exciton of TMDCs to the ‘dark’ surface plasmon mode of plasmonic nanostructures, which is an induced surface plasmon that dissipates this energy by absorption. This quenching process occurs via dipole-dipole

resonant nonradiative energy transfer that is highly sensitive to the donor-acceptor separation, dipole-dipole orientation, dipole moment strength of both the donor and the acceptor, and dipole-dipole resonance. For instance, if TMDCs are placed extremely close to plasmonic nanostructures, the non-radiative relaxation rates can dominate, sacrificing the advantage of the radiative decay rate enhancement of the plasmonic nanostructures. In weak pumping regime, these competing enhancement and quenching processes are quantified by the quantum yield η , $\eta = \Gamma_r / (\Gamma_{nr} + \Gamma_r)$, where Γ_r is the radiative and Γ_{nr} is the nonradiative decay rates.

Combined effects

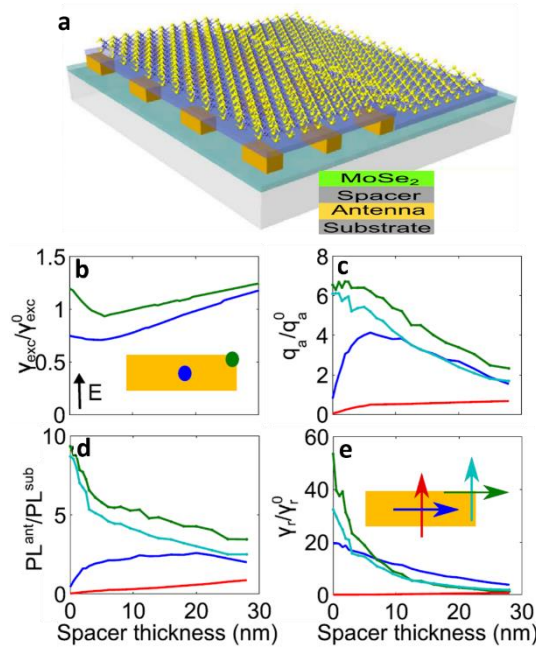


Figure 1.10 | MoSe₂-spacer-antenna and the related optical properties²². (a) Schematic view of the system. (b) The excitation rate of the electric field of a plane wave in the characteristic points of the antenna (center with dark blue and a top-end corner with green), normalized to the intensity of a plane wave in a setup without the antenna. The illumination plane wave is polarized along the short axis of the antenna as indicated by the inset arrow. Quantum yield (c), PL enhancement (d) and radiative decay rate (e) enhancement for a dipole emitter placed above the center of the antenna and polarized parallel to its long (dark blue) or short (red) axis; the quantities were calculated also for the case where the dipole emitter was placed above the top-end corner of the antenna and

parallel to its long (green) or short (light blue) axis. Figure reproduced with permission from: (a-e), ref. 22, © 2016, Nature Publishing Group.

PL modification is determined by a combined consideration of the excitation rate enhancement and the quantum yield. Chen *et al.* investigated the coupling between a MoSe₂ monolayer and gold antenna arrays (Fig. 1.10a)²², and provide a comprehensive analysis on the influence of spacer thickness on excitation rate (Fig. 1.10b), quantum yield (Fig. 1.10c), PL intensity (Fig. 1.10d), and radiative decay rate (Fig. 1.10e) of MoSe₂ with different dipole orientation and at different positions. They found that the excitation rate is not influenced much by spacer thickness due to the off-resonance excitation of the antenna, but the quantum yield varies a lot with spacer thickness. Therefore, the PL intensity in this case is determined by the quantum yield and can be manipulated from quenching to enhancement by changing the spacer thickness.

1.3.4 Other factors influencing PL

In addition to the plasmonics effects, there are many other factors such as charge transfer, strain, type of substrate and so on influencing the PL intensity of TMDCs. In the Au-MoS₂ hybrid system, Bhanu *et al.* reported PL quenching phenomenon (Fig. 1.11a) and attributed it to charge transfer from monolayer MoS₂ to gold nanoantennae via the Schottky barrier of 0.4 eV (Fig. 1.11b)²³. Conley *et al.* reported strain-induced decrease of PL intensity in MoS₂ monolayer²⁴ (Fig. 1.11c), indicating the direct-to-indirect transition of the optical band gap of MoS₂ with applied strain of ~1%. Strain can also influence Raman spectra (Fig. 1.11d). As the Raman peak position and intensity are sensitive to strain, so they can serve as a good indicator for the existence of strain at the interface of plasmonic nanostructures and TMDCs. The PL intensity of TMDCs can be influenced by the substrate as well. Mak *et al.*

reported suspended monolayer MoS₂ on a silicon substrate with etched holes has much larger PL than that on an unetched Si substrate²⁵. Buscema *et al.* quantitatively studied PL emission from monolayer MoS₂ on dielectrics (SiO₂, hexagonal boron nitride, mica and the polymeric dielectric gel-films) and conducting substrates (Au and few-layer graphene)²⁶. They found that on all studied substrates, monolayer MoS₂ shows a ~ 4 -fold PL enhancement, relative to the commonly used SiO₂ substrate²⁶. This is attributed to the combined effects of the substrate in MoS₂ doping and on the radiative decay rates of neutral and charged excitons.

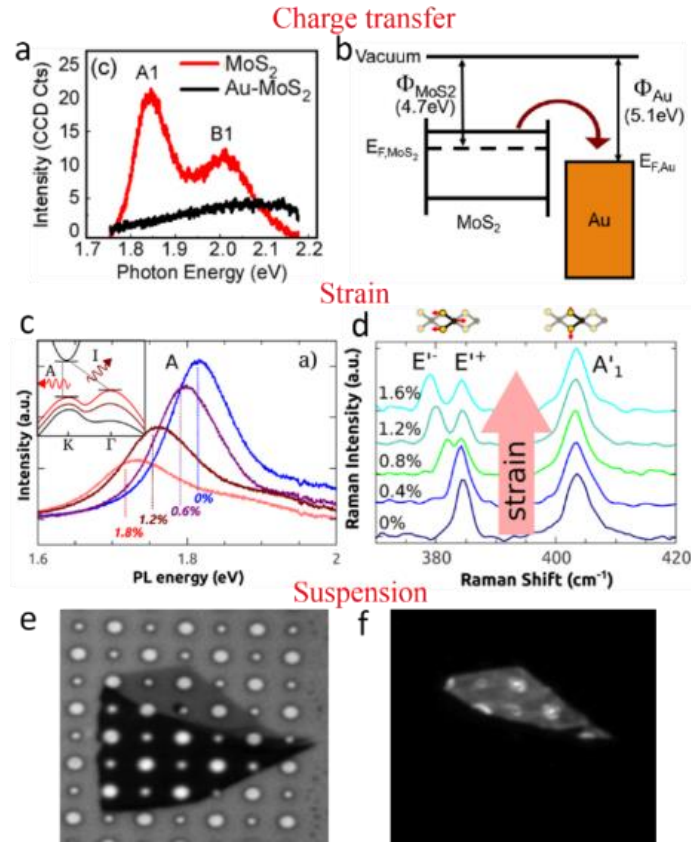


Figure 1.11 | PL is influenced by charge transfer, strain and suspension. (a) PL spectra of bilayer MoS₂ flake as exfoliated (red) and after 2.0 nm Au deposition (black)²³. (b) The energy band diagram for MoS₂ and Au²³. The direction of the arrow represents the transfer of electrons from MoS₂ to Au after the contact is established²⁴. (c) Evolution of the Raman spectrum as monolayer MoS₂ is strained from 0 to 1.6%. (d) PL spectra of monolayer MoS₂ as it is strained from 0 to 1.8%²⁴. (e) Optical image of mono- and few-layer MoS₂ crystals on a silicon substrate with etched holes²⁵. (f) PL image of the same samples in (e)²⁵.

Figure reproduced with permission from: (a-b), ref. 20, © 2016, Nature Publishing Group; (c-d), ref. 24, © 2013, American Chemistry Society; (e-f), ref. 25, © 2010, The American Physical Society.

These reviews lead to a summary of the factors that influence the PL of TMDCs integrated with metallic nanostructures and non-metallic nanocavities (Fig. 1.12). The PL intensity is dominantly determined by the excitation and emission processes. In the excitation process, spectral overlap of the resonance mode of metallic nanostructures or non-metallic nanocavities with pump laser wavelength gives rise to an enhanced near-field of incident light, leading to increased excitation rate of electron-hole pairs in TMDCs. Generally, the metallic nanostructure leads to a much larger near-field enhancement than non-metallic nanocavities. In the emission process, the spectral overlap of the resonance mode in metallic nanostructures and non-metallic cavities with the emission wavelength of the TMDCs can enhance the Purcell factor, leading to an enhanced spontaneous emission rate of the electron-hole pairs. The parameters that affect the Purcell factor between plasmonic nanostructure and optical cavity are compared here. Generally, the plasmonic nanostructure has smaller mode volume and lower quality factor than optical cavity. For the plasmonic nanostructure, the mode volume is close to the size of the nanoparticles or the gap between them, while for the optical cavity, the mode volume is on the order of wavelength. Therefore, the mode volume of plasmonic nanostructure can be $1/10^3$ of that of the optical cavity²⁷. Owing to the large imaginary part of permittivity of metal, the plasmonic nanostructure has lower quality factor than dielectric optical cavity that has negligible imaginary part of permittivity²⁷. Specific metal nanostructures, like gold and silver, can be

designed to exhibit high quality factors when their plasmon resonance deviates from the interband transition energies.

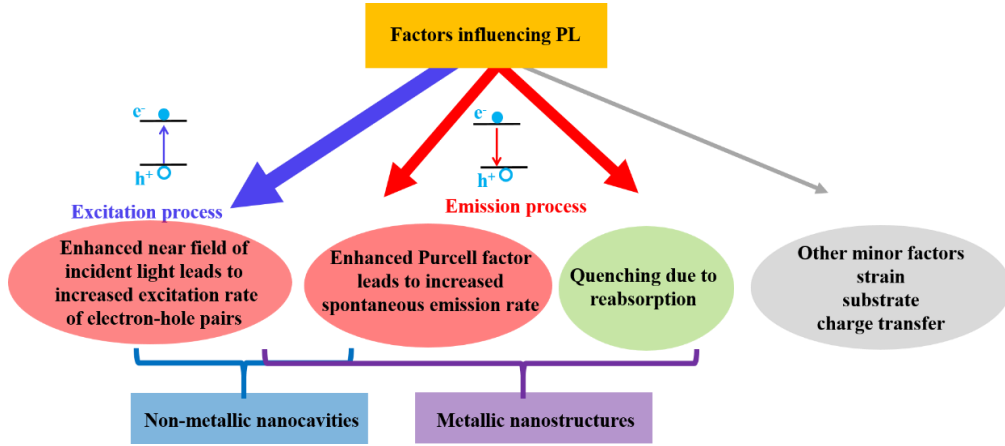


Figure 1.12 | Summary of the factors influencing the PL of TMDCs integrated with metallic nanostructures and non-metallic nanocavities.

Note that in the emission process, the metallic nanostructure may induce a quench channel due to reabsorption of the emitted light from TMDCs. These two major processes together with other minor factors need to be considered when we design a metallic nanostructures or non-metallic nanocavities to enhance the PL of TMDCs.

In Chapter 3, we report a new method for the giant enhancement of the PL of monolayer WSe₂ and systematically investigate the PL enhancement mechanism.

1.4 SHG of 2D TMDCs

Another optical effect resulting from light-matter interaction in TMDCs is second harmonic generation (SHG), namely, converting the incident light with frequency ω into light with frequency 2ω . SHG, the lowest order frequency mixing nonlinear optical process, plays an important role in frequency up-conversion in lasers and optoelectronic hybrid devices. Recent studies show that 2D TMDCs is an interesting class of nonlinear material for SHG^{28, 29}. This is

because the 2D TMDCs have thickness far below the optical coherence length, eliminating the requirement for phase matching. More importantly, despite the atomic thickness, 2D TMDCs under resonant excitation have an effective second order susceptibility³⁰ that is 1 order of magnitude larger than common transparent nonlinear crystals such as LiNbO₃ and β -BaB₂O₄. These unique properties make 2D TMDCs a promising nonlinear material in the design of smaller and thinner nonlinear optical and optoelectronic devices³¹. This section will briefly discuss the basic concept of nonlinear optics related to SHG, the motivation for SHG spectroscopy and the progress of nanostructure-enhanced SHG research on TMDCs.

1.4.1 Basic concept of SHG

When an electric field $\mathbf{E}(\omega)$ is applied to a material, a macroscopic electric dipole moment called the polarization, $\mathbf{P}(\omega)$, will be induced³². The induced polarization exhibits a linear dependence on the electric field as defined by the equation:

$$\mathbf{P}(\omega) = \epsilon_0 \chi(\omega) \cdot \mathbf{E}(\omega) \quad (1.1)$$

where $\chi(\omega)$ is the optical susceptibility of the material and ω is the angular frequency. As defined in the Eq. (1.1), all the linear optical properties of a material with the corresponding phenomena such as absorption, refraction, reflection are associated with the polarization, $\mathbf{P}(\omega)$. In these processes, the polarization oscillates at the same frequency as the incoming electric field, namely, acting as a source of radiation with frequency ω . When the electric field of the light becomes intense, χ itself depends on the electric field and thus the polarisation can be expressed as a power series of $\mathbf{E}$:

$$\mathbf{P} = \mathbf{P}^L + \mathbf{P}^{NL} = \epsilon_0 [\chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{E} \cdot \mathbf{E} + \chi^{(3)} \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E}] \quad (1.2)$$

where $\chi^{(1)}$ is the linear optical susceptibility, corresponding to the susceptibility at low electric field intensity; $\chi^{(2)}$ is the second-order nonlinear optical susceptibility and is a third rank tensor with 3^3 elements, corresponding to the possible combinations of the three Cartesian components of the polarization and of the two interacting electric fields; $\chi^{(3)}$ is the third-order nonlinear optical susceptibility and is a fourth rank tensor with 3^4 elements. The order of magnitude of the elements for $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ is 1, 10^{-12} m/V and 10^{-23} m²/V², respectively. When the light intensity equals 10^9 W/cm², the related electric field E_0 is 4.34×10^7 V/m, reaching a value that is in the same order as those existing between the charges, nuclei and electrons, constituting matter. Therefore, the optical properties of the material are modified. Such a strong electric field can be easily realized by a focused pulsed laser with an energy of 10 nJ/pulse.

The second-order polarization is the origin of well-known nonlinear phenomena such as second harmonic generation (SHG), sum frequency generation (SFG) and difference frequency mixing (DFM). Given a material with a second-order nonlinear susceptibility irradiated by an optical field oscillating at two frequencies, ω_1 and ω_2 , the polarization is given by:

$$\mathbf{P}_i^{(2)} = \varepsilon_0 \chi_{ijk}^{(2)} \cdot \mathbf{E}_j(\omega_1, \omega_2) \cdot \mathbf{E}_k(\omega_1, \omega_2) \quad (1.3)$$

where the indices i , j and k represent the Cartesian components of the polarization and of the incident fields, respectively, and $\chi_{ijk}^{(2)}$ denotes the relevant tensor element of the second-order nonlinear susceptibility, $\chi^{(2)}$. This equation shows that the nonlinear polarization oscillates at new frequencies of ω_3 which equals to $2\omega_1$, $2\omega_2$, $\omega_1 + \omega_2$ or $|\omega_1 - \omega_2|$, instead of ω_1 and ω_2 , thus acting

as source of radiation for achieving SHG, SFG or DFM. The intensity, I , of the field generated by the polarization at the new frequency, ω_3 , is given by:

$$I(\omega_3) \propto |\chi_{ijk}^{(2)}|^2 I_j I_k L^2 \cdot \text{sinc}^2 \left(\frac{\Delta k L}{2} \right) \quad (1.4)$$

where $\text{sinc}(x) = \sin(x)/x$, L is the optical path length considering the light propagation within a nonlinear medium of thickness L and Δk is the phase (wave vector) mismatch:

$$\Delta k = \mathbf{K}_{out} - \sum \mathbf{K}_{in} \quad (1.5)$$

where $\mathbf{K}_{out}$ and $\mathbf{K}_{in}$ are the wave vectors of the new outgoing field and original incident field, respectively, ($|\mathbf{k}|=k=n\omega/c$). The effect of phase mismatch is covered in the factor $\text{sinc}^2 \left(\frac{\Delta k L}{2} \right)$ as plotted in Fig. 1.13. The new field intensity I is the largest when $\Delta k = 0$, as it satisfies the momentum conservation condition (momentum $\mathbf{p} = \hbar \mathbf{k}$). Take SFG ($\omega_3 = \omega_1 + \omega_2$) as an example. The momentum conservation, namely, phase-matching condition ($\Delta k = 0$), requires that $\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2$. If this condition is not satisfied, the fields generated at different locations along the optical path in the material will destructively interfere with each other. As a result, no efficient frequency conversion can be achieved. For the second harmonic process, the severity of the phase mismatch can be easily quantified by the coherence length L_{coh} :

$$L_{coh} = \frac{\pi}{|\Delta k|} = \frac{\lambda}{4|n_2 - n_1|} \quad (1.6)$$

where n_1 and n_2 are refractive indices at the fundamental and second harmonic waves respectively, and λ is the wavelength of the fundamental wave in the vacuum. For typical optical materials, L_{coh} is a few tens of microns (μm). Reducing the dimensionality of the nonlinear materials to two dimension would eliminate the requirement for phase matching as the crystal thickness is far

below the coherence length. Therefore, 2D TMDCs provide an ideal platform for applying developing ultrathin nonlinear devices.

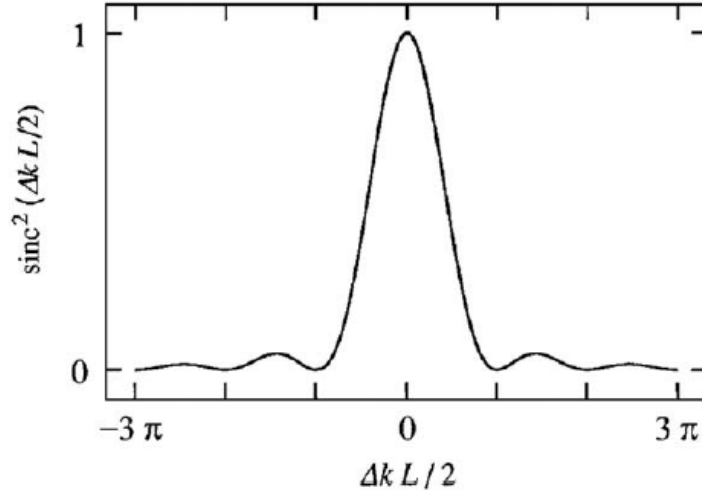


Figure 1.13 | Effects of wavevector mismatch on the efficiency of SHG or SFG³².

To observe these second-order nonlinear phenomena, the light has to fulfill phase-matching conditions and the material should have no central symmetric crystal structure. If the material has an inversion center, the second-order susceptibility will be zero. This can be demonstrated in a simple way by considering even order polarizations:

$$\mathbf{P}^{(2n)} = \epsilon_0 \chi^{(2n)} \mathbf{E}^{2n} \quad (n = 1, 2, 3, \dots) \quad (1.7)$$

In a centrosymmetric material, the sign of $\mathbf{P}^{(2n)}$ is reversed as the electric field is reversed:

$$-\mathbf{P}^{(2n)} = \epsilon_0 \chi^{(2n)} (-\mathbf{E})^{2n} \quad (1.8)$$

$$-\mathbf{P}^{(2n)} = \epsilon_0 \chi^{(2n)} \mathbf{E}^{2n} \quad (1.9)$$

Therefore $-\mathbf{P}^{(2n)} = \mathbf{P}^{(2n)}$. This is only possible when $\chi^{(2n)} = 0$. As a result, only materials with broken inversion symmetry have non-zero $\chi^{(2n)}$ and exhibit even order nonlinear optical properties. Centro-symmetric and isotropic materials such as liquids show only odd order nonlinear effects.

In order to develop smaller and thinner nonlinear media in next-generation optical devices, much effort has been devoted to develop ultrathin nonlinear crystals with high frequency conversion efficiency. Among them, monolayer 2H-phase TMDCs attract tremendous attention as they have inversion-symmetry breaking and have relatively large second order susceptibility despite of the atomic thin thickness³³. However, these materials still suffer in conversion efficiency owing to the short light-matter interaction length^{28, 34}. Since 2D TMDCs are interesting for fundamental study and applications in ultrathin nonlinear devices, it is important to further enhance their SHG intensity and explore their potential as a nonlinear medium.

1.4.2 Motivation for SHG spectroscopy

In 2D TMDCs, SHG has found several applications from microscopic and spectroscopic techniques to up-conversion lasing.

Characterizing crystal structure

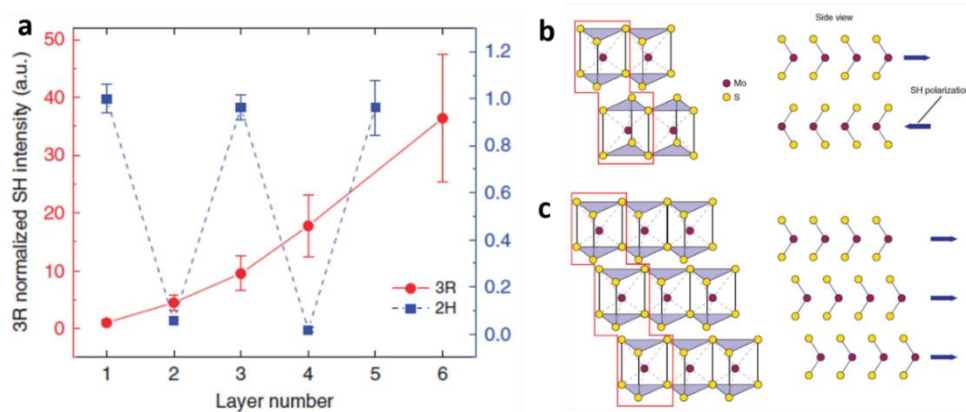


Figure 1.14 | SHG intensity and SHG polarization of 2H and 3R-MoS₂³¹. (a) SHG intensity of 2H and 3R-MoS₂ as a function of layer number. (b) Schematic of the crystal structure of 2H-MoS₂ (two layer unit cell outlined in red) with the side projection showing the flipped orientation of each layer and the anti-parallel orientation of the SH dipoles. (c) Crystal structure of 3R-MoS₂ (three layer unit cell outlined in red) with parallel SH polarization in each layer. Individual layers are identical to the 2H structure, however the unit cell and bulk crystal are noncentrosymmetric. Figures reproduced with permission from: (a-c), ref. 31, © 2016, Nature Publishing Group.

Firstly, SHG optical spectroscopy allows for non-destructive crystal structure studies of 2D TMDCs, as the amplitude of SHG strongly depends on the crystal structure and layer number. The 1T phase has negligible second harmonic emission as it has an inversion center in the crystalline unit cell, while the 2H and 3R phases show SHG signals correlated to the layer number. For 2H-MoS₂, the SHG intensity in the odd number of layers is much stronger than the response for even number of layers (Fig. 1.14a)³¹. This is because the odd-numbered layers are noncentrosymmetric, having a net nonlinear dipole, while the centrosymmetric even layers do not. This net nonlinear dipole in odd layered 2H-MoS₂ has enabled the probing of SHG due to the finite second-order nonlinearity ($\chi^{(2)} \neq 0$). An alternative way to understand this is to regard the source of second harmonic emission as dipoles. In the even number of layers, the second harmonic dipoles in adjacent two layers are oriented anti-parallel and cancel out (Fig. 1.14b). As shown in Fig. 1.14 a, unlike 2H-MoS₂, the SHG amplitude of 3R-MoS₂ increases with the number of layers as the SHG dipoles in each layer are all aligned in one direction (Fig. 1.14 c), allowing for constructive interference of the SHG light.

Secondly, the SHG signal of 2D TMDCs has been utilized to study the crystal orientation of monolayer and bilayer flakes or polycrystalline films. Hsu *et al.* found that the parallel (perpendicular) component of SHG intensity of monolayer TMDCs relative to the pump laser polarization varies with the angle between the pump laser polarization and the armchair direction³⁵. Therefore, the crystal-orientation-dependent SHG polar plot can be used to identify the armchair direction of the monolayer TMDCs. Jiang *et al.* obtained artificially folded bilayer MoS₂ with different folding angles by stacking exfoliated

monolayer flakes (Fig. 1.15a)³⁶. They found that the SHG intensity strongly relies on the folding angles between the top and bottom layers (Fig. 1.15b). After knowing the relative angle between the top and bottom layers confirmed by SHG, the crystal structure of bilayer MoS₂ can be identified from possible structures such as 2H-like (Mo), 2H-like (S), 3R-like and so on (Fig. 1.15c).

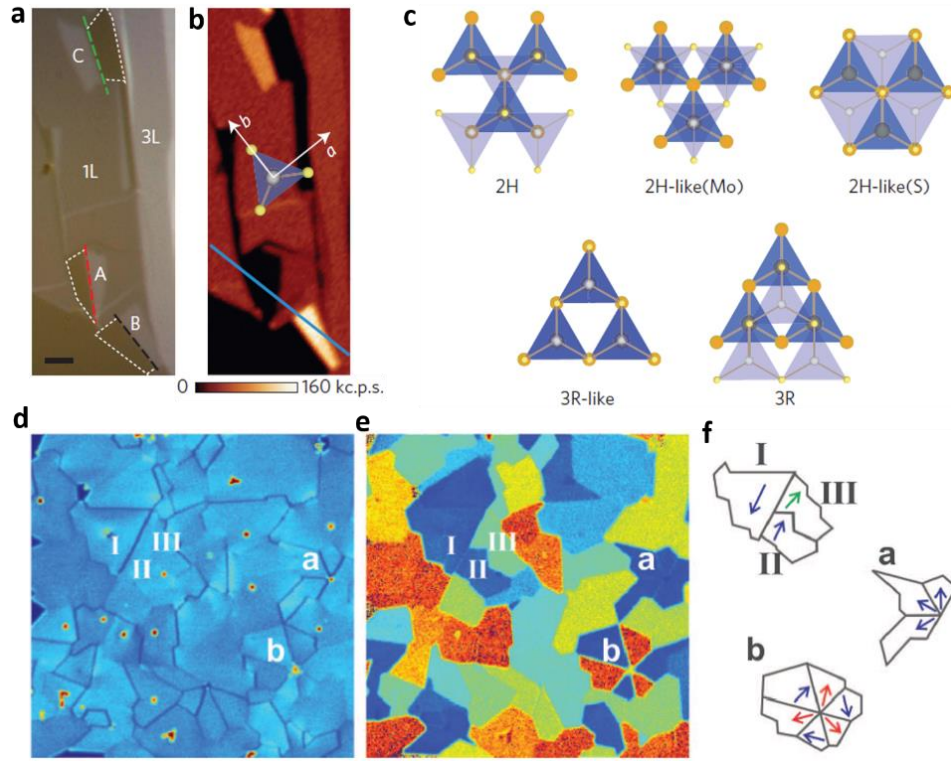


Figure 1.15 | Crystal structure determined by SHG spectroscopy. (a) OM of the exfoliated MoS₂ sample. A, B and C are folded bilayers³⁶. Scale bar: 2 μ m. (b) SHG microscope images³⁶ of the same region in (a). (c) Top views of atomic structures of the 2H, 2H-like (Mo), 2H-like (S), 3R-like and 3R bilayers, respectively³⁶. (d) SHG image of a polycrystalline monolayer of MoS₂³⁷. (e) The direct crystal orientation image shows the crystal orientations of the irregular-shaped polycrystalline aggregates³⁷. (f) Schematics show the flakes I and II are two crystals with opposite orientations, and flakes II and III have an orientation mismatch of $\sim 12^\circ$ ³⁷. Figure reproduced with permission from: (a-c), ref. 36, © 2014, Nature Publishing Group; (d-f), ref. 37, © 2014, American Association for the Advancement of Science.

Yin *et al.* reported a nonlinear optical imaging technique based on SHG to characterize the atomic edges and grain boundaries in polycrystalline MoS₂ films³⁷. As shown in Fig. 1.15d, while the grain boundaries are a few atoms in

width, they can still be clearly identified by the reduced total SHG intensity at the boundaries which shows obvious color contrast to the homogeneous SHG intensity within each grain. The suppressed total SHG at the boundaries are attributed to the destructive interference and cancellation of the nonlinear waves from the neighboring grains with different orientations. By analyzing the polarized components of the SHG, the crystal orientation of the polycrystalline atomic membrane is mapped (Fig. 1.15e) and demonstrated (Fig. 1.15f), allowing for the complete mapping of the crystal grain structures.

Determining excitonic states

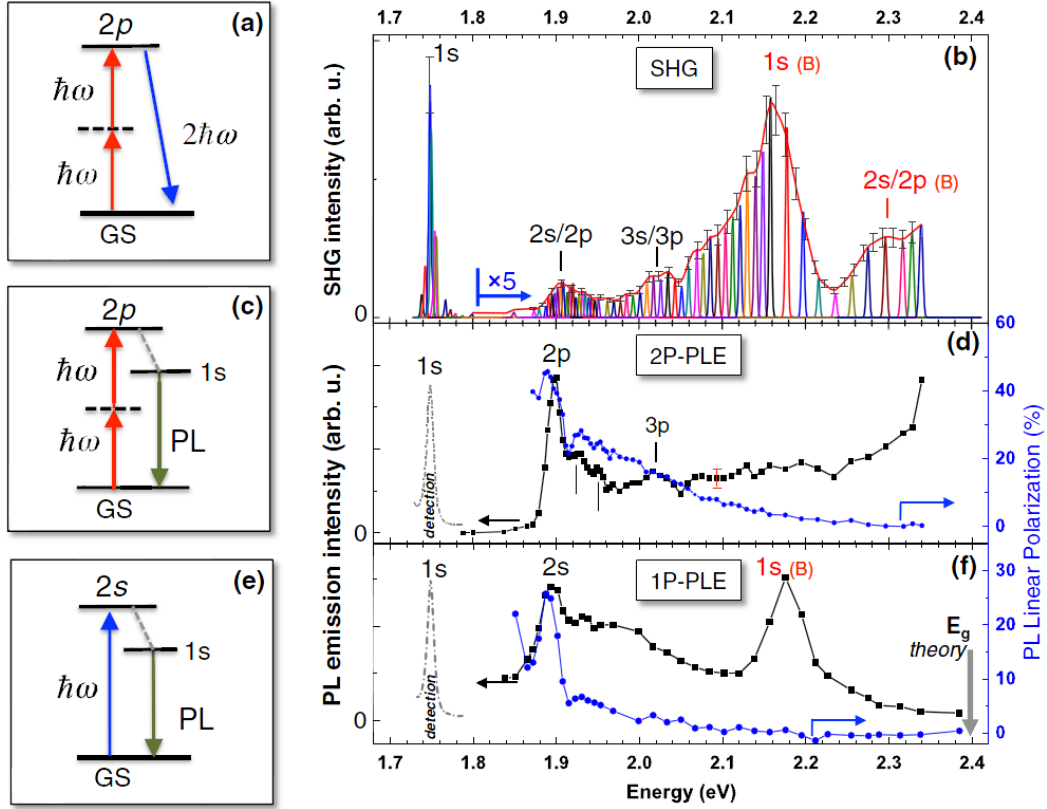


Figure 1.16 | Schematic for SHG, 2-photon PL and 1-photon PL processes, and the related emission intensity as a function of pump or emission energy³⁸. (a) Schematic for SHG when 2 incident photons are resonant with the 2p state of the A exciton. (b) Results of SHG spectroscopy as a function of $2\hbar\omega$. (c) Schematic for 2-photon PLE. (d) 2-photon PLE intensity (left axis, black squares), and linear polarization (right axis, blue circles) as a function of $2\hbar\omega$. (e) Schematic for 1-photon PLE. (f) 1-photon PLE intensity (left axis, black squares), and linear polarization (right axis, blue circles) as a function of $\hbar\omega$.

Figures reproduced with permission from: (a-f), ref. 38, © 2015 American Physical Society.

SHG generation at a fixed wavelength is commonly used for monolayer and few layer TMDCs to probe crystal inversion symmetry and structure as reviewed in the preceding section, whereas the intensity of the SHG signal as a function of the 2-photon laser excitation energy enables a spectroscopic method to study the excitonic structure. The broken inversion symmetry and rich linear and nonlinear optical properties make monolayer TMDCs an ideal material for applying this technique. Wang *et al.* demonstrated the variation of SHG intensity of monolayer WSe₂ with a 2-photon laser excitation laser in the energy range 1.7 to 2.4 eV. As shown in Fig. 1.16b, the SHG intensity varies over 3 orders of magnitude, with the strongest intensities at energies of the 1s A exciton (1.75 eV) and 1s B exciton ((2.17 eV)³⁸. In addition to the A and B excitons, clear resonances at 1.9, 2.03 and above 2.31 eV in the SHG spectrum were also observed. These were attributed to 2s/2p A exciton states, 3s/3p states and 2s/2p B exciton states, respectively, and confirmed experimentally by 2-photon and 1-photon PL excitation spectra (Fig. 1.16d and f). These SHG resonance features suggest that SHG spectroscopy can serve as a useful optical tool for the determination of exciton states.

Achieving frequency up-conversion

The SHG signal not only plays an important role in the characterization of 2D TMDCs, but also opens up a window for developing atomically thin nonlinear devices for frequency up-conversion. Li *et al.* demonstrated that monolayer 2H-MoS₂ has a much larger SHG than its few layer and bulk counterparts³⁰. Recent experimental results have demonstrated that the conversion efficiency represented by the second-order susceptibilities $\chi^{(2)}$

ranges from 5 and 500 pm/V in monolayer TMDCs depending on excitation wavelength³⁹ and sample quality⁴⁰. The typical value of $\chi^{(2)}$ in conventional crystals such as $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) and KH_2PO_4 (KDP) is in the range of 1 pm/V^{30, 41}.

In summary, relatively strong SH responses of 2D TMDCs has been achieved using pump lasers with appropriate wavelengths, demonstrating them to be promising materials for nonlinear optical devices. However, limited by the innate thickness of 2D TMDCs, the second harmonic conversion efficiency still needs to be improved for practical applications.

1.4.3 Methods to improve SHG

One method to improve SHG intensity is mentioned in Section 1.4.2, that is, using a 2-photon excitation pump with energy aligned to the exciton transitions. This is because the quantum mechanical expression for the second-order susceptibility $\chi^{(2)}$ of TMDCs includes matrix elements with one occupied and two unoccupied intermediate virtual states; when the virtual transition level is coincident with exciton states in TMDCs, the coupling between the second harmonic radiation and the $\chi^{(2)}$ becomes large. The exciton transition facilitates not only the resonance-enhanced SHG spectrum, but also makes the electrical tunability of the frequency-doubled signals feasible. Seyler *et al.* made a monolayer WSe_2 field-effect transistor, achieved impressive tunability of $\chi^{(2)}$ and the resulting SHG intensity was enabled through electrostatic doping induced by a gate bias¹⁰. To be specific, the SHG intensity at the A exciton energy can be tuned by over an order of magnitude in a cryogenic environment, albeit the performance is compromised at ambient temperature⁴². This approach utilizes electrostatic engineering of oscillator strength at the resonance

frequencies of various exciton states. As a result, the effect is inherently narrowband. When the energy of the pump laser is shifted by only tens of millielectronvolts, the gate-controlled modulation of the SHG dramatically diminishes. The researchers also demonstrated an interesting SHG selection rule, namely, the SHG signal is counter-circularly polarized to the fundamental wave³⁶, which is different from the optical selection rule of PL¹⁴.

The above methods to enhance SHG utilize the inherent exciton resonance of TMDCs. To further optimize the SHG signal, external strategies should also be incorporated. Optical resonators that can enhance the PL of TMDCs can also boost SHG. It has been reported that the SHG of TMDCs can be significantly enhanced by integrating them with optical cavities.

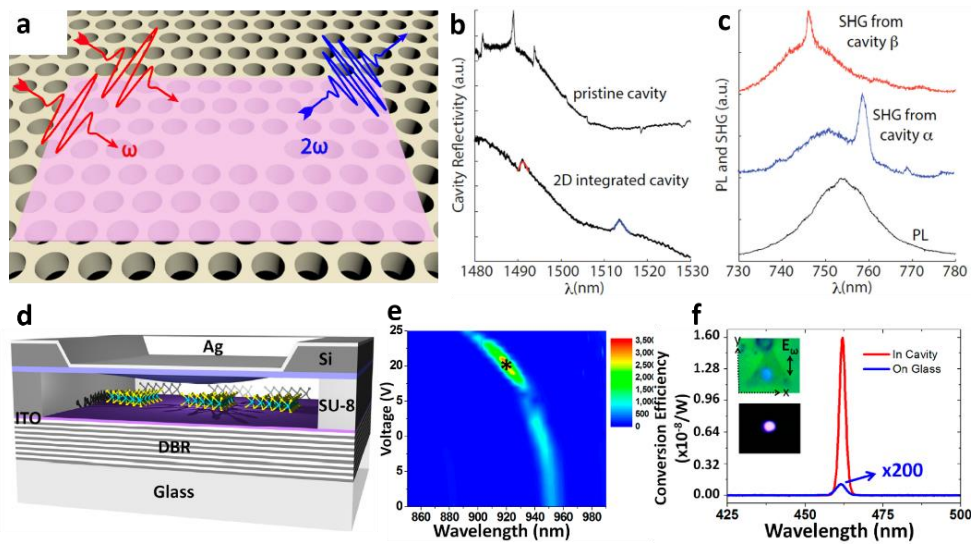


Figure 1.17 | SHG enhancement in 2D TMDCs by nanostructures. (a) Schematic of WSe₂ transferred on silicon photonic crystal⁴³. (b) Reflectivity of the higher order cavity modes before and after monolayer WSe₂ transfer⁴³. (c) PL from WSe₂ (black), SHG spectra from mode α (blue) and mode β (red)⁴³. (d) Schematic of the device structure formed by the dielectric mirror on a glass substrate and a silver mirror on a suspended membrane⁴⁴. (e) The measured voltage dependence of the total output SHG power enhancement factor normalized to a monolayer on glass substrate⁴⁴. (f) SHG signal generated from the MoS₂ flake inside the cavity (red solid line) and on a glass substrate (blue solid line)⁴⁴. Figures reproduced with permission from: (a-c), ref. 43, © 2016 IOP Publishing Ltd; (d-f), ref. 44, © 2016 American Chemical Society.

Fryett *et al.* transferred monolayer WSe₂ onto a silicon photonic crystal cavity⁴³, as shown in Fig. 1.17a. The choice of photonic crystal cavity is motivated by its modes with small mode volume and high quality factor (Fig. 1.17b), since for a nonlinear optical switch, the switching power scales as V_m/Q^3 for second order nonlinearity, where V_m is the mode volume and Q is the quality factor. When the device is pumped by ultrafast laser pulses near this cavity mode at the telecommunication wavelength, a SHG signal in the visible range with near unity linear polarization was observed (Fig. 1.17c), which originates from the coupling of the pump photon to the cavity mode. The photonic crystal cavity induces a two-fold increase in the average second-harmonic intensity from WSe₂ as compared to a monolayer WSe₂ on silicon. After normalization by comparing the nonlinear conversion efficiencies of WSe₂ on the cavity and on flat silicon, the cavity enhancement is estimated to be 200-fold.

Larger SHG enhancement was reported by Cubukcu *et al.* via integrating a MoS₂ monolayer into a doubly resonant optical cavity⁴⁴. As demonstrated in Fig. 1.17d, the device is based on a voltage controlled micro-Fabry-Perot (FP) cavity that consists of a Bragg reflector (DBR) mirror with high reflectivity and a voltage deformable silver mirror fabricated on a silicon nitride membrane. The nonlinear light-matter interaction in MoS₂ is engineered by optomechanical tuning of the FP cavity length via an applied voltage, which in turn controls the intracavity optical field strengths at the fundamental frequency (ω) and SH frequency (2ω). The SHG enhancement level is predicted by the field enhancement theoretical model. Since the intracavity electric field is related to the quality factor, this model can also be expressed as: $(Q_\omega)^2 \times (Q_{2\omega})$, where Q_ω and $Q_{2\omega}$ are the quality factors for the fundamental and second order

waves, respectively. The experimental SHG enhancement factor is defined as the ratio between the SHG signals from a MoS₂ monolayer in cavity and on a glass substrate at different voltages and wavelengths, and is shown as a map in Fig. 1.17 e. It is shown that the experimental results agree well with the theoretical model. The maximum SHG enhancement (3300-fold) is observed (Fig. 1.17f) in the case where both the fundamental and second harmonic waves are spectrally tuned with the two cavity modes, that is, in double resonance condition. The frequency doubling process is technologically important for the generation of tunable lasers sources in the visible spectrum, and methods to improve SHG need to be explored.

This thesis will provide a new method to significantly enhance the SHG of monolayer WSe₂ in Chapter 4.

1.5 Photocarriers of TMDCs

Another important feature stemming from light-matter interactions in 2D TMDCs is the optical generation of carriers. These carriers are fundamental to realize optoelectronic devices such as photodetectors and photovoltaic cells based on TMDCs. Given the impressive optical properties of 2D TMDCs, they are expected to exhibit superior performance in optoelectronic devices, with high efficiencies and fast responses. As the performance critically depends on efficient light absorption and excited carrier relaxation dynamics, it is important to understand the ultrafast optical phenomena of the semiconductors at the ultrafast timescale. This section will provide a brief discussion of the physics and applications related to photocarriers, introduce the techniques for measuring ultrafast behavior of photocarriers, followed by a review of current research on ultrafast photocarriers in TMDCs.

1.5.1 Physics and applications of photocarriers

The study of photocarriers in 2D optoelectronic devices encompass light absorption efficiency, photocarrier excitation, free carrier generation, free carrier collection, charge trapping, and recombination. Photocarriers are the building blocks of photodetectors and photovoltaic cells. They can be detected in the following ways: by photoconduction where photoexcited carriers increase conductance of the device, and by a photocurrent where photoexcited carriers are converted into a current with the aid of, for example, a built-in electric field at a p-n junction. Due to the extremely strong excitonic effects in TMDCs, a key issue for photodetectors is exciton dissociation by built-in or externally applied electric fields.

Experimental advances in photodetectors based on both in-plane and out-of-plane heterostructures of 2D TMDCs have been made. In-plane devices enable control of the material properties via electrostatic gating, whereas out-of-plane devices support a much higher bias field (up to $\sim 1 \text{ V nm}^{-1}$), offering a reduced excitonic binding energy in multilayer structures for more efficient exciton dissociation⁴⁵. Weak in-plane photoconduction was first observed by Mak *et al.* in illuminated 2D MoS₂ transistors⁴⁶. A high responsivity of 0.1 AW^{-1} and external quantum efficiency of 50% was demonstrated by Britnell *et al.* in vertical TMDC devices with graphene as top and bottom electrodes (Fig. 1.18a)², where the TMDC is not 2D but bulk with a thickness varying from 5 to 50 nm. The enhanced performance is attributed to Van Hove singularities in the electronic density of states of TMDC which enhances light-matter interactions, leading to enhanced photon absorption and electron-hole creation which are effectively collected at the graphene electrodes. In principle, the electrons/holes

generated in TMDCs have no preferred diffusion direction and, hence, no net photocurrent is measured (Left, Fig. 1.18b). However, the presence of a built-in electric field due to the doping between the graphene sheets or by gating (Right, Fig. 1.17b) across the TMDC can separate the electron-hole pairs and enable the flow of photocurrent.

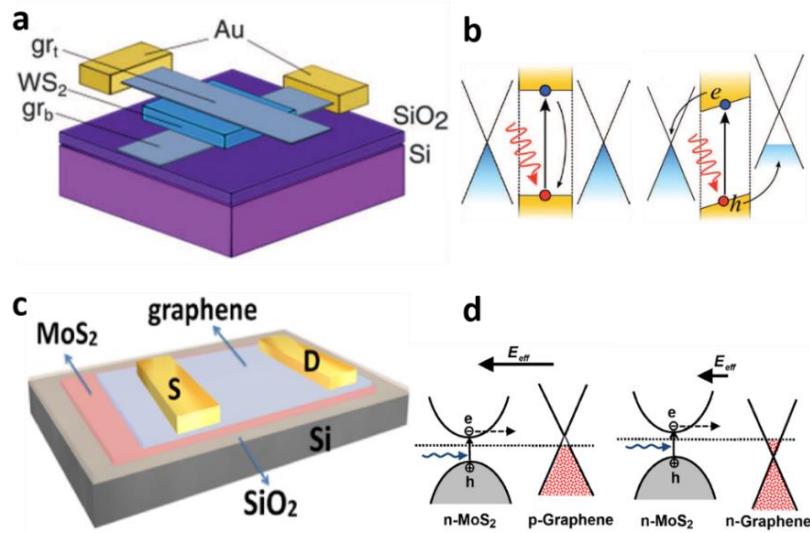


Figure 1.18 | Schematic view and band diagram of optoelectronic devices based on 2D TMDCs. (a) Schematic diagram of few-layer WS_2 vertical photoconductor with graphene as top and back electrodes². (b) Schematic band diagram for the heterostructure as shown in (a) with a built-in electric field to separate the generated electron-hole pair². (c) Schematic illustration of the photodetector based on graphene/ MoS_2 stacked layers⁴⁷. (d) Schematic illustration of the photoelectron transfer process in as shown in (c)⁴⁷. Figures reproduced with permission: (a-b), ref. 2, © 2013, American Association for the Advancement of Science; (c-d), ref. 47, © 2014, Nature Publishing Group.

Zhang *et al.* also reported an out-of-plane TMDC transistor with graphene electrodes (Fig. 1.18c)⁴⁷ and obtained a high photogain greater than 10^8 . This is because photoelectrons generated in MoS_2 can be effectively injected into graphene due to the presence of a perpendicular electric field caused by the combination of the built-in and applied electric field, as well as charged impurities or absorbants. The related photoelectron transfer process is demonstrated in Fig. 1.18d, where the effective electric field of the p-doped

graphene/MoS₂ heterostructure is larger than that of the n-doped graphene, resulting in easier separation of the photogenerated electron-hole pairs. These studies demonstrate the potential for efficient photodetection in out-of-plane heterostructures based on 2D materials.

Given the MoS₂/graphene heterostructure has superior optoelectronic properties, it is used as a model in this thesis to investigate the photocarrier dynamics. This work is presented in Chapter 5, where the steady-state measurement and sample preparation were done by me and the characterization of photocarrier dynamics were conducted by our collaborator Dr. Lei Wang in Jilin University, China. Further improvement of device performance is strongly dependent on an understanding of the photocarrier dynamics, which warrants an in-depth study. Next, the techniques used to characterize the carrier dynamics will be introduced.

1.5.2 Ultrafast spectroscopy

Insights into the photoresponse process, photocarrier origins and relaxation behaviors are crucial in optimizing device performance. The development of ultrafast (femtosecond) pulse laser techniques renders high temporal resolution, thus enabling ultrafast spectroscopies to directly monitor the carrier dynamics, whereby the decay time of the carriers in each path, and the mechanisms of the energy loss resulting from electron-exciton, exciton-exciton and electron-phonon interactions can be quantitatively analyzed. The general ultrafast spectroscopies include time-resolved PL (TRPL) spectroscopy and pump-probe spectroscopies such as transient absorption/reflection/transmission spectroscopies. TRPL is a tool used for probing bright excitons which can emit light through radiative decay.

Temperature-dependent TRPL studies reveal that the PL decay of monolayer MoS₂ is very fast (~ 4 ps) at low temperature, and an additional slow recombination process occurs at higher temperature due to exciton-phonon scattering⁴⁸.

Pump-probe spectroscopy is another ultrafast technique frequently employed to monitor the carrier dynamics in semiconductors. Unlike TRPL spectroscopy, pump-probe spectroscopy not only characterizes bright excitons but also interrogates the dynamics of dark states that cannot emit light, thereby providing comprehensive information about exciton states even in materials with low quantum yield. We next discuss pump-probe spectroscopy, taking transient absorption spectroscopy as an example.

As a typical pump-probe technique, transient absorption spectroscopy (TA), is taken as an example to introduce the working principle. In TA spectroscopy, an excitation (or pump) pulse is used to promote the sample to an electronically excited state. A weak probe pulse is also sent through the sample, but with a short time delay with respect to the pump pulse. The difference absorption spectrum (ΔA) is then calculated, namely, the absorption spectrum of the excited sample minus the absorption spectrum of the sample in the ground state. By changing the time delay between the pump and the probe, and recording a ΔA spectrum at each time delay τ , a ΔA profile as a function of time and wavelength is obtained. The ΔA spectrum contains information on the dynamic of photocarriers in the generation and relaxation processes. Details of the setup and data analysis will be shown in Chapter 2.

1.5.3 Pump-probe studies of TMDCs

The highly temporal and spatial resolution of the pump-probe technique enables it to be widely used to study the ultrafast behavior of photocarriers in TMDCs (Fig. 1.19a). Using this technique, Cui *et al.* directly determined the exciton lifetimes of ~ 18 ps in monolayer WSe₂ (Fig. 1.19b)⁷. They then adjusted the distance between the centers of the pump and probe spots on the sample, and measured the differential reflection signal as a function of the probe delay at each distance (Fig. 1.19c). In this way, they deduced the exciton transport property of these photocarriers such as exciton diffusion coefficient (15 ± 5 cm²/s), diffusion length (160 nm), mean free path (17 nm), mean free time (0.24 ps), electron mobility (200 cm²/(V s)), exciton mobility (600 cm²/(V s)) and so on. These parameters are useful for understanding the exciton behavior in WSe₂, which is important for applications in optoelectronics devices.

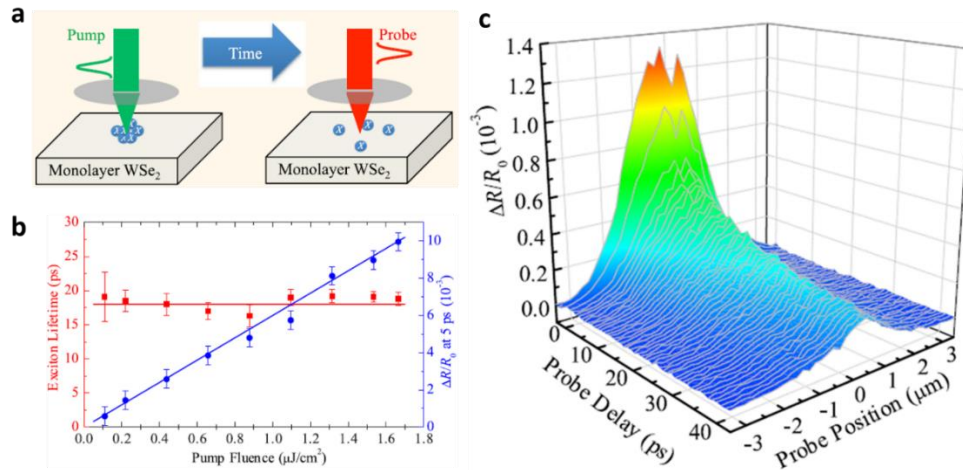


Figure 1.19 | Carrier dynamics and transport properties revealed by pump-probe technique⁷. (a) Schematic view of the pump-probe technique applied on monolayer WSe₂. (b) The exciton lifetime (red squares, left axis) as a function of the pump fluence. (c) Differential reflection signal as a function of both the probe delay and the probe position measured from the monolayer WSe₂ sample. Figures reproduced with permission from: (a-c), ref. 7, American Chemistry Society.

Unlike low-density exciton systems, high-density exciton processes such as in TMDCs would exhibit more complex dynamics due to the involvement of exciton-exciton interactions. For instance, exciton-exciton annihilation, a many-body interaction process where one electron-hole pair is destroyed and its energy transferred to another exciton, was identified in monolayer MoS₂ and MoSe₂ via pump-probe spectroscopy. This process can be considered the excitonic analog of the Auger recombination process, so studying this process is important for understanding the nonradiative decay channel. Under excitations with high injected density, the exciton-exciton annihilation rates in monolayer MoS₂⁴⁹ and MoSe₂⁵⁰ are deduced to be $(4.3 \pm 1.1) \times 10^{-2} \text{ cm}^2/\text{s}$ and $(33 \pm 6) \times 10^{-2} \text{ cm}^2/\text{s}$, respectively.

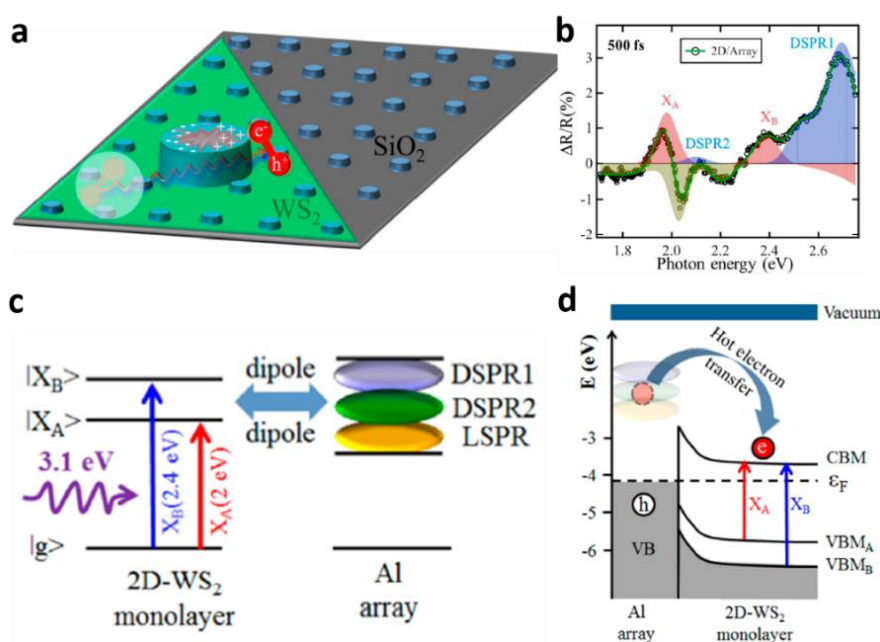


Figure 1.20 | Energy and electron transfer verified by pump-probe technique⁵¹. (a) Schematic view of a hybrid composed of monolayer WS₂ and Al disks. (b) Spectral cut at 500 fs from part (symbols) fit to a multiple-Gaussian function (solid line). (c) Schematic of the mechanism of energy transfer at the studied hybrid system. (d) Schematic of the proposed mechanism of charge transfer at the studied hybrid system. Figures reproduced with permission from: (a-d), ref. 51, © 2016, American Chemistry Society.

The pump-probe technique can also be used to characterize the energy and charge transfer between TMDCs and plasmonic nanostructures (Fig. 1.20a), as reported by Boulesbaa *et al.* in a hybrid composed of monolayer WS₂ and an array of aluminum (Al) nanodiscs⁵¹. Femtosecond pump-probe spectroscopy results indicate that within ~ 830 fs after photoexcitation of the monolayer WS₂, energy transfer from the WS₂ excitons excites the delocalized surface plasmon resonance (DSPR) of the Al array (Fig. 1.20b). Upon the damping of these excited plasmons, energy and/or electron transfer back to WS₂ occurs (Fig. 1.20 c and d) as indicated by an increase of the reflected probe signal at the WS₂ exciton transition energies at later time delays. This simultaneous exchange of energy and charges between the metal nanostructure and WS₂ leads to an extension of the average lifetime of the WS₂ excitons from ~ 15 ps to ~ 58 ps in the absence and presence of the Al nanodisks, respectively. The pump-probe technique quantitatively reveals the energy and charge transfer processes in the time domain, shedding light on the design of hybrid plasmonic/2D structures with long exciton-plasmon lifetimes for higher efficiencies in photovoltaics, photodetectors and photocatalysis applications.

1.6 Objective and scope of this thesis

The relative strong light-matter interactions in 2D TMDCs as compared with graphene brings about novel optical properties, making them attractive for applications in optoelectronics. However, there are still several challenges inhibiting their practical applications. One major challenge is to achieve stronger light-to-light conversion efficiencies for ultralow threshold lasing applications. Another challenge is to develop a good understanding of photon-

to-carrier conversion and exciton dissociation processes in 2D TMDC photo-conduction devices.

In the context of these challenges, this thesis reports the enhancement of light-to-light conversion efficiency and investigates the light-to-carrier conversion process of 2D TMDCs using PL, SHG and TA techniques. Chapter 2 provides a brief description of the fabrication and characterization techniques used in this study of 2D TMDCs. As the innate atomic-layer thickness limits light absorption and emission of 2D TMDCs, Chapters 3 and 4 focus on improving the first-order optical property (PL) and second-order optical property (SHG) of monolayer WSe₂ by gold plasmonic nanostructures, respectively. Detailed analyses of the enhancement mechanism as well as the interaction processes between the plasmonic nanostructure and monolayer WSe₂ are also presented. These studies provide an effective way to enhance the light emission properties of 2D TMDCs, paving the way towards plasmon-enhanced optoelectronic devices based on 2D materials.

Light-matter interactions in 2D TMDCs also gives rise to a photo-to-carrier conversion process. This process has been widely explored in optically active A and B excitons, whereas the study of C excitons in the band nesting region is less well studied. Chapter 5 uses the technique of third-order nonlinear TA spectroscopy to characterize the relaxation dynamics of photoexcited C excitons in MoS₂ and their collection efficiency in MoS₂/graphene heterostructures. This work provides a detailed understanding of the exciton dissociation and collection processes, and should motivate further studies on hot electron behaviors in 2D materials and their potential applications. In Chapter 6, a summary of the key results is presented, as well as a discussion on possible

future extensions to this thesis regarding exploring novel optical properties of plasmonic nanostructures with 2D TMDCs and their applications in novel optoelectronic devices.

1.7 References

1. Xia, F. *et al.* Two-dimensional material nanophotonics. *Nat. Photonics* **8**, 899-907 (2014).
2. Britnell, L. *et al.* Strong light-matter interactions in heterostructures of atomically thin films. *Science* **340**, 1311-1314 (2013).
3. Mak, K. F., Shan, J. Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides. *Nat. Photonics* **10**, 216-226 (2016).
4. Li, X., Zhu, J., Wei, B. Hybrid nanostructures of metal/two-dimensional nanomaterials for plasmon-enhanced applications. *Chem. Soc. Rev.* **45**, 3145-3187 (2016).
5. Wang, Q. H. *et al.* Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* **7**, 699-712 (2012).
6. Kumar, A., Ahluwalia, P. Electronic structure of transition metal dichalcogenides monolayers 1H-MX₂ (M= Mo, W; X= S, Se, Te) from ab-initio theory: new direct band gap semiconductors. *Eur. Phys. J. B* **85**, 186 (2012).
7. Cui, Q., Ceballos, F., Kumar, N., Zhao, H. Transient absorption microscopy of monolayer and bulk WSe₂. *ACS Nano* **8**, 2970-2976 (2014).
8. Carvalho, A., Ribeiro, R., Neto, A. C. Band nesting and the optical response of two-dimensional semiconducting transition metal dichalcogenides. *Phys. Rev. B* **88**, 115205 (2013).
9. Eda, G., Maier, S. A. Two-dimensional crystals: managing light for optoelectronics. *ACS Nano* **7**, 5660-5665 (2013).
10. Seyler, K. L. *et al.* Electrical control of second-harmonic generation in a WSe₂ monolayer transistor. *Nat. Nanotechnol.* **10**, 407-411 (2015).
11. Lopez-Sanchez, O. *et al.* Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotechnol.* **8**, 497-501 (2013).
12. Zeng, H. *et al.* Optical signature of symmetry variations and spin-valley coupling in atomically thin tungsten dichalcogenides. *Sci. Rep.* **3**, 1608 (2013).
13. Mak, K. F., He, K., Shan, J., Heinz, T. F. Control of valley polarization in monolayer MoS₂ by optical helicity. *Nat. Nanotechnol.* **7**, 494-498 (2012).
14. Zeng, H. *et al.* Valley polarization in MoS₂ monolayers by optical pumping. *Nat. Nanotechnol.* **7**, 490-493 (2012).
15. Jones, A. M. *et al.* Optical generation of excitonic valley coherence in monolayer WSe₂. *Nat. Nanotechnol.* **8**, 634-638 (2013).
16. Tonndorf, P. *et al.* Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂. *Opt. Express* **21**, 4908-4916 (2013).
17. Gan, X. *et al.* Controlling the spontaneous emission rate of monolayer MoS₂ in a photonic crystal nanocavity. *Appl. Phys. Lett.* **103**, 181119 (2013).
18. Butun, S., Tongay, S., Aydin, K. Enhanced light emission from large-area monolayer MoS₂ using plasmonic nanodisc arrays. *Nano Lett.* **15**, 2700-2704 (2015).

19. Lee, B. *et al.* Fano resonance and spectrally modified photoluminescence enhancement in monolayer MoS₂ integrated with plasmonic nanoantenna array. *Nano Lett.* **15**, 3646-3653 (2015).
20. Akselrod, G. M. *et al.* Leveraging nanocavity harmonics for control of optical processes in 2D semiconductors. *Nano Lett.* **15**, 3578-3584 (2015).
21. Chou, C.-H., Chen, F.-C. Plasmonic nanostructures for light trapping in organic photovoltaic devices. *Nanoscale* **6**, 8444-8458 (2014).
22. Chen, H. *et al.* Manipulation of photoluminescence of two-dimensional MoSe₂ by gold nanoantennas. *Sci. Rep.* **6**, (2016).
23. Bhanu, U., Islam, M. R., Tetard, L., Khondaker, S. I. Photoluminescence quenching in gold-MoS₂ hybrid nanoflakes. *Sci. Rep.* **4**, 5575 (2014).
24. Conley, H. J. *et al.* Bandgap engineering of strained monolayer and bilayer MoS₂. *Nano Lett.* **13**, 3626-3630 (2013).
25. Mak, K. F. *et al.* Atomically thin MoS₂: a new direct-gap semiconductor. *Phys. Rev. Lett.* **105**, 136805 (2010).
26. Buscema, M., Steele, G. A., van der Zant, H. S., Castellanos-Gomez, A. The effect of the substrate on the Raman and photoluminescence emission of single-layer MoS₂. *Nano Res.* **7**, 561-571 (2014).
27. Itoh, T., Yamamoto, Y. S., Ozaki, Y. Plasmon-enhanced spectroscopy of absorption and spontaneous emissions explained using cavity quantum optics. *Chem. Soc. Rev.*, (2017).
28. Zhao, M. *et al.* Atomically phase-matched second-harmonic generation in a 2D crystal. *Light: Sci. & Appl.* **5**, e16131 (2016).
29. Chen, H. *et al.* Enhanced second-harmonic generation from two-dimensional MoSe₂ on a silicon waveguide. (2017).
30. Li, Y. *et al.* Probing symmetry properties of few-layer MoS₂ and h-BN by optical second-harmonic generation. *Nano Lett.* **13**, 3329-3333 (2013).
31. Zhao, M. *et al.* Atomically phase-matched second-harmonic generation in a 2D crystal. *Light Sci. Appl.* **5**, e16131 (2016).
32. New, G. *Introduction to nonlinear optics*. Cambridge University Press (2011).
33. Janisch, C. *et al.* Extraordinary second harmonic generation in tungsten disulfide monolayers. *Sci. Rep.* **4**, (2014).
34. Shi, J. *et al.* 3R MoS₂ with Broken Inversion Symmetry: A Promising Ultrathin Nonlinear Optical Device. *Adv. Mater.*, (2017).
35. Hsu, W.-T. *et al.* Second harmonic generation from artificially stacked transition metal dichalcogenide twisted bilayers. *ACS Nano* **8**, 2951-2958 (2014).
36. Jiang, T. *et al.* Valley and band structure engineering of folded MoS₂ bilayers. *Nat. Nanotechnol.* **9**, 825-829 (2014).
37. Yin, X. *et al.* Edge nonlinear optics on a MoS₂ atomic monolayer. *Science* **344**, 488-490 (2014).
38. Wang, G. *et al.* Giant enhancement of the optical second-harmonic emission of WSe₂ monolayers by laser excitation at exciton resonances. *Phys. Rev. Lett.* **114**, 097403 (2015).
39. Clark, D. *et al.* Strong optical nonlinearity of CVD-grown MoS₂ monolayer as probed by wavelength-dependent second-harmonic generation. *Phys. Rev. B* **90**, 121409 (2014).
40. Kumar, N. *et al.* Second harmonic microscopy of monolayer MoS₂. *Phys. Rev. B* **87**, 161403 (2013).

41. Shen, Y.-R. The principles of nonlinear optics. *New York, Wiley-Interscience, 1984, 575 p.*, (1984).
42. Rodrigues, S. P., Cai, W. Nonlinear optics: tuning harmonics with excitons. *Nat. Nanotechnol.* **10**, 387-388 (2015).
43. Fryett, T. K. *et al.* Silicon photonic crystal cavity enhanced second-harmonic generation from monolayer WSe₂. *2D Mater.* **4**, 015031 (2016).
44. Yi, F. *et al.* Optomechanical enhancement of doubly resonant 2D optical nonlinearity. *Nano Lett.* **16**, 1631-1636 (2016).
45. Fiori, G. *et al.* Electronics based on two-dimensional materials. *Nat. Nanotechnol.* **9**, 768-779 (2014).
46. Mak, K. F., McGill, K. L., Park, J., McEuen, P. L. The valley Hall effect in MoS₂ transistors. *Science* **344**, 1489-1492 (2014).
47. Zhang, W. *et al.* Ultrahigh-gain photodetectors based on atomically thin graphene-MoS₂ heterostructures. *Sci. Rep.* **4**, 3826 (2014).
48. Korn, T. *et al.* Low-temperature photocarrier dynamics in monolayer MoS₂. *Appl. Phys. Lett.* **99**, 102109 (2011).
49. Sun, D. *et al.* Observation of rapid exciton–exciton annihilation in monolayer molybdenum disulfide. *Nano Lett.* **14**, 5625-5629 (2014).
50. Kumar, N. *et al.* Exciton-exciton annihilation in MoSe₂ monolayers. *Phys. Rev. B* **89**, 125427 (2014).
51. Boulesbaa, A. *et al.* Ultrafast dynamics of metal plasmons induced by 2D semiconductor excitons in hybrid nanostructure arrays. *ACS Photonics* **3**, 2389-2395 (2016).

Chapter 2 Fabrication and characterization techniques

This chapter will present a general review of the fabrication, transfer and characterization techniques used in 2D materials. The 2D materials WSe₂, MoS₂ and graphene used in this thesis were prepared by the chemical vapor deposition (CVD) method, and transferred to target substrates by wet transfer techniques. The gold plasmonic nanostructures were fabricated by the template-stripping method. The optical properties were characterized by photoluminescence (PL), Raman, second harmonic generation (SHG) and transient absorption (TA) spectroscopies. The morphologies of the samples were characterized by optical microscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). The detailed recipes and equipment are described in Chapter 3, 4 and 5 where they were used.

2.1 Preparation of 2D materials

Two major strategies have been employed to obtain monolayer 2D materials: one is the top-down method of mechanical or chemical exfoliation from bulk crystals; the other is the bottom-up method of chemical vapor deposition method (CVD)¹. The first method allows the production of high-quality and micrometer-sized monolayer samples. The second CVD method is more suitable for large-scale production as it generates high-quality 2D materials with a scalable size, controllable thickness as well as excellent optical and electronic properties.

2.1.1 Growth of TMDCs

For practical application of 2D TMDCs in electronic and optical devices, synthesis of atomically thin membrane with layer controllability and large-area uniformity by CVD is an indispensable requirement.

An early strategy for growing large-area MoS₂ layers reported by Lain-Jong Li's group is based on the direct chemical vapor phase reaction of MoO₃ and S powders^{2, 3}. The precursors MoO₃ and S powders are placed on separate ceramic or quartz boats, and the desired substrate such as *c*-face sapphire or silicon wafer are placed at the downstream of the furnace (Fig. 2.1a) or put facing down at the top of the boat containing MoO₃ (Fig. 2.1b). When MoO₃ is heated to 600 C°–700 C° by the furnace, S is heated to ~ 120 C° by heating belt (Fig. 2.1a)² or by utilizing the temperature variation (Fig. 2.1b)³ nearby the furnace, the gas Ar or mixture of H₂/Ar will carry the sulfur vapor to react with the diffused MoO₃ in the form of an intermediate phase MoO_{3-x} on the substrate. This approach renders the growth of single crystalline MoS₂ flakes on arbitrary substrates, and is thus widely used for producing synthetic monolayer TMDCs.

Figure 2.1c shows the process for producing wafer-scale MoS₂ membranes⁴. A MoO₃ thin layer with a desired thickness was initially thermally evaporated on *c*-face sapphire substrate. In the process of growth, the MoO₃-coated sapphire substrate is reduced to MoO₂ or other reduced Mo oxides in a H₂/Ar environment at 500 C°. The sample was then annealed in a sulfur-rich environment at 1000 C°, leading to the formation of a wafer-scale MoS₂ thin layer with semiconductor properties. Other TMDCs materials such as WSe₂ can be grown by similar method⁵. The monolayer WSe₂ with triangular shape used in Chapter 3 and 4 were grown by Lain-Jong Li's group and the monolayer MoS₂ film used in Chapter 5 was grown by myself via the method as shown in Figure 2.1 b, and the furnace was brought from MTI Corporation as shown in Fig. 2.2a.

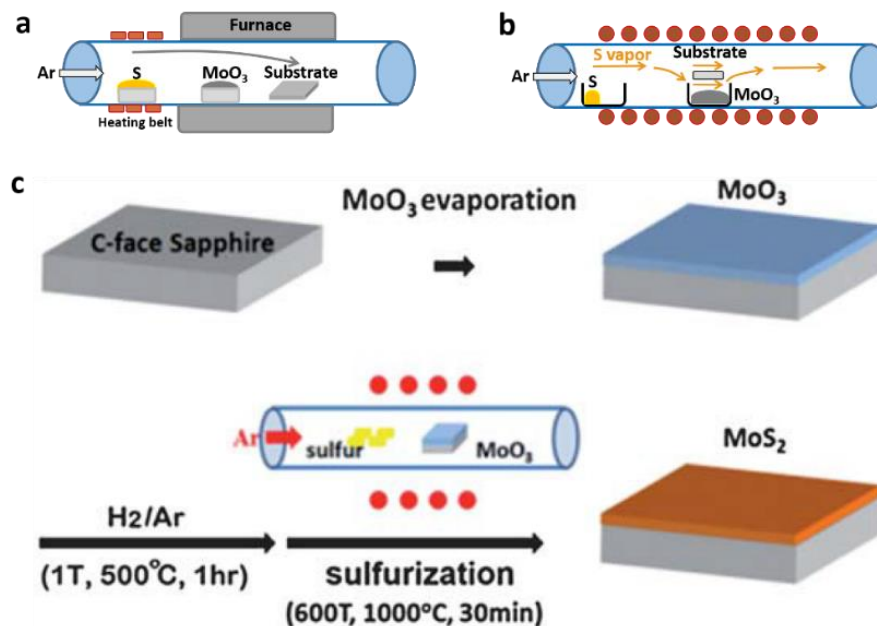


Figure 2.1 | Schematic illustration for the growth of TMDCs by CVD method. (a-b) Schematic of the synthesis process of MoS₂ by using precursors of MoO₃ and S powers. The temperature control of S power is achieved by heating tape (a) or by putting it at an appropriate place nearby the furnace (b). (c) Schematic illustration for the synthesis of MoS₂ layers by sulfurization of MoO₃ film on c-face sapphire⁴. Figure reproduced with permission from: (c), ref. 4, © 2012, the Royal Society of Chemistry.

2.1.2 Growth of graphene

Large-area graphene films can be grown on copper substrates at the temperature up to 1000 C° by CVD of carbon using a mixture of methane and hydrogen⁶. The films grown by this method are predominantly single-layer graphene with a small percentage (less than 5%) of the area having a few layers. They are continuous across copper surface steps and grain boundaries with the size of several centimeters. The low solubility of carbon in copper makes this growth process self-limiting, thus generating monolayer graphene on the copper foil substrate. The large-area monolayer graphene used in Chapter 5 was grown by myself via this CVD method. A separate furnace from the one used to grown MoS₂ was utilized to grow graphene so as to avoid contamination (Fig. 2.2b).

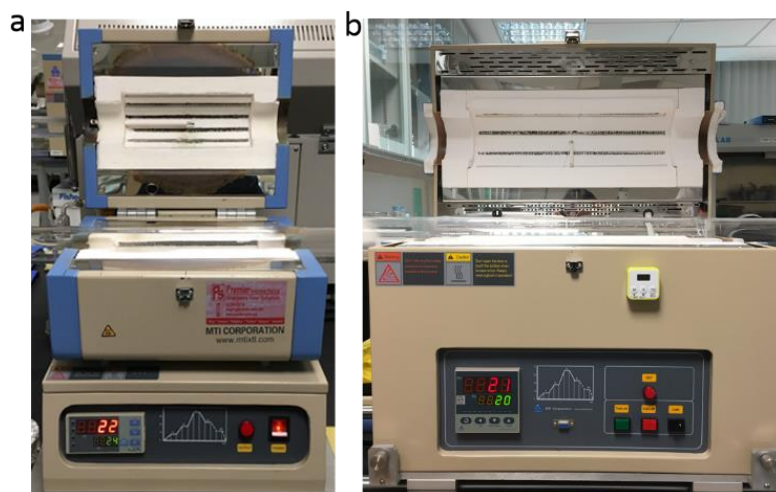


Figure 2.2 | Photos of the furnaces (MTI Corporation) that were used to grow 2D materials. (a) The furnace was used to grow monolayer MoS₂. (b) The furnace was used to grow monolayer graphene.

2.2 Transfer techniques

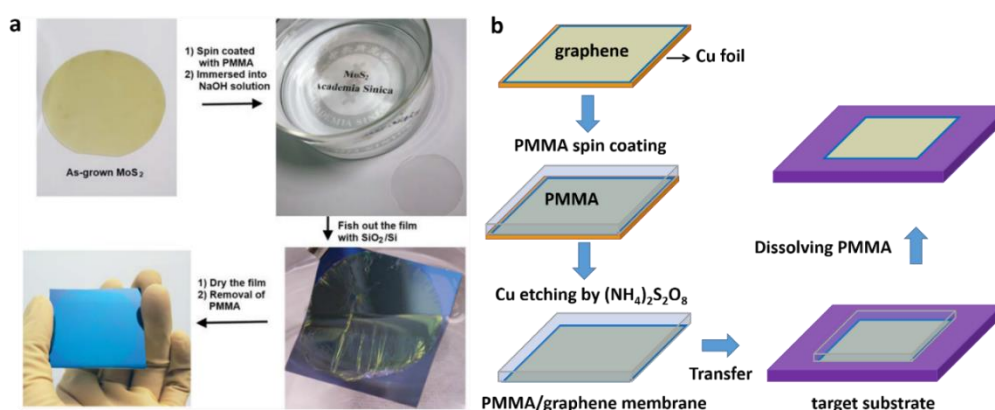


Figure 2.3 | Processes to transfer TMDCs or graphene on desired substrates. (a) Pictures showing the procedure to transfer as-synthesized MoS₂ layer from a sapphire to a SiO₂/Si wafer⁴. (b) Schematic view of the transfer process of graphene⁷. Figure reproduced with permission from: (a), ref. 4, © 2012, the Royal Society of Chemistry.

Exploring the potential of 2D materials requires us to perfectly transfer the CVD synthesized 2D materials from the growth substrates onto other substrates without compromising the sample quality and properties, as the substrates used for the growth of 2D materials may be different from those required for fundamental or applied research. The early strategy used to transfer

2D materials as demonstrated in Fig. 2.3 is called the wet transfer method^{4, 7}, namely, using polymethyl methacrylate (PMMA) to support the 2D materials and then etching the growth substrate by hot base solution to lift off the films followed by removal of PMMA. Subsequently, a dry transfer method was developed leveraging the penetration of water between hydrophobic TMDCs films with spin coated polystyrene (PS) and hydrophilic growth substrates to lift off the films⁸, and dry transferring the film to the desired substrate by tweezers. In this thesis, the wet transfer method was used to transfer TMDCs and graphene as it provides a better contact between the 2D materials and the target substrate.

2.3 Fabrication of metal nanostructures

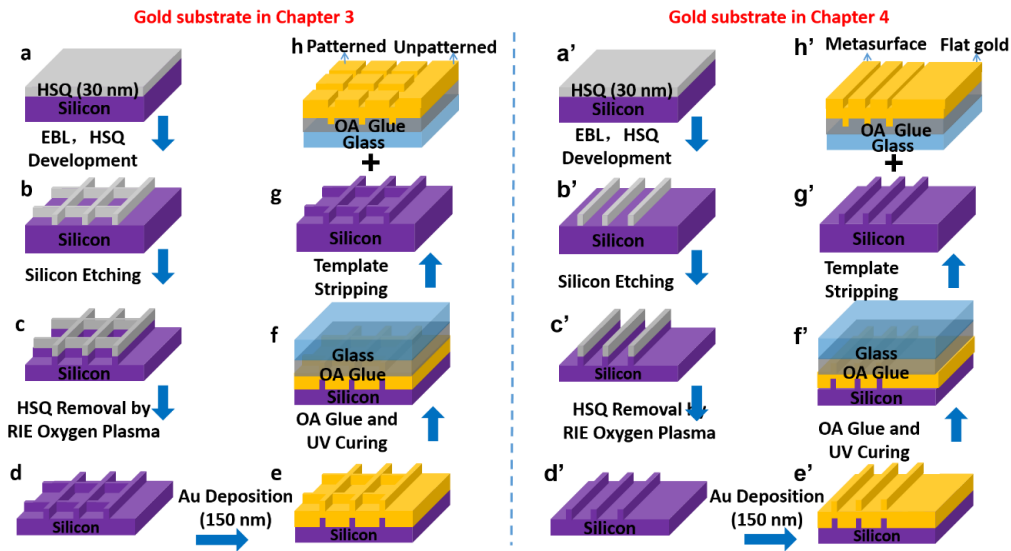


Figure 2.4 | Detailed illustration on the fabrication process of template-stripped gold substrates used in Chapter 3 (Left Panel) and Chapter 4 (Right Panel). (a, a') Spin coating of hydrogen silsesquioxane (HSQ) resist onto the silicon substrate. (b, b') Electron beam exposure of HSQ resist with the design pattern and NaOH/NaCl salty development of HSQ resist. (c, c') Silicon etching by inductively coupled plasma (ICP). (d, d') Residue HSQ resist mask sputtered away by reactive-ion etching (RIE) oxygen plasma. (e, e') Deposition of 150-nm-thick gold film by using e-beam evaporator. (f, f') Drop casting of optical adhesive (OA) glue onto the gold film and followed by a glass coverslip. OA glue is then cured by UV irradiation. (g, g')-(h, h') Template stripping process to fabricate the patterned gold nanostructures.

The metal nanostructures supporting localized surface plasmon can be used to enhance the optical or optoelectronic properties of 2D TMDCs as discussed in Chapter 1. In this thesis, the gold nanostructures used in Chapter 3 (Left Panel, Fig. 2.4) and Chapter 4 (Right Panel, Fig. 2.4) was made by template-stripping method⁹ as sub-20-nm-wide trenches can be easily obtained by this method. This narrow trenches can provide extremely strong localized field as compared with other nanostructures upon illumination of laser, thus rendering enhanced light emission from TMDCs. The fabrication was done by Dr. Zhaogang Dong in my co-supervisor A/P Joel K. W. Yang's group, Institute of Materials Research and Engineering (IMRE).

The gold substrate used in Chapter 3 has crossed trenches, while the one used in Chapter 4 has trenches all along one direction. Despite the slight difference in trenches, both substrates were patterned by the template-stripping method based on nano-patterned silicon templates, as shown in Fig. 2.4. First, 2% hydrogen silsesquioxane (HSQ) dissolved in methyl isobutyl ketone (MIBK) was spin coated onto a cleaned silicon substrate at 5000 rounds per minute (rpm). The thickness of the HSQ layer was around 30 nm. Then, the pattern of the HSQ resist was fabricated using electron beam lithography (EBL) with an electron acceleration voltage of 100 keV. The exposed HSQ was developed using NaOH/NaCl (1 wt %/4 wt %) in de-ionized water for 60 seconds before immersing in DI water for 60 seconds to stop the development. Next, silicon etching was carried out by inductively-coupled plasma (ICP) using a gas combination of Cl₂ and HBr. The HSQ feature functioned as a protection mask. After the silicon etching process, the HSQ mask was removed by using reactive-ion-etching (RIE) oxygen plasma, where the HSQ mask was sputtered away by

the reactive ions. Next, a 150-nm-thick gold film was evaporated onto the silicon substrate. Several droplets of the optical adhesive (OA) glue were put onto the sample surface using a pipette. A glass slide was then placed on top of the OA glue and the OA glue was cured using ultra-violet radiation, followed by template-stripping process, where the gold substrate was stripped from the silicon template.

2.4 Optical characterization

The optical properties of 2D TMDCs were carefully characterized before and after transferring them onto the desired substrate. This section will briefly review the working mechanism and optical equipment used to characterize 2D TMDCs.

2.4.1 PL and Raman

PL and Raman are importance nondestructive techniques to characterize the quality and thickness of the TMDCs. In PL and Raman measurement, a confocal setup (Fig. 2.5a) is used to excite the sample using a monochromic pump laser. The pump laser was focused by a microscope objective lens, and the PL or Raman was then collected by the same objective and detected by a nitrogen cooled charge coupled device. PL is the main technique used in Chapter 3, and the detailed measurement parameters will be shown there.

In monolayer TMDCs, electrons in the valence bands maximum (VBM) can be excited to the conduction bands minimum (CBM) by a pump laser, and the excited carriers can also recombine, releasing the energy by emitting light, as shown in Fig. 2.5b. The former process can be characterized by light absorption measurements, and the latter process can be characterized by PL measurements. More information about the origin of PL and the thickness-

dependence of PL intensity is described in Section 1.3. If lattice vibrations or phonons participate in the optical transitions, the generated photon will have a lower energy than the incident photon (Stoke shift), and the energy difference is associated with a specific phonon modes of the materials. This inelastic light scattering process is called Raman scattering, as shown in Fig. 2.5c.

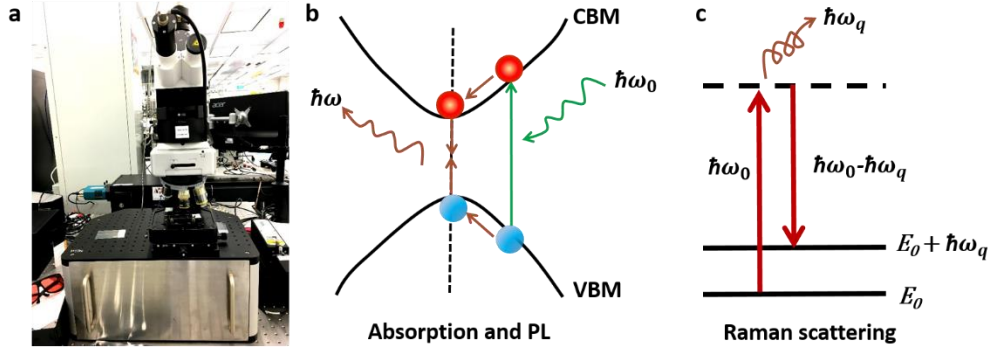


Figure 2.5 | Optical setup of PL and Raman, and the related physics process. (a) Photo of a typical PL and Raman setup (WITec). (b) Light absorption and emission process. $\hbar\omega_0$ is the energy of the incident light, $\hbar\omega$ is the energy of the emitted light in the PL process. (c) Raman scattering process. $\hbar\omega_q$ is the energy of the emitted phonon.

For the Raman spectrum of monolayer WSe₂, two dominant peaks are observed around 250 cm⁻¹ (Fig. 2.6a)¹⁰. However, few systematic trends could be observed on both the two modes as the film thickness increases. The Raman spectrum of MoS₂ also has two prominent peaks: an in-plane (E_{2g}^1) mode located around 383 cm⁻¹ and an out-of-plane (A_{1g}) mode located around 407 cm⁻¹, as shown in Fig. 2.6b¹¹. The in-plane mode is caused by sulphur atoms vibrating in one direction and the molybdenum atom in the other, while the out-of-plane mode results from just the sulphur atoms vibrating out-of-plane. These two modes evolve with the thickness of MoS₂. In the monolayer, the in-plane mode upshifts to 386 cm⁻¹ and the out-of-plane downshifts to 404 cm⁻¹. The peak difference of the two modes (~ 18 cm⁻¹) is a reliable identification for monolayer MoS₂.

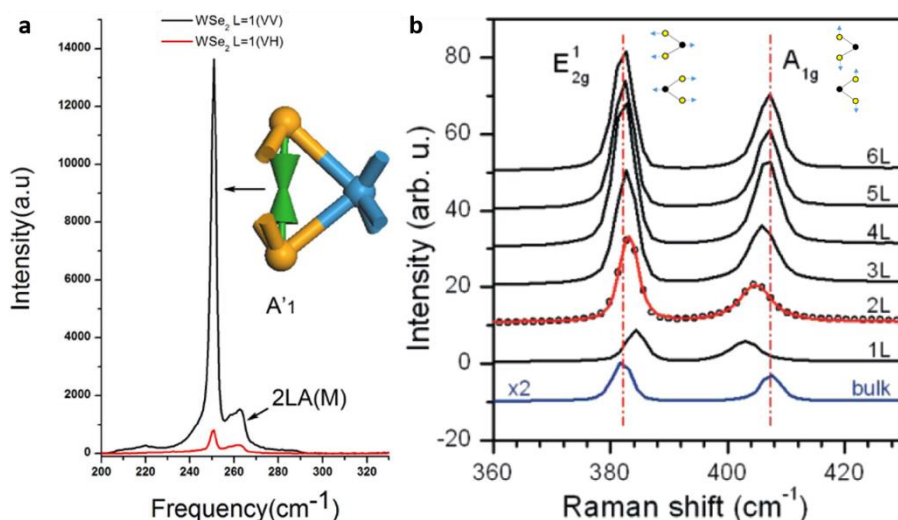


Figure 2.6 | Raman spectra of TMDCs. (a) Raman spectra of monolayer WSe₂ taken with a laser under conventional geometry (VV) and cross polarization (VH)¹⁰. (b) Raman of spectra of MoS₂ with various thickness¹¹. Figure reproduced with permission from: (a), ref. 10, © 2014, Nature Publishing Group; (b), ref. 11, © 2015, American Chemical Society.

2.4.2 SHG spectroscopy

Discovery of second harmonic generation (SHG) in 1961 by Peter Franken *et al.* at University of Michigan opened up a window for exploring nonlinear optics. Shortly after the construction of the first laser by Theodore Harold Maiman, this field underwent dramatic advances. As more information about the origin of SHG and its function in characterizing TMDCs has already been presented in Chapter 1, this section will only demonstrate a brief comparison of SHG and PL techniques. Both techniques can be used in microscopy and spectroscopy modes to characterize the material properties. However, they have several differences in their origin, requirements for samples and optical set for conducting experiments. First, SHG is a second order coherent process where two lower energy photons are up-converted to exactly twice the incident frequency (half the wavelength) of an excitation laser. This process is carried out via an intermediate virtual state (Fig. 2.7a), requiring the materials to have no inversion symmetry. In contrast, PL is a process for

materials absorbing light with higher energy and emitting light with lower energy (Fig. 2.7b), requiring the materials to be semiconductors. The energy of the emitted light is associated with the optical bandgap of the materials. Second, the SHG experiment is generally conducted by pulsed laser, as the SHG is a nonlinear process requiring high electric field, while PL experiment is often conducted with a continuous-wave laser with energy larger than bandgap of the samples. The detailed parameters for SHG experiment will be discussed in Chapter 4.

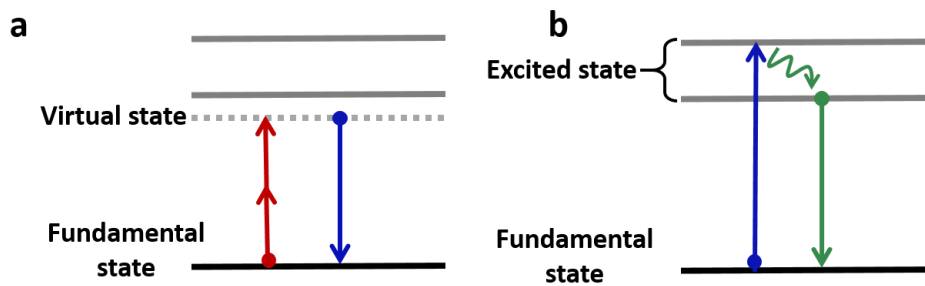


Figure 2.7 | Comparison of SHG and PL processes. (a) Demonstration of the process related with SHG. (b) Demonstration of the process related with PL.

2.4.3 Reflectance spectroscopy

Reflectance spectroscopy is a useful tool to deduce the absorbance of the materials on an opaque substrate and to identify the plasmon resonant wavelength of metal nanostructures. The reflectance spectrum is the plot of the reflectance as a function of wavelength. Generally, the resonant wavelength of the nanostructure is featured as a dip in the reflectance spectrum, as the nanostructure has strong absorption there. In Chapter 3 and 4, the plasmon resonant wavelength was quantitatively determined by this simple approach.



Figure 2.8 | Photo of the CRAIC UV-VIS-NIR micro-spectrophotometer (model QDI 2010) used to measure reflectance spectra.

Reflectance is defined by the fraction of incident electromagnetic power that is reflected at an interface. The absolute reflectance spectrum of a target sample is normally determined by comparison with a standard substrate such as aluminum or gold substrate with known reflectivity via the equation:

$$\rho_t = \rho_s \frac{L_t}{L_s} \quad (2.1)$$

where ρ_t is the reflectance of the target sample with unit of percentage, ρ_s is the reflectance of the standard with known reflectance spectrum profile, L_t and L_s are the reflected signal of the target and standard substrate, respectively, which are collected by the charge-coupled device (CCD) of the equipment with the unit of CCD counts. The main purpose for using the standard sample here is to calibrate the intensity of the incident light as its intensity varies with wavelength. The optical reflectance spectra of the sample shown in Chapter 3 and 4 were measured using a CRAIC UV-VIS-NIR micro-spectrophotometer model QDI 2010 (equipped with a $36\times$ objective lens with $NA = 0.5$). The picture of the setup is shown in Fig. 2.8.

2.4.4 Transient absorption spectroscopy

Experimental setup

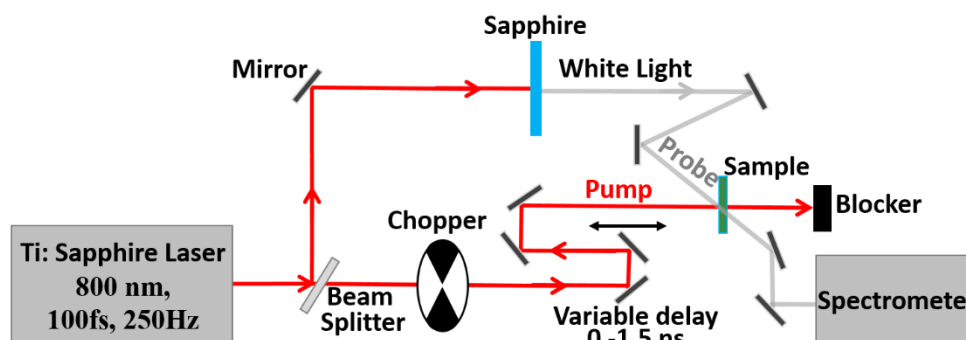


Figure 2.9 | Pump-probe setup. A schematic view of a typical two colour pump-probe setup. Pump (red) comes from the Ti: sapphire oscillator. The continuum white light (silver) generated from the sapphire crystal (blue) is used as the probe.

The experimental setup for transient absorption (TA) spectroscopy is illustrated in Fig. 2.9. The TA spectra is measured by using a Kerr-lens mode-locked Ti: sapphire oscillator and a standard two-color pump-probe setup. The output of the oscillator with certain wavelength is split into two beams by a beam splitter. One beam with a diameter of hundreds of μm was focused on the sample as the pump and blocked after the sample. The other beam is focused on a sapphire, calcium fluoride plate, quartz or water to generate a supercontinuum white light with wavelength normally ranging from 400 to 1100 nm (depending on the material) and used as a broadband probe. The probe has low intensity so as to avoid multiphoton/multistep processes during probing, namely it does not transfer a significant population from the ground to the excited states (or vice versa), and has a diameter slightly smaller than the pump. In order to vary the time delay (τ) between the pump and probe pulses, the pump is sent through an optical delay line, which consists of a retroreflector mounted on a computer-controlled translation stage.

A TA experiment proceeds as follows¹²: tuning the time delay between the pump and probe beams to a fixed duration by the optical delay line, and using an optical chopper to block every other excitation pulse. In this way, the sample is being excited by the pump and not excited alternately. The detector alternately records the spectrally resolved intensity of the probe that passes through (transmission mode) or reflected from (reflection mode) the sample being ‘pumped’ and ‘unpumped’, $I(\lambda)_{\text{pumped}}$ and $I(\lambda)_{\text{unpumped}}$. An absorbance difference spectrum $\Delta A(\lambda)$ is reconstructed according to:

$$\Delta A(\lambda) = -\log I(\lambda)_{\text{pumped}}/I(\lambda)_{\text{unpumped}} \quad (2.2)$$

where λ is the detection wavelength. Subsequently, the delay line is moved to another time delay between the pump and probe, and the above procedures are repeated. In this way, the entire dataset $\Delta A(\lambda, \tau)$ is collected.

Contributing processes to the spectrum

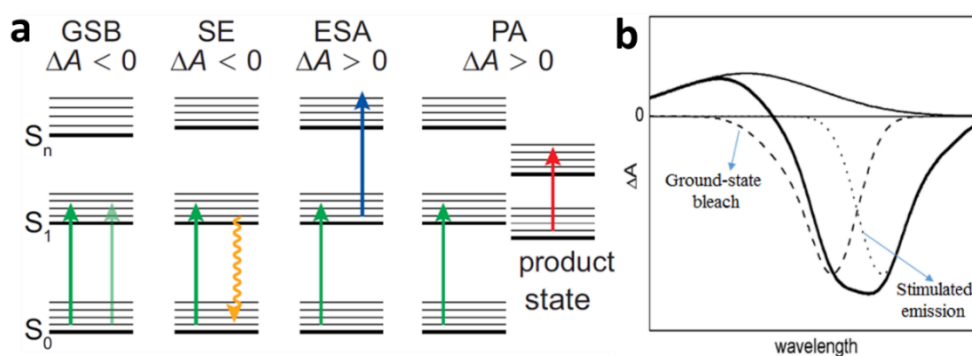


Figure 2.10 | Contributions in TA spectra. (a) Physics process of signal contributions in transient absorption spectroscopy¹³. Both the ground state bleaching (GSB) and the stimulated emission (SE) result in a negative change in absorbance $\Delta A < 0$. The excited-state absorption (ESA) and the absorption of a photoproduct (PA) give a positive signal $\Delta A > 0$. (b) Components comprising transient absorption spectrum: ground-state bleaching (dashed line), stimulated emission (dotted line), excited-state absorption (gray line), sum of these contributions (thick solid line)¹⁴. Figure reproduced with permission from: (b), ref. 13, © 2009, Photosynthesis Research, Springer.

As shown in Fig. 2.10, a ΔA spectrum contains contributions from various processes¹⁴:

- (1) The first contribution is ground-state bleaching. When the pump pulse excites the sample, a fraction of the molecules leave the ground states and transfer to the excited state (dark green arrow, Fig. 2.10a). This means the number of ground-state molecules in the excited sample is less than that in unexcited sample. As a result, a negative signal in the ΔA spectrum is observed in the wavelength region of ground state absorption (dashed line, Fig. 2.10b).
- (2) The second contribution is stimulated emission. It occurs when the probe pulse finds optically allowed transition of excited state in molecules, and the photons of the probe pulse stimulate the emission of the molecules (yellow dashed arrow, Fig. 2.10a). This process increases the intensity of the detected probe, resulting in a negative signal in ΔA spectrum (dotted line, Fig. 2.10b).
- (3) The third contribution is excited-state absorption. Upon excitation with the pump beam, the molecules in the excited state can be excited to a higher excited state (blue arrow, Fig. 2.10) in certain wavelength regions, and absorption of the probe at these wavelengths emerges. As a result, a positive signal in the ΔA spectrum is observed in the wavelength region of excited-state absorption (gray line, Fig. 2.10b).
- (4) The fourth possible contribution to the ΔA spectrum stemming from product absorption. Upon excitation of the photosynthetic or photochemical system, reactions may occur that generate a transient or a long-lived molecular state, such as triplet states, charge-separated states and isomerized states (red arrow, Fig. 2.10a). The absorption of such a product will arise as a positive signal in the ΔA spectrum.

Note that the intensity of the probe pulse is so weak that the excited-state population is not affected appreciably by these processes.

Data analysis and interpretation

TA spectroscopy yields multidimensional data sets $\Delta A(\lambda, \tau)$ where one independent dimension is given by the delay-time τ , and the other one by the probe wavelength λ . The large amounts of data collected can be analyzed by global and target analysis techniques. The common global analysis procedure is global lifetime analysis (GLA), where the data, $\Delta A(t, \lambda_i)$, is represented by a discrete sum-of-exponentials function:

$$\Delta A(t, \lambda_i) = \sum_{j=1}^n DAS(\tau, \lambda_i) \exp(-t/\tau_j) \quad (2.3)$$

where the global parameters spanning the dataset are the lifetimes, τ , and the $DAS(\tau, \lambda_i)$ are pre-exponential amplitudes. The DAS are decay-associated spectra, representing the kinetic information of different states. It is plotted against detection wavelength, λ , as shown in Fig. 2.11a.

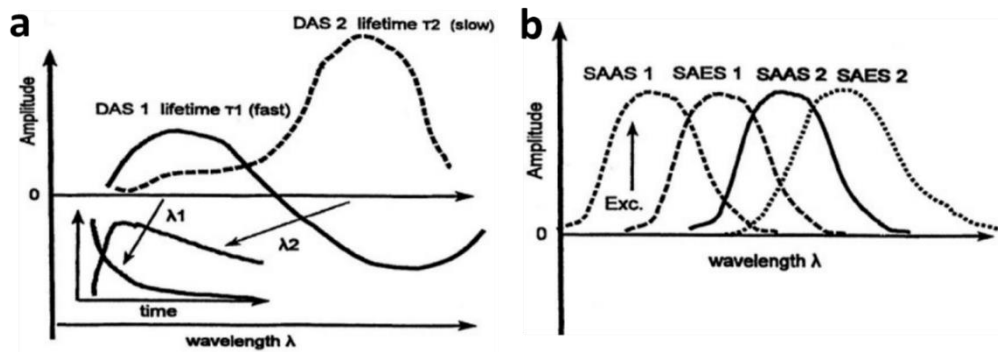


Figure 2.11 | TA spectra¹⁵. (a) Decay-associated spectra (DAS) of the two lifetime τ_1 and τ_2 , and time course of absorption intensity for two detection wavelength λ_1 and λ_2 . (b) States-associated absorption (SAAS) and states-associated emission spectra (SAES) of the two-component system.

For a coupled N-states system, we have in general $n = N$, namely, the number of kinetic components (lifetimes) equals the number of distinguishable states in the system. Take a system with $n = 2$ for example. The lifetime for a certain state is constant at all detection wavelength, *i.e.*, $\tau_1(\lambda_1) = \tau_1(\lambda_2) = \dots \tau_1(\lambda_i)$ and $\tau_2(\lambda_1) = \tau_2(\lambda_2) = \dots \tau_2(\lambda_i)$. Then we need to do target analysis, namely, fitting

a ‘spectral model’ to the data. The physical parameters of interest are not DAS, but the SAAS (Fig. 2.11b) which represents state-associated absorption spectrum. The following equations show the relationships between these parameters¹⁵:

$$DAS_1(\lambda_{em}) = c_{11} * SAAS_1 + c_{12} * SAAS_2 \quad (2.4)$$

$$DAS_2(\lambda_{em}) = c_{21} * SAAS_1 + c_{22} * SAAS_2 \quad (2.5)$$

The DAS are linear combinations of SAAS with coefficient c_{lm} . The lifetimes τ_i are functions of rate constants and the kinetic connecting scheme of the system under study. The coefficients for the SAAS are complicated functions of both the rate constants, the excitation wavelength, and the extinction coefficients of the species involved.

Comparison of TA and steady-state spectroscopy

TA spectroscopy is an extension of steady-state absorption spectroscopy, but their working mechanism and setup are totally different. TA spectroscopy is an example of non-linear spectroscopy based on the pump-probe technique, measuring signal change of the probe passing through the sample in the case of illumination and blocking of the pump laser. Here, the absorbance at a particular wavelength or a range of wavelengths is measured as a function of time after excitation by a flash of pulsed laser. The time resolution relies on the ability to resolve two physical actions of the pump and probe in real time. In principle, the shorter the detection time, the better the resolution. Therefore, in TA spectroscopy, a femtosecond laser is frequently used as it offers a better resolution than a nanosecond laser. In contrast, the steady-state absorption spectroscopy only uses one light source covering a broad range of wavelengths

for radiating the sample. It provides spectral information of the absorbance of the material but cannot give temporal information about the carrier dynamics.

TA is the major technique used in Chapter 5, where the setup is similar to the one shown in Fig. 2.9 and detailed experimental parameters are listed there. The TA experiments in Chapter 5 were done and analyzed by Dr. Lei Wang in Prof. Hongbo Sun's group, Jilin University, China. This part is included for completeness and better understanding of Chapter 5.

2.5 Characterization of morphology

The morphology of 2D materials and nanostructure were characterized by optical microscopy (OM), atomic-force microscopy (AFM) and scanning electron microscopy (SEM).

2.5.1 AFM

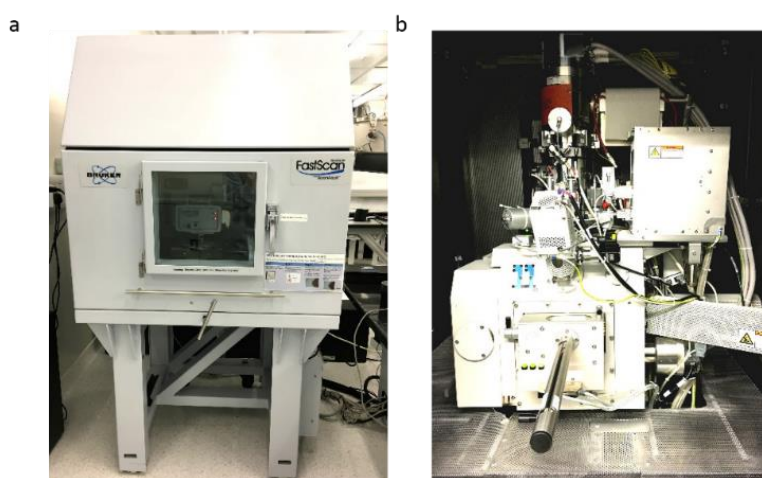


Figure 2.12 | Setup for morphology characterization. (a) Atomic Force Microscopy (FastScan, Bruker). (b) Field Emission Scanning Electron Microscopy (FEI Verios 460).

AFM is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The height and

roughness of the samples in this thesis were measured by a BRUKER Dimension FastScan AFM (Fig. 2.12a).

2.5.2 SEM

SEM produces images of a sample by scanning it with a focused beam of electrons. These electrons interact with atoms in the sample, generating various signals that contain information about the sample surface topography. SEM images shown in this thesis were measured by FEI Verios 460 Field Emission SEM (Fig. 2.12b) with a current of 100 pA and electric field of 10 kV.

2.6 Scanning tunneling macroscopy

Scanning tunneling microscopy (STM) measurements in Chapter 5 were carried out by Dr. Yuli Huang in my main supervisor Prof. Andrew T. S. Wee' group in National University of Singapore (NUS). Scanning tunneling spectroscopy (STS), an extension of STM, provides information about the density of electrons in a sample as a function of their energy. The STM/STS measurements were conducted in an ultra-high vacuum system housing an Omicron LT-STM interfaced to a Nanonis controller. The sample was degassed overnight at 350 °C before STM/STS analysis was performed, and kept at 77 K during the measurements. For dI/dV spectra, the tunneling current was obtained by a lock-in amplifier, with a modulation of 625 Hz and 40 mV. Note that the bias voltage (V_{tip}) is applied on the STM tip; hence negative values correspond to the conduction band and positive values to the valence band.

2.7 References

1. Shi, Y., Li, H., Li, L.-J. Recent advances in controlled synthesis of two-dimensional transition metal dichalcogenides via vapour deposition techniques. *Chem. Soc. Rev.* **44**, 2744-2756 (2015).
2. Lee, Y. H. *et al.* Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. *Adv. Mater.* **24**, 2320-2325 (2012).

3. Lee, Y.-H. *et al.* Synthesis and transfer of single-layer transition metal disulfides on diverse surfaces. *Nano Lett.* **13**, 1852-1857 (2013).
4. Lin, Y.-C. *et al.* Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization. *Nanoscale* **4**, 6637-6641 (2012).
5. Zhou, H. *et al.* Large area growth and electrical properties of p-type WSe₂ atomic layers. *Nano Lett.* **15**, 709-713 (2014).
6. Li, X. *et al.* Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science* **324**, 1312-1314 (2009).
7. Liang, X. *et al.* Toward clean and crackless transfer of graphene. *ACS Nano* **5**, 9144-9153 (2011).
8. Gurarslan, A. *et al.* Surface-energy-assisted perfect transfer of centimeter-scale monolayer and few-layer MoS₂ films onto arbitrary substrates. *ACS Nano* **8**, 11522-11528 (2014).
9. Dong, Z. *et al.* Second-harmonic generation from sub-5 nm gaps by directed self-assembly of nanoparticles onto template-stripped gold substrates. *Nano Lett.* **15**, 5976-5981 (2015).
10. Terrones, H. *et al.* New first order Raman-active modes in few layered transition metal dichalcogenides. *Sci. Rep.* **4**, 4215 (2014).
11. Lee, C. *et al.* Anomalous lattice vibrations of single-and few-layer MoS₂. *ACS Nano* **4**, 2695-2700 (2010).
12. Klimov, V. I., McBranch, D. W. Femtosecond high-sensitivity, chirp-free transient absorption spectroscopy using kilohertz lasers. *Optics letters* **23**, 277-279 (1998).
13. Kanal, F. Femtosecond Transient Absorption Spectroscopy –Technical Improvements and Applications to Ultrafast Molecular Phenomena. *Thesis*, 11 (2015).
14. Berera, R., van Grondelle, R., Kennis, J. T. Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems. *Photosynth. Res.* **101**, 105-118 (2009).
15. Ames, J., Hoff, A. J. *Biophysical techniques in photosynthesis*. Springer Science & Business Media (2006).

Chapter 3 Giant PL Enhancement in WSe₂-Gold Plasmonic Hybrid Structures

3.1 Introduction

Distinct from semimetal graphene with no band gap, crystalline monolayers of transition metal dichalcogenides (TMDCs) are direct bandgap two-dimensional (2D) semiconductors that are promising as light-active materials for optoelectronic applications^{1, 2}. Recently, TMDCs have shown great potential in ultrasensitive photodetectors and ultrathin light absorbers and emitters³⁻⁵. However, their application in photonic devices is limited by their low absolute photoluminescence (PL), albeit the direct band gap in monolayer TMDCs leads to much larger PL than the bilayer, few-layer and bulk counterparts. The low PL is caused by low quantum efficiency arising from low radiative decay rate and weak absorption owing to the innate thin thickness⁶. Fortunately, integrating noble metal nanostructures supporting localized surface plasmons (LSPs)⁷⁻¹³ and propagating surface plasmon polaritons (SPPs)^{14, 15} can afford significant PL enhancement owing to the increase of optical density of states.

Among TMDCs, tungsten diselenide (WSe₂) attracts tremendous research interests as it is a promising material for creating electrically excited light-emitting diodes¹ and heterostructures with MoS₂ (ref. 5). It has been shown to be a promising emitter at ~ 750 nm wavelength with a quantum yield that is two orders of magnitude larger than that of MoS₂ (refs 16, 17) at room temperature. However, the research of PL enhancements from WSe₂-plasmonic hybrid nanostructures is limited. Recently reported enhancements in MoS₂ are potentially close to the ultimate limit that can be achieved from this material⁹,

¹⁸. While it is generally more challenging to achieve large enhancements from systems with a higher quantum yield, it is significant to explore the ultimate limit in the PL enhancements that can be achieved in WSe₂.

We obtained giant PL enhancement factor (EF) of ~ 20,000-fold from a single crystal monolayer of WSe₂ by suspending it over sub-20-nm-wide trenches that support lateral gap plasmons. By systematically tuning the gap plasmon resonances to the 633-nm pump laser, a close correlation was observed between the local near-field intensity, the Purcell factor and the measured PL enhancements. This character sheds light on the utility of lateral gap plasmons in promoting excitation of electron-hole pairs at the pump laser wavelength and their radiative emission at 750 nm, providing an effective way to obtain giant PL in TMDCs. Unlike previous plasmon-enhanced structures^{8, 9, 12, 13}, our hybrid plasmon-enhanced design provides full access to the top surface of WSe₂, facilitating stacking of other 2D materials, adding electrical top contacts or optical waveguiding, and conducting chemical doping.

3.2 Experimental and simulation methodology

3.2.1 Growth and transfer of WSe₂

The triangular-shape monolayer WSe₂ was grown on sapphire by the chemical vapor deposition (CVD) method. It was conducted by Dr. Yung-Huang Chang in our collaborator Prof. Lain-Jong Li's group, at the King Abdullah University of Science and Technology (KAUST). The WO₃ powder (0.3 g) was placed in a ceramic boat located in the center of the furnace and the Se powders were placed in a separate ceramic boat at the upper stream side maintained at 270 °C during the reaction. The sapphire substrates for growing WSe₂ were put at the downstream side, where the Se and WO₃ vapors

were brought to the sapphire substrates by an Ar/H₂ flowing gas (Ar = 80 sccm, H₂ = 20 sccm, chamber pressure = 1 Torr). The center heating zone was heated to 925 °C at a ramp rate of 25 °C /min. Note that the temperature of the sapphire substrates is ~750 to 850 °C when the center heating zone reaches 925 °C. After reaching 925 °C, the heating zone was kept at that temperature for 15 min and the furnace was then naturally cooled down to room temperature. The quality of WSe₂ was characterized by optical microscopy, PL and Raman techniques (Fig. 3.1). The optical microscopy in Fig. 3.1a shows that the triangular-shape WSe₂ with a size of ~ 4.5 μm is well crystallized and densely distributed on sapphire. It has one pronounced emission peak at 768 nm (1.61 eV), *i.e.* the A direct excitonic transition¹⁹⁻²¹, which is a typical PL spectrum of a pristine monolayer WSe₂ (Fig. 3.1b). The Raman spectrum excited by 532-nm laser is shown in the inset of Fig. 3.1b, where there are two characteristic peaks for monolayer WSe₂ on sapphire at 248 cm⁻¹ and 259 cm⁻¹, which are from the degenerate E'/A₁' mode and 2LA(M) mode, respectively²².

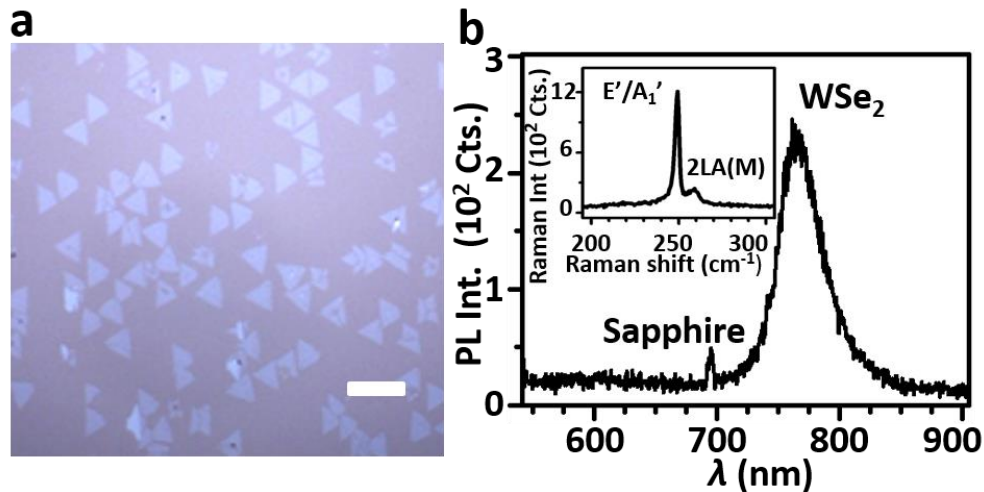


Figure 3.1 | Characterization results of WSe₂ on as-grown sapphire. (a) Optical microscope image of WSe₂ grown on sapphire. The scale bar is 10 μm. The black dots are nucleation points of WSe₂ in the growth process. (b) Raman and PL spectra of WSe₂ on sapphire as measured by 532-nm pump laser. The laser

powers for measuring PL and Raman spectra were 110 μW and 450 μW respectively, and the corresponding integration times were 0.5 s and 15 s, respectively.

After growth, the WSe_2 was transferred from the sapphire substrate to the gold substrate by a wet transfer method. First, the WSe_2 on sapphire substrate was coated with a layer of PMMA (950K, A3) by spin-coating (step 1: 500 rpm for 10 s; step 2: 2000 rpm for 70 s), followed by baking at 130 $^\circ\text{C}$ for 2 min. The PMMA at the edge of the sapphire substrate was cut off by a knife in order to facilitate the following exfoliation of PMMA-capped WSe_2 from the substrate. Then, a NaOH (3 mol/L) solution at 100 $^\circ\text{C}$ was used to exfoliate PMMA-capped WSe_2 from sapphire. After that, the PMMA-supported WSe_2 film was transferred to deionized (DI) water so as to remove the etchant and residues. A fresh gold substrate was then used to ‘fish out’ the PMMA-capped WSe_2 film, followed by drying on a hot-plate (75 $^\circ\text{C}$ for 5 min and then 100 $^\circ\text{C}$ for 10 min). The PMMA was finally removed by acetone vapor and cleaned by isopropyl alcohol (IPA).

3.2.2 Characterizations

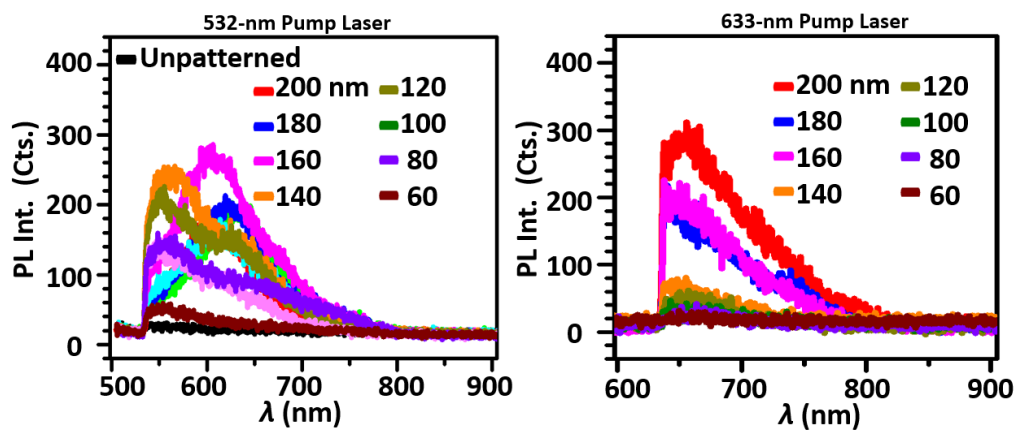


Figure 3.2 | PL signal of unpattern gold film and gold nanostructure without WSe_2 . The pitches range from 60 to 200 nm. The PL signal measured by 532-nm (a) and 633-nm pump laser (b), respectively.

AFM images and SEM images as well as reflectance spectra were measured by systems as discussed in Chapter 2. A confocal micro-photoluminescence setup was used to excite the sample by using a 532-nm or 633-nm CW pump laser, which is focused by a 100x microscope objective lens (NA = 0.65). Photoluminescence (PL) emission was then collected by the same objective and detected by a nitrogen cooled charge coupled device. The spot sizes of the 532-nm and 633-nm pump lasers were approximately 600 nm and 1.2 μm , respectively. The PL mappings were measured by the 532-nm laser as the smaller laser spot size of this gave a better PL mapping resolution. The background PL signals of pure gold nanostructures (Fig. 3.2) without WSe₂ were subtracted from all the PL spectra of WSe₂ on patterned gold nanostructures. The PL EF is defined as the ratio of integrated PL intensity of WSe₂ on patterned gold nanostructure to that on unpatterned gold film.

3.2.3 Numerical simulation method

The simulation was done by Dr. Yinghong Gu in my co-supervisor Prof. Cheng-Wei Qiu's group, National University of Singapore. A commercial software package, Lumerical Finite-Difference Time-Domain (FDTD) Solutions, was used to simulate the optical field distributions and Purcell factors. Periodic boundary conditions were used along x - and y -axes, while perfect-matched layer (PML) was used along z -axis. The finest mesh size was set to be 0.5 nm in the structure. The geometries of the metal nanostructures in the simulations were designed to match with the corresponding SEM images with a trench depth of 75 nm. This fine adjustment in the geometry was done for every pitch, which explains the discontinuous jumps in the numerical data points (Fig. 3.8a and b).

3.3 WSe₂-plasmonic hybrid nanostructures.

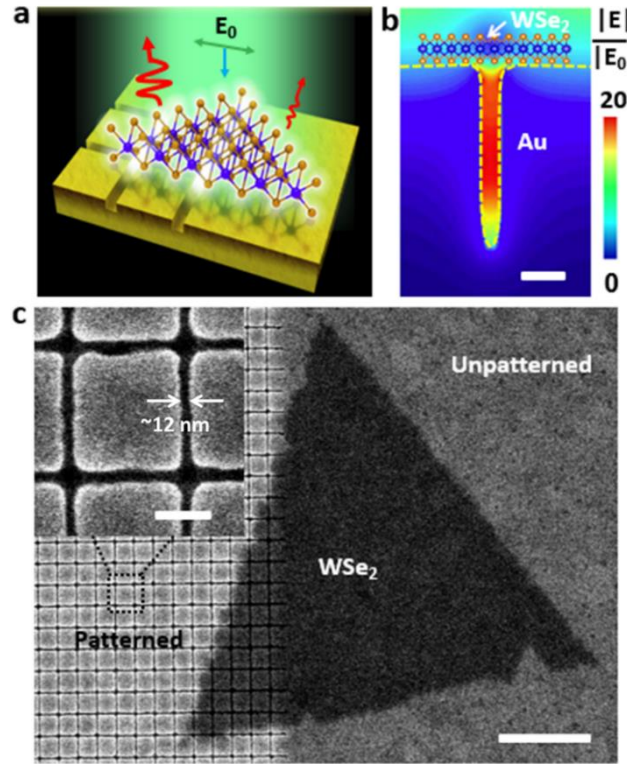


Figure 3.3 | Schematic of WSe₂-gold plasmonic hybrid structure with strong optical absorption. (a) Schematic of PL emission from a single crystal monolayer of WSe₂ flake on a gold substrate. Part of the triangular flake rests on the patterned region of the substrate consisting of sub-20 nm wide trenches. (b) Representative simulation of the electric field distribution of the lateral gap plasmons with a WSe₂ monolayer flake suspended over a single trench. The polarization of the incident laser field is across the gap. The dashed yellow line denotes the boundary between air and gold. The scale bar is 20 nm. (c) Representative Scanning electron micrograph (SEM) image of WSe₂ on square arrays with a trench width of 12 nm (Patterned) and unpatterned gold film (Unpatterned). The scale bars in the main figure and the inset are 1 μm and 100 nm, respectively.

A schematic of the investigated system is shown in Figure 3.3a. We transferred CVD grown WSe₂ monolayer flakes onto gold substrates with trenches as narrow as sub-20 nm. The gold substrate was fabricated by template-stripping method (see details in Section 2.3). This sample enables a direct comparison of PL emission from the same single crystal WSe₂ flake, where regions over unpatterned gold were taken as the base reference. The template-stripping method used to prepare the gold nanostructures has advantages over

other commonly used electron beam lithography (EBL) method to make gold nano-bowties, nano-rods or nano-discs^{8, 12, 13}, where 4 or 5 pieces of gold substrate with nanostructures are reproducible from one piece of patterned silicon substrate, critical for high-throughput and time-saving manufacturing^{23, 24}. Moreover, we do template-stripping right before the transfer process of WSe₂ so as to reduce contamination from adsorbed air-borne molecular species and preserve the hydrophilic nature of freshly stripped gold²⁵.

The trenches in gold support strong field enhancements as shown in the FDTD simulation results in Fig. 3.3b, where a monolayer WSe₂ flake is placed over the trench. The resonances are in the form of lateral gap plasmons in the sub-20 nm trenches with **E**-fields predominantly parallel to the plane of WSe₂ to promote strong light absorption²⁶. This resonance can be tuned to be matched with the pump laser wavelength by varying the pitch of the structures, which are critical for plasmon coupling with light to achieve optimal field confinement^{27, 28}. Figure 3.3c presents a scanning electron micrograph (SEM) image of a triangular WSe₂ single crystal monolayer as transferred onto the gold substrate with a trench width of ~ 12 nm.

3.4 Observation of PL enhancement in WSe₂.

Here, we show that the lateral gap plasmons are able to enhance the PL emission significantly. A template-stripped gold substrate with a large pitch (760 nm) and 532-nm pump laser were chosen for this purpose so that the enhanced PL due to lateral gap plasmons in the trench could be spatially resolved. Fig. 3.4a and Fig. 3.4b present the SEM image and the corresponding PL mapping across the same WSe₂ flake, respectively, so that it enables us to have a self-consistent comparison of PL enhancement from a single flake, thus

avoiding potential variations in PL emission between different flakes. The PL experiment was carried out using a 532-nm pump laser with a power of 30 μ W and the intensity value at each pixel of Fig. 3.4b was obtained by integrating the PL spectra across the spectrum window of 700-820 nm. This PL mapping shows that the sub-20 nm trenches on gold substrate were able to enhance the PL emission considerably. The weaker PL enhancement at Point C is due to the tear defect in the flake that is observable in the SEM image.

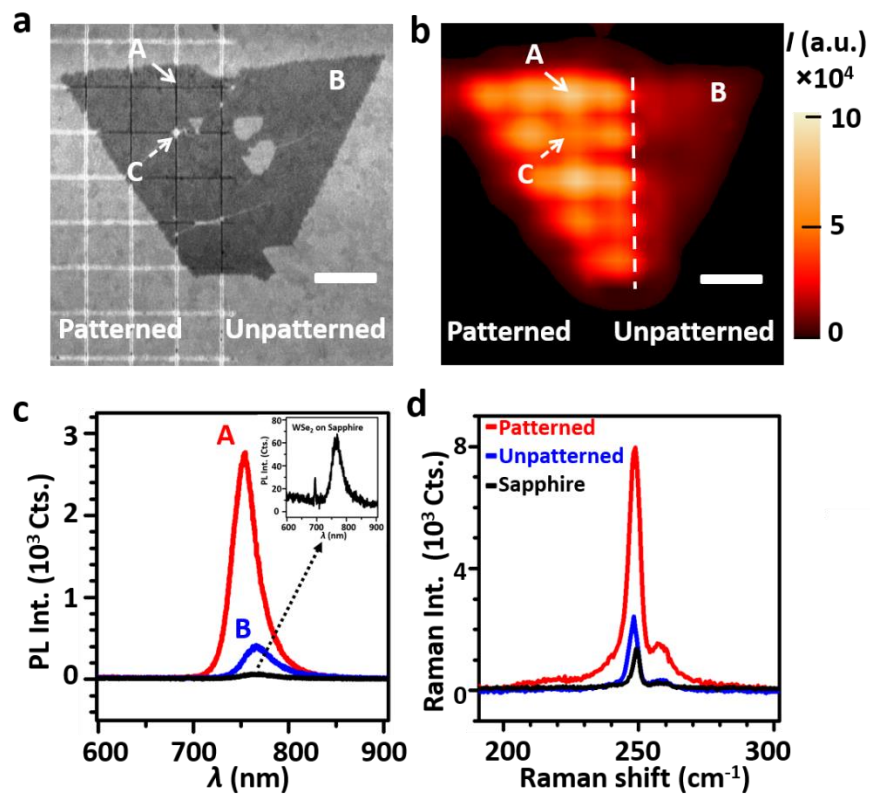


Figure 3.4 | Characterization results of WSe₂-gold plasmonic hybrid structure. (a) SEM image of a WSe₂ flake on a patterned nanostructure with a pitch of 760 nm. "A" points to a portion of WSe₂ suspended above an intersection of two underlying trenches, while "B" corresponds to WSe₂ on unpatterned gold film. "C" points to a tear defect. The scale bar is 1 μ m. (b) PL intensity (I) mapping of the WSe₂-gold plasmonic hybrid structure. A 532-nm pump laser was chosen for a fine PL mapping resolution. (c) PL spectra from A, B and as-grown WSe₂ on sapphire. The 532-nm laser power is 30 μ W and integration time is 0.5 s. (d) Comparison of Raman spectra from WSe₂ on patterned and unpatterned gold film, and on sapphire. The pump laser is 532 nm with the power of 450 μ W. The integration time was 15 s.

Figure 3.4c presents a quantitative comparison of PL spectra from WSe₂ on patterned gold nanostructures (*i.e.* Point A), unpatterned gold film (*i.e.* Point B) and on sapphire. In this particular sample with a pitch of 760 nm, the 9-nm-wide trenches enhance the PL emission from WSe₂ of up to 37-fold as compared to the emission from WSe₂ on sapphire. Moreover, PL emission from WSe₂ on unpatterned gold film is enhanced by 7-fold as compared to the emission from WSe₂ on sapphire, which might be due to the substrate-induced p-doping²⁵ and field enhancement by the gold. The PL of monolayer WSe₂ on unpatterned gold and sapphire are decomposed into emission from positively charged exciton (trion) and neutral exciton by Lorentz fitting (Fig. 3.5). The emission ratio of trion to exciton is higher in WSe₂ on unpatterned gold than WSe₂ on sapphire, indicating the p-doping of the former caused by the gold substrate. The change in doping level could also be induced from the downshift of Raman peak in WSe₂ when transferred from sapphire onto gold substrate^{29, 30} (Fig. 3.4d).

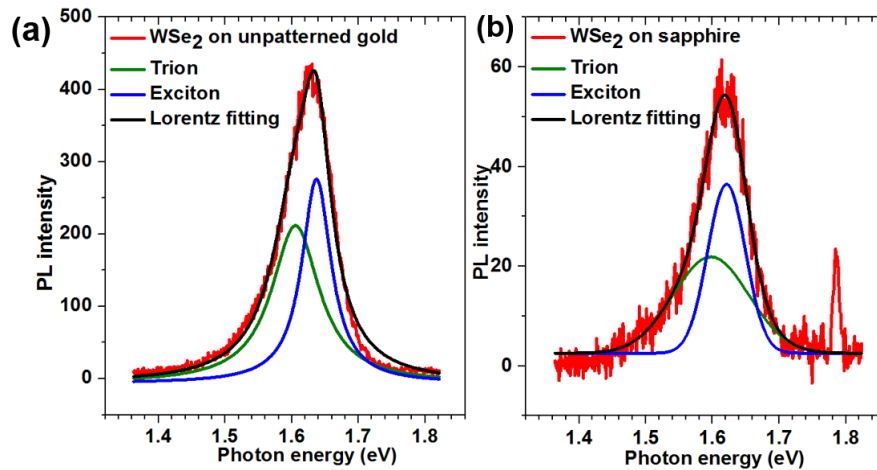


Figure 3.5 | Comparison of Lorentz-fitted PL spectra of WSe₂ on unpatterned gold (a) and on as-grown sapphire (b), respectively. PL spectra of monolayer WSe₂ (red curve) are fitted (black curve) with Lorentz functions and decomposed into exciton (blue curve) and trion (green curve) peaks.

3.5 PL enhancement mechanism.

The physical processes involved in the PL enhancement are investigated next. The PL intensity of emitters is determined by its excitation rate (*i.e.* absorption of the pump laser) and its emission efficiency (*i.e.* Purcell factor). When the plasmon resonance of WSe₂-gold nanostructures matches the wavelength of the pump laser, the excitation rate of WSe₂ will be enhanced³¹, *i.e.* $\gamma_{\text{exc}} \sim |\mathbf{E}_{\text{NF}}|^2$ (near-field intensity enhancement). In addition, the plasmon resonance at the emission wavelength enhances the radiative decay rate and quantum efficiency via the Purcell effect³².

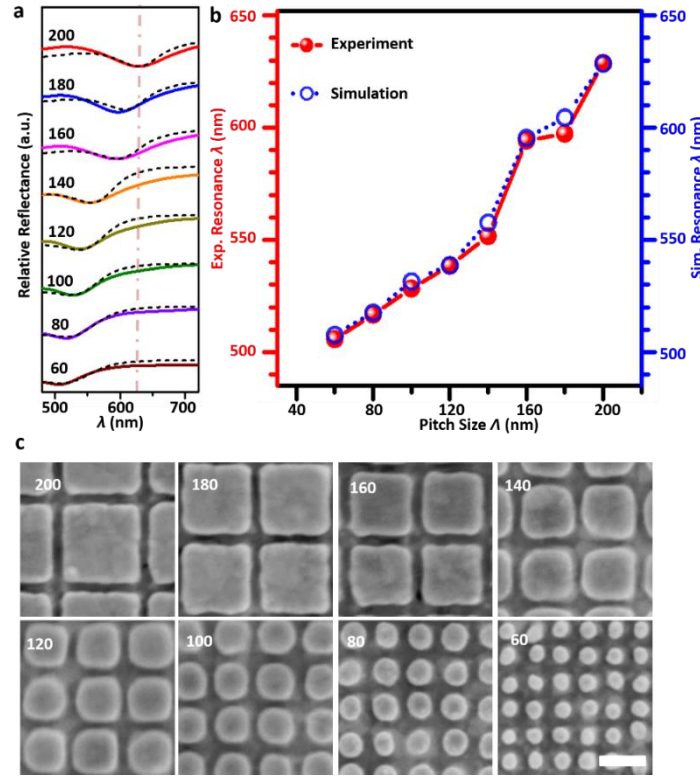


Figure 3.6 | Optical characteristics of patterned gold nanostructures with different pitch sizes. (a) Relative reflectance spectra of patterned gold nanostructures with pitch sizes of 60 – 200 nm with respect to the unpatterned gold film. The solid and dashed curves present the experimental and simulated spectra, respectively. The dash dot line indicates the position of the pump laser of 633 nm. (b) Experimental (Exp.) and simulated (Sim.) resonance wavelength of the patterned gold nanostructures as a function of pitch size. (c) SEM images of the template-stripped gold nanostructures with respective pitch sizes. The inset numbers denote the pitch sizes in the unit of nm. The scale bars in the SEM images are 100 nm.

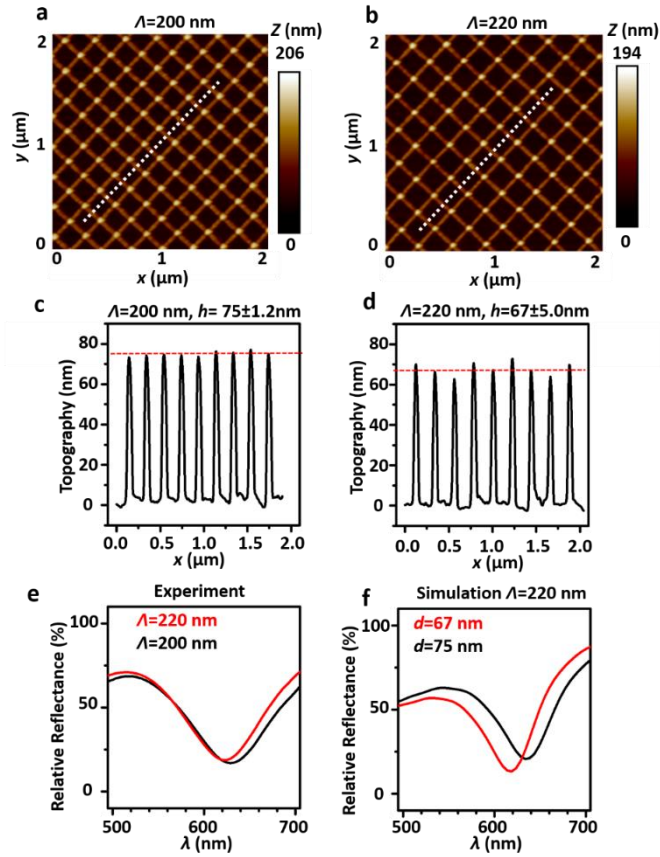


Figure 3.7 | Comparison of gold patterned nanostructure with pitches of 200 and 220 nm. Atomic force microscope (AFM) measurement results of nanostructured silicon templates with the pitch sizes of 200 nm (a) and 220 nm (b), and the corresponding height profile along the white dashed lines (c) and (d). (e) Experimentally measured relative reflectance spectrum with respect to unpatterned gold film for gold nanostructure substrates with the pitch sizes of 220 nm and 200 nm. (f) Simulated relative reflectance spectrum of gold patterned nanostructure with different trench depths (the pitch size is 220 nm).

The simulations show an excellent agreement with the measured spectra, as seen in Fig. 3.6a. Moreover, the dependence of the plasmon resonance on the pitch size is summarized in Fig. 3.6b, where the plasmon resonance was red-shifted from 507 to 633 nm as the pitch size is increased from 60 to 200 nm. Figure 3.6c presents the SEM images of the patterned trenches of different pitches. Well-defined square structures are observed in the patterned gold nanostructures for large pitch sizes of 140 – 200 nm while the shape evolves into rounded disks as the pitch was reduced to 60 nm. This effect is due to the

nanofabrication process, *i.e.* proximity effects in EBL and micro-loading effects during etching. Resonance wavelengths beyond 633 nm were not been obtained in our patterned nanostructures as the resonance wavelength for nanostructures with pitches larger than 200 nm exhibited a blue shift due to a shallower trench depth as caused by imperfections in the fabrication process (Fig. 3.7). In the simulation, the surface geometry of the trenches is based on the SEM images (Fig. 3.6c) and the trench depth is based on the height profile of the ridges on the silicon template measured by AFM (Fig. 3.7c)

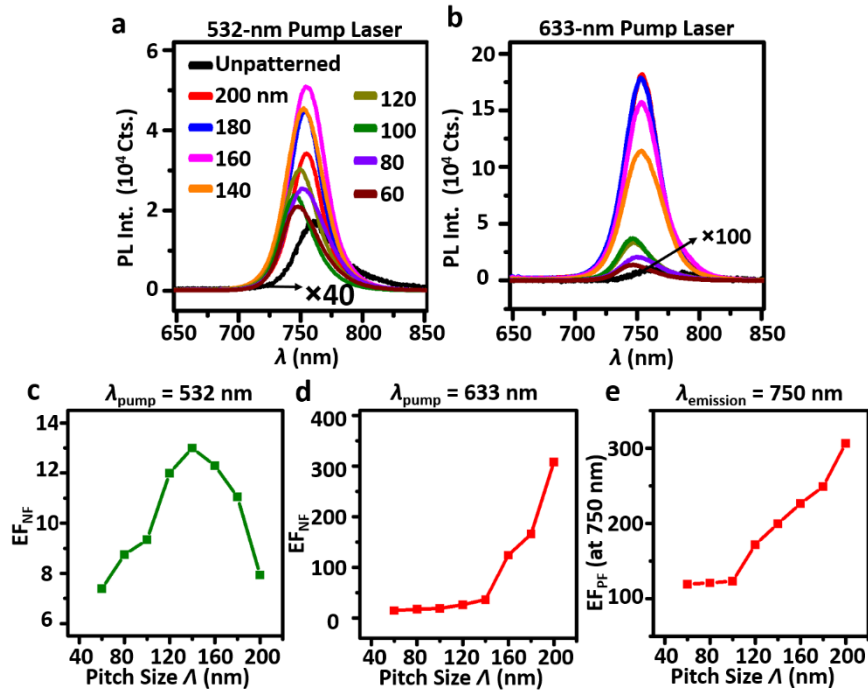


Figure 3.8 | Photoluminescence spectra, near-field intensity enhancement, Purcell factor enhancement and PL enhancement of WSe₂ on patterned gold nanostructures with different pitch sizes. (a, b) PL spectra measured by 532-nm and 633-nm pump laser, respectively. (c, d) Simulated enhancement factor of the near-field intensity for the WSe₂ monolayer flake as placed on the trench region of the gold substrate compared to that on unpatterned gold film at the pump laser wavelength of 532 nm and 633 nm, respectively. This enhancement factor for the near-field intensity is denoted as “ EF_{NF} ”, which accounts for the excitation process. (e) Simulated enhancement factor for the Purcell factor at the PL emission wavelength of WSe₂ (750 nm) denoted as “ EF_{PF} ”, accounting for the emission process.

Both 532-nm and 633-nm pump lasers were used to investigate the effect of plasmon-enhanced PL emission from monolayer WSe₂. Figure 3.8a-b presents the corresponding PL spectra as extracted from the PL mapping. We note that the 633-nm pump laser gives a higher PL emission as compared to the 532-nm pump laser. We simulated the enhancement factor (EF) of near-field intensity, which is defined as the ratio of the simulated $|\mathbf{E}|^2$ on top of the trench to the simulated $|\mathbf{E}|^2$ on the unpatterned gold film at pump laser wavelength of 532 and 633 nm, respectively (Fig. 3.8c-d). To estimate the emission enhancement, we calculated the Purcell factors for dipoles located on top of the trenches of gold nanostructures and for dipoles on top of the unpatterned gold film³³. The emission enhancement was then determined by the ratio of these Purcell factors (Fig. 3.8e). The Purcell factors were obtained directly from the FDTD analysis³⁴, where the Purcell factors were equivalent to the emitter power of dipole arrays on the patterned or unpatterned gold substrates divided by that in the free space. Note that the classical calculations of Purcell factors do take into consideration both radiative and non-radiative rates for the dipole in the different environments³⁵. Classically, the non-radiative decay rates are due to Ohmic losses in the metallic structures adjacent to the dipole. Despite the higher intrinsic absorption at 532 nm as compared to that at 633 nm in WSe₂, excitation at 532 nm resulted in low field enhancements (Fig. 3.8c-d) and PL enhancements (Fig. 3.9a), due to inter-band transitions of electrons in gold at 532 nm³⁶.

Figure 3.9b presents the experimental PL EF (corrected by the trench area fraction) excited by the 633-nm laser and the product of the simulated EF of near-field intensity and Purcell factor as a function of pitch sizes. Despite the

higher density of trenches on the smaller pitch structures, on-resonance excitation with the pitch of 200 nm results in the strongest near-field intensity and Purcell factor enhancements which were computed 1 nm above the gold substrate, *i.e.* at the expected z -plane of WSe₂. The standard deviation in Fig. 3.8a and b was obtained by statistically analyzing ten spectra of WSe₂ on each patterned gold nanostructure. Variations could be attributed to the slight trench size and shape variation of the patterned gold nanostructures, or optical non-uniformity among different triangular single crystals of WSe₂.

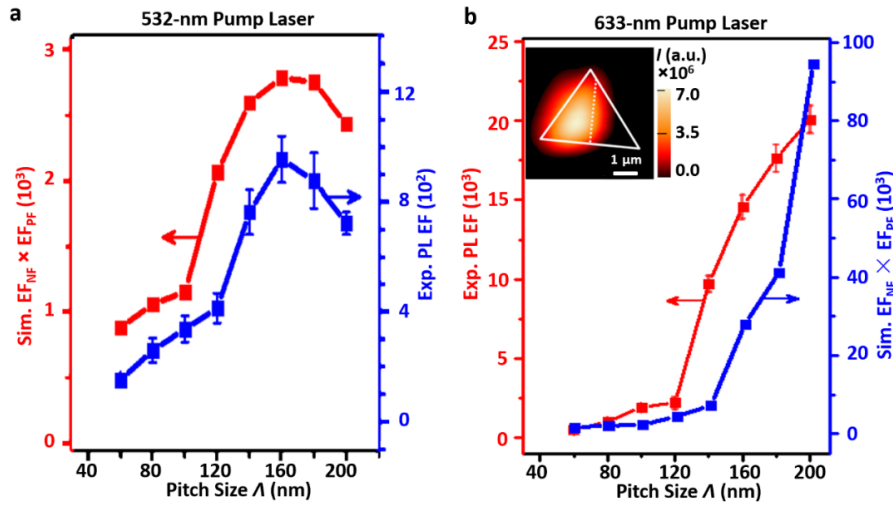


Figure 3. 9 | Experimental PL enhancement factor (EF) (after correcting for the trench area fraction) and the simulated product of near-field enhancement factor (EF_{NF}) at the related excitation wavelength and Purcell factor enhancement factor (EF_{PF}) at the emission wavelength (750 nm). The excitation pump is 532-nm laser (a) and 633-nm laser (b), respectively. The data points and corresponding error bars are obtained, respectively, by calculating the mean value and standard error of PL EF based on ten experimental PL spectra for each nanostructure. The inset in (b) shows the PL mapping of a WSe₂ monolayer flake sited on patterned gold nanostructure with a pitch of 200 nm (on the left of the dashed line) and unpatterned gold film (on the right of the dashed line) under the illumination of 633-nm pump laser. The intensity value at each pixel was obtained by integrating the PL spectrum across the spectrum window of 700 – 820 nm. The solid line presents the shape of the flake and the dashed line presents the boundary of the patterned and unpatterned substrate. The laser power was 30 μ W and integration time was 0.5 s.

As seen in Fig. 3.8b, the maximum PL enhancement was achieved by pumping WSe₂ on a nanostructure with the pitch of 200 nm via 633-nm laser.

With the gap plasmon resonance tuned to the 633-nm pump laser wavelength, the integrated PL intensity from WSe₂ on this gold nanostructure was enhanced up to 1,810-fold (without correction by the trench area fraction) compared to the reference on unpatterned gold film (see Fig. 3.9a-b).

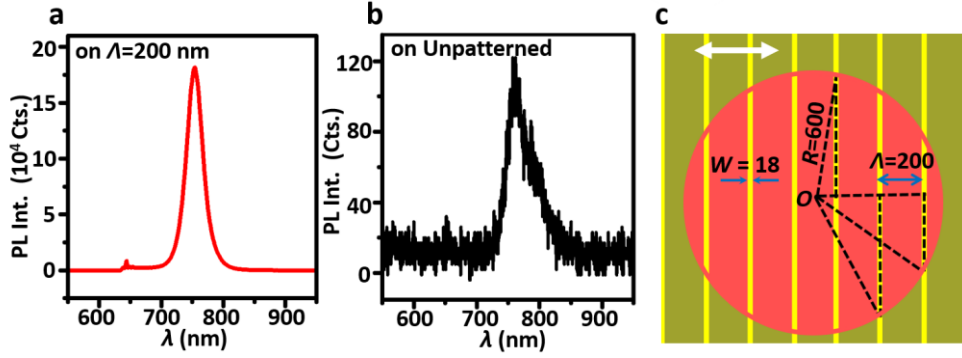


Figure 3.10 | The method to calculate the PL enhancement factor of WSe₂ over the trench. (a, b) Comparison of PL spectrum of WSe₂ on pitch 200 nm and on unpatterned gold measured by 633-nm laser. The PL peak energy and full-width at half-maximum (FWHM) in (a) are 1.64 eV and 65 meV respectively, while the corresponding values in (b) are 1.62 eV and 101 meV. The pump laser power was 30 μ W and integration time was 0.5 s. (c) Diagram showing the area of multiple trenches perpendicular to the polarization direction of the laser within a laser spot. The trench parallel to the polarization direction of the laser is not shown for simplicity. The white arrow denotes the polarization direction of the laser and the red circle represents the laser spot. Λ denotes the pitch size and W denotes the trench width. The dashed lines illustrate how Pythagorean theorem was used to calculate the length of the trenches.

Due to the small pitch size of 200 nm, the modulation of WSe₂ PL intensity by the array of trenches could no longer be resolved in the PL mapping (see the inset of Fig. 3.8b). From Fig. 3.3b and Fig. 3.10b as shown later, we assume that the enhancements are still localized to WSe₂ at the trenches, where this assumption will be supported by the PL mappings as shown in Fig. 3.10d and Fig. 3.10f. As measurements here were done with the pump laser polarized along the x -axis, fields are confined only within the trenches along the y -axis. Correcting for the small area occupied by these trenches, we obtain the

maximum effective PL EF of ~20,000 in WSe₂ over the trench using the formula⁹:

$$\langle \text{EF} \rangle = \frac{I_{\text{patterned}}}{I_{\text{unpatterned}}} \frac{A_0}{A_{\text{gap}}} \quad (3.1)$$

where $I_{\text{patterned}}$ is the PL intensity from WSe₂ on the patterned gold nanostructure and $I_{\text{unpatterned}}$ is the PL intensity from WSe₂ on the unpatterned gold film. A_0 represents the excitation area of the laser spot size ($\pi \times 600^2 \text{ nm}^2$) and A_{gap} represents the area of the trenches ($1.0 \times 10^5 \text{ nm}^2$) perpendicular to the polarization direction of the laser within the laser spot (see Fig. 3.9c). To the best of our knowledge, this magnitude of enhancement has not been previously observed from 2D materials⁷⁻¹⁵.

Such a giant EF for the measured PL emission is due to the plasmon-enhanced excitation process and the plasmon-enhanced emission process. To be more specific, as shown in Fig. 3.7c, the plasmonic nanostructure is able to enhance the excitation intensity by ~310-fold, at the pump laser wavelength of 633 nm, when the pitch size is 200 nm. Furthermore, as shown in Fig. 3.7e, the Purcell factor on this 200-nm-pitch nanostructure is able to be enhanced by ~307-fold, as compared to the one on unpatterned gold film. Therefore, the experimental EF of PL emission could be predicted by the product of these two enhancement factors (EFs), which is calculated to be more than 9×10^4 , as shown in Fig. 3.8b for the pitch size of 200 nm. In addition, we would like to mention that it is unlikely that phase transition of WSe₂ is at play here, although the direct contact between WSe₂ and gold plasmonic structures. The semiconducting 2H to metallic 1T phase transition, which has only been observed in high-vacuum and low-temperature conditions³⁷, has associated

Raman and PL quenching effects³⁸. However, we observed strong PL enhancement instead of quenching.

3.6 Polarization dependence of PL emission

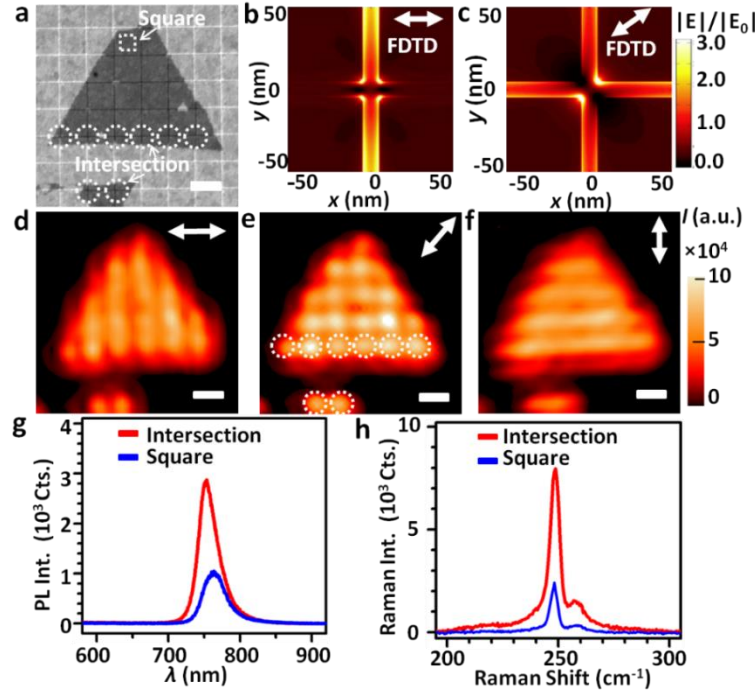


Figure 3.11 | Polarization-dependent characteristics of PL emission from WSe₂ flake on gold nanostructures with a pitch size of 920 nm and a pump laser of 532 nm. (a) SEM image of WSe₂ flake on the gold nanostructures. The white dashed circles denote the region, where the trenches in the gold film intersect and the dashed square denotes the center of the square region. (b, c) Simulated electric field distribution at a plane 1 nm above the surface of patterned gold nanostructures with 0-degree and 45-degree polarizations, respectively. (d, e, f) Corresponding PL intensity mappings with polarization angles of 0, 45 and 90 degrees, respectively. The intensity value at each pixel was obtained by integrating the PL spectrum across the spectrum window of 700 – 820 nm. The white arrows show the polarization directions of the pump laser. (g, h) PL and Raman spectra of WSe₂ taken at the intersection of gold trenches and square center, respectively. All the scale bars are 1 μ m. The laser power and integration time for measuring PL (Raman) is 30 μ W and 0.5 s (450 μ W and 15 s).

Next, we investigate the polarization-dependent characteristics of the PL emission from WSe₂ on patterned gold nanostructures. To resolve the PL enhanced regions, we chose a 920-nm-pitch substrate and a 532-nm pump laser to do the PL mapping. Here, we choose the 532-nm pump laser to do the PL

mapping simply because the 532-nm pump laser has a smaller spot size due to the shorter wavelength, as compared to the 633-nm pump laser. As a result, the imaging resolution of the PL mapping as obtained by the 532-nm pump laser is much clearer to show the enhanced PL emissions from trench regions. Figure 3.10a shows an SEM image of the sample. Figures 3.10b-c present the simulated electric field distributions of lateral gap plasmons at the intersection of two trenches with 0- and 45-degree polarizations for the excitation.

The simulated electric field distributions of this nanostructure agree with the experimental PL mappings in Fig. 3.10d-f. The maximum field enhancement occurs in trenches perpendicular to the polarization direction (Fig. 3.10b) and at the intersection of the trenches under 45-degree polarization (Fig. 3.10c). A plot of PL intensity intersecting several trenches indicates a laser beam waist of ~ 600 nm. These results provide further evidence that the highest PL enhancements are from WSe₂ directly above the trenches, where the optical fields are localized. It is noted that when the pitch size is larger than the pump laser wavelength, both lateral gap plasmons at the trenches and SPP on the flat squares are excited. However, the intensity of the SPP is only 1/6 of that of the lateral gap plasmon. Thus, the contribution to the PL enhancement of WSe₂ still dominantly stems from the lateral gap plasmons supported by the trenches. Figures 3.10g-h present the PL and Raman spectra of WSe₂ on the intersection and on the square center, respectively. Both Raman and PL intensities of WSe₂ at the intersection are found to be larger than the ones at the square center. The un-shifted Raman peak of WSe₂ over trenches and square center suggests that no strain is induced by the trench and thus it also confirms that the observed PL enhancement was not induced by strain³⁹.

3.7 Discussion

Furthermore, the WSe₂-gold plasmonic hybrid nanostructure allows us to conveniently evaluate a recent claim in the literature⁴⁰ which states that suspended 2D materials are expected to have larger PL than the counterparts on a substrate, because the substrate depopulates the density of states in 2D materials through charger transfer. Nevertheless, as shown in Fig. 3.10d and Fig. 3.10f, the gaps parallel to the pump laser polarization do not exhibit any stronger PL over its surrounding, although WSe₂ is suspended here. Therefore, it suggests that the suspension nature of WSe₂ by the trenches contributes little to the PL enhancement.

It should be noted here, that the square geometry chosen has the advantage of being independent of the incident polarization. In other words, if the incident polarization is either purely *x*-polarized or *y*-polarized, we will achieve the same EF. Therefore, for any other polarizations in-between, we always could decompose the incident optical field into the respective *x*-polarized component and *y*-polarized component. Since the PL emission intensity is linear with the excitation intensity, the EF remains the same.

Lastly, we would like to mention that there were no observable local heating effects in our experiments. In hybrid structure of MoS₂-gold nanoantenna, an increased absorption of the laser light at the nanoantenna may cause local heating so as to red shift and broaden the MoS₂ PL emission peak. Simultaneously, the local heating might cause a reduction in PL intensity of MoS₂ (ref. 12). In our experiment, the PL peak position and its full-width-at-half-maximum (FWHM) of WSe₂ on both patterned and unpatterned gold film have no power dependence (Fig. 3.11a-d). Hence, for the range of laser power

used, the integrated PL and peak intensity increase linearly with respect to the laser power (Fig. 3.11e-f), showing no signs of local heating effect.

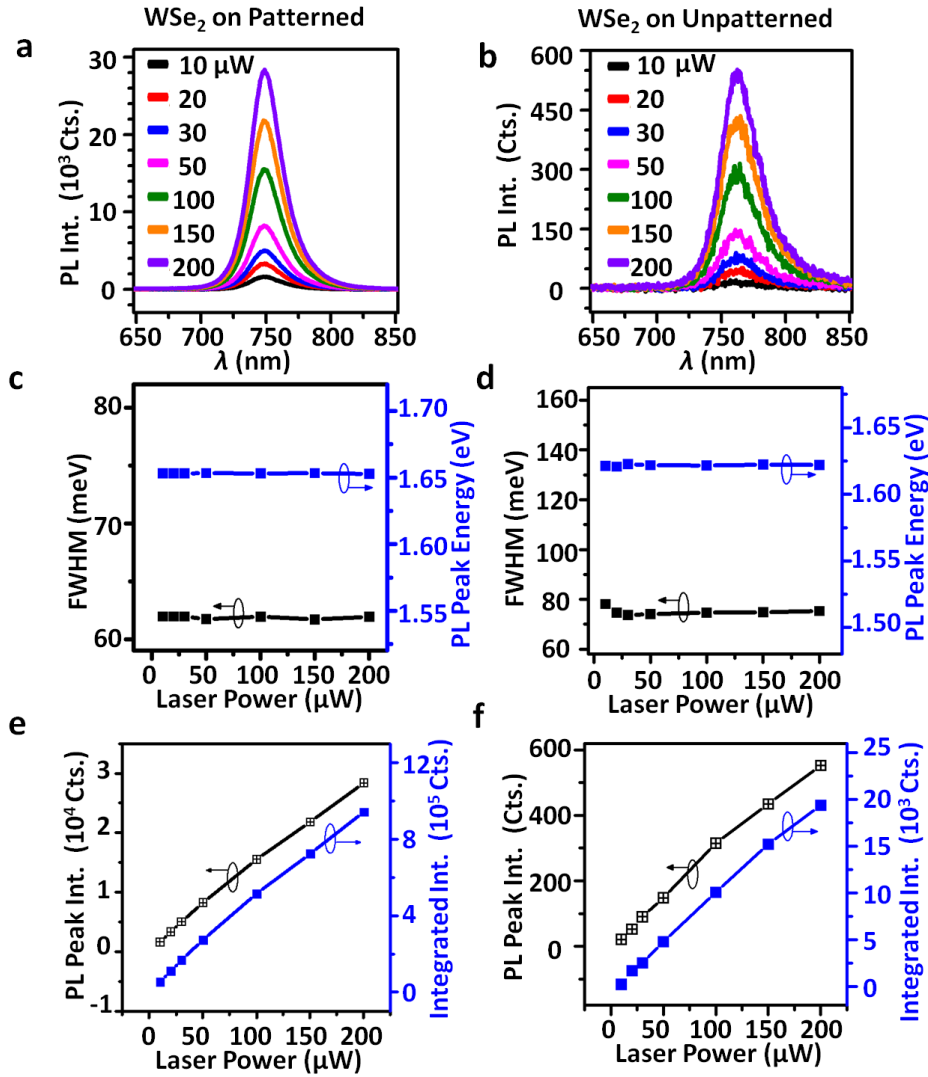


Figure 3.12 | Power dependence of monolayer WSe₂ PL spectra from patterned gold nanostructures. (a) and unpatterned gold film (b), by varying pumping power of 532-nm laser. The integration time in PL measurements was 0.1 s. PL FWHM and peak energy of WSe₂ on the patterned gold substrates (c) and on the unpatterned gold film (d), as a function of laser power. PL peak intensity and integrated intensity of WSe₂ on the patterned gold nanostructures (e) and on the unpatterned gold film (f), as a function of laser power.

3.7 Summary

In summary, concentrating and manipulating the electromagnetic field in sub-20 nm trenches can achieve unprecedented PL enhancement of WSe₂. Tuning the resonance of lateral gap plasmons to be aligned with the pump laser

wavelength effectively boosts the light–matter interactions in WSe₂, thus enhancing the light emission efficiency of WSe₂. A giant PL EF of ~20,000 was observed in WSe₂ when using the 633-nm pump laser. We expect further PL enhancements to be achieved through the design of double-resonance structures with directionality control. This work demonstrates an important method to enhance the PL of TMDCs since it could enable high-efficiency and high-quality photodetectors and sensors, where photon absorption and emission dictate the device performance. The incorporation of gold arrays with sub-20 nm wide trenches onto WSe₂ monolayers opens up a new platform for investigating novel electrical/optical properties in 2D materials, such as electroluminescence and second harmonic generation, speeding up the applications of novel optoelectronic devices.

3.8 References

1. Ross, J. S. *et al.* Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ pn junctions. *Nat. Nanotechnol.* **9**, 268-272 (2014).
2. Radisavljevic, B. *et al.* Single-layer MoS₂ transistors. *Nat. Nanotechnol.* **6**, 147-150 (2011).
3. Zhang, W. *et al.* High-Gain Phototransistors Based on a CVD MoS₂ Monolayer. *Adv. Mater.* **25**, 3456-3461 (2013).
4. Koperski, M. *et al.* Single photon emitters in exfoliated WSe₂ structures. *Nat. Nanotechnol.* **10**, 503-506 (2015).
5. Chiu, M.-H. *et al.* Determination of band alignment in the single-layer MoS₂/WSe₂ heterojunction. *Nat. Commun.* **6**, (2015).
6. Tonndorf, P. *et al.* Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂. *Opt. Express* **21**, 4908-4916 (2013).
7. Lee, K. C. *et al.* Plasmonic gold nanorods coverage influence on enhancement of the photoluminescence of two-dimensional MoS₂ monolayer. *Sci. Rep.* **5**, 16374 (2015).
8. Lee, B. *et al.* Fano resonance and spectrally modified photoluminescence enhancement in monolayer MoS₂ integrated with plasmonic nanoantenna array. *Nano Lett.* **15**, 3646–3653 (2015).
9. Akselrod, G. M. *et al.* Leveraging nanocavity harmonics for control of optical processes in 2D semiconductors. *Nano Lett.* **15**, 3578-3584 (2015).
10. Zhou, K. *et al.* Demonstration of Photoluminescence and Metal-Enhanced Fluorescence of Exfoliated MoS₂. *Chem. Phys. Chem.* **13**, 699-702 (2012).

11. Sobhani, A. *et al.* Enhancing the photocurrent and photoluminescence of single crystal monolayer MoS₂ with resonant plasmonic nanoshells. *Appl. Phys. Lett.* **104**, 031112 (2014).
12. Najmaei, S. *et al.* Plasmonic pumping of excitonic photoluminescence in hybrid MoS₂–Au nanostructures. *ACS Nano* **8**, 12682–12689 (2014).
13. Butun, S., Tongay, S., Aydin, K. Enhanced light emission from large-area monolayer MoS₂ using plasmonic nanodisc arrays. *Nano Lett.* **15**, 2700–2704 (2015).
14. Goodfellow, K. M. *et al.* Integrated nanophotonics based on nanowire plasmons and atomically thin material. *Optica* **1**, 149–152 (2014).
15. Lee, H. S. *et al.* Efficient Exciton–Plasmon Conversion in Ag Nanowire/Monolayer MoS₂ Hybrids: Direct Imaging and Quantitative Estimation of Plasmon Coupling and Propagation. *Adv. Opt. Mater.* **3**, 943–947 (2015).
16. Mouri, S. *et al.* Nonlinear photoluminescence in atomically thin layered WSe₂ arising from diffusion-assisted exciton-exciton annihilation. *Phys. Rev. B* **90**, 155449 (2014).
17. Wu, S. *et al.* Monolayer semiconductor nanocavity lasers with ultralow thresholds. *Nature* **520**, 69–72 (2015).
18. Amani, M. *et al.* Near-unity photoluminescence quantum yield in MoS₂. *Science* **350**, 1065–1068 (2015).
19. Huang, J.-K. *et al.* Large-area synthesis of highly crystalline WSe₂ monolayers and device applications. *ACS Nano* **8**, 923–930 (2014).
20. Zhou, H. *et al.* Large area growth and electrical properties of p-type WSe₂ atomic layers. *Nano Lett.* **15**, 709 (2015).
21. Srivastava, A. *et al.* Valley Zeeman effect in elementary optical excitations of monolayer WSe₂. *Nature Physics*, (2015).
22. Terrones, H. *et al.* New first order Raman-active modes in few layered transition metal dichalcogenides. *Sci. Rep.* **4**, 4215 (2014).
23. Nagpal, P., Lindquist, N. C., Oh, S.-H., Norris, D. J. Ultrasoft patterned metals for plasmonics and metamaterials. *Science* **325**, 594–597 (2009).
24. Liu, H. *et al.* Enhanced surface plasmon resonance on a smooth silver film with a seed growth layer. *ACS Nano* **4**, 3139–3146 (2010).
25. Mak, K. F. *et al.* Atomically thin MoS₂: a new direct-gap semiconductor. *Phys. Rev. Lett.* **105**, 136805 (2010).
26. Chen, X. *et al.* Atomic layer lithography of wafer-scale nanogap arrays for extreme confinement of electromagnetic waves. *Nat. Commun.* **4**, (2013).
27. Siegfried, T., Ekinici, Y., Martin, O. J., Sigg, H. Gap plasmons and near-field enhancement in closely packed sub-10 nm gap resonators. *Nano Lett.* **13**, 5449–5453 (2013).
28. Tan, S. F. *et al.* Quantum plasmon resonances controlled by molecular tunnel junctions. *Science* **343**, 1496–1499 (2014).
29. Mukherjee, B. *et al.* Raman analysis of gold on WSe₂ single crystal film. *Mater. Res. Express* **2**, 065009 (2015).
30. Chen, C.-H. *et al.* Hole mobility enhancement and p-doping in monolayer WSe₂ by gold decoration. *2D Mater.* **1**, 034001 (2014).
31. Wientjes, E. *et al.* Strong antenna-enhanced fluorescence of a single light-harvesting complex shows photon antibunching. *Nat. Commun.* **5**, (2014).
32. Purcell, E. M. Spontaneous emission probabilities at radio frequencies. *Phys. Rev.* **69**, 681 (1946).

33. Zhou, W. *et al.* Lasing action in strongly coupled plasmonic nanocavity arrays. *Nat. Nanotechnol.* **8**, 506-511 (2013).
34. Zhou, W. *et al.* Lasing action in strongly coupled plasmonic nanocavity arrays. *Nat. Nanotechnol.* **8**, 506-511 (2013).
35. Anger, P., Bharadwaj, P., Novotny, L. Enhancement and quenching of single-molecule fluorescence. *Phys. Rev. Lett.* **96**, 113002 (2006).
36. Ngoc, L. L. T., Wiedemair, J., van den Berg, A., Carlen, E. T. Plasmon-modulated photoluminescence from gold nanostructures and its dependence on plasmon resonance, excitation energy, and band structure. *Opt. Express* **23**, 5547-5564 (2015).
37. Li, Z. *et al.* Active light control of the MoS₂ monolayer exciton binding energy. *ACS Nano* **9**, 10158-10164 (2015).
38. Ma, Y. *et al.* Reversible semiconducting-to-metallic phase transition in chemical vapor deposition grown monolayer WSe₂ and applications for devices. *ACS Nano* **9**, 7383-7391 (2015).
39. Desai, S. B. *et al.* Strain-induced indirect to direct bandgap transition in multilayer WSe₂. *Nano Lett.* **14**, 4592-4597 (2014).
40. Jin, W. *et al.* Substrate interactions with suspended and supported monolayer MoS₂: Angle-resolved photoemission spectroscopy. *Phys. Rev. B* **91**, 121409 (2015).

Chapter 4 Enhanced Second Harmonic Generation of WSe₂ by Metasurfaces

4.1 Introduction

Second harmonic generation (SHG) is the lowest order frequency mixing nonlinear optical process in a nonlinear medium, where two photons are effectively combined and converted to a new photon with half the wavelength of the input photons¹. SHG plays an important role in frequency up-conversion in lasers and optoelectronic hybrid devices²⁻⁵. Recent studies have shown that two-dimensional transition metal dichalcogenides (2D TMDCs)⁶, especially tungsten diselenide (WSe₂)⁷, have advantages over conventional nonlinear materials in serving as SHG source materials⁸ as their atomic crystal thickness is far below the optical coherence length eliminating the requirement for phase matching and satisfies the design trend for smaller and thinner nonlinear optical and optoelectronic devices⁹⁻¹¹. However, this sub-nanometer length for light-matter interaction in 2D TMDCs also limits the total SHG conversion efficiency and limits their applicability. Exciton-enhanced SHG, namely, the enhancement of SHG efficiency at the exciton resonance energy, has been reported¹²⁻¹⁴. At the temperature of 4 K, SHG emission intensity from monolayer WSe₂ can be tuned by changing the wavelength of the pump laser, and it is enhanced by three orders of magnitude when the SHG emission energy is aligned with exciton resonance¹². At cryogenic temperatures, the SHG intensity of a field-effect-transistor device based on monolayer WSe₂ can be tuned over an order of magnitude by an electrostatic field and is strong at the A-exciton energy¹³. The tunability of the SHG intensity originates from the electrostatic modulation of oscillator strength at the resonance frequencies of various exciton species. As

such, these exciton-based methods are inherently narrowband, so when the two-photon energy of the fundamental wave is shifted away from exciton resonance, the SHG decreases dramatically¹⁵. Furthermore, these enhancement and tunability effects are compromised to a factor of four at room temperature¹⁵.

An approach to boost the SHG at room temperature is to use photonic nanostructures that can concentrate the electromagnetic field of the incident light so as to enhance SHG¹⁶⁻²⁰. It was reported that a 200-fold SHG enhancement in TMDC can be obtained by coupling of a pump laser to a silicon cavity mode. However, this results in an unfavorable broad background in the SHG spectra¹⁶. Sharp and tunable SHG spectra were achieved in TMDC integrated in a Fabry–Perot microresonator with resonances at both the fundamental and the second-harmonic frequencies, where a maximum enhancement of 3000-fold was obtained¹⁷.

Metasurfaces refers to surfaces covered by ultrathin plasmonic structures²¹, enable us to engineer the spatial distribution of amplitude, phase and polarization response of optical signals from materials surrounding them²². Similar to the work on PL enhancement in Chapter 3²³, this chapter reports that a gold metasurface with sub-20 nm trenches can also significantly boost the SHG from monolayer WSe₂ at room temperature, with an enhancement factor of ~13,000 as compared with its counterpart on flat gold film. This is among the highest SHG enhancement factor for TMDCs reported so far. The enhancement is attributed to the enhanced localized near-field of the fundamental wave at the sub-20-nm-wide trenches, which then boosts the SHG from monolayer WSe₂. Furthermore, this strategy allows for easy tuning of the total SHG intensity with an extinction ratio of 33 by rotating the polarization direction of the pump laser.

The sharp peak profile of the SHG spectra is not influenced by the pump laser polarization. This hybrid system of metasurface and monolayer WSe₂ can be utilized to configure a tunable “nonlinear mirror” with excellent monochromaticity, and also it has a flat surface with overall thickness of only 150 nm, facilitating the development of miniaturized on-chip optoelectronic devices.

4.2 Methods

4.2.1 Material growth and quality of WSe₂.

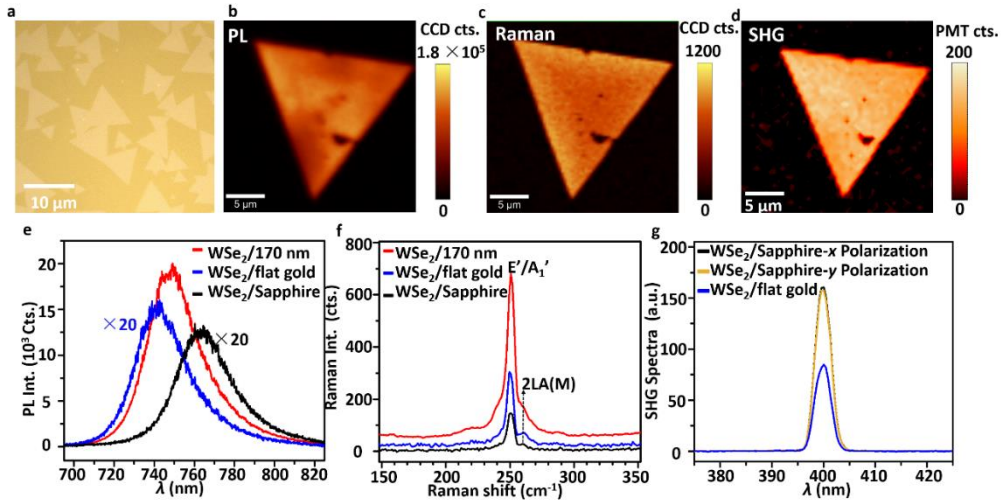


Figure 4.1 | Characterization results of WSe₂ on sapphire, flat gold and the metasurface. (a) Optical microscope image of WSe₂ grown on sapphire. (b-c) Raman, PL and SHG mappings of a triangular-shape WSe₂ on sapphire. The intensity value at each pixel for PL mapping was obtained by integrating the PL spectrum across the spectrum window of 700 – 820 nm, for Raman is the spectrum window of 245 – 265 cm⁻¹ and for SHG is the peak intensity at 400 nm. The PL and Raman were measured by 532-nm CW laser, and SHG was measured by 800-nm fs laser. (e-g) Comparison of PL, Raman and SHG spectra from WSe₂ on different substrates.

The monolayer WSe₂ single crystal was grown on *c*-cut sapphire by the chemical vapor deposition (CVD) method (see Section 3.2.1). The growth was carried out by Dr. Ming-Hui Chiu in Prof. Lain-Jong Li's group, King Abdullah University of Science and

Technology. This technique yields high quality monolayer WSe₂ with a crystal size ranging from 4 to 15 μm (Fig. 4.1a). The typical PL spectrum of a pristine

monolayer WSe₂ (Fig. 4.1e) is dominated by an emission peak at 768 nm (1.62 eV) that arises from the A direct excitonic transition. For monolayer WSe₂ on sapphire, the Raman spectrum excited by a 532-nm laser shown Fig. 4.1f, and has two characteristic peaks at 251 cm⁻¹ and 260 cm⁻¹ that originate from the degenerate E'/A'₁ mode and 2LA(M) mode.

4.2.2 Fabrication of gold substrate and transferring of WSe₂

The gold substrate consisting of metasurface and flat gold film was prepared by a template-stripping method (see detailed fabrication processes in Section 2.3). The gold substrate used here has trenches all aligned in one direction, which is slightly different from the one in Chapter 3. Then WSe₂ flake was transferred onto the gold substrate by a wet transfer approach (Section 3.2.1).

4.2.3 Characterization

AFM images, reflectance spectra and SEM images were obtained as described in Chapter 2. A confocal micro-PL/Raman setup was used to excite the sample using a 532-nm CW pump laser, which is focused by a 100x microscope objective lens. The SHG was measured by a femtosecond laser beam with tunable central wavelength of 800 – 900 nm and repetition rate of 80 MHz. The detailed setup is shown in Fig. 4.3c. The SHG enhancement factor is defined by the ratio of the total SHG intensity from WSe₂ on the metasurface to the emission from its counterpart on the flat gold film. The total SHG intensity does not depend on the crystal orientation.

4.2.4 Numerical simulations

The simulation was done by Miss Lei Jin in my co-supervisor Prof. Cheng-Wei Qiu's group, National University of Singapore. A commercial

software package, Lumerical FDTD Solutions, was used to simulate the optical field distributions and reflectance spectra. Periodic boundary conditions were used along the x - and y -axes, while a perfect-matched layer (PML) was used along z -axis. The finest mesh size was set to be 0.5 nm in the structure. The width of the metal nanostructures in the simulations were designed to match with the related SEM image (Fig. 4.4c and Fig. 4.6a, respectively), with a trench depth of ~ 102 nm for 170nm pitch and ~ 30 nm for 910 nm pitch. The depth of the trenches were estimated from the height of the ridge of the silicon template as shown in the AFM profile (Fig. 4.2).

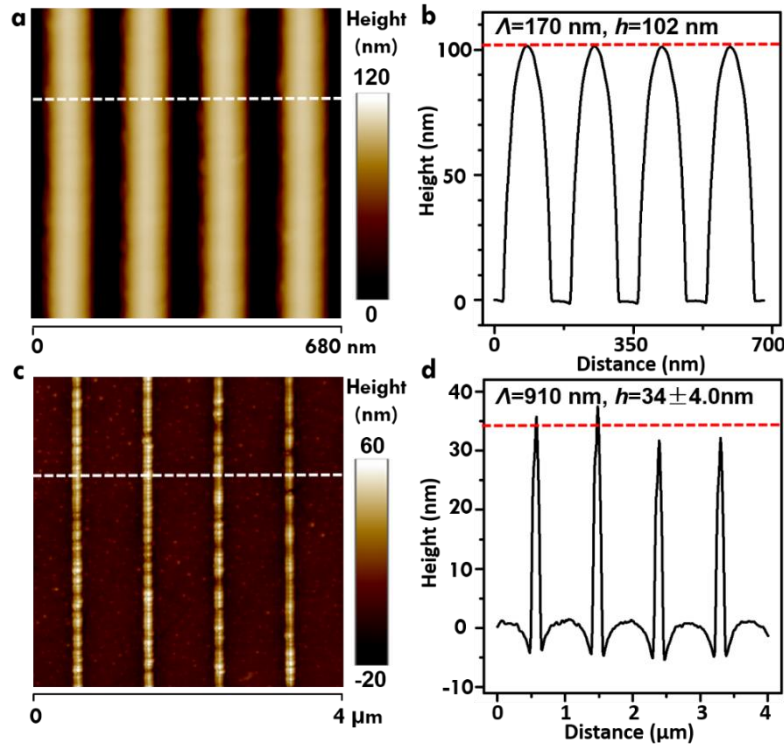


Figure 4.2 | Height of the ridges on silicon template. AFM measurements of patterned silicon template with pitch sizes of 170 nm (a) and 910 nm (b), and the associated height profile along the white dashed lines (c) and (d).

4.3 Results and discussion

4.3.1 Hybrid structure and characterization facility

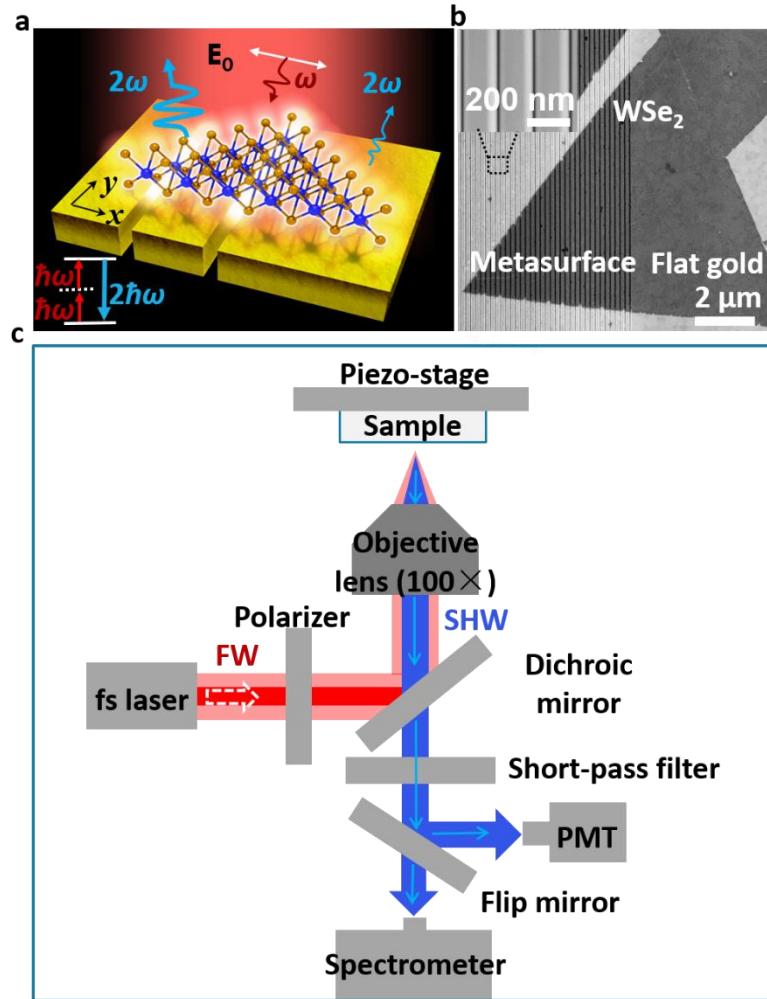


Figure 4.3 | Schematic of second-harmonic generation (SHG) from monolayer WSe₂ flake on a gold substrate. Part of the flake was on the metasurface consisting of sub-20-nm-wide trenches and the rest on flat gold film. (b) Representative scanning electron micrograph (SEM) image of WSe₂ on metasurface with a trench width of 16 nm (Metasurface) and flat gold film (Flat gold). (c) Optical setup for measuring SHG mappings and SHG spectra. This fundamental-wave (FW) laser was linearly polarized via a polarizer. Then it was reflected by a dichroic mirror (Semrock, FF750-SDiO2-25 $\times$ 36) and focused on the sample through a 100 $\times$ air objective with a numerical aperture (NA) of 0.90 (Nikon, Ti-U inverted microscope, TU Plan Fluor). The sample was mounted on a piezo-actuated 3D nanopositioning stage (Physik Instrumente, P545.2R7). The generated second-harmonic wave (SHW) was then back collected by the same objective and passed through the dichroic mirror. Next, the SHW went through a short pass filter (Laser 2000, FF01-750/SP-25) that was used to completely filter out the FW laser. Finally, a flip mirror was used to redirect the SHW to either a photomultiplier tube (PicoQuant, PMA 182) for SHG mapping or a spectrometer (Princeton Instruments, 2300i) for spectrum measurement.

Figure 4.3a shows a schematic view of SHG from the hybrid nanostructure of monolayer WSe₂ and gold substrate, which consists of the metasurface with sub-20-nm-wide trenches and flat gold film. Inversion symmetry breaking²⁴ in crystal structure of monolayer 2H-type WSe₂ brings about nonzero second-order susceptibility, enabling WSe₂ to convert incident light with frequency ω into light with double frequency 2ω , *i.e.*, SHG. Monolayer WSe₂ on metasurface especially over trenches has much larger SHG than on flat gold film owing to the gap-plasmon-enhanced electric field of pump laser and strengthened light-matter interaction in WSe₂. Unlike our previously reported crossed trenches used to obtain giant photoluminescence of WSe₂²³, the trenches here are all aligned along the y -axis direction so that the pump laser with electric field polarized along the x -axis can excite gap plasmons. In contrast, the pump laser with electric field polarized along the y -axis cannot excite gap plasmons. In this case, tuning the polarization direction of incident light can switch on or off of the gap plasmon in the trenches, thus tuning the SHG intensity of WSe₂, which will be discussed in detail later. Figure 4.3b shows the scanning electron micrograph (SEM) image of monolayer WSe₂ flakes covering both the gold metasurface and flat gold film. The CVD-grown monolayer WSe₂ flakes were transferred onto a freshly prepared gold metasurface with sub-20 nm width trenches (see details of WSe₂ growth, transfer and metasurface fabrication in Section 2.1-2.3, respectively). The quality and layer number of WSe₂ were confirmed by optical microscopy (OM), Raman and photoluminescence before transfer (see details in Fig. 4.1).

Figure 4.3c demonstrates the optical setup for the SHG experiments of WSe₂ on gold substrate. A femtosecond laser beam with a tunable central

wavelength of 800 – 900 nm and repetition rate of 80 MHz, generated from a Ti: sapphire oscillator (Coherent, Chameleon Ultra II), was linearly polarized then focused on the sample through a 100 $\times$ air objective with a numerical aperture (NA) of 0.90 (Nikon, Ti-U inverted microscope). The sample was raster scanned by a piezo-actuated 3D nanopositioning stage (Physik Instrumente, P545.2R7). At each pixel, the back scattered SHG signal was collected through the same objective, and passed through a dichroic mirror and a short-pass filter which completely filtered out the fundamental beam before being detected by either a photomultiplier tube (PicoQuant, PMA 182) or a spectrograph (Princeton Instruments, 2300i). There was no analyzer before the detectors except in the experiment of investigating the influence of crystal and trench orientation. For all SHG measurements, the pump laser power on the sample was typically at 0.5 mW to prevent possible damage, with the exception of the experiment on power dependence.

4.3.2 Giant SHG enhancement

To make a precise comparison on SHG from WSe₂ flakes on the metasurface (dark grey) and flat gold film (grey), monolayer WSe₂ flakes covering both regions were chosen here, as shown in the scanning electron microscopy (SEM) image in Fig. 4.4a. To maximize the electric field enhancement in this experiment, the metasurface with dense trench distribution (pitch of 170 nm) was designed to have a resonance mode covering the fundamental wavelength of the pump laser at 800 nm. In order to investigate the localized gap plasmon resonance, the reflectance spectra of the metasurface and flat gold film were measured by white light with electric field polarized along x and y respectively as shown in Fig. 4.4b. In both polarization conditions, the

reflectance spectra of flat gold film (black and orange lines) almost overlap due to the isotropic dielectric properties of gold in the x - y plane, where no localized plasmon resonance mode is observed. In comparison, the polarization direction of incidence light can switch on or off the localized gap plasmon mode in the metasurface. Specifically, x -polarized incident light, with electric field polarization perpendicular to the trench direction, can excite plasmon resonance in the metasurface so as to result in a broad absorption dip ~ 800 nm in the reflectance spectrum (red line). On the other hand, y -polarized incident light with electric field polarization along the trench direction cannot excite gap plasmons, since the incidence light interacts with the metasurface in a way similar to the flat gold film, resulting in a similar reflectance spectrum as the flat gold film (blue line). The former case is referred to as “resonant excitation” and the latter “non-resonant excitation” for simplicity. The dips around 400 and 470 nm in all reflectance spectra are attributed to the absorption of gold caused by inter-band transitions²⁵.

The localized lateral gap plasmon plays a significant role in SHG conversion efficiency. Figures 4.4c and d are the SHG mappings of WSe₂ on metasurface and flat gold film. The 800-nm pump laser was incident normal to the surface and polarized along x - (Fig. 4.4c) and y -axis (Fig. 4.4d), respectively. SHG was measured without any analyzer in front of the detector, so the total SHG intensity was independent of the crystal orientation of WSe₂ with respect to the polarization direction of pump laser. Regardless of whether resonant or non-resonant excitation was used, the metasurface (areas outlined by white dashed square) enhances SHG of WSe₂ dramatically as compared with the flat gold film (the rest part). There is no observable SHG signal from the bare gold

metasurface (Fig. 4.4f), indicating that the measured SHG signal is only from active nonlinear material WSe₂.

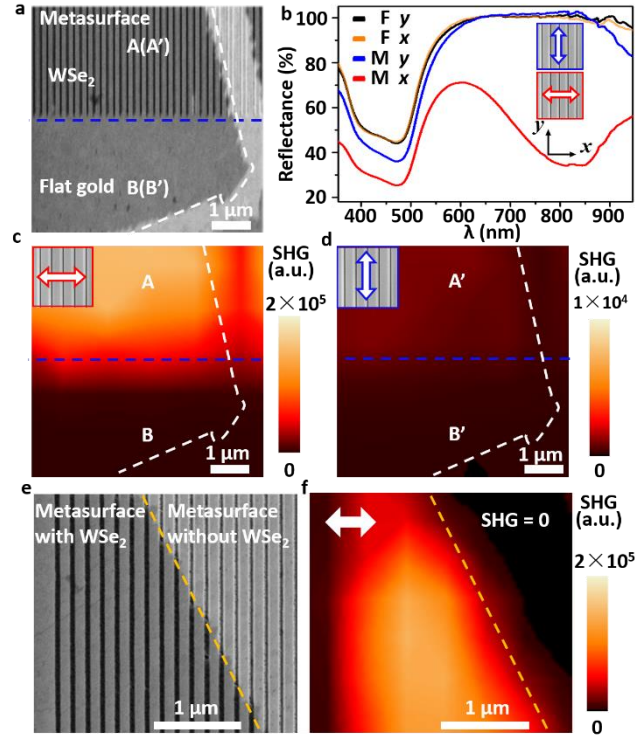


Figure 4.4 | Large SHG enhancement observed in WSe₂ on metasurface. (a) SEM image of WSe₂ flakes on gold metasurface (dark grey) and on flat gold film (grey). The white dashed square shows the region of metasurface. The colour of gold substrate without WSe₂ is light grey. (b) Reflectance spectra of gold metasurface (M) and flat gold film (F) under the illumination of white light polarized parallel (x) and perpendicular (y) to the trenches orientation. (c-d) SHG peak intensity mapping of WSe₂ on gold metasurface (A/A') and flat gold film (B and B') under resonant excitation and non-resonant excitation, respectively. The pump laser is 800 nm with power on the sample of 0.5 μ w. (e-f) SEM image (e) of metasurface with and without WSe₂, and the related SHG mapping (f).

For a quantitative comparison, 4 SHG spectra from WSe₂ on the metasurface (A or A') and flat gold film (B or B') under resonant or nonresonant excitation conditions are shown in Fig. 4.5a. In resonant excitation, the SHG from monolayer WSe₂ flake on metasurface (A) is enhanced by ~1600-fold as compared to the one on flat gold film (B). This enhancement is because the trenches support lateral gap plasmons which can concentrate the

electromagnetic field of the pump laser into the trench region, so that it enhances the light-matter coupling in the plane of the WSe₂ flake and enables the WSe₂ flake to efficiently convert 800-nm light into 400-nm light. Further simulation and experiments as shown in Fig. 4.7 will verify that SHG enhancement in the sample occurs at the trenches. Considering the area fraction of the trenches within a laser spot, the maximum SHG enhancement of WSe₂ over the trenches is calculated to be $\sim 13,000$ -fold as compared with emission from the reference sample on flat gold. Since the flat gold plane is near the node of the incident electric magnetic radiation at 800 nm, this may be not the optimal condition for a reference signal. As compared with WSe₂ on sapphire, the PL enhancement factor for WSe₂ over the trench is ~ 7000 . This normalization method is similar to the one used in Chapter 3 (see more detail in Fig. 3.9c). In non-resonant excitation, the SHG enhancement of WSe₂ on metasurface (A') as compared with the counterpart on flat gold drops to ~ 400 -fold (with normalization of trench occupation) owing to the lack of gap plasmon mode, while SHG of WSe₂ on flat gold (B') maintains the same value as it is under resonant excitation (B). Therefore, rotating the polarization of pump laser can dynamically tune the total SHG intensity of WSe₂ on metasurface with an extinction ratio of ~ 33 , demonstrating its advantage over WSe₂ on flat gold or as-grown sapphire (Fig. 4.1g) whose intensity cannot be influenced by polarization direction of incident light. It is noted that in both excitation cases, SHG spectra of WSe₂ on metasurface was evidenced by a sharp peak at the second-harmonic wavelength (400 nm) with no spectral broad background or two-photon photoluminescence, allowing for obtaining light source at shorter wavelength and with high purity which is not possible by linear photoluminescence (Fig. 4.1f).

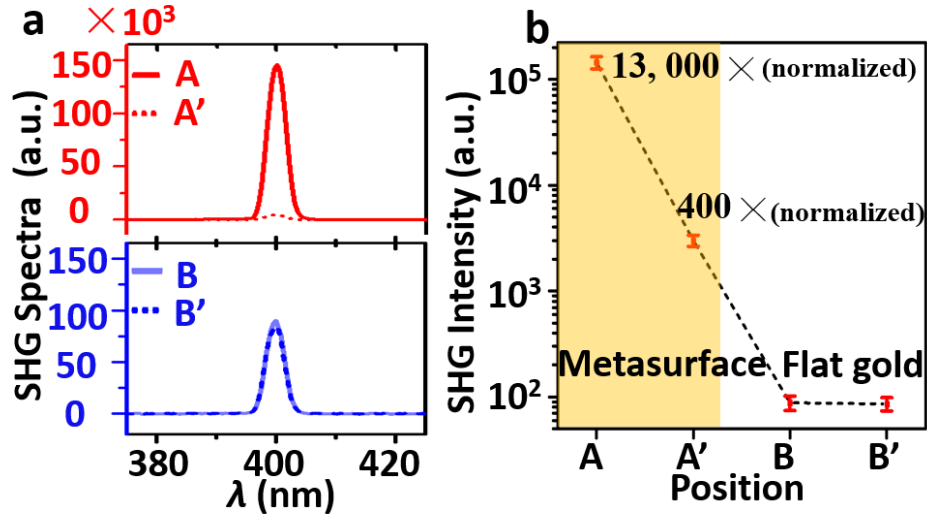


Figure 4.5 | Quantitative comparison of SHG intensity. (a) Representative SHG spectra of Points A, A', B and B' as shown in SHG mappings. (b) SHG intensity with an error bar of WSe₂ on metasurface and on flat gold film.

Moreover, unlike previously reported nanocavities^{16, 18}, the 150 nm thick hybrid structure that provides a flat top surface can serve as an important nonlinear element for realizing ultrathin optical information processors on chip. In addition, the integration of WSe₂ on metasurfaces can promote the application of ‘nonlinear mirrors’. The nonlinear mirror that generates the second harmonic back toward the fundamental source is a significant concept in nonlinear metasurface and metamaterials^{26, 27}, where the difficulty in obtaining the backward phase-matching condition requires judiciously design of the metamaterials²⁸. In contrast, in our hybrid structure, monolayer WSe₂ as a nonlinear medium eliminates the requirement for phase matching and provides a source for second harmonic wave with a propagation direction opposite to the fundamental wave, and where the metasurface supporting the gap plasmon resonance absorbs most of the fundamental wave and enhances the backward SHG intensity. The forward propagation of the second-harmonic wave is blocked by the 150-nm-thick gold substrate as the penetration depth for gold at

400 nm wavelength is ~ 16 nm. Therefore, the hybrid structure can be regarded as a potential WSe₂-mediated gap-plasmon nonlinear mirror.

4.3.3 SHG enhancement mechanism and position

Next, the SHG enhancement mechanism is analyzed in detail. For monolayer WSe₂ with D_{3h} point-group symmetry, the second-order susceptibility tensor has a single nonzero element: $\chi_{WSe_2}^{(2)} = \chi_{bbb}^{(2)} = -\chi_{aab}^{(2)} = -\chi_{aba}^{(2)} = -\chi_{baa}^{(2)}$, where a and b are the principle axes in crystal coordinates. Here a corresponds to a zigzag direction and b corresponds to an armchair direction that has a mirror plane symmetry (Fig. 4.6a). This leads to a theoretical estimate of the total SHG signal:

$$I_{2\omega} = C |\mathbf{E}_{2\omega}|^2 \propto |\chi_{bbb}^{(2)}|^2 |\mathbf{E}_\omega|^4, \quad (4.1)$$

where $\mathbf{E}_{2\omega}$ is the electric field of the double frequency wave, and $\mathbf{E}_\omega$ is the electric field of the fundamental wave and C is a constant. The metasurface is designed to enhance the nonlinear effects of WSe₂ by providing near-field enhancement of the fundamental wave ($\mathbf{E}_\omega$) at the trenches via coherent oscillations of positive and negative charges at the two edges of the trenches in the form of lateral gap plasmons.

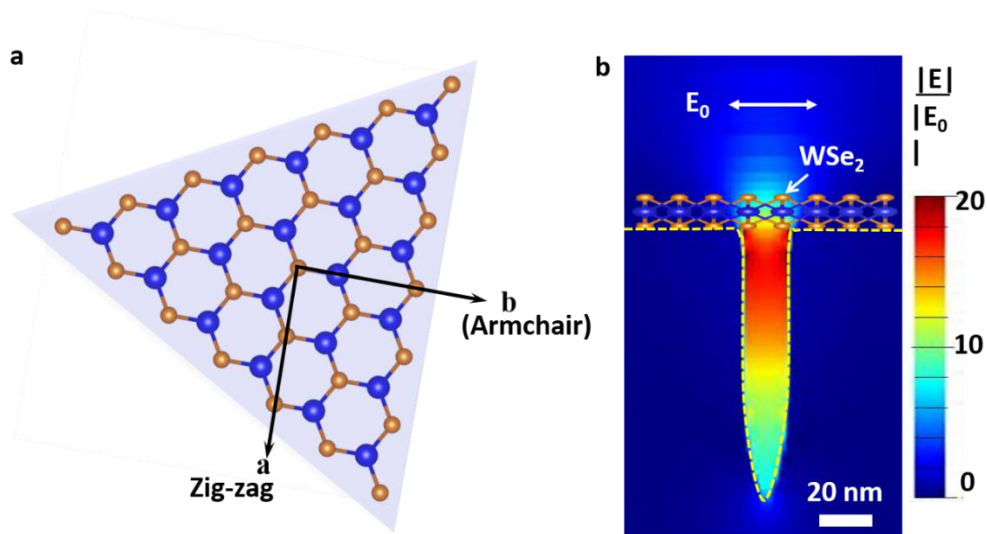


Figure 4.6 | SHG enhancement mechanism. (a) Lattice structure of single crystalline monolayer WSe₂ with triangular shape. a and b are principle axes in the monolayer plane in the crystal coordinates (a , b , c), where a corresponds to a zigzag direction, b corresponds to an armchair direction that has a mirror plane symmetry and c is the out-of-plane 3-fold rotation axis. (b) Simulation of the electric field distribution of the lateral gap plasmons with a WSe₂ monolayer flake being suspended over a single trench with a width of 18 nm and a pitch of 170 nm. The polarization of the incident laser field is across the gap. The dashed yellow line denotes the boundary between air and gold.

Figure 4.6b shows simulated electric field distribution over a trench using FDTD simulation, where the spatial overlap of the enhanced near field of $\mathbf{E}_\omega$ and monolayer WSe₂ strengthens the light coupling in WSe₂ and boosts SH emission, and the near-field of $\mathbf{E}_\omega$ is enhanced by ~ 13 -fold as compared to the electric field of the pump laser in the air ($\mathbf{E}_0$), predicting a theoretical SHG enhancement factor of 13^4 ($\sim 29,000$). Our maximum SHG enhancement extent (13,000-fold) is less than this predicted value as the gold substrate may cause loss of SHG signal at 400 nm due to interband-transition and reabsorption. The reabsorption of 400-nm signal can be seen in both metasurface and flat gold (Fig. 4.4b). This also accounts for the weaker SHG intensity from WSe₂ on flat gold as compared with the emission from WSe₂ on as-grown sapphire (Fig. 4.1g). Although the near-field enhancement near 800 nm is well controlled by the gold metasurface, the absorption of gold below 500 nm causes the emitted SHG to be partially absorbed. Thus, the device could be improved by using a different metal that has low absorbance ~ 400 nm. The effective second order susceptibility $\chi_{eff}^{(2)}$ was computed by using the measured SHG spectra as²⁹:

$$\chi_{eff}^{(2)} \propto (I_{2\omega})^{1/2}/I_\omega, \quad (4.2)$$

where I_ω and $I_{2\omega}$ are the pump laser and second-harmonic intensities.

According to this method, the effective second order susceptibility $\chi_{eff}^{(2)}$ of

WSe₂ on metasurface is calculated to be $\sim 7.44 \times 10^3$ pm/V without normalization of the trench occupation. The $\chi_{eff}^{(2)}$ of our CVD-grown WSe₂ on sapphire is ~ 9.24 pm/V, which is slightly lower than that of the mechanically exfoliated monolayer TMDCs as reported by refs. 13, 3. If mechanical exfoliated WSe₂ had been transferred onto the metasurface, the $\chi_{eff}^{(2)}$ could have been even higher.

To experimentally verify the SHG enhancement mechanism and position, triangular WSe₂ flake on trenches with large pitch size of 910 nm was prepared for SHG mapping. Figure 4.7a shows the SEM image of a triangular WSe₂ flake covering 6 trenches. Fig. 4.7b presents the simulated electric field distributions over one of these trenches with pump polarization perpendicular (left panel) and parallel (right panel) to the trench. Corresponding to the SEM image, there are 6 brighter SHG strips in the SHG mapping (Fig. 4.7c) when the polarization direction of incident light is perpendicular to the trench orientation, proving that the SHG enhancement position is located at the trenches that support lateral gap plasmons. It is also noted that the SHG amplitude at WSe₂ between the trenches is almost the same as that at WSe₂ on flat gold (Fig. 4.7c), indicating that the SHG enhancement only occurs at WSe₂ over the trenches. This observation can be confirmed by the localized electric field distribution over the trenches with the pitch of 910 nm (left panel in Fig. 4.7b). As expected, when the incident light is rotated 90 degrees, the brighter strips almost disappear (Fig. 4.7d), confirming trenches without generation of gap plasmons (right panel in Fig. 4.7b) have little influence on SHG from WSe₂.

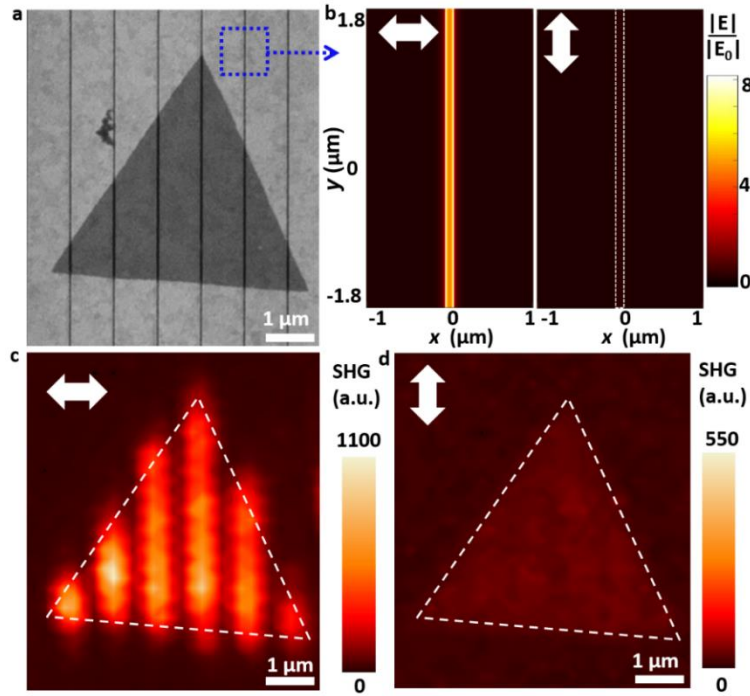


Figure 4.7 | SHG enhancement positions. (a) SEM image of single-crystalline monolayer WSe₂ flake on metasurface with a pitch size of 910 nm. We purposely chose the large pitch size here so that the SHG emission from the neighbouring trenches could be spatially resolved. (b) Simulated electric field distribution at a plane 1 nm above the surface of metasurface with pump polarization perpendicular (left panel) and parallel (right panel) to the trench. The short dot line denote the geometry of the trench. (c-d) SHG mappings of WSe₂ flake on metasurface as shown in the SEM image under resonant excitation and non-resonant excitation, respectively. The white dashed lines outline the borders of the WSe₂ flake. The white arrows show the polarization directions of the pump laser.

4.4.4 Influence of crystal and trench orientation

Due to the sensitivity of the SHG to the crystal symmetry, crystal-orientation-dependent SHG measurements provide important crystallographic information of WSe₂ atomic layers if the collected SHG signal was sent through a linear-polarized analyzer. The components of the second-order susceptibility are normally provided in terms of the crystal axes (a , b , c). However, it is convenient to describe the nonlinear polarization in terms of the laboratory axes (x , y , z) as the direction of propagation and polarizations of the interacting waves are defined relative to the laboratory axes. According to the transformation from

the crystal coordinate to the laboratory coordinate, we can derive the effective second-order susceptibility along x and y axes. As such, the parallel ($E_{2\omega}^{\parallel}$) and perpendicular ($E_{2\omega}^{\perp}$) components of the second-harmonic electric field with respect to the fundamental polarization can be expressed as³⁰:

$$\mathbf{E}_{2\omega}^{\parallel} \propto |\chi_{bbb}^{(2)}| \cos 3(\Theta + \Theta_0), \quad (4.3)$$

$$\mathbf{E}_{2\omega}^{\perp} \propto |\chi_{bbb}^{(2)}| \sin 3(\Theta + \Theta_0), \quad (4.4)$$

where Θ is the rotated angle of the sample. Θ_0 is the initial angle between armchair direction (b) of the WSe₂ and polarization direction of the fundamental wave (y). The total SHG intensity (without the analyzer) is expressed as follows:

$$I_{2\omega} = I_{2\omega}^{\parallel} + I_{2\omega}^{\perp} = C^2 [(E_{2\omega}^{\parallel})^2 + (E_{2\omega}^{\perp})^2] \propto C^2 |\chi_{bbb}^{(2)}|^2, \quad (4.5)$$

where $I_{2\omega}$ is constant with respect to the crystal orientation. For the experiments in Fig. 4.8 b-c, we placed an analyzer before the spectrometer with its polarization direction aligned with the polarizer for the pump laser, so we only need to consider the parallel component of SHG intensity. This can be employed to determine and distinguish the contributions of SHG signals influenced by the monolayer WSe₂ crystal orientation and the trench orientation, respectively. A triangular monolayer WSe₂ flake covering both metasurface and flat gold film (Fig. 4.8a) was rotated by 5-degree steps and the SHG spectra from these two positions were respectively recorded at each rotation angle (Θ).

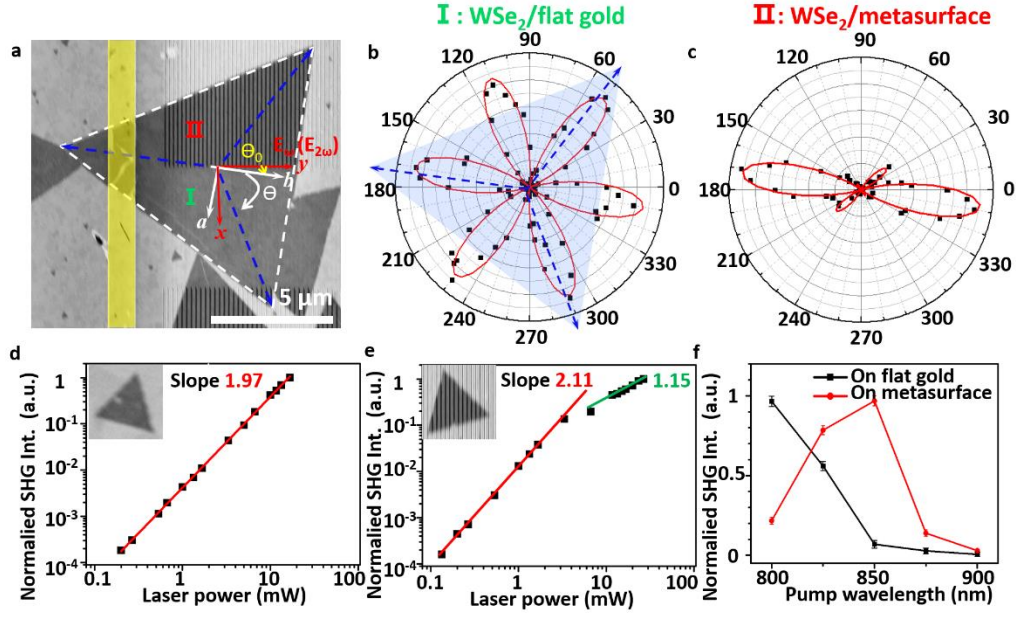


Figure 4.8 | Influence of crystal and trench orientation (a) SEM image of WSe₂ flake on flat gold film (I) and metasurface (II). White dashed line denotes the region of the investigated WSe₂ flake with the armchair directions denoted by blue dashed arrow. a and b are principle axes in the monolayer plane in the crystal coordinates. x and y are from laboratory coordinates (x, y, z), where x is perpendicular to y , y corresponds to the polarization of pump laser. The SHG components detected parallel to the polarization of pump laser, *i.e.*, $\mathbf{E}_\omega \parallel \mathbf{E}_{2\omega}$. θ is the rotate angle of the sample. θ_0 is the initial angle between the b and $\mathbf{E}_\omega$. The yellow bar denotes the orientation of the trench. (b-c) Polar plot of the normalized SHG intensity from I and II , respectively. The black squares are experimental data which are fitted by red curve according to the symmetry analysis in the text. The blue triangle with white dashed arrow are used to denote the crystal orientation. (d-e) Normalized SHG intensity from I and II as a function of laser power in log-log scale plot, respectively. (f) Normalized SHG intensity from I and II as a function of laser wavelength, respectively. The data points and corresponding error bars are obtained, respectively, by calculating the mean value and standard deviation of the SHG peak amplitude based on 10 spectra for each regions.

Figures 4.8b and c shows the polar plot of WSe₂ on flat gold (Region I) and metasurface (Region II), respectively, where the SHG intensity is plotted as a function of the rotation angle. A clear petal pattern with six-fold symmetry can be observed in Fig. 4.8b for WSe₂ on flat gold where the SHG pattern follows an equation derived from Eq. (4.3): $I_{2\omega} \propto C_1 \cos^2[3(\theta + \theta_0)]$, where C_1 is a constant obtained from the largest SHG intensity. The peaks of SHG

intensity point to the armchair directions in monolayer WSe₂ lattice, *i.e.*, the perpendicular bisectors of the single crystalline flake (white dashed arrow). The fitting denoted by the red curves shows that the initial offset angle (Θ_0) between the armchair direction of the single crystalline WSe₂ and fundamental wave polarization is 10°, indicating that the armchair was initially rotated with respect to the fundamental wave. Unlike the polar pattern of Region I, Region II shows a polar pattern with two large and two small petals that can be well fitted by the equation:

$$I'_{2\omega} = C_2 \cos^2[3(\Theta + \Theta_0)] \cdot \cos^4\Theta, \quad (4.6)$$

where C_2 is a constant that is fitted by normalizing the SHG intensity at each angle. The first cosine term represents the influence of the crystal orientation and the second cosine term reflects how the angle between the trench and the y axis influences the SHG intensity. The trenches were initially oriented perpendicular to the polarization of fundamental wave, in which case, the near field of the fundamental wave localized at the gap has the largest value: $\mathbf{E}_{\text{gap}}^{\parallel} = f\mathbf{E}_{\omega}$, where $\mathbf{E}_{\text{gap}}^{\parallel}$ is the enhanced local electric field with the same polarization direction as $\mathbf{E}_{\omega}$ and f is the enhancement factor defined by $\mathbf{E}_{\text{gap}}/\mathbf{E}_0$. As the trenches rotate an angle of Θ , the near field enhanced by the gap plasmon is given by $\mathbf{E}_{\text{gap}}^{\parallel} = f\mathbf{E}_{\omega}\cos\Theta$. Therefore, the SHG intensity of the WSe₂ on metasurface varies with the rotation of the trench accordingly to the $\cos^4\Theta$ function.

In addition, the power-dependent total SH signal from both WSe₂ on flat gold film and metasurface (Figs. 4.8d-e) exhibits quadratic input power dependence, and the fitting line (red) has a slope of ~ 2 , confirming the second-order nature of the nonlinear process. As shown in Fig. 4.8e, at high pump

powers, the SHG intensity deviating from a quadratic dependence may be due to absorption processes. In particular, the pump laser is absorbed via two-photon absorption and the second harmonic signal is absorbed linearly³¹, resulting in a power-dependence slope of 1.15. Figure 4.8f shows the influence of pump laser wavelength on SHG intensity where the power of fundamental wave remains the same at each wavelength. With increasing pump wavelength, the SHG intensity of WSe₂ on flat gold film drops, whereas for WSe₂ on metasurface, the SHG intensity first goes up then decreases, reaching a maximum at the wavelength of 850 nm corresponding to the plasmon resonance of the nanostructure (Fig. 4.8b). It is also worth noting that for WSe₂ on metasurface, there is a strong SH response in a broad wavelength range even at room temperature, showing its advantage over the method of exciton-enhanced SHG.

4.5 Summary

Transferring WSe₂ onto metasurfaces with plasmon resonance that approach the fundamental wavelength of 800 nm can significantly enhance SH emission at 400 nm by 13, 000-fold, without emission peak broadening or increased spectral background. The large enhancement can be maintained in a broad wavelength range even at room temperature. As validated by experiments and simulation, the augmented SHG mainly originates from the intensification of the local fields at excitation wavelength induced by gap plasmons located over the trenches. Furthermore, the anisotropic gold substrate composed of trenches aligned in single direction allows for dynamic tuning of the SHG amplitude from WSe₂ by rotating the polarization direction of pump laser. This method is superior to the previously reported isotropic photonic cavity which fixes the SHG intensity from TMDCs. This hybrid system comprising a

metasurface and monolayer WSe₂ provides a convenient and practical means to obtain blue emission from a near-infrared laser in monolayer TMDCs. It can also serve as a nonlinear mirror with applications ranging from nanoscale nonlinear optical frequency converters, highly monochromatic lasers, and all-optical signal processors.

4.6 References

1. New, G. *Introduction to nonlinear optics*. Cambridge University Press (2011).
2. Kumar, N. *et al.* Second harmonic microscopy of monolayer MoS₂. *Phys. Rev. B* **87**, 161403 (2013).
3. Malard, L. M. *et al.* Observation of intense second harmonic generation from MoS₂ atomic crystals. *Phys. Rev. B* **87**, 201401 (2013).
4. Kuo, P. S., Bravo-Abad, J., Solomon, G. S. Second-harmonic generation using-quasi-phasematching in a GaAs whispering-gallery-mode microcavity. *Nat. Commun.* **5**, (2014).
5. Yu, H. *et al.* Charge-Induced Second-Harmonic Generation in Bilayer WSe₂. *Nano Lett.* **15**, 5653-5657 (2015).
6. Wang, C.-Y., Guo, G.-Y. Nonlinear Optical Properties of Transition-Metal Dichalcogenide MX₂ (M= Mo, W; X= S, Se) Monolayers and Trilayers from First-Principles Calculations. *J. Phys. Chem. C* **119**, 13268-13276 (2015).
7. Ribeiro-Soares, J. *et al.* Second Harmonic Generation in WSe₂. *2D Mater.* **2**, 045015 (2015).
8. Shoji, I. *et al.* Absolute scale of second-order nonlinear-optical coefficients. *J. Opt. Soc. Am. B* **14**, 2268-2294 (1997).
9. Zhao, M. *et al.* Atomically phase-matched second-harmonic generation in a 2D crystal. *Light Sci. Appl.* **5**, e16131 (2016).
10. Klein, J. *et al.* Electric-field switchable second-harmonic generation in bilayer MoS₂ by inversion symmetry breaking. *Nano Lett.*, (2016).
11. Li, Y. *et al.* Probing symmetry properties of few-layer MoS₂ and h-BN by optical second-harmonic generation. *Nano Lett.* **13**, 3329-3333 (2013).
12. Wang, G. *et al.* Giant enhancement of the optical second-harmonic emission of WSe₂ monolayers by laser excitation at exciton resonances. *Phys. Rev. Lett.* **114**, 097403 (2015).
13. Seyler, K. L. *et al.* Electrical control of second-harmonic generation in a WSe₂ monolayer transistor. *Nat. Nanotechnol.* **10**, 407-411 (2015).
14. Janisch, C. *et al.* Extraordinary second harmonic generation in tungsten disulfide monolayers. *Sci. Rep.* **4**, 5530 (2014).
15. Rodrigues, S. P., Cai, W. Nonlinear optics: tuning harmonics with excitons. *Nat. Nanotechnol.* **10**, 387-388 (2015).
16. Fryett, T. K. *et al.* Silicon photonic crystal cavity enhanced second-harmonic generation from monolayer WSe₂. *2D Mater.* **4**, 015031 (2016).
17. Yi, F. *et al.* Optomechanical enhancement of doubly resonant 2D optical nonlinearity. *Nano Lett.* **16**, 1631-1636 (2016).

18. Day, J. K., Chung, M.-H., Lee, Y.-H., Menon, V. M. Microcavity enhanced second harmonic generation in 2D MoS₂. *Opt. Mater. Express* **6**, 2360-2365 (2016).
19. Grinblat, G. *et al.* High-efficiency second harmonic generation from a single hybrid ZnO nanowire/Au plasmonic nano-oligomer. *Nano Lett.* **14**, 6660-6665 (2014).
20. Liu, X. *et al.* Cooperative enhancement of second-harmonic generation from a single CdS nanobelt-hybrid plasmonic structure. *ACS Nano* **9**, 5018-5026 (2015).
21. Zheng, G. *et al.* Metasurface holograms reaching 80% efficiency. *Nat. Nanotechnol.* **10**, 308-312 (2015).
22. Yu, N., Capasso, F. Flat optics with designer metasurfaces. *Nat. Mater.* **13**, 139-150 (2014).
23. Wang, Z. *et al.* Giant photoluminescence enhancement in tungsten-diselenide-gold plasmonic hybrid structures. *Nat. Commun.* **7**, (2016).
24. Wang, Q. H. *et al.* Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* **7**, 699-712 (2012).
25. Maier, S. A. *Plasmonics: fundamentals and applications*. Springer Science & Business Media (2007).
26. Rose, A., Huang, D., Smith, D. R. Controlling the second harmonic in a phase-matched negative-index metamaterial. *Phys. Rev. Lett.* **107**, 063902 (2011).
27. Lee, J. *et al.* Giant nonlinear response from plasmonic metasurfaces coupled to intersubband transitions. *Nature* **511**, 65-69 (2014).
28. Lan, S. *et al.* Backward phase-matching for nonlinear optical generation in negative-index materials. *Nat. Mater.* **14**, 807-811 (2015).
29. Aouani, H. *et al.* Multiresonant broadband optical antennas as efficient tunable nanosources of second harmonic light. *Nano Lett.* **12**, 4997-5002 (2012).
30. Ko, T. Y. *et al.* On-stack two-dimensional conversion of MoS₂ into MoO₃. *2D Mater.* **4**, 014003 (2016).
31. Buckley, S., Radulaski, M., Biermann, K., Vučković, J. Second harmonic generation in photonic crystal cavities in (111)-oriented GaAs. *Appl. Phys. Lett.* **103**, 211117 (2013).

Chapter 5 Slow Cooling and Efficient Extraction of C-Exciton Hot Carriers in MoS₂ Monolayer

5.1 Introduction

Controlling the relaxation behaviour of electron-hole pairs in low cost is significant for hot carrier-related optoelectronic applications^{1, 2}. For bulk semiconductor photovoltaics, phonon-assisted hot-carrier cooling generates heat, so the maximum theoretical light-into-electricity conversion efficiency is limited to only ~31% (ref. 3). This value could double if all hot carriers could be extracted efficiently by suitable conductors⁴. To overcome this shortcoming, slowing down the hot-carrier relaxation by circumventing the phonon-assisted relaxation is the typical approach investigated⁵.

Slow hot-carrier cooling can be achieved by reducing the material dimensionality to achieve quantum confinement from one (two-dimensional material) to all three (quantum dot) dimensions, as the enlarged energy spacing arising from quantum confinement causes a ‘phonon bottleneck’⁶. However, the initial hot-carrier extraction efficiency in typical quasi-zero-dimensional semiconductor quantum dot systems at room temperature is still low. For CdSe/CdS/ZnS core-shell quantum dots, only about a third of the photogenerated hot electrons located in the CdS shell will transfer to the electron acceptor (methyl viologen)⁷. Moreover, for bare CdSe quantum dots adsorbed within methyl viologen, this hot electron extraction is negligible, because an extremely fast hot-carrier extraction process is required to compete against phonon-assisted relaxation⁸. Additional relaxation mechanisms that come into play are Auger-like processes and surface-state trapping, which

are efficient in quantum dots^{9, 10}, unless the photogenerated electrons and holes are spatially separated to a certain extent^{5, 7}.

Two-dimensional systems such as semiconducting transition metal dichalcogenides (TMDCs) with finite bandgaps^{11, 12} have been recently shown to be very promising for ultrathin and flexible energy conversion and storage devices¹³⁻¹⁷. Due to the parallel bands in their density of states or the so-called band nesting effect¹⁸, these atomically thin materials present strong optical responses even for excitation energies far exceeding their bandgaps. Recent work in atomically thin molybdenum disulfide (MoS₂) have suggested that the photoexcited electron-hole pairs in the ‘band nesting’ region (denoted as C-excitons) could exhibit a very fast intraband relaxation and a very slow indirect emission process due to spontaneous charge-separation in momentum space^{19, 20}. The band nesting refers to regions in the band structure with conduction band and valence band parallel to each other in energies, implying that when a material absorbs a photon, the resulting electrons and holes will move to the lower energy states. As a result, they propagate with the same but opposite velocities, reducing the possibility of the electron-hole combination.

Therefore, it can be expected that the resulting hot-carrier relaxation for the C-exciton state would be different from that associated with the band-edge excitons in atomically thin TMDCs. Moreover, because of the renormalized bandgap and enhanced electron-electron interactions induced by the reduced Coulomb screening²¹, as well as an indirect to direct bandgap transition attributed to the quantum confinement effect^{22, 23} in two dimensions, this C-exciton relaxation is expected to be distinguishable from its few-layer and bulk counterparts. Indeed, previous time-resolved studies have shown that the

intervalley (K– Γ) transfer in MoS₂ bulk is very efficient due to the dominant indirect bandgap characteristic²⁴, while for the few-layer MoS₂ case, although there is efficient charge carrier photogeneration²⁵, the decay of neutral C-excitons is still faster than neutral band-edge excitons. However, the fundamental photophysical mechanism and detailed processes of hot-carrier relaxation and follow-up extraction for the C-exciton state in single-layer TDMCs have not yet been elucidated²⁶, and could be crucial to understand the working mechanisms in related two-dimensional nanophotonic devices.

In this chapter, we report the transient characteristics of the intrinsic high-energy C-exciton state in MoS₂ monolayers and MoS₂ monolayer/graphene heterostructures by studying its femtosecond broadband transient absorption (TA) spectrum. We observe a slower hot-carrier relaxation for the C-excitons, in comparison with band-edge A/B-excitons, indicating the presence of an additional mechanism for the suppression of phonon-assisted relaxation which is not dominated by the quantum confinement effect. In combination with scanning tunneling spectroscopic (STS) analysis and steady-state optical spectroscopies, we identify the screening-sensitive bandgap renormalization of single-layer MoS₂ with and without graphene as a substrate. The relevant initial charge transfer processes in MoS₂ monolayer/graphene heterostructures are confirmed, and a direct hot-carrier extraction with a remarkable efficiency of ~80% is demonstrated for the C-exciton at room temperature, with corresponding values for A/B-excitons of 93%/81%. These results show that atomically thin TMDCs provide opportunities for modifying the electronic structure and manipulating the hot-carrier relaxation behavior in two-dimensional *d*-electron systems.

In this work, my contribution is growing graphene and MoS₂ as well as characterizing their quality by AFM, Raman and PL techniques. As part of our collaboration, the transient absorption experiment was conducted by Dr. Lei Wang in Prof. Hongbo Sun's group in Jilin University, China.

5.2 Preparation of 2D materials

5.2.1 Growth and transfer of graphene film

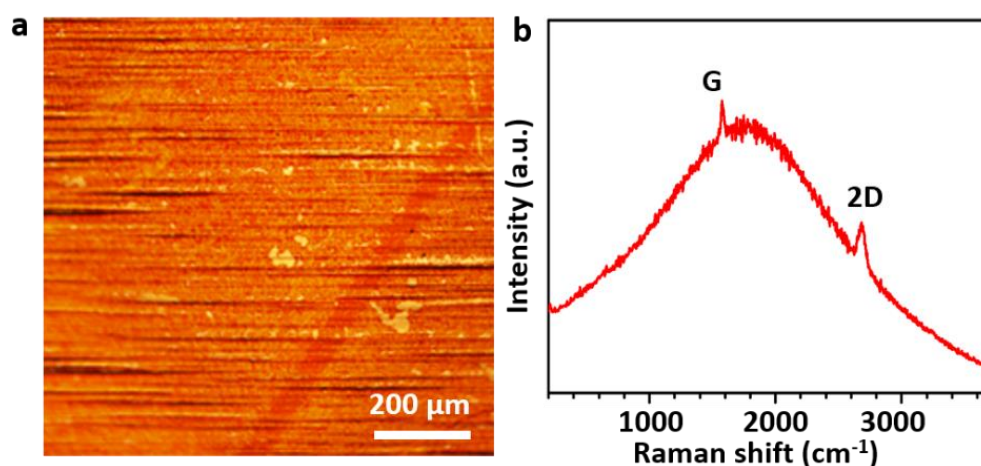


Figure 5. 1 | Properties of graphene grown on copper. (a) OM of graphene grown on copper. (b) Raman spectrum of graphene grown on copper.

Large-area monolayer graphene was grown on copper foils (ALFA10950.GZ, 99.999%) at 1000 °C by a CVD method using a mixture of methane and hydrogen gases as reported elsewhere (Fig. 5.1a). The 1 cm by 2 cm copper foil sample was heated to 1000 °C inside a quartz tube under a H₂ atmosphere with 15 sccm flow at 150 mTorr and followed by thermal annealing at the same temperature. The growth of single-layer graphene was then started with a CH₄/H₂ gas mixture (60 and 15 sccm, respectively) for 30 min at 750 mTorr. Subsequently the furnace was rapidly cooled to room temperature. The quality of graphene on copper is verified by Raman spectra where there are characteristic G and 2D peaks at 1450 cm⁻¹ and 2650 cm⁻¹ respectively, and no

defect peak is observed. The broad background is caused by the signal from the copper foil.

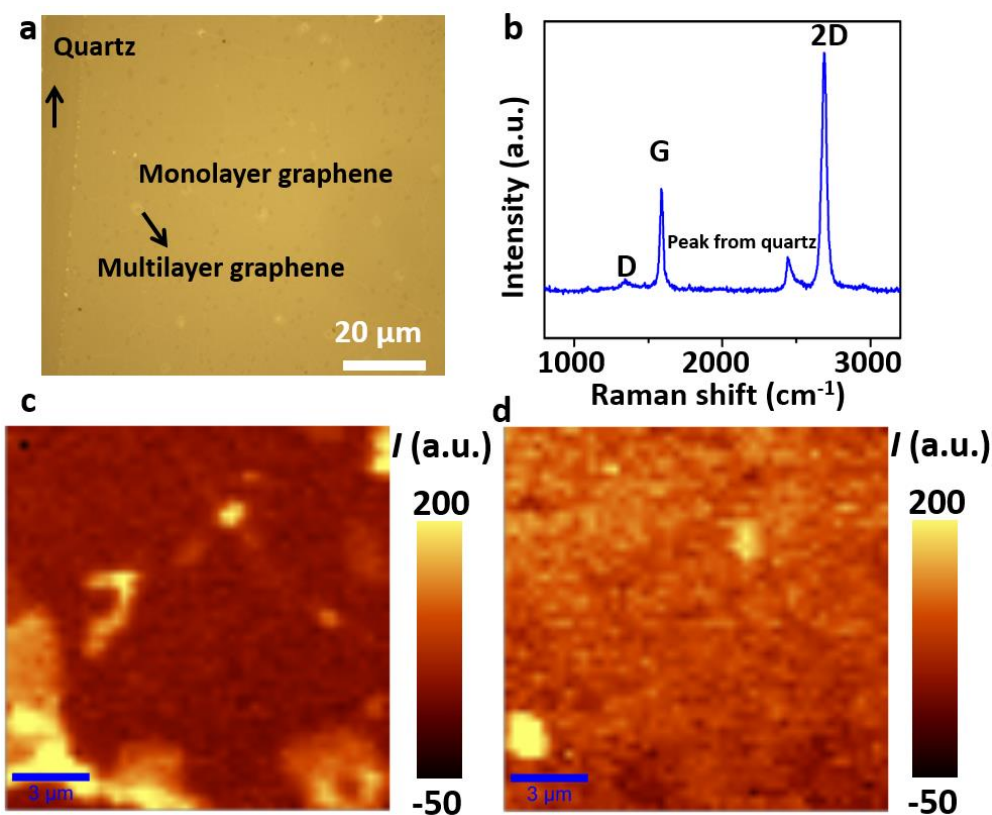


Figure 5.2 | Properties of graphene transferred onto quartz. (a) Optical microscope image of graphene on quartz under 100× objective. (b) Raman spectrum of graphene on quartz. (c) G peak ($1562\text{--}1640\text{ cm}^{-1}$) mapping of graphene on quartz. (d) 2D peak ($2638\text{--}2739\text{ cm}^{-1}$) mapping of graphene on quartz.

The transfer process for graphene is slightly different from that for TMDCs in the substrate etching solution used. The former uses ammonium peroxydisulfate to etch copper foil, but other processes are similar (see details in Section 3.2.1). The quality of graphene transferred on quartz was carefully characterized by OM and Raman, as shown in Fig. 5.2. The OM image (Fig. 5.2a) shows that the transferred graphene is dominated by continuous monolayer film with few multilayer flakes. The layer number of the graphene can be identified by analysing the Raman intensity ratio of 2D peak and G peak. As shown in Raman spectrum (Fig. 5.2b) and mappings (Fig. 5.2c-d), this film

shows a typical monolayer feature with the intensity ratio of ~ 2 . The D peak $\sim 1300\text{ cm}^{-1}$ in the Raman spectrum (Fig. 5.2b), which is associated with defects, is near the background level.

5.2.2 Growth and transfer of MoS₂ film

MoS₂ monolayers were grown by CVD on SiO₂/Si substrates²⁷. The substrate was placed at the centre of the furnace, while the precursor powder (sulfur, 0.15 g) was placed in a quartz boat in a suitable upstream position. The smooth side of the SiO₂/Si substrate was placed face down on a customized quartz half rod leaving a 2- μm gap between the substrate and the rod, and 0.05 g of MoO₃ was put on the back of the substrate. The quartz tube was heated from room temperature to 650 °C with inlet of 50-sccm Ar, and when the temperature reached the maximum value, the Ar flow was adjusted to 10 sccm. The furnace was kept for 20 min at 650 °C for the growth of MoS₂. Uniform MoS₂ monolayers were obtained on the smooth side of the SiO₂/Si substrate. The MoS₂ transfer²⁸ method is similar to that used to transfer WSe₂ (cf. Section 3.2.1). Here, the target substrate is quartz with or without graphene. Hence, both MoS₂ monolayer and MoS₂ monolayer/graphene heterostructure samples on quartz substrates were obtained. To confirm the sample quality of MoS₂, OM, AFM, PL and Raman characterization were performed before and after transfer, as shown in Figs. 5.3 and 5.4. The monolayer MoS₂ grown on Si wafer is continuous film (Fig. 5.3a) with a typical PL emission peak at $\sim 660\text{ nm}$ (Fig. 5.3b) and Raman modes (E_{2g}^1 and A_{1g}) at $\sim 390\text{ cm}^{-1}$ and $\sim 410\text{ cm}^{-1}$, respectively. After transferred onto quartz, the monolayer MoS₂ remains to be a continuous film with a thickness of 0.75 nm (Fig. 5.4).

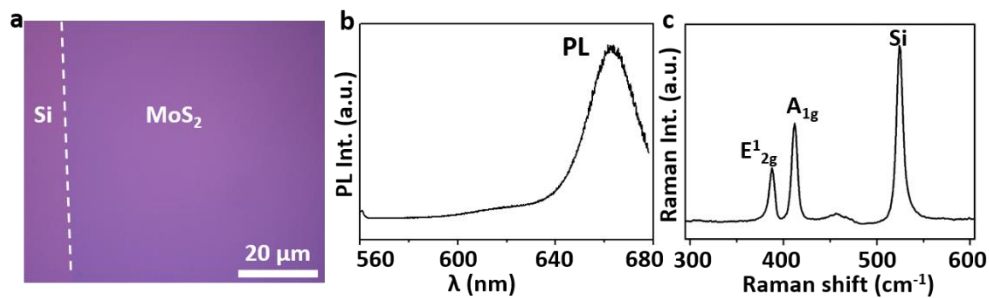


Figure 5.3 | Characterization of MoS₂ on Si wafer. (a) Optical microscope image of MoS₂ on quartz under 100× objective. (b, c) PL and Raman of MoS₂ on Si wafer.

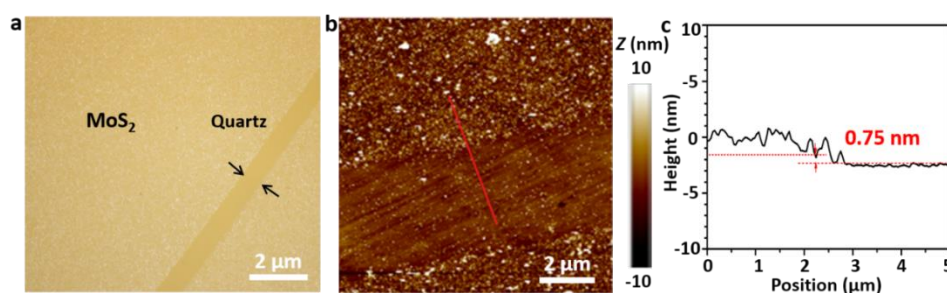


Figure 5.4 | Characterization of MoS₂ transferred onto quartz. (a) Optical microscope image of MoS₂ on quartz under 100× objective. (b) AFM height profile of MoS₂ on quartz. (c) Cross-sectional profile along the red line in (b).

5.2.3 Characterization setup

The optical imaging was performed in a Nikon Eclipse LV 100D system, and the AFM imaging was performed by a BRUKER Dimension FastScan system using the tapping mode. The Raman/PL spectra and mapping were collected in a confocal system (The Alpha 300R). The wavelength of the excitation laser was 532 nm with a spot size of approximately 0.5 mm. The steady-state PL spectra and mapping were obtained with a 600 grooves mm⁻¹ grating, while a 1,800 grooves mm⁻¹ grating was used to obtain detailed line shapes of the Raman band. The experimental conditions for STM/STS measurements were described in Section 2.6.

The TA setup is described in Section 2.4.4. In the TA setup for both transmission and reflection modes, a mode-locked Ti: sapphire laser/amplifier

system (Solstice, Spectra-Physics) was used (800 nm wavelength, 1.5-mJ pulse energy, 100 fs pulse width, 250 Hz repetition rate). The low frequency was set to allow matching of the signal with the collection system. The output of the amplifier was split into two parts, with the stronger beam used to generate the desired excitation light. For 600 nm and 650 nm excitation, a TOPAS system was adopted, while 400 nm excitation was directly doubled from 800 nm laser pulses. The broad-band white-light probe pulses from 400 nm to 850 nm generated from 2 mm thick water. The TA data were collected by a fiber-coupled spectrometer connected to a computer. The group velocity dispersion of the transient spectra was compensated by a chirp program²⁹. All the measurements were performed at room temperature.

5.3 Theoretical calculations.

We collaborated with Xianbin Li in Jilin University and performed the calculations using the DFT as implemented in the VASP codes. The exchange correlation energy was described by the generalized gradient approximation, in the scheme proposed by Perdew, Burke and Ernzerhof (PBE)^{30, 31}. A unit cell with vacuum region of 16 Å was used for the calculation, and a $9 \times 9 \times 1$ Monkhorst-Pack mesh grid was used to sample the Brillouin zone. The cutoff energy of the plane wave basis was 520 eV. All atoms were relaxed until the Hellman-Feynman forces on individual atoms were less than 0.02 eV Å⁻¹. The effect of spin-orbit coupling was also included. Although the PBE calculation could underestimate the MoS₂ bandgap³², the resulting profile of energy band is expected to be correct.

5.4 Steady-state optical characterization.

MoS₂ monolayers and graphene were grown by chemical vapor deposition (CVD) on SiO₂/Si substrates and copper foils, respectively²⁷, and then transferred to a fresh quartz substrate using a standard poly(methylmethacrylate) (PMMA) transfer method²⁸. Details of MoS₂ monolayer and MoS₂ monolayer/graphene sample preparation and steady-state characterizations are presented in Section 5.2. The OM of MoS₂ transferred on graphene is shown in Fig. 5.5a.

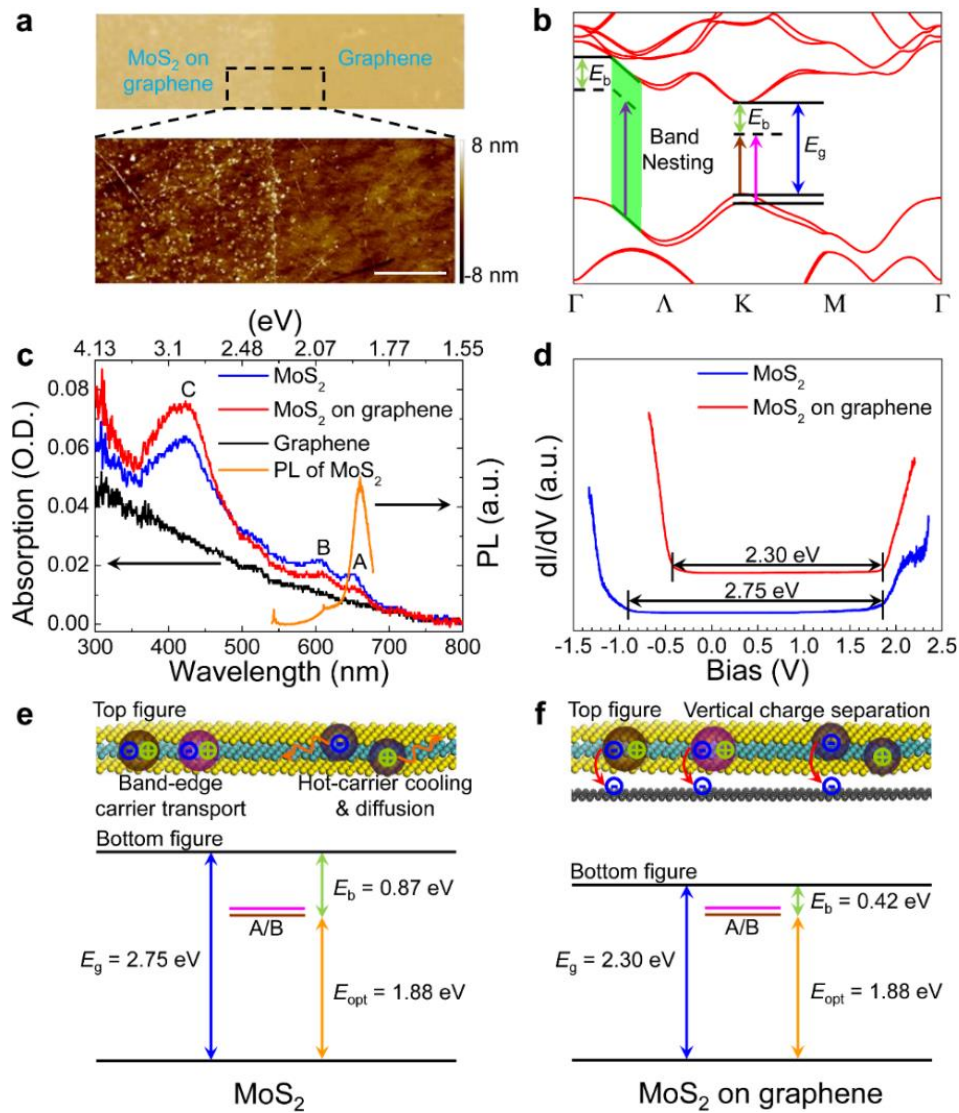


Figure 5.5 | Influence of graphene on the electronic bandgap of MoS₂ monolayer. (a) Optical microscope and AFM images of MoS₂ monolayer/graphene heterostructure. The scale bar is 2 μm . (b) Theoretically predicted energy band structure

corresponding to the direct transitions in the momentum space of MoS₂ monolayers considering the spin-orbit coupling. E_g , energy gap; E_b , exciton binding energy. The green area is the band nesting region. The vertical brown, pink, and purple arrows in b represent the optical transitions of A/B/C-exciton, respectively. (c) Steady-state absorption spectra of graphene, MoS₂ monolayer, and MoS₂ monolayer/graphene heterostructure. The orange solid line is the PL spectrum of MoS₂ monolayer under 532 nm excitation. (d) STS spectra for MoS₂ monolayer and MoS₂ monolayer/graphene heterostructure. (e) Sketch of electronic and optical bandgaps for MoS₂ monolayer (bottom figure). The top image illustrates the MoS₂ monolayer (sky blue solid sphere represents the Mo atom, and yellow solid sphere represents the S atom); brown, pink, and purple spheres represent the A/B/C-exciton, respectively; the orange curves represent the hot-carrier cooling and diffusion processes. (f) Sketch of electronic and optical bandgaps for MoS₂ monolayer/graphene heterostructure (bottom figure). The top illustration schematizes the MoS₂ monolayer/graphene heterostructure (black solid sphere represents the C atom); the red arrows indicate the vertical electron extraction processes. E_{opt} , optical bandgap.

Figure 5.5b-c exhibit, respectively, the *ab initio* calculation of the band structure related to the band nesting region for MoS₂ and the corresponding measured steady-state absorption and PL spectra. According to Fig. 5.5c, when MoS₂ monolayers are placed on a graphene substrate, the oscillator strengths of band-edge A/B-excitons around 650 nm and 600 nm decrease slightly, while for the high-energy C-exciton around 430 nm the oscillator strength increases. The resulting PL of the MoS₂ monolayer/graphene heterostructure (not shown) is found to be strongly quenched, in contrast to the reference case of MoS₂ monolayers alone (Fig. 5.5c), where the PL peak at around 660 nm (1.88 eV) is observed, corresponding to the optical bandgap (E_{opt}) of the MoS₂ monolayer. These results imply complex interactions between the MoS₂ monolayer and substrates³³ that need to be understood.

5.5 Electronic bandgap measurement and transient experiment

To shed light on the correlations between the electronic structures of MoS₂ monolayer on different substrates and internal exciton relaxations, electronic bandgap and time-resolved ultrafast spectroscopy studies were performed. The influence of graphene on the electronic bandgap (E_g , equal to

the quasiparticle bandgap, E_q) of MoS₂ monolayer is revealed by the STS analysis shown in Fig. 5.5d. It is found that E_g is reduced from 2.75 eV for MoS₂ monolayer alone to 2.30 eV for the MoS₂ monolayer/graphene heterostructure. Moreover, the measurements indicate that graphene lowers the conduction band minimum (CBM, left) of the MoS₂ monolayer by ~ 0.45 eV, while the corresponding valence band maximum (VBM, right) is pinned at ~ 1.85 eV below the Fermi level. The exciton binding energy, $E_b = E_g - E_{opt}$, is calculated to be 0.42 eV and 0.87 eV for the MoS₂ monolayer with and without graphene, respectively. The former value approximates well to the previously reported values of E_b of 0.48 eV and associated E_g of 2.40 eV for CVD MoS₂ monolayers grown directly on cleaved graphite (HOPG) substrates³⁴, and the latter is close to the reported theoretical predictions (E_b of 1.0 eV and E_g of 2.8 eV)³⁵⁻³⁸. This indicates a screening-sensitive bandgap renormalization, similar to that reported for the MoSe₂ monolayer²¹. In addition, the reduced E_b measured for MoS₂ monolayer/graphene heterostructures could facilitate the charge transfer from MoS₂ monolayer to graphene, and this phenomenon will be discussed later. The relevant energy levels for MoS₂ monolayer and MoS₂ monolayer/graphene heterostructure are presented in Fig. 5.5e-f respectively, as extracted from the steady-state experimental data. According to our experimental observations and density functional theory (DFT) calculations, the location of Dirac point of graphene is close in energy to the middle of bandgap of MoS₂ monolayer, about 1.20 eV higher than its VBM (Fig. 5.6).

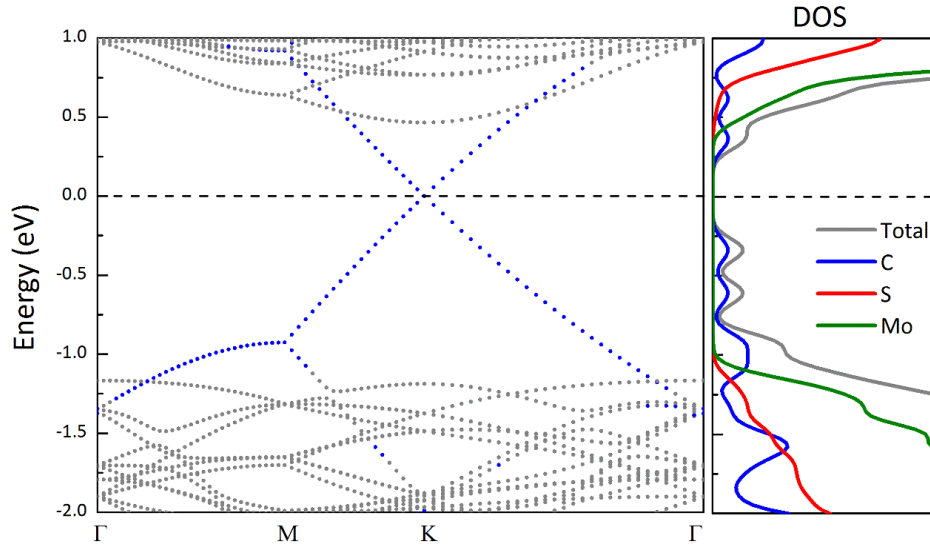


Figure 5.6 | DFT calculation of the projected band structure (left) and density of states (right) of MoS₂-graphene heterostructure. The blue dots (left figure) represent the contribution of carbon atoms in graphene.

The inherent excited-state relaxation processes for A/B/C-excitons in MoS₂ monolayers and MoS₂ monolayer/graphene heterostructures are elucidated by broadband TA experiments in transmission mode^{39,40}. Typical TA spectra of MoS₂ monolayers under 400 nm excitation (pump density of 5 $\mu\text{J cm}^{-2}$, initial exciton density of $1.28 \times 10^{12} \text{ cm}^{-2}$) are shown in Fig. 5.7a. These spectra represent the pump-induced absorption changes observed in the samples, namely the differential optical density with and without pump light excitation ($\Delta O.D. = O.D._{\text{pump}} - O.D._{\text{w/o pump}}$). As can be seen in Fig. 5.7a, there are three distinct negative transient species (bleaching signals) at around 656 nm, 608 nm and 430 nm (1.89 eV, 2.04 eV and 2.88 eV), corresponding to the energy states of A/B/C-excitons observed in the steady-state absorption spectrum (Fig. 5.5c), respectively. The positive peaks for atomically thin TMDCs as shown in Fig. 5.7a are usually attributed to peak shift and broadening of A/B/C-exciton states⁴¹⁻⁴³, excited-state absorption and/or the absorption of new photogenerated transient species, for example, the effect of charges at high pump conditions^{2,25},

Through a global analysis:

$$\Delta O.D. = \sum_{i=1}^n \alpha_i(\lambda) \exp(-t / \tau_i) \quad (5.1)$$

where $\alpha_i(\lambda)$ are the pre-exponential factors used for the calculation of decay-associated spectra (DAS), λ is the probe wavelength, t is the time delay between pump and probe, τ_i are λ -independent lifetimes^{39, 44}, and i is the number of molecule states. Global analysis is a mathematical method to extract useful lifetime components, *i.e.*, molecule states, from an overwhelming amount of data, *i.e.*, spectra intensity as a function of wavelength (transient absorption spectrum) at different delay time between the pump and probe. To be specific, as shown in Eq. 5.1, all the transient absorption spectra regardless of the time delay can be represented by the sum product of a few number of decay associated spectra resulting from molecule states and the associated exponential factors. More details can be seen in Section 2.4.4. As shown in Fig. 5.7b, it is deduced that there are at least four lifetime components for MoS₂ monolayers. For the band-edge bleaching region, the first two shortest lifetime components mainly represent the contributions of A/B-exciton populations. The lifetime component of 0.27 ps (blue) that is dominant in this spectral region could arise from fast nonradiative recombination, for example, exciton-exciton annihilation^{45, 46}, while the next lifetime component of 1.3 ps (green) not only matches the spectral positions of steady-state PL peaks well, but also agrees with the fast decay component of band-edge emission⁴⁷. As such, it could be responsible for the radiative recombination of band-edge excitons. Concerning the bleaching region of the high-energy C-exciton state, the longer lifetime component of 23 ps (orange) is dominant, and could represent contributions of

charge populations generated by self-separation of C-excitons in momentum space forming hot carriers.

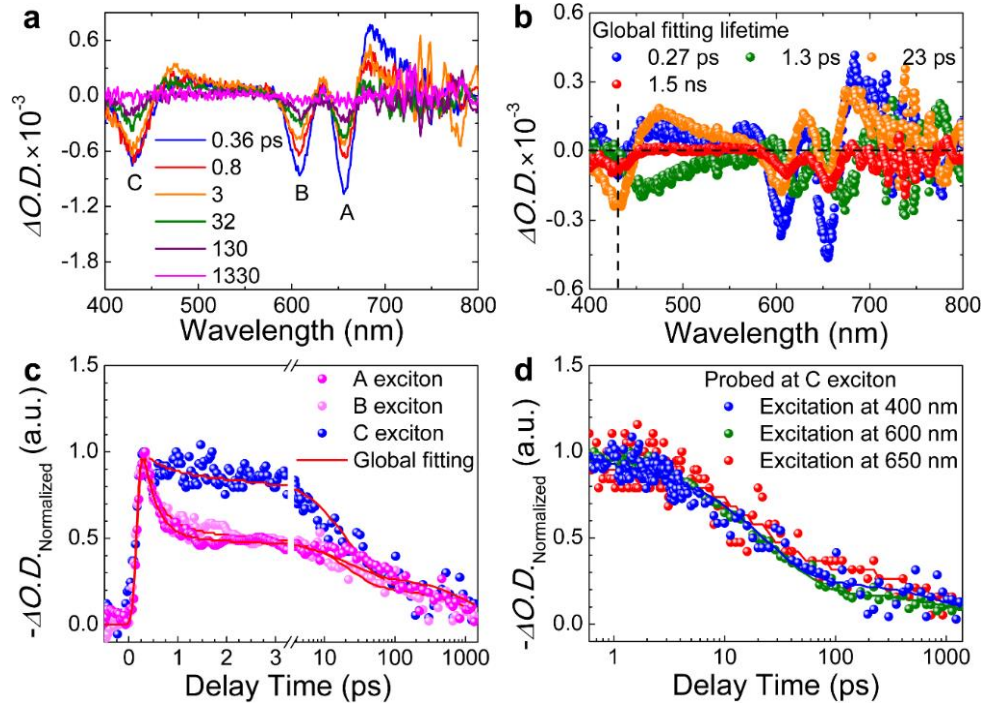


Figure 5.7 | Global fitting for transient absorption spectra of MoS₂ monolayers. (a) Transient absorption spectra of MoS₂ monolayers probed at different delay times under 400 nm excitation (pump density of $5 \mu\text{J cm}^{-2}$, initial exciton density of $1.28 \times 10^{12} \text{ cm}^{-2}$). (b) Global analysis for the transient absorption data in a. The vertical dashed line indicates the position of the C-exciton state, while the horizontal dashed line indicates $\Delta O.D. = 0$. (c) Normalized decay dynamics of A-, B-, and C-exciton states under the pump condition in (a). The red solid lines are the global fitting results. (d) Normalized decay dynamics of the C-exciton state under 400 nm, 600 nm and 650 nm excitation with similar initial exciton density. The solid lines are the global fitting results.

Finally, the remaining lifetime component in the nanosecond range (red) is used to match the long-lifetime decay background. It is therefore suggested that the global analysis on the TA data of MoS₂ monolayer should be applied when the initial exciton density is low enough, for example, less than $2 \times 10^{12} \text{ cm}^{-2}$ adopted here. This analysis demonstrates a slower decay for the hot-carriers associated with the C-exciton state, especially at the first tens of picoseconds, as observed in Fig. 5.7c. The resulting characteristic population

decay dynamics for the C-exciton state generated by the different excitations give an average hot-carrier lifetime of 350 ± 50 ps (Fig. 5.7d).

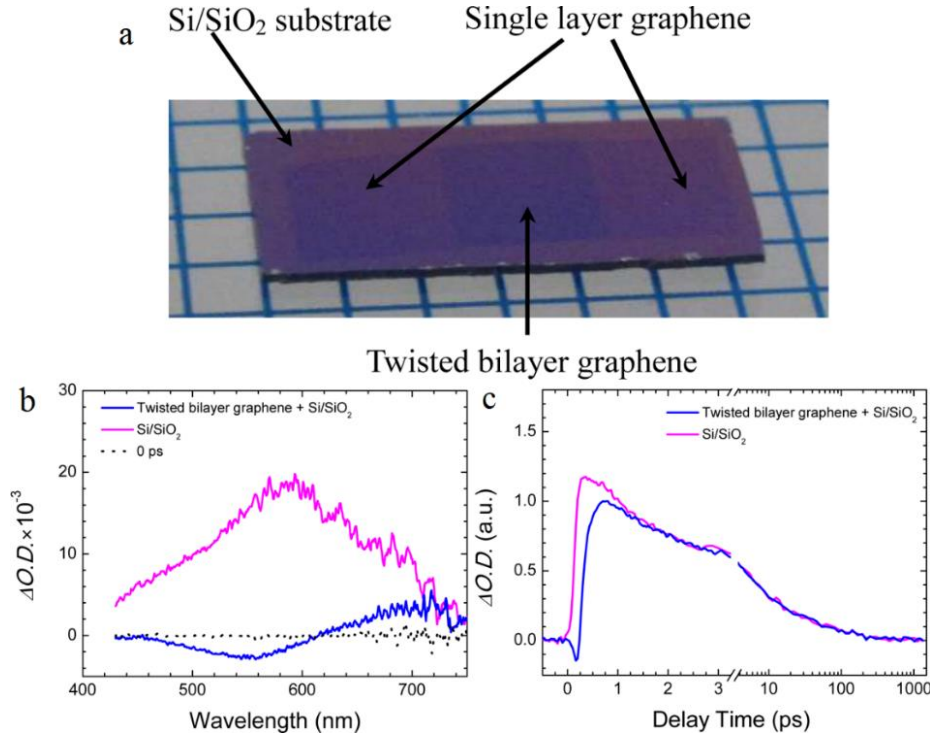


Figure 5.8 | Transient absorption of bilayer graphene. (a) Photography of the twisted bilayer graphene on Si/SiO₂ studied here. (b) Transient absorption spectra of the twisted bilayer graphene (blue line), and pure Si/SiO₂ substrate (magenta line) probed at 0.2 ps under 400 nm excitation ($300 \mu\text{J cm}^{-2}$). The dot line indicates the spectrum probed at 0 ps. (c) The dynamics probed at 580 nm for the twisted bilayer graphene, and Si/SiO₂ substrate.

It is worth noting that this anomalous relaxation behavior is contrary to the expected faster decay for the C-exciton when considering only its electronic instability. In fact, the parallel bands in the density of states will induce very fast carrier relaxation, as demonstrated in bilayer graphene. Bilayer graphene was prepared by manual transfer of two monolayer graphene films (Fig. 5.8a) and transient absorption spectra was measured with 400 nm excitation (Fig. 5.8b). The dynamics probed at 580 nm (Fig. 5.8c) demonstrates that the average carrier lifetime for twisted bilayer graphene is only ~ 0.2 ps. However, for MoS₂ monolayers, in the case where the excited-states of lower energy band-edge

exciton states are already occupied, the C-exciton state under 400 nm excitation could cause a transient and complex excited-state Coulomb environment in the pump spectral region. In this context, the high-energy C-exciton relaxation in the band nesting region will slow down.

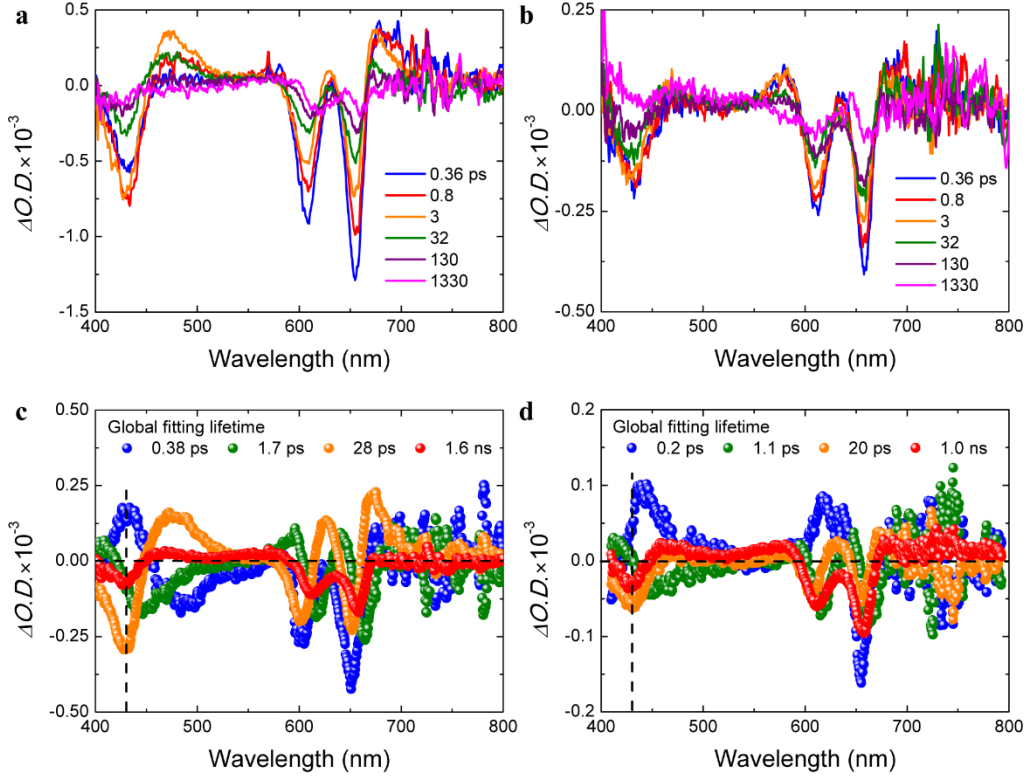


Figure 5.9 | Transient absorption spectra of MoS₂ monolayer measured by 600 nm and 650 nm pump laser, respectively as well as their global analysis (a) Transient absorption spectra of MoS₂ monolayers probed at different delay times under 600 nm excitation (initial exciton density of $1.27 \times 10^{12} \text{ cm}^{-2}$). (b) Transient absorption spectra of MoS₂ monolayers probed at different delay times under 650 nm excitation (initial exciton density of $1.13 \times 10^{12} \text{ cm}^{-2}$). (c) Global analysis for the transient absorption data in panel (a). (d) Global analysis for the transient absorption data in panel (b).

To verify this hypothesis, we performed band-edge excitation TA experiments using 600/650 nm excitation (Fig. 5.9), for which the high-energy C-exciton state is still observed (that is, there is an efficient up-conversion process). For these band-edge excitation conditions, the initial exciton densities were set close to that for the 400 nm excitation case as presented in Fig. 5.7a–c. In the global analysis results of band-edge excitations (Fig. 5.9 c and d) and 400

nm excitation (Fig. 5.7b), the main difference comes from the shortest lifetime components. For the 600 nm excitation case (Fig. 5.9c), there is a positive excited-state absorption peak in the lifetime component of 0.38 ps, which is located at the same spectral position of the C-exciton state. And this kind of positive excited-state absorption peak also appears in the lifetime component of 0.2 ps for the 650 nm excitation case (Fig. 5.9c), although a little red-shifted. In contrast, in the global analysis of the 400 nm excitation TA experiment (Fig. 5.7b), there is no positive signal around the position of the C-exciton state in the lifetime component of 0.27 ps.

Since band-edge excitations cannot directly generate the high-energy C-excitons, this positive excited-state absorption peak could be related to the formation of C-excitons. The reason for the formation of C-exciton under band-edge excitations involves photogenerated band-edge excitons jumping firstly into the high excited states by the exciton-exciton annihilation, and then fast tunneling to the C-exciton state by an energy state hybridization³⁶. Furthermore, these subtle differences between the band-edge excitation and 400 nm excitation TA experiments, suggesting a fast tunneling mechanism from the high excited states of band-edge excitons to the C-exciton state³⁵, which is consistent with our hypothesis.

TA experiments for higher exciton densities at 400 nm pump condition reveal another remarkable characteristic of the C-exciton state, which is an extremely weak initial exciton-density dependent relaxation. As shown in Fig. 5.10a, by increasing the pump density from 5 to 80 $\mu\text{J cm}^{-2}$ (initial exciton density $\sim 10^{12} - 10^{13} \text{ cm}^{-2}$), the initial TA signal amplitude of the C-exciton state probed at 0.36 ps increases and exhibits a linear behaviour even up to 240 μJ

cm^{-2} . Moreover, while the normalized decay traces at different pump densities for the C-exciton state show similar profiles, the band-edge bound optical exciton states are strongly affected by the high initial exciton density. This implies a transient and reversible method to control the optical responses of band-edge excitons in ultrashort timescales⁴⁸ by changing the carrier population in the C-exciton state.

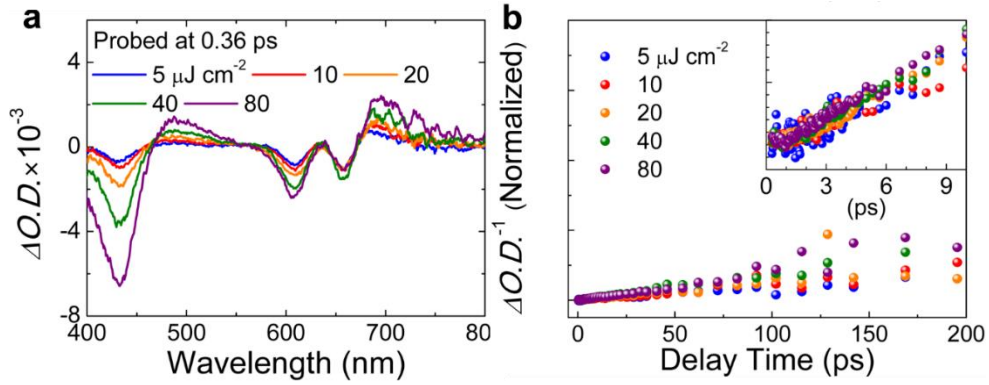


Figure 5.10 | Excitation-density dependent transient behaviours on MoS₂ monolayers. (a) Transient absorption spectra of MoS₂ monolayers probed at 0.36 ps under 400 nm excitation with different excitation power densities. (b) Reciprocal of decay traces of the C-exciton state (430 nm) under different excitation power densities, normalized at the minimum $\Delta O.D.^{-1}$. Inset shows the traces in the main panel within the first 10 ps.

5.6 Free-carrier relaxation feature for C-exciton hot carriers

Based on the rate equation⁴⁹ that describes the non-geminate/free carrier recombination:

$$\frac{n_0}{n_t} - 1 = kn_0t \quad (5.2)$$

where n_0 is the initial exciton density, t is time, and k is the second-order rate constant for recombination, a linear relationship between $\Delta O.D.^{-1}$ at the C-exciton state and t is observed in Fig. 5.10b. This linearity is consistent with a two-body recombination mechanism, and supports our hypothesis that photocarriers in the C-exciton state are hot carriers with free-carrier properties. In addition, this linearity is weakly dependent on the initial exciton density,

which suggests that the exciton dissociation occurs efficiently in the C-exciton state, in agreement with the self-separation of photocarriers in the nesting region in momentum space. From linear fits using the rate equation at different pump densities, we can obtain the value representing the slope of each fitting line as kn_0 . As n_0 can be calculated based on the related pump laser density and the absorption of the monolayer MoS₂, we can calculate the value of k . As such, we can estimate a second-order recombination rate constant of $(3.8 \pm 0.2) \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ at the extremely low initial exciton density limit ($n_0 \rightarrow 0$) by extrapolating an exponential-decay phenomenological expression.

We now turn to the detailed description of hot-carrier relaxation processes in single-layer MoS₂. It is well known in low-dimensional systems that many-body processes represent an important obstacle for achieving slow hot-carrier cooling. For the anomalous C-exciton relaxation in two-dimensional TMDCs, the band nesting effect is crucial, as it does not only provide an alternative high-energy exciton state, but also promotes self-separation of photocarriers in the nesting region in momentum space, which helps circumvent the Auger recombination channel owing to momentum mismatching. The quantum confinement in the two-dimensional system also changes the energy level alignment between the C-exciton and band-edge optical exciton (A/B-exciton) states. As the conduction and valence band energy levels for the former are higher than those for the latter, hot carriers in the C-exciton state will eventually jump to the lowest energy states in momentum space. This process will then dominate over the indirect bandgap recombination that predominates in bulk and few-layers cases. Furthermore, when photoinduced band-edge excitons and their excited states generate C-excitons by an up-

conversion/many-body process^{26, 36}, they also play a role in slowing down the C-exciton relaxation due to the transient excited-state Coulomb interactions^{50, 51}. By those factors together, a free-carrier recombination feature is created for the hot carriers in the C-exciton state of MoS₂ monolayer.

5.7 Initial extraction process for C-exciton hot carriers

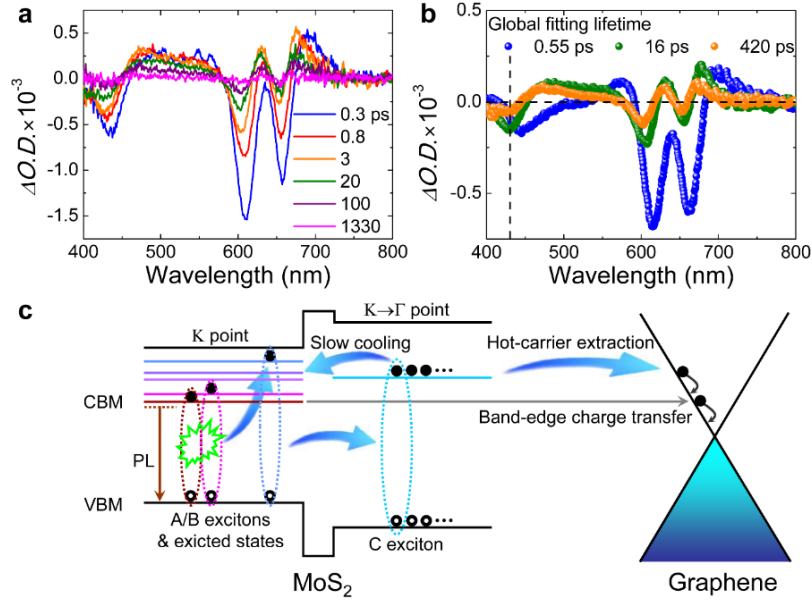


Figure 5.11 | Initial carrier extraction in MoS₂ monolayer/graphene heterostructure. (a) Transient absorption spectra of MoS₂ monolayer/graphene heterostructures probed at different delay times under 400 nm excitation (initial exciton density of $1.73 \times 10^{12} \text{ cm}^{-2}$). (b) Global analysis for the transient absorption data in (a). The vertical dashed line indicates the position of the C-exciton state, while the horizontal dashed line indicates $\Delta O.D. = 0$. (c) Illustration of the photophysical processes in the MoS₂ monolayer and initial charge transfer in the MoS₂ monolayer/graphene heterostructure.

Finally, we use the MoS₂ monolayer/graphene heterostructure to examine the initial carrier extraction processes. Figure 5.11a and b shows the TA spectra of MoS₂ monolayer/graphene films at room temperature (400 nm excitation, initial exciton density of $1.73 \times 10^{12} \text{ cm}^{-2}$) and global fitting results, respectively. It is found that due to the influence of graphene, only three lifetime components compared to four previously are needed in the global analysis. Comparing with the results in bare MoS₂ monolayers, we calculate that the

heterostructures present an initial carrier extraction efficiency of 93%, 81%, and 80% for the A-, B-, and C-exciton states, respectively. Detailed fitting data are presented in Table 5.1.

Table 5.1 Femtosecond time-resolved TA dynamics parameters obtained by global fitting under 400 nm excitation.

	Lifetime component (ps)	τ_1 (0.27)	τ_2 (1.3)	τ_3 (23)	τ_4 (1500)	τ_{ave}	
MoS ₂ monolayer	A exciton	0.59	0.02	0.17	0.22	334 ± 10	
	B exciton	0.54	0.06	0.24	0.16	246 ± 8	
	C exciton	0.14	0.04	0.59	0.23	360 ± 12	
	Lifetime component (ps)		τ_1 (0.55)	τ_2 (16)	τ_3 (420)	τ_{ave}	η
MoS ₂ monolayer /Graphene	A exciton		0.80	0.15	0.05	24 ± 1	0.93 ± 0.01
	B exciton		0.63	0.27	0.10	47 ± 1	0.81 ± 0.01
	C exciton		0.30	0.55	0.15	72 ± 2	0.80 ± 0.01

Carrier extraction efficiency: $\eta = 1 - \tau_{\text{MoS}_2\text{-Graphene}} / \tau_{\text{MoS}_2}$.

The normalized dynamics of A-, B- and C-exciton states with and without the graphene substrate are shown in Fig. 5.12. For the band-edge A-exciton, a high charge transfer efficiency (>90%) is expected, as reported in other atomically thin van der Waals heterojunctions^{49,50}. In contrast, for the initial hot-carrier extraction in the C-exciton state, this is the first time to our knowledge that such a highly efficient hot-carrier transfer is demonstrated in the MoS₂ monolayer/graphene heterostructure. The related physical picture is illustrated in Fig. 5.11c. This observation could open new avenues for hot-carrier driven optoelectronic applications², such as water photolysis and singlet

exciton fission based on atomically thin TMDCs, when other special electron acceptors are utilized to replace the graphene adopted here.

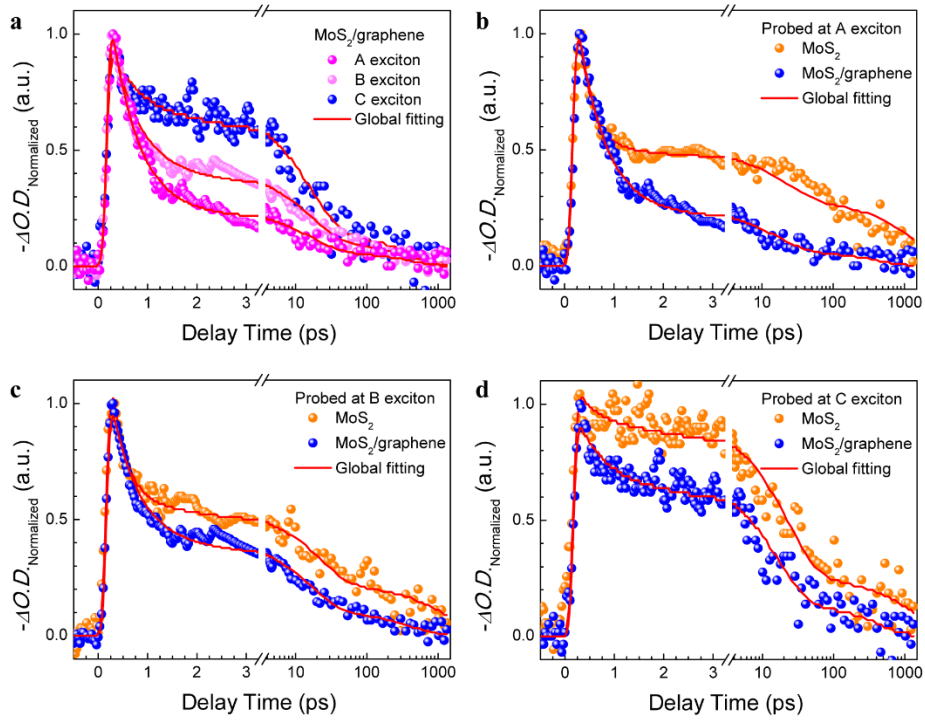


Figure 5.12 | Decay dynamics of A-, B- and C-exciton state. (a), Normalized decay dynamics of A-, B-, and C-exciton state for MoS₂ monolayer/graphene heterostructures under the pump condition in Fig. 5.11, panel a. A direct comparison for the exciton dynamics in the TA experiments of MoS₂ with and without graphene substrate under 400 nm excitation. (b), (c) and (d) show, respectively, the normalized dynamics of A-, B- and C-exciton state. The red solid lines are the global fitting results.

5.8 Discussion

One novel transient feature found here is the slower carrier relaxation (~ 350 ps) compared to the band-edge A/B-excitons, which stems from the favorable band alignment and complex excited-state Coulomb environment, rather than solely on quantum confinement in two-dimension systems. As a result, the hot-carrier relaxation in the C-exciton state is three orders of magnitude slower than the typical carrier relaxation for parallel bands in the density of states (such as ~ 0.2 ps in twisted bilayer graphene). Thus, two lateral carrier transport modes in MoS₂ monolayers are revealed: slow hot-carrier

diffusion and traditional band-edge carrier transport (Fig. 5.5e, top), which are highly important for understanding the working mechanisms of two-dimensional optoelectronic devices based on TMDC monolayers⁵². It is worth noting that the hot-carrier diffusion in the C-exciton state of MoS₂ monolayer not only possesses the free-carrier relaxation feature, but also exhibits an initial-exciton-density-dependent second-order recombination rate constant. The latter could reflect the initial excited-state Coulomb environment around the photogenerated C-excitons. This contrasts with the band-edge free-carrier relaxation behaviour, such as in organometallic halide perovskite films⁴⁹, where the second-order recombination rate constant is invariant under different pump fluences.

5.9 Summary

In summary, our results establish a fundamental photophysical model in MoS₂ monolayers by carefully analyzing the excited-state relaxation processes, especially the hot-carrier cooling and initial extraction for the C-exciton state in the band nesting region. A two-body recombination mechanism for the hot-carrier relaxation in the C-exciton state is proposed. In addition, an unprecedented initial hot-carrier extraction efficiency of 80% for the C-exciton state at room temperature is further identified when we use graphene as the electron acceptor (scheme in Fig. 5.5f, top). This highly efficient initial charge separation in the vertical direction occurs among the band-edge states (the initial carrier extraction efficiency is 93% and 81% for the band-edge A- and B-exciton states, respectively) and all high-energy excited-states indicate the optimized fabrication route for the construction of all two-dimensional van der Waals heterostructure devices. The heterostructure also yields a two-fold

reduction of E_b in comparison with the pristine MoS₂ monolayer (Fig. 5.5f, bottom). This further implies one approach to modulate the E_g of single TMDC monolayer crystals is by locally overlapping with other dielectric screening materials. Further theoretical research such as time-dependent quantum calculations are necessary for a better understanding of many-body processes involving the hot-carrier generation, relaxation and initial extraction in these atomically thin two-dimensional heterostructures.

5.10 References

1. Gabor, N. *et al.* Hot Carrier-Assisted Intrinsic Photoresponse in Graphene. *Science* **334**, 648-652 (2011).
2. Brongersma, M. L., Halas, N. J., Nordlander, P. Plasmon-induced hot carrier science and technology. *Nat. Nanotechnol.* **10**, 25-34 (2015).
3. Shockley, W., Queisser, H. J. Detailed balance limit of efficiency of p-n junction solar cells. *J. Appl. Phys.* **32**, 510-519 (1961).
4. Ross, R. T., Nozik, A. J. Efficiency of hot-carrier solar energy converters. *J. Appl. Phys.* **53**, 3813-3818 (1982).
5. Nozik, A. J. Spectroscopy and hot electron relaxation dynamics in semiconductor quantum wells and quantum dots. *Annu. Rev. Phys. Chem.* **52**, 193-231 (2001).
6. Wang, Y.-F. *et al.* Electron extraction dynamics in CdSe and CdSe/CdS/ZnS quantum dots adsorbed with methyl viologen. *J. Phys. Chem. C* **118**, 17240-17246 (2014).
7. Tisdale, W. A. *et al.* Hot-electron transfer from semiconductor nanocrystals. *Science* **328**, 1543-1547 (2010).
8. Efros, A. L., Kharchenko, V., Rosen, M. Breaking the phonon bottleneck in nanometer quantum dots: Role of Auger-like processes. *Solid State Commun.* **93**, 281-284 (1995).
9. Cooney, R. R. *et al.* Breaking the phonon bottleneck for holes in semiconductor quantum dots. *Phys. Rev. Lett.* **98**, 177403 (2007).
10. Pandey, A., Guyot-Sionnest, P. Slow electron cooling in colloidal quantum dots. *Science* **322**, 929-932 (2008).
11. Chhowalla, M. *et al.* The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chem.* **5**, 263-275 (2013).
12. Xu, M., Liang, T., Shi, M., Chen, H. Graphene-like two-dimensional materials. *Chem. Rev.* **113**, 3766-3798 (2013).
13. Bonaccorso, F. *et al.* Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* **347**, 1246501 (2015).
14. Eda, G., Maier, S. A. Two-dimensional crystals: managing light for optoelectronics. *ACS Nano* **7**, 5660-5665 (2013).
15. Memaran, S. *et al.* Pronounced photovoltaic response from multi-layered transition-metal dichalcogenides PN-junctions. *arXiv preprint arXiv:1411.2086*, (2014).

16. Wang, Q. H. *et al.* Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* **7**, 699-712 (2012).
17. Xia, F. *et al.* Two-dimensional material nanophotonics. *Nat. Photonics* **8**, 899-907 (2014).
18. Carvalho, A., Ribeiro, R., Neto, A. C. Band nesting and the optical response of two-dimensional semiconducting transition metal dichalcogenides. *Phys. Rev. B* **88**, 115205 (2013).
19. Kozawa, D. *et al.* Photocarrier relaxation pathway in two-dimensional semiconducting transition metal dichalcogenides. *Nat. Commun.* **5**, 4543-4543 (2013).
20. Kumar, R., Verzhbitskiy, I., Eda, G. Strong Optical Absorption and Photocarrier Relaxation in 2-D Semiconductors. *IEEE J. Quantum Electron.* **10**, 1-6 (2015).
21. Ugeda, M. M. *et al.* Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor. *Nat. Mater.* **13**, 1091-1095 (2014).
22. Mak, K. F. *et al.* Atomically thin MoS₂: a new direct-gap semiconductor. *Phys. Rev. Lett.* **105**, 136805 (2010).
23. Splendiani, A. *et al.* Emerging photoluminescence in monolayer MoS₂. *Nano Lett.* **10**, 1271-1275 (2010).
24. Kumar, N. *et al.* Charge carrier dynamics in bulk MoS₂ crystal studied by transient absorption microscopy. *J. Appl. Phys.* **113**, 133702 (2013).
25. Borzda, T. *et al.* Charge Photogeneration in Few-Layer MoS₂. *Adv. Funct. Mater.* **25**, 3351-3358 (2015).
26. Pogna, E. A. *et al.* Photo-induced bandgap renormalization governs the ultrafast response of single-layer MoS₂. *ACS Nano* **10**, 1182-1188 (2016).
27. Lee, Y. H. *et al.* Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. *Adv. Mater.* **24**, 2320-2325 (2012).
28. Lin, Y.-C. *et al.* Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization. *Nanoscale* **4**, 6637-6641 (2012).
29. Wang, L. *et al.* Common origin of green luminescence in carbon nanodots and graphene quantum dots. *ACS Nano* **8**, 2541-2547 (2014).
30. Perdew, J. P., Burke, K., Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
31. Wang, D. *et al.* Determination of formation and ionization energies of charged defects in two-dimensional materials. *Phys. Rev. Lett.* **114**, 196801 (2015).
32. Komsa, H.-P., Krasheninnikov, A. V. Effects of confinement and environment on the electronic structure and exciton binding energy of MoS₂ from first principles. *Phys. Rev. B* **86**, 241201 (2012).
33. Mertens, J. *et al.* Excitons in a mirror: Formation of “optical bilayers” using MoS₂ monolayers on gold substrates. *Appl. Phys. Lett.* **104**, 191105 (2014).
34. Huang, Y. L. *et al.* Bandgap tunability at single-layer molybdenum disulfide grain boundaries. *Nat. Commun.* **6**, (2015).
35. Cheiwchanamangij, T., Lambrecht, W. R. Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS₂. *Phys. Rev. B* **85**, 205302 (2012).
36. Qiu, D. Y., Felipe, H., Louie, S. G. Optical spectrum of MoS₂: many-body effects and diversity of exciton states. *Phys. Rev. Lett.* **111**, 216805 (2013).

37. Ramasubramaniam, A. Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides. *Phys. Rev. B* **86**, 115409 (2012).
38. Shi, H., Pan, H., Zhang, Y.-W., Yakobson, B. I. Quasiparticle band structures and optical properties of strained monolayer MoS₂ and WS₂. *Phys. Rev. B* **87**, 155304 (2013).
39. Wang, L. *et al.* Ultrafast optical spectroscopy of surface-modified silicon quantum dots: unraveling the underlying mechanism of the ultrabright and color-tunable photoluminescence. *Light Sci. Appl.* **4**, 245 (2015).
40. Wang, L. *et al.* Direct Observation of Quantum-Confined Graphene-Like States and Novel Hybrid States in Graphene Oxide by Transient Spectroscopy. *Adv. Mater.* **25**, 6539-6545 (2013).
41. Moody, G. *et al.* Intrinsic homogeneous linewidth and broadening mechanisms of excitons in monolayer transition metal dichalcogenides. *Nat. Commun.* **6**, (2015).
42. Moody, G., Schaibley, J., Xu, X. Exciton dynamics in monolayer transition metal dichalcogenides *J. Opt. Soc. Am. B* **33**, C39-C49 (2016).
43. Sim, S. *et al.* Exciton dynamics in atomically thin MoS₂: interexcitonic interaction and broadening kinetics. *Phys. Rev. B* **88**, 075434 (2013).
44. Lackowicz, J. R. *Principles of fluorescence spectroscopy*, 3 edn. Springer (1983).
45. Kumar, N. *et al.* Exciton-exciton annihilation in MoSe₂ monolayers. *Phys. Rev. B* **89**, 125427 (2014).
46. Sun, D. *et al.* Observation of rapid exciton–exciton annihilation in monolayer molybdenum disulfide. *Nano Lett.* **14**, 5625-5629 (2014).
47. Docherty, C. J. *et al.* Ultrafast transient terahertz conductivity of monolayer MoS₂ and WSe₂ grown by chemical vapor deposition. *ACS Nano*, (2014).
48. Chernikov, A. *et al.* Population inversion and giant bandgap renormalization in atomically thin WS₂ layers. *Nat. Photonics* **9**, 466-470 (2015).
49. Manser, J. S., Kamat, P. V. Band filling with free charge carriers in organometal halide perovskites. *Nat. Photonics* **8**, 737-743 (2014).
50. Klimov, V. I. Spectral and dynamical properties of multiexcitons in semiconductor nanocrystals. *Annu. Rev. Phys. Chem.* **58**, 635-673 (2007).
51. Mueller, M. L., Yan, X., Dragnea, B., Li, L.-s. Slow hot-carrier relaxation in colloidal graphene quantum dots. *Nano Lett.* **11**, 56-60 (2010).
52. Lee, C.-H. *et al.* Atomically thin p–n junctions with van der Waals heterointerfaces. *Nat. Nanotechnol.* **9**, 676-681 (2014).

Chapter 6 Summary and outlook

6.1 Summary

2D transition metal dichalcogenides (TMDCs) have recently attracted tremendous attention owing to their remarkable optical and electronic properties arising from their atomically thin nature. However, there are still several challenges hindering practical applications. One main challenge is to achieve stronger light-to-light conversion efficiency in 2D TMDCs for the application in ultrathin lasing. The other challenge is to develop a good understanding of photo-to-carrier conversion process and exciton dissociation of 2D TMDCs in photoconduction devices. This thesis has demonstrated strategies to enhance the light-to-light conversion efficiency and investigated the light-to-carrier conversion process of 2D TMDCs by using photoluminescence (PL), second harmonic generation (SHG) and transient absorption (TA) techniques.

Chapter 3 demonstrated that tuning the resonance of lateral gap plasmons to be aligned with the 633-nm pump laser effectively boosts the light-matter interactions in WSe₂, thus enhancing the PL of WSe₂ by ~20,000-fold. The giant enhancement arises from the judiciously designed sub-20-nm-wide trenches that can bring in large field enhancement at the excitation wavelength and large Purcell factor at the emission wavelength. The unique feature of the trenches is the small mode volume that can support large optical density of states, enabling the possibility of enhancing the PL of other TMDCs. The trench geometry can be improved by making the side wall smoother and a Fabry-Perot cavity system such as gold array with trenches/2D materials/meta film can be designed to enhance PL of the entire piece of 2D materials instead of localized positions. Further PL enhancements are expected to be achieved

through the design of double-resonance structures with directionality control. This work opens up a new platform for investigating novel electrical/optical properties in 2D materials, such as electroluminescence and second harmonic generation.

Chapter 4 reports that gold substrate with sub-20-nm-wide trenches can enhance SHG of monolayer WSe₂ to 13,000-fold, owing to the strong local electric field enhancement of the fundamental wave. This work provides a practical method to obtain blue emission from a near-infrared laser in monolayer TMDCs, and has applications as nanoscale nonlinear optical frequency converters. Further optimization of the SHG efficiency can be achieved by using silver nanostructure with less loss at the wavelength of the SHG signal. Note that the nanostructure with plasmon resonance at ~ 800 nm that is efficient to enhance SHG is not very efficient to enhance PL and Raman as the field enhancement at pump wavelength of 532 nm for PL and Raman measurement is low. This indicates that for certain optical property, we need to design specific nanostructure and try to reduce quenching effect.

The light-matter interaction in 2D TMDCs also gives rise to a photon-to-carrier conversion process. This process has been widely explored in optically active A and B excitons, whereas the study of C excitons in the band nesting region is often neglected. Chapter 5 characterized the relaxation dynamics of photoexcited C excitons in MoS₂ and their collection efficiency in MoS₂/graphene heterostructures by TA spectroscopy. This work provides a detailed good understanding of the exciton dissociation and collection processes, motivating further studies on the hot electron behaviors in 2D materials and their potential applications.

6.2 Outlook

The enhanced PL and SHG of TMDCs by plasmonic nanostructures pave the way toward lateral gap plasmon-enhanced optoelectronic devices such as light emission diode (LED) and photocurrent transistors. In particular, the work regarding plasmon-enhanced PL allows us to increase the quantum efficiency of LED by lateral gap plasmon, where TMDCs heterostructures serve as light active materials and nanostructures serve as light enhancement tool. We can first make transistors on silicon wafer based on TMDCs heterostructure and then pattern nanostructure consisting of metal arrays with small gaps on it. Alternatively, we can first make the metal arrays on silicon wafer and then transfer TMDCs on top of them. The nanostructure should be designed to have plasmon resonance wavelength aligned with the light emission wavelength of the TMDCs heterostructure. In this case, when the TMDCs heterostructure emits light under electric field, the nanostructure with narrow gaps will dramatically enhance the out-coupling of the light in the far field, thus enhancing the quantum efficiency of the LED devices. Note that we should avoid direct connection of the metal nanostructure with the electrodes of the devices to avoid a “short circuit”. The work on plasmon-enhanced SHG point to the use of lateral gap plasmon to increase other second-order nonlinear processes such as two-photon absorption and make photon sensors based on this effect. The structure of these sensors is similar to the one used for LED, but the plasmon resonance should be designed to align with the pump laser. Unlike conventional photon sensors based on linear light absorption and photocurrent conversion, the one based on two-photon absorption and current generation will have

broader working spectral range. Furthermore, the nanostructure will increase the photocurrent via increasing the two-photon absorption.

There are many interesting follow-up studies from the work on exciton dynamics in TMDCs such as the charge and energy transfer in WSe₂ and MoS₂ heterostructure and in hybrid system of TMDCs and metallic nanostructures.

Recent advances in the development of other 2D semiconductors and van der Waals heterostructures bring about more exciting opportunities. A few examples are worth further investigation. First, the unique valley-dependent properties are intriguing for applications in information processing. An example is coupling 2D TMDCs to microcavities or plasmonics nanostructures and enhancing the valley-polarization degree of the PL and SHG by making use of the valley optical selection rule in 2D TMDCs^{1, 2}. Second, achieving strong-coupling between light and excitons in 2D TMDCs by integration of the plasmonic nanostructures with TMDCs. The strong coupling can lead to light-matter hybrid states and new quasi-particles such as exciton polaritons, allowing for the observation of intriguing coherent phenomena such as Bose-Einstein condensation as well as enabling novel photonics devices such as polariton lasers³. Third, the use of complex excitonic species in optoelectronics devices is not well studied, for example utilizing trions (charged excitons) to transport photoexcited carriers⁴. Here the usage of pump-probe techniques such as transient absorption spectroscopy will help to reveal the exciton dynamics in terms of excitation and relaxation in the light absorption, emission and carrier transport processes. Last but not least is the recent discovery of new 2D semiconductors with anisotropic optical and optoelectronic properties,

including phosphorene. Together with 2D TMDCs, they provide a material toolbox for 2D semiconductors with gap energies spanning the visible to near-infrared spectral range. Fabricating novel heterostructures by stacking these 2D materials or integrating them with plasmonic nanostructures are intriguing for exploring novel optical properties and developing new optoelectronic devices.

6.3 References

1. Li, Z. *et al.* Tailoring MoS₂ Exciton-Plasmon Interaction by Optical Spin-Orbit Coupling. *ACS Nano* **11**, 1165-1171 (2016).
2. Zeng, H. *et al.* Valley polarization in MoS₂ monolayers by optical pumping. *Nat. Nanotechnol.* **7**, 490-493 (2012).
3. Liu, W. *et al.* Strong Exciton-Plasmon Coupling in MoS₂ Coupled with Plasmonic Lattice. *Nano Lett.* **16**, 1262-1269 (2016).
4. Lui, C. *et al.* Trion-induced negative photoconductivity in monolayer MoS₂. *Phys. Rev. Lett.* **113**, 166801 (2014).

Appendices

Copyright Permission

Figures in Chapter 1 and 2

Figure 1.1

NATURE PUBLISHING GROUP LICENSE TERMS AND CONDITIONS

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4238040562023
License date	Nov 29, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Electronics and optoelectronics of two-dimensional transition metal dichalcogenides
Licensed Content Author	Qing Hua Wang, Kourosh Kalantar-Zadeh, Andras Kis, Jonathan N. Coleman, Michael S. Strano
Licensed Content Date	Nov 6, 2012
Licensed Content Volume	7
Licensed Content Issue	11
Type of Use	reuse in a dissertation / thesis
Requestor type	non-commercial (non-profit)
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
High-res required	no
Figures	Figure 1
Author of this NPG article	no
Your reference number	

Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Estimated size (number of pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing Address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang
Total	0.00 USD

Terms and Conditions

Terms and Conditions for Permissions

Nature Publishing Group hereby grants you a non-exclusive license to reproduce this material for this purpose, and for no other use, subject to the conditions below:

1. NPG warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to Nature Publishing Group and does not carry the copyright of another entity (as credited in the published version). If the credit line on any part of the material you have requested indicates that it was reprinted or adapted by NPG with permission from another source, then you should also seek permission from that source to reuse the material.
2. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to the work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version. Where print permission has been granted for a fee, separate permission must be obtained for any additional, electronic re-use (unless, as in the case of a full paper, this has already been accounted for during your initial request in the calculation of a print run). NB: In all cases, web-based use of full-text articles must be authorized

separately through the 'Use on a Web Site' option when requesting permission.

3. Permission granted for a first edition does not apply to second and subsequent editions and for editions in other languages (except for signatories to the STM Permissions Guidelines, or where the first edition permission was granted for free).
4. Nature Publishing Group's permission must be acknowledged next to the figure, table or abstract in print. In electronic form, this acknowledgement must be visible at the same time as the figure/table/abstract, and must be hyperlinked to the journal's homepage.
5. The credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

Note: For republication from the *British Journal of Cancer*, the following credit lines apply.

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

6. Adaptations of single figures do not require NPG approval. However, the adaptation should be credited as follows:

Adapted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)

Note: For adaptation from the *British Journal of Cancer*, the following credit line applies.

Adapted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

7. Translations of 401 words up to a whole article require NPG approval. Please visit <http://www.macmillanmedicalcommunications.com> for more information. Translations of up to a 400 words do not require NPG approval. The translation should be credited as follows:

Translated by permission from Macmillan Publishers Ltd:
[JOURNAL NAME] (reference citation), copyright (year of
publication).

**Note: For translation from the *British Journal of Cancer*, the
following credit line applies.**

Translated by permission from Macmillan Publishers Ltd on behalf of
Cancer Research UK: [JOURNAL NAME] (reference citation),
copyright (year of publication)

We are certain that all parties will benefit from this agreement and wish you
the best in the use of this material. Thank you.

Special Terms:
v1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in
the US) or +1-978-646-2777.

Figure 1.2

**SPRINGER LICENSE
TERMS AND CONDITIONS**

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and Springer ("Springer")
consists of your license details and the terms and conditions provided by
Springer and Copyright Clearance Center.

License Number	4238041475334
License date	Nov 29, 2017
Licensed Content Publisher	Springer
Licensed Content Publication	The European Physical Journal B - Condensed Matter and Complex Systems
Licensed Content Title	Electronic structure of transition metal dichalcogenides monolayers 1H-MX ₂ (M = Mo, W; X = S, Se, Te) from ab-initio theory: new direct band gap semiconductors
Licensed Content Author	A. Kumar, P. K. Ahluwalia
Licensed Content Date	Jan 1, 2012
Licensed Content Volume	85
Licensed Content Issue	6
Type of Use	Thesis/Dissertation

Portion	Figures/tables/illustrations
Number of figures/tables/illustrations	1
Author of this Springer article	No
Order reference number	
Original figure numbers	Figure 9 and Figure 13
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Estimated size(pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing Address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang
Total	0.00 USD
Terms and Conditions	

Introduction

The publisher for this copyrighted material is Springer. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

Limited License

With reference to your request to reuse material on which Springer controls the copyright, permission is granted for the use indicated in your enquiry under the following conditions:

- Licenses are for one-time use only with a maximum distribution equal to the number stated in your request.

- Springer material represents original material which does not carry references to other sources. If the material in question appears with a credit to another source, this permission is not valid and authorization has to be obtained from the original copyright holder.
 - This permission
 - is non-exclusive
 - is only valid if no personal rights, trademarks, or competitive products are infringed.
 - explicitly excludes the right for derivatives.
 - Springer does not supply original artwork or content.
 - According to the format which you have selected, the following conditions apply accordingly:
 - **Print and Electronic:** This License include use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
 - **Print:** This License excludes use in electronic form.
 - **Electronic:** This License only pertains to use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
- For any electronic use not mentioned, please contact Springer at permissions.springer@spi-global.com.
- Although Springer controls the copyright to the material and is entitled to negotiate on rights, this license is only valid subject to courtesy information to the author (address is given in the article/chapter).
 - If you are an STM Signatory or your work will be published by an STM Signatory and you are requesting to reuse figures/tables/illustrations or single text extracts, permission is granted according to STM Permissions Guidelines: <http://www.stm-assoc.org/permissions-guidelines/>
- For any electronic use not mentioned in the Guidelines, please contact Springer at permissions.springer@spi-global.com. If you request to reuse more content than stipulated in the STM Permissions Guidelines, you will be charged a permission fee for the excess content.
- Permission is valid upon payment of the fee as indicated in the licensing process. If permission is granted free of charge on this occasion, that does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.
- If your request is for reuse in a Thesis, permission is granted free of charge under the following conditions:
- This license is valid for one-time use only for the purpose of defending your thesis and with a maximum of 100 extra copies in paper. If the thesis is going to be published, permission needs to be reobtained.
- includes use in an electronic form, provided it is an author-created version of the thesis on his/her own website and his/her university's repository, including UMI (according to the definition on the Sherpa website: <http://www.sherpa.ac.uk/romeo/>);
 - is subject to courtesy information to the co-author or corresponding author.
- Geographic Rights: Scope
- Licenses may be exercised anywhere in the world.
- Altering/Modifying Material: Not Permitted
- Figures, tables, and illustrations may be altered minimally to serve your work.

You may not alter or modify text in any manner. Abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of the author(s).

Reservation of Rights

Springer reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction and (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

License Contingent on Payment

While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by Springer or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received by the date due, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and Springer reserves the right to take any and all action to protect its copyright in the materials.

Copyright Notice: Disclaimer

You must include the following copyright and permission notice in connection with any reproduction of the licensed material:

"Springer book/journal title, chapter/article title, volume, year of publication, page, name(s) of author(s), (original copyright notice as given in the publication in which the material was originally published) "With permission of Springer"

In case of use of a graph or illustration, the caption of the graph or illustration must be included, as it is indicated in the original publication.

Warranties: None

Springer makes no representations or warranties with respect to the licensed material and adopts on its own behalf the limitations and disclaimers established by CCC on its behalf in its Billing and Payment terms and conditions for this licensing transaction.

Indemnity

You hereby indemnify and agree to hold harmless Springer and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

No Transfer of License

This license is personal to you and may not be sublicensed, assigned, or transferred by you without Springer's written permission.

No Amendment Except in Writing

This license may not be amended except in a writing signed by both parties (or, in the case of Springer, by CCC on Springer's behalf).

Objection to Contrary Terms

Springer hereby objects to any terms contained in any purchase order,

acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

Jurisdiction

All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in the Federal Republic of Germany, in accordance with German law.

Other conditions:

V 12AUG2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Figure 1.4

AMERICAN PHYSICAL SOCIETY LICENSE TERMS AND CONDITIONS

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and American Physical Society ("American Physical Society") consists of your license details and the terms and conditions provided by American Physical Society and Copyright Clearance Center.

License Number	4238050302057
License date	Nov 29, 2017
Licensed Content Publisher	American Physical Society
Licensed Content Publication	Physical Review B
Licensed Content Title	Band nesting and the optical response of two-dimensional semiconducting transition metal dichalcogenides
Licensed Content Author	A. Carvalho, R. M. Ribeiro, and A. H. Castro Neto
Licensed Content Date	Sep 12, 2013
Licensed Content Volume	88
Type of Use	Thesis/Dissertation
Requestor type	Student

Format	Print, Electronic
Portion	chart/graph/table/figure
Number of charts/graphs/tables/figures	1
Portion description	Figure 1
Rights for	Main product
Duration of use	Life of Current Edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Worldwide
In the following language(s)	Original language of publication
With incidental promotional use	no
The lifetime unit quantity of new product	0 to 499
The requesting person/organization is:	Zhuo Wang, NUS
Order reference number	
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Expected size (number of pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing Address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang

Total 0.00 USD

Terms and Conditions

Terms and Conditions

The American Physical Society (APS) is pleased to grant the Requestor of this license a non-exclusive, non-transferable permission, limited to [**print** and/or **electronic** format, depending on what they chose], provided all criteria outlined below are followed.

1. You must also obtain permission from at least one of the lead authors for each separate work, if you haven't done so already. The author's name and affiliation can be found on the first page of the published Article.
2. For electronic format permissions, Requestor agrees to provide a hyperlink from the reprinted APS material using the source material's DOI on the web page where the work appears. The hyperlink should use the standard DOI resolution URL, <http://dx.doi.org/{DOI}>. The hyperlink may be embedded in the copyright credit line.
3. For print format permissions, Requestor agrees to print the required copyright credit line on the first page where the material appears: "Reprinted (abstract/excerpt/figure) with permission from [(FULL REFERENCE CITATION) as follows: Author's Names, APS Journal Title, Volume Number, Page Number and Year of Publication.] Copyright (YEAR) by the American Physical Society."
4. Permission granted in this license is for a one-time use and does not include permission for any future editions, updates, databases, formats or other matters. Permission must be sought for any additional use.
5. Use of the material does not and must not imply any endorsement by APS.
6. Under no circumstance does APS purport or intend to grant permission to reuse materials to which it does not hold copyright. It is the requestors sole responsibility to ensure the licensed material is original to APS and does not contain the copyright of another entity, and that the copyright notice of the figure, photograph, cover or table does not indicate that it was reprinted by APS, with permission from another source.
7. The permission granted herein is personal to the Requestor for the use specified and is not transferable or assignable without express written permission of APS. This license may not be amended except in writing by APS.
8. You may not alter, edit or modify the material in any manner.
9. You may translate the materials only when translation rights have been granted.
10. You may not use the material for promotional, sales, advertising or marketing purposes.
11. The foregoing license shall not take effect unless and until APS or its agent, Copyright Clearance Center (CCC), receives payment in full in accordance with CCC Billing and Payment Terms and Conditions, which are incorporated herein by reference.
12. Should the terms of this license be violated at any time, APS or CCC may revoke the license with no refund to you and seek relief to the fullest extent of the laws of the USA. Official written notice will be made using the contact

information provided with the permission request. Failure to receive such notice will not nullify revocation of the permission.

13. APS reserves all rights not specifically granted herein.

14. This document, including the CCC Billing and Payment Terms and Conditions, shall be the entire agreement between the parties relating to the subject matter hereof.

Other Terms and Conditions

Version 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Figure 1.5a



[Home](#) [Account Info](#) [Help](#)

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Two-Dimensional Crystals:
Managing Light for
Optoelectronics

Author: Goki Eda, Stefan A. Maier

Publication: ACS Nano

Publisher: American Chemical Society

Date: Jul 1, 2013

Copyright © 2013, American Chemical Society

Logged in as:
Zhuo Wang
Account #: 3001100639

[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

[BACK](#) [CLOSE WINDOW](#)

Copyright © 2017 Copyright Clearance Center, Inc. All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#). Comments? We would like to hear from you. E-mail us at customercare@copyright.com

150

Figure 1.5b**NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS**

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4238050805488
License date	Nov 29, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Electrical control of second-harmonic generation in a WSe ₂ monolayer transistor
Licensed Content Author	Kyle L. Seyler, John R. Schaibley, Pu Gong, Pasqual Rivera, Aaron M. Jones et al.
Licensed Content Date	Apr 20, 2015
Licensed Content Volume	10
Licensed Content Issue	5
Type of Use	reuse in a dissertation / thesis
Requestor type	non-commercial (non-profit)
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
High-res required	no
Figures	Fig.1
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Estimated size (number of pages)	140

Requestor Location Zhuo Wang
Physics Department, Faculty of Science
2 Science Drive 3
National University of Singapore
Singapore, Singapore 117551
Singapore
Attn: Zhuo Wang

Billing Type Invoice

Billing Address Zhuo Wang
Physics Department, Faculty of Science
2 Science Drive 3
National University of Singapore
Singapore, Singapore 117551
Attn: Zhuo Wang

Total 0.00 USD

Terms and Conditions

Terms and Conditions for Permissions

Nature Publishing Group hereby grants you a non-exclusive license to reproduce this material for this purpose, and for no other use, subject to the conditions below:

1. NPG warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to Nature Publishing Group and does not carry the copyright of another entity (as credited in the published version). If the credit line on any part of the material you have requested indicates that it was reprinted or adapted by NPG with permission from another source, then you should also seek permission from that source to reuse the material.
2. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to the work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version. Where print permission has been granted for a fee, separate permission must be obtained for any additional, electronic re-use (unless, as in the case of a full paper, this has already been accounted for during your initial request in the calculation of a print run). NB: In all cases, web-based use of full-text articles must be authorized separately through the 'Use on a Web Site' option when requesting permission.
3. Permission granted for a first edition does not apply to second and subsequent editions and for editions in other languages (except for signatories to the STM Permissions Guidelines, or where the first edition permission was granted for free).

4. Nature Publishing Group's permission must be acknowledged next to the figure, table or abstract in print. In electronic form, this acknowledgement must be visible at the same time as the figure/table/abstract, and must be hyperlinked to the journal's homepage.
5. The credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

Note: For republication from the *British Journal of Cancer*, the following credit lines apply.

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

6. Adaptations of single figures do not require NPG approval. However, the adaptation should be credited as follows:

Adapted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)

Note: For adaptation from the *British Journal of Cancer*, the following credit line applies.

Adapted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

7. Translations of 401 words up to a whole article require NPG approval. Please visit <http://www.macmillanmedicalcommunications.com> for more information. Translations of up to a 400 words do not require NPG approval. The translation should be credited as follows:

Translated by permission from Macmillan Publishers Ltd:
[JOURNAL NAME] (reference citation), copyright (year of publication).

Note: For translation from the *British Journal of Cancer*, the

following credit line applies.

Translated by permission from Macmillan Publishers Ltd on behalf of
Cancer Research UK: [JOURNAL NAME] (reference citation),
copyright (year of publication)

We are certain that all parties will benefit from this agreement and wish you
the best in the use of this material. Thank you.

Special Terms:

v1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free
in the US) or +1-978-646-2777.

Figure 1.5c

**NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS**

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and Nature Publishing Group
("Nature Publishing Group") consists of your license details and the terms and
conditions provided by Nature Publishing Group and Copyright Clearance
Center.

License Number	4238050931565
License date	Nov 29, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Ultrasensitive photodetectors based on monolayer MoS2
Licensed Content Author	Oriol Lopez-Sanchez, Dominik Lembke, Metin Kayci, Aleksandra Radenovic, Andras Kis
Licensed Content Date	Jun 9, 2013
Licensed Content Volume	8
Licensed Content Issue	7
Type of Use	reuse in a dissertation / thesis
Requestor type	non-commercial (non-profit)
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1

High-res required	no
Figures	Fig.1
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Estimated size (number of pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing Address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang
Total	0.00 USD

Terms and Conditions

Terms and Conditions for Permissions

Nature Publishing Group hereby grants you a non-exclusive license to reproduce this material for this purpose, and for no other use, subject to the conditions below:

1. NPG warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to Nature Publishing Group and does not carry the copyright of another entity (as credited in the published version). If the credit line on any part of the material you have requested indicates that it was reprinted or adapted by NPG with permission from another source, then you should also seek permission from that source to reuse the material.
2. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to the work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print

version. Where print permission has been granted for a fee, separate permission must be obtained for any additional, electronic re-use (unless, as in the case of a full paper, this has already been accounted for during your initial request in the calculation of a print run). NB: In all cases, web-based use of full-text articles must be authorized separately through the 'Use on a Web Site' option when requesting permission.

3. Permission granted for a first edition does not apply to second and subsequent editions and for editions in other languages (except for signatories to the STM Permissions Guidelines, or where the first edition permission was granted for free).
4. Nature Publishing Group's permission must be acknowledged next to the figure, table or abstract in print. In electronic form, this acknowledgement must be visible at the same time as the figure/table/abstract, and must be hyperlinked to the journal's homepage.
5. The credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

Note: For republication from the *British Journal of Cancer*, the following credit lines apply.

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

6. Adaptations of single figures do not require NPG approval. However, the adaptation should be credited as follows:

Adapted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)

Note: For adaptation from the *British Journal of Cancer*, the following credit line applies.

Adapted by permission from Macmillan Publishers Ltd on behalf of

Cancer Research UK: [JOURNAL NAME] (reference citation),
copyright (year of publication)

7. Translations of 401 words up to a whole article require NPG approval. Please visit <http://www.macmillanmedicalcommunications.com> for more information. Translations of up to a 400 words do not require NPG approval. The translation should be credited as follows:

Translated by permission from Macmillan Publishers Ltd:
[JOURNAL NAME] (reference citation), copyright (year of
publication).

**Note: For translation from the *British Journal of Cancer*, the
following credit line applies.**

Translated by permission from Macmillan Publishers Ltd on behalf of
Cancer Research UK: [JOURNAL NAME] (reference citation),
copyright (year of publication)

We are certain that all parties will benefit from this agreement and wish you
the best in the use of this material. Thank you.

Special Terms:

v1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in
the US) or +1-978-646-2777.

Figure 1.7a,c



[Home](#) [Account Info](#) [Help](#)

**ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Enhanced Light Emission from Large-Area Monolayer MoS₂ Using Plasmonic Nanodisc Arrays
Author: Serkan Butun, Sefaattin Tongay, Koray Aydin
Publication: Nano Letters
Publisher: American Chemical Society
Date: Apr 1, 2015
Copyright © 2015, American Chemical Society

Logged in as:
Zhuo Wang
Account #: 3001100639
[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

[BACK](#) [CLOSE WINDOW](#)

Figure 1.7b,d



[Home](#) [Account Info](#) [Help](#)

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Fano Resonance and Spectrally Modified Photoluminescence Enhancement in Monolayer MoS₂ Integrated with Plasmonic Nanoantenna Array
Author: Bumsu Lee, Joohee Park, Gang Hee Han, et al
Publication: Nano Letters
Publisher: American Chemical Society
Date: May 1, 2015
Copyright © 2015, American Chemical Society

Logged in as:
Zhuo Wang
Account #:
3001100639
[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

[BACK](#)[CLOSE WINDOW](#)

Figure 1.11c,d



[Home](#) [Account Info](#) [Help](#)

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Bandgap Engineering of Strained Monolayer and Bilayer MoS₂
Author: Hiram J. Conley, Bin Wang, Jed I. Ziegler, et al
Publication: Nano Letters
Publisher: American Chemical Society
Date: Aug 1, 2013
Copyright © 2013, American Chemical Society

Logged in as:
Zhuo Wang
Account #:
3001100639
[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

Figure 1.11c,d

License Number	4238070335235
License date	Nov 29, 2017
Licensed Content Publisher	American Physical Society
Licensed Content Publication	Physical Review Letters
Licensed Content Title	Atomically Thin MoS_2 : A New Direct-Gap Semiconductor
Licensed Content Author	Kin Fai Mak et al.
Licensed Content Date	Sep 24, 2010
Licensed Content Volume	105
Type of use	Thesis/Dissertation
Requestor type	Student
Format	Print, Electronic
Portion	image/photo
Number of images/photos requested	1
Portion description	Fig.1
Rights for	Main product
Duration of use	Life of Current Edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Worldwide
In the following language(s)	Original language of publication
With incidental promotional use	no
Lifetime unit quantity of new product	0 to 499
The requesting person/organization	WANG Zhuo, NUS
Order reference number	
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Expected size (number of pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang
Total	0.00 USD

Figure 1.14



[Home](#)[Account Info](#)[Help](#)



Title: Atomically phase-matched second-harmonic generation in a 2D crystal
Author: Mervin Zhao, Ziliang Ye, Ryuji Suzuki, Yu Ye, Hanyu Zhu et al.
Publication: Light: Science & Applications
Publisher: Nature Publishing Group
Date: Aug 26, 2016
Copyright © 2016, Rights Managed by Nature Publishing Group

Logged in as:
Zhuo Wang
Account #:
3001100639

LOGOUT

Creative Commons

The request you have made is considered to be non-commercial/educational. As the article you have requested has been distributed under a Creative Commons license (Attribution-Noncommercial), you may reuse this material for non-commercial/educational purposes without obtaining additional permission from Nature Publishing Group, providing that the author and the original source of publication are fully acknowledged (please see the article itself for the license version number). You may reuse this material without obtaining permission from Nature Publishing Group, providing that the author and the original source of publication are fully acknowledged, as per the terms of the license. For license terms, please see <http://creativecommons.org/>

Figure 1.15a,b,c

NATURE PUBLISHING GROUP LICENSE TERMS AND CONDITIONS

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4238070904326
License date	Nov 29, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Valley and band structure engineering of folded MoS ₂ bilayers
Licensed Content Author	Tao Jiang, Hengrui Liu, Di Huang, Shuai Zhang, Yingguo Li et al.
Licensed Content Date	Aug 31, 2014
Licensed Content Volume	9
Licensed Content Issue	10
Type of Use	reuse in a dissertation / thesis
Requestor type	non-commercial (non-profit)
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
High-res required	no
Figures	Fig. 1 and 2
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017

Estimated size (number of pages) 140

Requestor Location Zhuo Wang
Physics Department, Faculty of Science
2 Science Drive 3
National University of Singapore
Singapore, Singapore 117551
Singapore
Attn: Zhuo Wang

Billing Type Invoice

Billing Address Zhuo Wang
Physics Department, Faculty of Science
2 Science Drive 3
National University of Singapore
Singapore, Singapore 117551
Attn: Zhuo Wang

Total 0.00 USD

Terms and Conditions

Terms and Conditions for Permissions

Nature Publishing Group hereby grants you a non-exclusive license to reproduce this material for this purpose, and for no other use, subject to the conditions below:

1. NPG warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to Nature Publishing Group and does not carry the copyright of another entity (as credited in the published version). If the credit line on any part of the material you have requested indicates that it was reprinted or adapted by NPG with permission from another source, then you should also seek permission from that source to reuse the material.
2. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to the work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version. Where print permission has been granted for a fee, separate permission must be obtained for any additional, electronic re-use (unless, as in the case of a full paper, this has already been accounted for during your initial request in the calculation of a print run). NB: In all cases, web-based use of full-text articles must be authorized separately through the 'Use on a Web Site' option when requesting permission.
3. Permission granted for a first edition does not apply to second and subsequent editions and for editions in other languages (except for signatories to the STM Permissions Guidelines, or where the first

edition permission was granted for free).

4. Nature Publishing Group's permission must be acknowledged next to the figure, table or abstract in print. In electronic form, this acknowledgement must be visible at the same time as the figure/table/abstract, and must be hyperlinked to the journal's homepage.
5. The credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

Note: For republication from the *British Journal of Cancer*, the following credit lines apply.

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

6. Adaptations of single figures do not require NPG approval. However, the adaptation should be credited as follows:

Adapted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)

Note: For adaptation from the *British Journal of Cancer*, the following credit line applies.

Adapted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

7. Translations of 401 words up to a whole article require NPG approval. Please visit <http://www.macmillanmedicalcommunications.com> for more information. Translations of up to a 400 words do not require NPG approval. The translation should be credited as follows:

Translated by permission from Macmillan Publishers Ltd:
[JOURNAL NAME] (reference citation), copyright (year of publication).

Note: For translation from the *British Journal of Cancer*, the following credit line applies.

Translated by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

We are certain that all parties will benefit from this agreement and wish you the best in the use of this material. Thank you.

Special Terms:
v1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Figure 1.15d,e,f

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE LICENSE TERMS AND CONDITIONS

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and The American Association for the Advancement of Science ("The American Association for the Advancement of Science") consists of your license details and the terms and conditions provided by The American Association for the Advancement of Science and Copyright Clearance Center.

License Number	4238071331302
License date	Nov 29, 2017
Licensed Content Publisher	The American Association for the Advancement of Science
Licensed Content Publication	Science
Licensed Content Title	Edge Nonlinear Optics on a MoS ₂ Atomic Monolayer
Licensed Content Author	Xiaobo Yin,Ziliang Ye,Daniel A. Chenet,Yu Ye,Kevin O'Brien,James C. Hone,Xiang Zhang
Licensed Content Date	May 2, 2014
Licensed Content Volume	344
Licensed Content Issue	6183

Volume number	344
Issue number	6183
Type of Use	Thesis / Dissertation
Requestor type	Scientist/individual at a research institution
Format	Print and electronic
Portion	Figure
Number of figures/tables	1
Order reference number	Fig. 1
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Estimated size(pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing Address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang
Total	0.00 USD

Terms and Conditions

American Association for the Advancement of Science TERMS AND CONDITIONS

Regarding your request, we are pleased to grant you non-exclusive, non-transferable permission, to republish the AAAS material identified above in your work identified above, subject to the terms and conditions herein. We must be contacted for permission for any uses other than those specifically identified in your request above.

The following credit line must be printed along with the AAAS material: "From [Full Reference Citation]. Reprinted with permission from AAAS." All required credit lines and notices must be visible any time a user accesses any part of the AAAS material and must appear on any printed copies and authorized user might make.

This permission does not apply to figures / photos / artwork or any other content or materials included in your work that are credited to non-AAAS sources. If the requested material is sourced to or references non-AAAS sources, you must obtain authorization from that source as well before using that material. You agree to hold harmless and indemnify AAAS against any claims arising from your use of any content in your work that is credited to non-AAAS sources.

If the AAAS material covered by this permission was published in Science during the years 1974 - 1994, you must also obtain permission from the author, who may grant or withhold permission, and who may or may not charge a fee if permission is granted. See original article for author's address. This condition does not apply to news articles.

The AAAS material may not be modified or altered except that figures and tables may be modified with permission from the author. Author permission for any such changes must be secured prior to your use.

Whenever possible, we ask that electronic uses of the AAAS material permitted herein include a hyperlink to the original work on AAAS's website (hyperlink may be embedded in the reference citation).

AAAS material reproduced in your work identified herein must not account for more than 30% of the total contents of that work.

AAAS must publish the full paper prior to use of any text.

AAAS material must not imply any endorsement by the American Association for the Advancement of Science.

This permission is not valid for the use of the AAAS and/or Science logos.

AAAS makes no representations or warranties as to the accuracy of any information contained in the AAAS material covered by this permission, including any warranties of merchantability or fitness for a particular purpose.

If permission fees for this use are waived, please note that AAAS reserves the right to charge for reproduction of this material in the future.

Permission is not valid unless payment is received within sixty (60) days of the issuance of this permission. If payment is not received within this time period then all rights granted herein shall be revoked and this permission will be considered null and void.

In the event of breach of any of the terms and conditions herein or any of CCC's Billing and Payment terms and conditions, all rights granted herein shall be revoked and this permission will be considered null and void.

AAAS reserves the right to terminate this permission and all rights granted herein at its discretion, for any purpose, at any time. In the event that AAAS elects to terminate this permission, you will have no further right to publish, publicly perform, publicly display, distribute or otherwise use any matter in which the AAAS content had been included, and all fees paid hereunder shall be fully refunded to you. Notification of termination will be sent to the contact information as supplied by you during the request process and termination shall be immediate upon sending the notice. Neither AAAS nor CCC shall be liable for any costs, expenses, or damages you may incur as a result of the termination of this permission, beyond the refund noted above. This Permission may not be amended except by written document signed by both parties.

The terms above are applicable to all permissions granted for the use of AAAS material. Below you will find additional conditions that apply to your particular type of use.

FOR A THESIS OR DISSERTATION

If you are using figure(s)/table(s), permission is granted for use in print and electronic versions of your dissertation or thesis. A full text article may be used in print versions only of a dissertation or thesis.

Permission covers the distribution of your dissertation or thesis on demand by ProQuest / UMI, provided the AAAS material covered by this permission remains in situ.

If you are an Original Author on the AAAS article being reproduced, please refer to your License to Publish for rules on reproducing your paper in a dissertation or thesis.

FOR JOURNALS:

Permission covers both print and electronic versions of your journal article, however the AAAS material may not be used in any manner other than within the context of your article.

FOR BOOKS/TEXTBOOKS:

If this license is to reuse figures/tables, then permission is granted for non-exclusive world rights in all languages in both print and electronic formats (electronic formats are defined below).

If this license is to reuse a text excerpt or a full text article, then permission is granted for non-exclusive world rights in English only. You have the option of securing either print or electronic rights or both, but electronic rights are not automatically granted and do garner additional fees. Permission for translations of text excerpts or full text articles into other languages must be obtained separately.

Licenses granted for use of AAAS material in electronic format books/textbooks are valid only in cases where the electronic version is equivalent to or substitutes for the print version of the book/textbook. The AAAS material reproduced as permitted herein must remain in situ and must not be exploited separately (for example, if permission covers the use of a full text article, the article may not be offered for access or for purchase as a stand-alone unit), except in the case of permitted textbook companions as noted below.

You must include the following notice in any electronic versions, either adjacent to the reprinted AAAS material or in the terms and conditions for use of your electronic products: "Readers may view, browse, and/or download material for temporary copying purposes only, provided these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published, or sold in whole or in part, without prior written permission from the publisher."

If your book is an academic textbook, permission covers the following companions to your textbook, provided such companions are distributed only in conjunction with your textbook at no additional cost to the user:

- Password-protected website
- Instructor's image CD/DVD and/or PowerPoint resource
- Student CD/DVD

All companions must contain instructions to users that the AAAS material may be used for non-commercial, classroom purposes only. Any other uses require the prior written permission from AAAS.

If your license is for the use of AAAS Figures/Tables, then the electronic rights granted herein permit use of the Licensed Material in any Custom Databases that you distribute the electronic versions of your textbook through, so long as the Licensed Material remains within the context of a chapter of the title identified in your request and cannot be downloaded by a user as an independent image file.

Rights also extend to copies/files of your Work (as described above) that you are required to provide for use by the visually and/or print disabled in compliance with state and federal laws.

This permission only covers a single edition of your work as identified in your request.

FOR NEWSLETTERS:

Permission covers print and/or electronic versions, provided the AAAS material reproduced as permitted herein remains in situ and is not exploited separately (for example, if permission covers the use of a full text article, the article may not be offered for access or for purchase as a stand-alone unit)

FOR ANNUAL REPORTS:

Permission covers print and electronic versions provided the AAAS material reproduced as permitted herein remains in situ and is not exploited separately (for example, if permission covers the use of a full text article, the article may not be offered for access or for purchase as a stand-alone unit)

FOR PROMOTIONAL/MARKETING USES:

Permission covers the use of AAAS material in promotional or marketing pieces such as information packets, media kits, product slide kits, brochures, or flyers limited to a single print run. The AAAS Material may not be used in any manner which implies endorsement or promotion by the American Association for the Advancement of Science (AAAS) or Science of any product or service. AAAS does not permit the reproduction of its name, logo or text on promotional literature.

If permission to use a full text article is permitted, The Science article covered by this permission must not be altered in any way. No additional printing may be set onto an article copy other than the copyright credit line required above. Any alterations must be approved in advance and in writing by AAAS. This includes, but is not limited to, the placement of sponsorship identifiers, trademarks, logos, rubber stamping or self-adhesive stickers onto the article copies.

Additionally, article copies must be a freestanding part of any information package (i.e. media kit) into which they are inserted. They may not be physically attached to anything, such as an advertising insert, or have anything attached to them, such as a sample product. Article copies must be easily removable from any kits or informational packages in which they are used. The only exception is that article copies may be inserted into three-ring binders.

FOR CORPORATE INTERNAL USE:

The AAAS material covered by this permission may not be altered in any way. No additional printing may be set onto an article copy other than the required credit line. Any alterations must be approved in advance and in

writing by AAAS. This includes, but is not limited to the placement of sponsorship identifiers, trademarks, logos, rubber stamping or self-adhesive stickers onto article copies.

If you are making article copies, copies are restricted to the number indicated in your request and must be distributed only to internal employees for internal use.

If you are using AAAS Material in Presentation Slides, the required credit line must be visible on the slide where the AAAS material will be reprinted. If you are using AAAS Material on a CD, DVD, Flash Drive, or the World Wide Web, you must include the following notice in any electronic versions, either adjacent to the reprinted AAAS material or in the terms and conditions for use of your electronic products: "Readers may view, browse, and/or download material for temporary copying purposes only, provided these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published, or sold in whole or in part, without prior written permission from the publisher." Access to any such CD, DVD, Flash Drive or Web page must be restricted to your organization's employees only.

FOR CME COURSE and SCIENTIFIC SOCIETY MEETINGS:

Permission is restricted to the particular Course, Seminar, Conference, or Meeting indicated in your request. If this license covers a text excerpt or a Full Text Article, access to the reprinted AAAS material must be restricted to attendees of your event only (if you have been granted electronic rights for use of a full text article on your website, your website must be password protected, or access restricted so that only attendees can access the content on your site).

If you are using AAAS Material on a CD, DVD, Flash Drive, or the World Wide Web, you must include the following notice in any electronic versions, either adjacent to the reprinted AAAS material or in the terms and conditions for use of your electronic products: "Readers may view, browse, and/or download material for temporary copying purposes only, provided these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published, or sold in whole or in part, without prior written permission from the publisher."

FOR POLICY REPORTS:

These rights are granted only to non-profit organizations and/or government agencies. Permission covers print and electronic versions of a report, provided the required credit line appears in both versions and provided the AAAS material reproduced as permitted herein remains in situ and is not exploited separately.

FOR CLASSROOM PHOTOCOPIES:

Permission covers distribution in print copy format only. Article copies must be freestanding and not part of a course pack. They may not be physically attached to anything or have anything attached to them.

FOR COURSEPACKS OR COURSE WEBSITES:

These rights cover use of the AAAS material in one class at one institution. Permission is valid only for a single semester after which the AAAS material must be removed from the Electronic Course website, unless new permission

is obtained for an additional semester. If the material is to be distributed online, access must be restricted to students and instructors enrolled in that particular course by some means of password or access control.

FOR WEBSITES:

You must include the following notice in any electronic versions, either adjacent to the reprinted AAAS material or in the terms and conditions for use of your electronic products: "Readers may view, browse, and/or download material for temporary copying purposes only, provided these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published, or sold in whole or in part, without prior written permission from the publisher."

Permissions for the use of Full Text articles on third party websites are granted on a case by case basis and only in cases where access to the AAAS Material is restricted by some means of password or access control.

Alternately, an E-Print may be purchased through our reprints department (brocheleau@rockwaterinc.com).

**REGARDING FULL TEXT ARTICLE USE ON THE WORLD WIDE WEB
IF YOU ARE AN 'ORIGINAL AUTHOR' OF A SCIENCE PAPER**

If you chose "Original Author" as the Requestor Type, you are warranting that you are one of authors listed on the License Agreement as a "Licensed content author" or that you are acting on that author's behalf to use the Licensed content in a new work that one of the authors listed on the License Agreement as a "Licensed content author" has written.

Original Authors may post the 'Accepted Version' of their full text article on their personal or on their University website and not on any other website. The 'Accepted Version' is the version of the paper accepted for publication by AAAS including changes resulting from peer review but prior to AAAS's copy editing and production (in other words not the AAAS published version).

FOR MOVIES / FILM / TELEVISION:

Permission is granted to use, record, film, photograph, and/or tape the AAAS material in connection with your program/film and in any medium your program/film may be shown or heard, including but not limited to broadcast and cable television, radio, print, world wide web, and videocassette. The required credit line should run in the program/film's end credits.

FOR MUSEUM EXHIBITIONS:

Permission is granted to use the AAAS material as part of a single exhibition for the duration of that exhibit. Permission for use of the material in promotional materials for the exhibit must be cleared separately with AAAS (please contact us at permissions@aaas.org).

FOR TRANSLATIONS:

Translation rights apply only to the language identified in your request summary above.

The following disclaimer must appear with your translation, on the first page of the article, after the credit line: "This translation is not an official translation by AAAS staff, nor is it endorsed by AAAS as accurate. In crucial matters, please refer to the official English-language version originally published by AAAS."

FOR USE ON A COVER:

Permission is granted to use the AAAS material on the cover of a journal issue, newsletter issue, book, textbook, or annual report in print and electronic formats provided the AAAS material reproduced as permitted herein remains in situ and is not exploited separately

By using the AAAS Material identified in your request, you agree to abide by all the terms and conditions herein.

Questions about these terms can be directed to the AAAS Permissions department permissions@aaas.org.

Other Terms and Conditions:

v 2

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Figure 1.16

**AMERICAN PHYSICAL SOCIETY LICENSE
TERMS AND CONDITIONS**

Nov 29, 2017

This Agreement between Zhuo Wang ("You") and American Physical Society ("American Physical Society") consists of your license details and the terms and conditions provided by American Physical Society and Copyright Clearance Center.

License Number	4238071504366
License date	Nov 29, 2017
Licensed Content Publisher	American Physical Society
Licensed Content Publication	Physical Review Letters
Licensed Content Title	Giant Enhancement of the Optical Second-Harmonic Emission of WSe_2 Monolayers by Laser Excitation at Exciton Resonances
Licensed Content Author	G. Wang et al.
Licensed Content Date	Mar 4, 2015
Licensed Content Volume	114
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print, Electronic
Portion	image/photo

Number of images/photos requested	1
Portion description	Fig.2
Rights for	Main product
Duration of use	Life of Current Edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Worldwide
In the following language(s)	Original language of publication
With incidental promotional use	no
The lifetime unit quantity of new product	0 to 499
The requesting person/organization is:	Zhuo Wang
Order reference number	
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Expected size (number of pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing Address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang
Total	0.00 USD

Terms and Conditions

Terms and Conditions

The American Physical Society (APS) is pleased to grant the Requestor of this license a non-exclusive, non-transferable permission, limited to [**print** and/or **electronic** format, depending on what they chose], provided all criteria outlined below are followed.

1. You must also obtain permission from at least one of the lead authors for each separate work, if you haven't done so already. The author's name and affiliation can be found on the first page of the published Article.
2. For electronic format permissions, Requestor agrees to provide a hyperlink from the reprinted APS material using the source material's DOI on the web page where the work appears. The hyperlink should use the standard DOI resolution URL, <http://dx.doi.org/{DOI}>. The hyperlink may be embedded in the copyright credit line.
3. For print format permissions, Requestor agrees to print the required copyright credit line on the first page where the material appears: "Reprinted (abstract/excerpt/figure) with permission from [(FULL REFERENCE CITATION) as follows: Author's Names, APS Journal Title, Volume Number, Page Number and Year of Publication.] Copyright (YEAR) by the American Physical Society."
4. Permission granted in this license is for a one-time use and does not include permission for any future editions, updates, databases, formats or other matters. Permission must be sought for any additional use.
5. Use of the material does not and must not imply any endorsement by APS.
6. Under no circumstance does APS purport or intend to grant permission to reuse materials to which it does not hold copyright. It is the requestors sole responsibility to ensure the licensed material is original to APS and does not contain the copyright of another entity, and that the copyright notice of the figure, photograph, cover or table does not indicate that it was reprinted by APS, with permission from another source.
7. The permission granted herein is personal to the Requestor for the use specified and is not transferable or assignable without express written permission of APS. This license may not be amended except in writing by APS.
8. You may not alter, edit or modify the material in any manner.
9. You may translate the materials only when translation rights have been granted.
10. You may not use the material for promotional, sales, advertising or marketing purposes.
11. The foregoing license shall not take effect unless and until APS or its agent, Copyright Clearance Center (CCC), receives payment in full in accordance with CCC Billing and Payment Terms and Conditions, which are incorporated herein by reference.
12. Should the terms of this license be violated at any time, APS or CCC may revoke the license with no refund to you and seek relief to the fullest extent of the laws of the USA. Official written notice will be made using the contact information provided with the permission request. Failure to receive such notice will not nullify revocation of the permission.
13. APS reserves all rights not specifically granted herein.

14. This document, including the CCC Billing and Payment Terms and Conditions, shall be the entire agreement between the parties relating to the subject matter hereof.

Other Terms and Conditions

Version 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Figure 1.17d,e,f

 **Copyright Clearance Center**

 **RightsLink[®]**

[Home](#) [Account Info](#) [Help](#)

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Optomechanical Enhancement of Doubly Resonant 2D Optical Nonlinearity
Author: Fei Yi, Mingliang Ren, Jason C. Reed, et al
Publication: Nano Letters
Publisher: American Chemical Society
Date: Mar 1, 2016
Copyright © 2016, American Chemical Society

Logged in as:
Zhuo Wang
Account #: 3001100639
[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

Figure 1.18a,b

License Number	4238090142725
License date	Nov 29, 2017
Licensed Content Publisher	The American Association for the Advancement of Science
Licensed Content Publication	Science
Licensed Content Title	Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films
Licensed Content Author	L. Britnell,R. M. Ribeiro,A. Eckmann,R. Jalil,B. D. Belle,A. Mishchenko,Y.-J. Kim,R. V. Gorbachev,T. Georgiou,S. V. Morozov,A. N. Grigorenko,A. K. Geim,C. Casiraghi,A. H. Castro Neto,K. S. Novoselov
Licensed Content Date	Jun 14, 2013
Licensed Content Volume	340
Licensed Content Issue	6138
Volume number	340
Issue number	6138
Type of Use	Thesis / Dissertation
Requestor type	Scientist/individual at a research institution
Format	Print and electronic
Portion	Figure
Number of figures/tables	2
Order reference number	
Title of your thesis / dissertation	OPTICAL PROPERTIES OF 2D TRANSITION METAL DICHALCOGENIDES ENHANCED BY PLASMONIC NANOSTRUCTURES
Expected completion date	Nov 2017
Estimated size(pages)	140
Requestor Location	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Singapore Attn: Zhuo Wang
Billing Type	Invoice
Billing address	Zhuo Wang Physics Department, Faculty of Science 2 Science Drive 3 National University of Singapore Singapore, Singapore 117551 Attn: Zhuo Wang
Total	0.00 USD

Figure 1.19



[Home](#) [Account Info](#) [Help](#)

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Transient Absorption Microscopy of Monolayer and Bulk WSe₂

Author: Qiannan Cui, Frank Ceballos, Nardeep Kumar, et al

Publication: ACS Nano

Publisher: American Chemical Society

Date: Mar 1, 2014

Copyright © 2014, American Chemical Society

Logged in as:
Zhuo Wang
Account #: 3001100639

[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

Figure 1.20



[Home](#) [Account Info](#) [Help](#)

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Ultrafast Dynamics of Metal Plasmons Induced by 2D Semiconductor Excitons in Hybrid Nanostructure Arrays

Author: Abdelaziz Boulesbaa, Viktoriia E. Babicheva, Kai Wang, et al

Publication: ACS Photonics

Publisher: American Chemical Society

Date: Dec 1, 2016

Copyright © 2016, American Chemical Society

Logged in as:
Zhuo Wang
Account #:
3001100639

[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

Figure 2.6



[Home](#) [Account Info](#) [Help](#)

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂

Author: Changgu Lee, Hugen Yan, Louis E. Brus, et al

Publication: ACS Nano

Publisher: American Chemical Society

Date: May 1, 2010

Copyright © 2010, American Chemical Society

Logged in as:
Zhuo Wang
Account #: 3001100639

[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

Figures and contents in Chapter 3



[Home](#) [Account Info](#) [Help](#) 



Title: Giant photoluminescence enhancement in tungsten-diselenide-gold plasmonic hybrid structures

Author: Zhuo Wang, Zhaogang Dong, Yinghong Gu, Yung-Huang Chang, Lei Zhang et al.

Publication: Nature Communications

Publisher: Nature Publishing Group

Date: May 6, 2016

Copyright © 2016, Rights Managed by Nature Publishing Group

Logged in as:
Zhuo Wang
Account #:
3001100639

[LOGOUT](#)

Author Use

Authors of NPG articles do not require permission to use content from their article in most cases as stated in the [author's guidelines](#).

Authors wishing to use their article for commercial purposes must request permission in the normal way.

For further questions, please contact NPG's permissions department: permissions@nature.com

Figures and contents in Chapter 5



[Home](#) [Account Info](#) [Help](#) 



Title: Slow cooling and efficient extraction of C-exciton hot carriers in MoS2 monolayer

Author: Lei Wang, Zhuo Wang, Hai-Yu Wang, Gustavo Grinblat, Yu-Li Huang et al.

Publication: Nature Communications

Publisher: Nature Publishing Group

Date: Jan 5, 2017

Copyright © 2017, Rights Managed by Nature Publishing Group

Logged in as:
Zhuo Wang
Account #:
3001100639

[LOGOUT](#)

Author Use

Authors of NPG articles do not require permission to use content from their article in most cases as stated in the [author's guidelines](#).

Authors wishing to use their article for commercial purposes must request permission in the normal way.

For further questions, please contact NPG's permissions department: permissions@nature.com