Transient Nonlinear Optics of Two-Dimensional Materials

Yadong Wang
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Yadong Wang

A doctoral thesis completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Electrical Engineering, Remote Zoom meeting, on 4th March 2022.

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# Abstract

Two-dimensional (2D) layered materials with remarkable optical and electronic properties, are promising for a variety of applications in the area of electronics, photonics, and optoelectronics. Recently, increasing efforts are targeted toward the nonlinear optical properties of 2D materials, which are not only fascinating in terms of fundamental physics, but also intriguing for various potential applications. Beneficial from their atomically thin nature, 2D materials are the ideal material to address the subjects on how the materials respond to the light excitation without considering phase-matching effects.

In this thesis, I devote main efforts to studying the relation between carrier dynamics and nonlinear optical responses in 2D materials and to developing potential applications in the area of ultrafast nonlinear optics. Details are expressed as below:

1. Transient linear optical absorption of monolayer MoS2 is studied in the sub-bandgap region from 860 nm to 1400 nm. A significant absorption enhancement of up to 4.2% is observed due to the pump-induced absorption at the excited carrier states.

2. Transient second-harmonic generations in transition metal dichalcogenide monolayers are investigated in a broadband energy range. The pump modified excitonic oscillation strength enables to enhance the SHG at dark exciton states and bleach the SHG at bright exciton states. The enhancement of SHG is achieved as high as 386 times. Further, the SHG modulation has been realized with a modulation depth of up to 60% and a response time of ~600 fs.

3. Transient higher-order harmonic generations are finally studied. Broadband third-harmonic spectroscopy displays a series of electronic states in monolayer MoS2 with high signal contrast up to 800 times. The ultrafast photocarrier dynamics of electronic states in MoS2 are explored by transient third-harmonic generation. Further, the all-optical modulation of high-harmonic generation in monolayer MoS2 is demonstrated with a modulation depth up to 90%, offering a promising platform for the ultrafast optical signal processing of nonlinear optics.

# Keywords
Nonlinear Optics, Two-Dimensional Materials, Pump-Probe Spectroscopy, Excitonic States, Harmonic Generations, Ultrafast All-Optical Modulation

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“It's not enough to read, to listen, to be passive. One must act.”
— Adam Weishaupt

Espoo, 26 June 2021
Yadong Wang
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# List of Abbreviations and Symbols

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<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Absorptivity</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DFG</td>
<td>Difference-frequency generation</td>
</tr>
<tr>
<td>DM</td>
<td>Dichroic mirror</td>
</tr>
<tr>
<td>EOM</td>
<td>Electro-optic modulator</td>
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<tr>
<td>FWM</td>
<td>Four-wave mixing</td>
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<tr>
<td>GEOM</td>
<td>Graphene electro-optic modulator</td>
</tr>
<tr>
<td>h-BN</td>
<td>Hexagonal boron nitride</td>
</tr>
<tr>
<td>HHG</td>
<td>High-harmonic generation</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting devices</td>
</tr>
<tr>
<td>ME</td>
<td>Mechanical exfoliation</td>
</tr>
<tr>
<td>NLO</td>
<td>Nonlinear optical</td>
</tr>
<tr>
<td>NRZ</td>
<td>Non-return-to-zero</td>
</tr>
<tr>
<td>OC</td>
<td>Optical fiber coupler</td>
</tr>
<tr>
<td>OPA</td>
<td>Optical parametric amplification</td>
</tr>
<tr>
<td>OPO</td>
<td>Optical parametric oscillation</td>
</tr>
<tr>
<td>OSC</td>
<td>Oscilloscope</td>
</tr>
<tr>
<td>PD</td>
<td>Photodetector</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>SA</td>
<td>Saturable absorption</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SFG</td>
<td>Sum-frequency generation</td>
</tr>
<tr>
<td>SHG</td>
<td>Second-harmonic generation</td>
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<td>TA</td>
<td>Transient absorption</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
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<tr>
<td>TFBG</td>
<td>Tilted fiber Bragg grating</td>
</tr>
<tr>
<td>THG</td>
<td>Third-harmonic generation</td>
</tr>
<tr>
<td>TMD</td>
<td>Transition metal dichalcogenides</td>
</tr>
<tr>
<td>WDM</td>
<td>Wavelength division multiplexing</td>
</tr>
<tr>
<td>2DM</td>
<td>Two-dimensional materials</td>
</tr>
<tr>
<td>$\chi^{(2)}$</td>
<td>Second-order nonlinear susceptibility</td>
</tr>
<tr>
<td>$\chi^{(3)}$</td>
<td>Third-order nonlinear susceptibility</td>
</tr>
<tr>
<td>$\chi^{(n)}$</td>
<td>n-order nonlinear susceptibility</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>$\sigma^+$</td>
<td>Left-circular polarized</td>
</tr>
<tr>
<td>$\sigma^-$</td>
<td>Right-circular polarized</td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>Short-circuit current</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Light frequency</td>
</tr>
<tr>
<td>Re(x)</td>
<td>Real part of x</td>
</tr>
<tr>
<td>Im(x)</td>
<td>Imaginary part of x</td>
</tr>
</tbody>
</table>
This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals


3. **Yadong Wang**, Susobhan Das, Fadil Iyikanat, Yunyun Dai, Shisheng Li, Xiangdong Guo, Xiaoxia Yang, Jinluo Cheng, Xuerong Hu, Masood Ghotbi, Fangwei Ye, Harri Lipsanen, Shiwei Wu, Tawfique Hasan, Xuetao Gan, Kailui Liu, Dong Sun, Qing Dai, F. Javier García de Abajo, Jianlin Zhao and Zhipei Sun, Giant all-optical modulation of second-harmonic generation mediated by dark excitons. ACS Photonics, 8 (8), 2320 (2021).


6. Hui Xue†, **Yadong Wang†**, Yunyun Dai, Wonjae Kim, Henri Jussila, Mei Qi, Jannatul Susoma, Zhaoyu Ren, Qing Dai, Jianlin Zhao, Kari Holonen, Harri Lipsanen, Xiaomu Wang, Xuetao Gan, and Zhipei Sun, A MoSe\textsubscript{2}/WSe\textsubscript{2} heterojunction-based photodetector at telecommunication wavelengths. Advanced Functional Materials, 28 (47), 1804388 (2018). †**Equal contribution.**


Author’s Contribution

**Publication 1:** Difference frequency generation in monolayer MoS$_2$

The author performed all the major experiments except the polarization dependent measurement. Co-authors fabricated the samples and performed the corroborative polarization measurement.

**Publication 2:** All-optically controlled slow and fast lights in graphene-coated tilted fiber Bragg grating

The author prepared the sample, conducted all the major experiments with collaborators, analysed the data, and wrote the manuscript together with the co-authors.

**Publication 3:** Giant all-optical modulation of second-harmonic generation mediated by dark excitons

The author conceived the idea, performed all the major experiments (except the power dependent modulation part) and wrote the manuscript. Co-authors fabricated the samples and theoretically analysed the data and optimized the manuscript.

**Publication 4:** Probing electronic states in monolayer semiconductors with third-harmonic spectroscopies

The author conceived the idea, conducted all the major experiments (except the sample characterization part), wrote the manuscript together with the co-authors. Co-authors grew the samples and theoretically analysed the data and optimized the manuscript.

**Publication 5:** Graphene actively mode-locked lasers

The author performed the modulator measurements and laser system characterizations, and wrote the modulator part of the manuscript.

**Publication 6:** A MoSe$_2$/WSe$_2$ heterojunction-based photodetector at telecommunication wavelengths.

The author set up the photocurrent measurement system and laser source at telecommunication band, took part in writing the manuscript.

**Publication 7:** Ultrafast transient sub-bandgap absorption of monolayer MoS$_2$. 

The author set up the transient absorption experimental system, analysed the data, took part in writing the manuscript.

**Publication 8:** Electrical control of interband resonant nonlinear optics in monolayer MoS$_2$.

The author set up the four-wave mixing experimental system, took part in writing the manuscript.

**Publication 9:** Broadband Plasmon-Enhanced Four-Wave Mixing in Monolayer MoS$_2$.

The author set up the four-wave mixing experimental system, took part in writing the manuscript.

**Publication 10:** Nonlinear optics with 2D layered materials

The author wrote the saturable absorption section of the manuscript and prepared Figures 2, 3, 5, 11, organized the references and took part in writing the manuscript.

**Publication 11:** Active synchronization and modulation of fiber lasers with a graphene electro-optic modulator

The author assisted the experimental measurements, and took part in writing the manuscript.

**Publication 12:** Graphene actively Q-switched lasers

The author assisted the experimental measurement, and took part in writing the manuscript.
1. Introduction

Nonlinear optics is the branch of optics that examines the light behaviour in nonlinear optical media, which plays an increasingly important role in various technologies in our modern information society. Harmonic generations (HGs) are a series of nonlinear optical processes, in which incident photons generate new photons with harmonic frequencies of the incident photons. As the most widely used nonlinear optical effects, second-harmonic generation (SHG), originating from second-order nonlinear optical susceptibility \( \chi^{(2)} \) mainly in noncentro-symmetric materials, was first reported in 1961 immediately after the invention of the laser.[1] It is normally regarded as one of the most efficient nonlinear optical processes and has been widely exploited for various important applications, such as coherent light generation [2], crystalline characterization [3], bio-imaging [4], and spectroscopy [5]. In addition, the third-harmonic generation (THG) with third-order nonlinear optical susceptibility \( \chi^{(3)} \) is also primarily useful for many applications.[6] Different from SHG, THG could occur in the materials without considering symmetry breaking. THG can also be directly dependent on one-, two-, and three-photon transition resonances with electronic states, which gives additional freedom of 3-photon resonance than that of SHG.[6] Further, the development of high-harmonic generation (HHG) has also played a basis for attosecond science.[7] Normally, nonlinear optical processes have relatively low efficiency. And high-order harmonic generation requires higher intense incident light due to the relatively low higher-order nonlinear susceptibility. Therefore, reinforcing the conversion efficiency of HGs is of significant importance for numerous applications of nonlinear optics.

There are many approaches to enhance the conversion efficiency of nonlinear optics, such as employing materials with high nonlinear optical susceptibility, increasing the light-matter interaction length and optimizing phase matching condition. Currently, the commercial nonlinear optical materials are mainly bulk crystals, such as potassium titanyl phosphate (KTP), beta barium borate (BBO), and lithium iodate (LiIO3). They have enabled the great success of nonlinear optics in practical applications. While the emerging and future technology typically demands miniaturization of the photonic and optoelectronic devices for on-chip integration. To achieve this objective, on-chip nonlinear photonic devices have been demonstrated by using highly confined electromagnetic fields (such as, high Q-factor resonators or plasmonic resonances). It offers one possible way for enhancement of nonlinear optics, while the nonlinear optical susceptibility itself is low but with high loss, which drives scientists to search for
novel materials with strong nonlinear optical susceptibility (such as low-dimensional materials).

In addition to optical nonlinearity enhancement, active control of nonlinear optical processes is desirable for practical applications, in analogy to the linear active optical devices. In particular, it is extremely fascinating to all-optically modulate nonlinear optical responses of materials with high efficiency and ultrafast speed, for a large range of applications [8], such as optical data processing, optical communications [9], optical frequency comb generation, and quantum optics [10]. However, the active control of traditional bulk materials is distressful due to their slow speed or less efficiency. To address these challenges, thin films have been first employed (such as metals [11] and semiconductors [12],) but their performance on nonlinear optical modulation is generally very weak (typically with enhancement factors of < 2 [13-15]). The efficient all-optical modulation strategies to control nonlinear optical processes still have remained elusive.

The recent discovery and development of two-dimensional (2D) materials offer a promising platform for actively engineered nonlinear optics. Indeed, 2D materials such as graphene, transition metal dichalcogenides (TMDs) have attracted huge interest in the field of photonics and optoelectronics.[16,17] The 2D structure naturally confines the electrons into the atomic level, which gives an opportunity to form a strong light interaction. For example, graphene with 0.3 nm thickness has as high as 2.3% broadband linear optical absorption [18] and the nonlinear optical susceptibility up to $\chi^{(3)} \sim 10^{-7}$ esu [19] due to the resonance in the linear-dispersion band structure. On the other hand, with the extreme quantum confinement and reduced screening effect, monolayer TMDs have significant excitonic quasi-particles induced resonance, which prominently dominates their linear and nonlinear optical properties.[20-25] Further, 2D materials with atomic thickness naturally have large mechanical deformation and flexible structure, which can be easily integrated with other devices, such as on-chip waveguides without considering lattice matching. It thus holds great promises for future integrated devices both in optoelectronics and photonics.[26,27] However, the conversion efficiency in 2D materials remains relatively low with the atomic thickness, comparing to bulk materials, which hinders their potential applications.

This thesis aims to study the transient linear and nonlinear optical processes in different 2D materials, and demonstrate new methods to control and enhance their nonlinear optical responses, specifically SHG, THG, HHG. More specifically, the key objectives of this thesis are described as follows:

1. Transient linear optical absorption in the transparent region of monolayer MoS$_2$: The ultrafast transient optical absorption of monolayer MoS$_2$ is investigated in the sub-bandgap region from 860 nm to 1400 nm. A significant absorption enhancement of up to 4.2% is observed due to the pump-induced re-absorption at the excited carrier states.

2. SHG modulation in TMD monolayers: A giant and broadband all-optical ultrafast modulation of SHG in TMD monolayers has been investigated. The pump modified excitonic oscillation strength enables to enhance the
SHG at dark exciton states and bleach the SHG at bright exciton states. The enhancement of SHG has been achieved as high as 386 times, two orders of magnitude larger than previous results. Further, the SHG modulation has been realized with a modulation depth of up to 60% and response time of < 600 fs.

3. Probing Rydberg states of excitons in 2D transition TMDs with THG spectroscopies: Series of electronic states in monolayer MoS$_2$, such as multiple excitonic Rydberg states and free-particle energy bands, have been explored, with significant contrast of up to 800 times via broadband (from ~1.77 to 3.10 eV) third-harmonic spectroscopy. Further, the photocarrier dynamics of electronic states in MoS$_2$ have been explored by transient THG, giving direct evidence of various carrier relaxation processes, such as exciton formation and electron-phonon interaction.

4. Optical control of HHG in 2D TMDs: The all-optical modulation of HHG in monolayer MoS$_2$ has been demonstrated with the assistance of the modified interlayer transitions. Thanks to the strong resonance oscillation of excitons in monolayer MoS$_2$, the HHG is largely modulated with a modulation depth of 90% by a pump light at a wavelength of 400 nm.

This thesis is arranged as follows: After chapter 1 (this chapter), it begins by presenting the fundamentals of 2D materials and related electrical, optical properties in chapter 2. The fundamental of nonlinear optics and the current state-of-the-art nonlinear optics with 2D materials are detailly discussed in chapter 3. Chapters 4–6 introduce the transient linear, SHG, THG, HHG in 2D materials, respectively. Finally, chapter 7 summarizes this thesis and presents a perspective outlook of the above results from the fundamental and technological points of view.
2. Fundamentals of 2D materials

Two-dimensional materials (2D materials), are the natural layered materials with a thickness on the atomic scale and normally with a much large surface area ($\geq \mu m$), where electrons in these materials are confined to move within the two-dimensional plane. Graphene with a single sheet of carbon atoms is discovered as the first 2D material in 2004, which broke the argument about the non-existence of strictly 2D crystalline materials.[28] Since then, hundreds of 2D materials, such as transition metal dichalcogenides (TMDs), phosphorene, hexagonal boron nitride (h-BN), Xenes, have been fabricated with various methods (such as mechanical exfoliation (ME), liquid exfoliation, and chemical vapor deposition (CVD)). With isolation into single or few-layer from bulk materials, 2D materials exhibit remarkable physical and chemical properties [28] mainly due to: i) removal of van der Waals interactions, ii) an increase in the ratio of surface-area-to-volume, iii) confinement of electrons in an atomic plane. Such properties could be employed for vast promising applications [29], such as transistors[30], ultrafast lasers [31], photodetectors [32], valleytronics [33]. This chapter will give a brief introduction to optical and electrical properties of 2D materials, specifically graphene and monolayer TMDs.

2.1 Graphene

2.1.1 Electrical and optical properties

Graphene is a single carbon layer, in which each carbon atom is covalently sp$^2$ hybridized bonding with three other carbon atoms in an arrangement of a honeycomb lattice. In graphene, the conduction and valence bands meet at the K point (i.e. Dirac points) of the Brillouin zone, as shown in Figure 2.1(a).[34] Therefore, graphene is regarded as a semimetal. And the electron band in graphene obeys a linear dispersion relation of $E = \nu_F h k$, where $\nu_F = 10^6$ m/s is the Fermi velocity, $h$ is the Planck constant, $k$ is the wave vector. This unique band structure enables distinctive electronic properties. Figure 2.1(b) shows the evolution of graphene’s conductivity ($\sigma$) as a function of gate voltage[35], which increases linearly with the substantial electron (hole) doping. The linear dependence of conductivity gives the carrier mobilities $\mu = \sigma / ne$ as high as 200000 cm$^2$/Vs, where $n$ is the concentration of electrons or holes and $e$ is the electron charge.[36] This high carrier mobility is promising for ultrafast electronics [37],

including digital logic, high-frequency transistor, circuits (e.g., mixers and radio-frequency amplifiers).

![Figure 2.1](image)

(a) Electronic band structures of graphene.[34] (b) Changes of graphene’s conductivity as a function of gate voltage $V_g$.[35]

Due to the linear dispersion of the massless Dirac fermions, the optical conductivity of graphene in the near-IR and visible regions has a universal value.[18] The absorption of graphene within this broadband frequency region is around 2.3%. Thus, it can be even observed under optical microscopy with naked eyes after contrast engineering. If considering the 0.334-nm thickness of graphene, the absorption coefficient in graphene is $\sim 7 \times 10^7$ m$^{-1}$, which is $\sim 50$ times higher than that of GaAs at the telecommunication band.[38] While the absorption index of graphene at higher energy (normally $> 3$ eV) shows the deviated value with the universal one due to many-body effects.[39] Excitingly, the optical responses in graphene are highly dependent on the relation of optical energy and Fermi level, owing to Pauli blocking effect. The interband transitions are essentially blocked when photon energies $\omega < 2|E_F|$, where $E_F$ is the Fermi level. The $E_F$ in graphene can be adjusted with chemical or physical doping, enabling actively tunable optics with graphene. Figure 2.2 shows the optical transmission of our homemade graphene device at the photon energy of 0.8 eV with the relation of gate voltage.[40] Another exciting property of graphene is ultrafast carrier dynamics, where the carriers in the excited state decay and recombine very fast within several picoseconds, much faster than the bulk materials (normally as hundreds of picoseconds to nanoseconds).[41] Such ultrafast carrier interaction is crucial to ultrafast optoelectronic applications.[42]

Besides the linear optical properties, the nonlinear optical responses of graphene have been found with remarkable strong and broadband features. By comparing with a thin gold layer, the third-order optical susceptibility is obtained as $\chi^{(3)} \sim 10^{-7}$ esu [19], which is 8 orders of magnitude larger than that in transparent dielectric materials. Thus far, the nonlinear optical properties of graphene such as broadband saturable absorption [31], photothermal effect [26,27,43], third-harmonic generation [44-46], four-wave mixing [19,47], self-phase modulations [48-50], high-harmonic generation [51,52], optical limiting [53] and nonlinear Kerr effect [54-56] have been widely investigated. Although graphene has a centrosymmetric structure, the second-harmonic generation has
been found from the interface with a substrate or from quadrupole re-
response.[57,58] Meanwhile, the inversion symmetry can be broken by many
methods such as electrical gating [59-61], chemical etching [62]. Similar to the
linear response, nonlinear optical responses in graphene are sensitive to carrier
doping, which gives an opportunity for tunable nonlinear optics.[63-66]

![Figure 2.2](image_url)

Figure 2.2. Gate tunable optical transmittance of graphene at the photon energy of 0.8 eV, where
blue dots are experimental results and red curve is theoretical calculation. Inset curve is the
calculated Fermi energy as a function of the gate voltage. Adapted from Publication 12.

### 2.1.2 Photonic and optoelectronic applications

The richness of optical and electronic properties of graphene gives rise of poten-
tial applications in photonics and optoelectronics, ranging from solar cells and
light-emitting devices to touch screens, photodetectors, and ultrafast lasers.[67] For instance, the broadband absorption in monolayer graphene makes it a
promising material for broadband optical devices (e.g., wideband photodetec-
tors [29,67], saturable absorbers [67-69], and modulators [70]), covering an ex-
tremely wide spectral range from the ultraviolet to microwave regions. Here,
two examples of graphene’s applications are introduced: actively modulated
pulsed lasers, and optically controlled slow and fast light.

![Figure 2.3](image_url)

Figure 2.3. Graphene electro-optic modulators and pulsed laser generations. (a) Schematic illus-
tration (up) and cross-section (down) of a graphene modulator. (b) Optical image of fabricated
GEOM device. (c) Operation of frequency bandwidth at 1550 nm. (d) Actively mode-locked laser pulse train synchronized with modulation voltage. Inset, autocorrelation trace of the output pulses. (e) The modulated signal (top panel) and synchronously Q-switched laser pulse trains at 2 μm (middle panel) and 1.5 μm (bottom panel). Figure (a)-(d) are adapted from Publication 5, Figure (e) is adapted from Publication 11.

Generally, pulsed lasers are vital for widespread applications in various fields such as spectroscopy, materials processing, and digital telecommunications [71], which can be implemented with either active or passive methods. With the active method, the optical modulator is inserted into the laser cavity to actively switch the loss of intra-cavity light, while the passive one typically relies on saturable absorbers (SAs) by introducing all-optical self-modulation effect.[31] In comparison to the passive one, the active method allows more freedoms for electrically tunable laser parameters, such as repetition rate, pulse duration, and energy, which is favourable for applications. Graphene electro-optic modulators (GEOMs) have been demonstrated to achieve actively modulated pulsed lasers. An example of the GEOM is shown in Figure 2.3. The modulator consists of metal contacts, an insulator layer, and monolayer graphene. Figure 2.3(a) and (b) give the schematic illustration and optical image of GEOM, respectively. The diameter of GEOM is around 80 μm to fit the diameter size of the laser spot. Besides the optical tunable absorption of GEOM, the other key parameter is the operation bandwidth for the modulator. Figure 2.3(c) shows the dynamic electro-optical response of a free-space GEOM device, which exhibits a flat response with a 3-dB bandwidth of ~13.2 MHz. By employing the GEOM, actively Q-switched (1550 nm and 2000 nm [40]) and mode-locked (1550 nm in Figure 2.3(d) [72]) have been demonstrated. The broadband operation of GEOM allows another important application: actively synchronized pulsed lasers (e.g., 1550 nm and 2000 nm laser synchronization in Figure 2.3(e) [73]).

![Graphene based tunable TFBG](image)

**Figure 2.4.** Graphene based tunable TFBG. (a) Schematic diagram of the graphene coated TFBG. (b) SEM Image of the graphene coated TFBG. (b) Delay times of signal pulses at the wavelength of 1554.81 nm as a function of pump power. Adapted from Publication 2.

On the other hand, graphene has been employed as an effective media to delay or accelerate light pulses, which is promising in the area of signal processing and optical communication networks.[74] Figure 2.4(a) shows the schematic diagram of a 6° slanted tilted fiber Bragg grating (TFBG) coated by few-layered graphene. The scanning electron microscopy (SEM) image further confirms the tight joint between graphene and TFBG. By employing graphene’s photothermal effect, the refractive index of TFBG is changed with pump light excitation. Thus,
the group delay of the graphene-coated TFBG (GTFBG) can be well controlled by a pump light. Figure 2.4(b) shows the delay time of the signal as a function as pump power, which have been achieved as large as 200 ps and enable to be tuned continuously. This simple, broad-bandwidth, compact approach to actively control the slow and fast light offers potential applications for tunable optical data synchronizations and optical memories. Similar design with optical properties of graphene could also be promising for other platforms such as an on-chip scheme for active optical devices.[75]

2.2 Transition metal dichalcogenide monolayers

2.2.1 Electrical and optical properties

In contrast to the zero bandgap of graphene, transition metal dichalcogenides (TMDs), MX$_2$ (M = Mo, W; X$_2$ = S, Se) are typically semiconductors with bandgaps ranging from near-infrared to the visible region. As shown in Figure 2.5(a), TMDs consist of a single layer of transition metal atoms sandwiched by two layers of chalcogen atoms with the trigonal prismatic structure. In the out-plane, they have mirror symmetry, while in-plane inversion symmetry is broken. Limiting to the monolayer, these materials become direct bandgap semiconductors at the K and K’ points.[17,24] This is due to the increased indirect-gap value with the strong quantum confinement effect in the out-of-plane direction, while the direct gap at the K (K’) point remains mostly unchanged.[76] The electronic bands of TMD monolayers can be calculated (e.g., the GW-BSE method), yielding reliable predictions for the exciton properties of ultra-thin transition metal dichalcogenides.[77,78] Figure 2.5(b) shows the electronic band structure calculated within the GGA and G$_0$W$_0$ approximations for monolayer MoS$_2$.

Compared with graphene, the spin-orbit interaction in TMDs is much stronger mainly originated from their relatively heavy elements and the involvement of the transition metal $d$ orbitals. In TMD monolayers, the spin splitting at the K (K’) point in the valence band is found ~0.2 eV (Mo) and ~0.4 eV (W).[79,80] This coupling leads to the two valence sub-bands, corresponding to two types of excitons, A and B. With D$_{3h}$ point symmetry, optically generated electrons and holes are both valley and spin polarized. Therefore, with the circular-polarized excitation, the exciton emission in TMD monolayers can be co-polarized followed by the selection rule.[24]

Due to the weak dielectric screening and strong confinement, TMD monolayers give rise to an extraordinarily strong Coulomb interaction, which leads to various fascinating many-particle phenomena. For example, the formation of different types of excitons: neutral exciton, trion, biexciton formed, as well as interlayer exciton states from with different layers.[24,81] The excitons in TMD monolayers exhibit binding energies ~0.5 eV which is one to two orders of magnitude larger than in conventional bulk materials, such as GaAs.[82] Therefore, excitonic features are stable at room temperature and dominate the optical responses of these materials. As shown in the upper panel of Figure 2.5(c), the
reflectance contrast from monolayer MoS$_2$ on a sapphire substrate exhibits three prominent peaks at 1.85, 2.00, 2.84 eV in room temperature, corresponding to the well-known $1s_A$, $1s_B$, $1s_C$ excitons, respectively. By mathematically 2nd-derivative of the spectrum, the relatively weak excitons also appear. As shown in the down panel of Figure 2.5(c), the dips at 2.17, 2.38, 3.05 eV, corresponding to the $2s$, $3s$, and $1s_D$ exciton states, respectively.[83] It matches well with the absorption calculation with the GW-BSE approach [84], as shown in Figure 2.5(d).

Figure 2.5. (a) Trigonal prismatic structure of monolayer TMDs [17]. (b) Electronic bands of monolayer MoS$_2$ calculated with the GGA and G$_0$W$_0$ approximations. (c) Reflectance contrast in monolayer MoS$_2$. (d) Calculated absorption states in monolayer MoS$_2$ within the G$_0$W$_0$−BSE approximation. Figure (b-d) are adapted from Publications 3 and 4.

2.2.2 Photonic and optoelectronic applications

With their amazing optical and electrical properties, 2D TMDs are finding various applications for next-generation electronics and optoelectronic devices, especially for photodetectors, light-emitting devices (LEDs), and valleytronics.[17] While graphene-based photodetectors suffer high dark currents due to the semimetal feature of graphene, 2D TMD based photodetectors exhibit lower dark currents and higher responsivity, typically with the operation of photovoltaic effect. Lopez-Sanchez et al. have reported a monolayer MoS$_2$ photodetector with responsivity as high as 880 A/W.[85] A potentially efficient way is to construct a build-in electric field with a heterostructure. For example, heterostructure devices have been demonstrated for photodetection.[86,87] Figure 2.6(a) shows a heterostructure photodetector with few-layer MoSe$_2$ and WSe$_2$ on a
280-nm SiO$_2$/Si substrate. This heterostructure device with a build-in electrical field shows a strong photon response when vias voltage and the gate voltage is zero, as shown in Figure 2.6(b). The maximum photoresponsivity is obtained with 2 A/W at 532 nm with a power of 100 nW, indicating high photodetection performance. Clearly, the heterostructure region reveals pronounced photocurrent generation, exhibiting an attractive platform for the electrical engineered TMD heterostructures for high-performance optoelectronic devices.

Figure 2.6. The heterostructure photodetector. (a) the optical image of MoSe$_2$/WSe$_2$ device. Inset: Raman mapping. (b) Photocurrent mapping of the heterostructure. Adapted from Publication 6.
3. Nonlinear optics in 2D materials

Nonlinear optics has grown rapidly with the development of lasers, originating from the study of the interactions of intense light with dielectric media, the applications such as coherent laser sources, material characterizations, and optical signal processing. Along with the long-existing knowledge and techniques of bulk materials, 2D materials have given new insights into nonlinear optics from a fundamental point of view to their potential applications. This chapter gives a brief review of the current state-of-the-art nonlinear optics based on 2D materials.

3.1 Introduction to nonlinear optics

The nonlinear optical effect normally occurs when intense light modifies the optical properties of a material system. And the optical response of the material reacts in a nonlinear manner with the strength of the optical field. To describe this factor, the optical response of materials to the applied electrical field \( (E) \) can be expressed by expanding the resulting polarization \( (P) \):

\[
P(t) = \varepsilon_0 (\chi^{(1)}E(t) + \chi^{(2)}E(t)E(t) + \chi^{(3)}E(t)E(t)E(t) + \cdots) \quad (3.1)
\]

where the coefficients \( \chi^{(n)} \) are the \( n \)-th-order susceptibilities of the material and \( \varepsilon_0 \) is the vacuum permittivity. The first term \( \chi^{(1)} \) is the linear susceptibility with second-rank tensor, which describes the linear optical effects, such as absorption and refraction. The quantities \( \chi^{(2)} \) and \( \chi^{(3)} \) are known as the second- and third-order nonlinear optical (NLO) susceptibilities, respectively, which are normally weaker than \( \chi^{(1)} \). In general, the interaction strength of the nonlinear optical processes typically decreases with a relation of \( |\chi^{(n)}|/|\chi^{(n-1)}| \approx 1/|E_0| \), where \( E_0 \) is average electrical strength in atom (For example \( E_0 \) in a hydrogen atom is \( \sim 10^{11} \) V/m). When the optical field is strong enough, the phenomena caused by higher-order \( (n \geq 2) \) terms become significant, which could induce new radiation at different frequencies, pulse shaping, or change of refractive index.

The second-order NLO effects, including SHG, difference- and sum-frequency generation (DFG and SFG), the Pockels effect, and optical rectification, are typically induced by the second-order NLO susceptibility \( \chi^{(2)} \) in Equation (3.1). The third-order NLO effects, such as THG, four-wave mixing (FWM), optical Kerr effect, and saturable absorption (SA), normally interact with the third-order NLO susceptibility \( \chi^{(3)} \) in Equation (3.1). Although higher-order NLO interac-
tions are normally weak, the HHG, multiphoton absorption/scattering/ luminescence with the \( n^{\text{th}} \)-order NLO susceptibility \( \chi^{(n)} \), appears when the laser intensity is extremely high.

**Figure 3.1.** Examples of photon diagrams of second- and third-order NLO processes.

Different nonlinear optical processes are commonly explained with photon diagrams, shown in Figure 3.1. In general, harmonic generation is utilized to convert an optical signal to higher frequencies. In SHG (THG), two (three) incident photons at the frequency \( \omega \) create light radiation at the frequency \( 2\omega \) (3\( \omega \)), as shown in Figure 3.1. SHG and THG are the most frequently used nonlinear optical processes for various frequency conversion applications. In SFG, which is analogous to SHG with the difference that the two input photons have different frequencies (i.e., \( \omega_1 \) and \( \omega_2 \)) and the energy from the \( \omega_1 \) and \( \omega_2 \) waves is converted into that at the sum frequency \( \omega_3 \) (i.e., \( \omega_3 = \omega_1 + \omega_2 \)). Note that nonlinear processes (in particular various parametric processes, such as SHG, SFG, FWM) are typically phase sensitive, therefore efficient nonlinear frequency conversion requires a proper phase relationship between the interacting waves (i.e., phase-matching). In the case of SHG, perfect phase-matching requires an identical refractive index at different interacting waves (i.e., \( n(\omega_i) = n(2\omega_i) \)), which is challenging in materials that typically exhibit normal dispersion. To achieve ideal phase-matching, common phase-matching methods involve the use of crystal birefringence and the periodic poling of the crystal. In DFG, the frequency of the generated photon is the difference of the two input frequencies, (i.e., \( \omega_3 = \omega_1 - \omega_2 \)), shown in Figure 3.1. When two optical waves at frequencies \( \omega_1 \) and \( \omega_2 \) interact inside a \( \chi^{(2)} \) nonlinear crystal, an additional input light at frequency \( \omega_2 \) can be
amplified in the DFG process. This is called optical parametric amplification (OPA), which can be utilized to create tunable light amplifiers by mixing the output of two lasers operating at different frequencies. When such an amplification process happens inside an optical resonator, the gain from DFG can produce light oscillation if the gain is larger than cavity loss. These kinds of devices are called optical parametric oscillators (OPO) and they are commonly used to produce wavelength-tunable coherent light (e.g., from the near- to mid-infrared or even terahertz spectral regions). The wavelength tuning in OPOs is achieved by varying the phase-matching condition with the orientation or the temperature of the nonlinear optical crystals. This makes OPOs technologically valuable devices to produce broadband wavelength-tunable light at frequencies that are difficult to achieve with conventional lasers.[88,89]

Because the input optical field and its dielectric polarization in materials are vector quantities, the nonlinear susceptibility is a tensor, which depends on the symmetry of the nonlinear optical material. For example, $\chi^{(2)}$ is a third-rank tensor with 27 Cartesian components. A complete description of the nonlinear interaction in the case of SFG, therefore, requires 12 of these tensors yielding a total of 324 different and possible complex components that need to be specified.[88,89] Fortunately, intrinsic permutation symmetry and crystal symmetry decrease the number of independent components. This makes nonlinear optical effects (e.g., SHG DFG, THG, FWM, Figure 3.1) a very sensitive method for probing the crystal symmetry of given materials.[88,89] Furthermore, the second-order or other even-order nonlinear optical effects can only occur in a material that lacks the centre of inversion symmetry. Therefore, the second-order nonlinear optical effects, such as SHG, are dipole-forbidden in centrosymmetric materials. However, second-order nonlinear optical effects can occur at the surface (or interface) of a centrosymmetric material by surface (or interface) induced symmetry breaking [90]. On the contrary, third-order nonlinear optical
effects are allowed in all materials regardless of the crystal symmetry. Nevertheless, the components both second-, third-, and high-order susceptibility tensors all strictly depend on the crystal symmetry of the materials. Nevertheless, SHG, THG and HHG can be very sensitive to the orientation of the sample and the polarization of the incident field. For these reasons, nonlinear optical processes provide a convenient method for probing the crystal symmetries of various materials.

Research on nonlinear optics is growing daily and the field of nonlinear optics plays a major role in emerging photonic and optoelectronic technologies, such as coherent laser sources, signal processing, ultrafast switching, ultrashort pulsed laser, imaging, sensors and so on (Figure 3.2). Thus, it has attracted huge interest, and this has led to significant progress over the past decade. In below Sections, the current state-of-the-art 2D materials based representative NLO processes is presented.

3.2 Harmonic generations in 2D materials

After the first experimental demonstrations of harmonic generation in 2D materials (e.g., surface SHG in graphene [91], SHG in MoS₂ [22,92-95], THG from graphene [45,46] and MoS₂ [96-99]), significant research efforts have been directed to this topic. Since then, demonstrations of SHG and THG have been reported from a wide range of monolayer and few-layer 2D materials, including BP [100-102], WSe₂ [21,25,103,104], WS₂ [105-108], MoSe₂ [109,110], GaSe [111-115], GaTe [116], h-BN [92,117,118], MoTe₂ [119-121], InSe [122], ReS₂ [123], CrI₃ [124], and AgInP₂S₆ [125]. Most of these results have revealed that 2D materials exhibit exceptionally large NLO susceptibilities (e.g., \( \chi^{(2)} \approx 10^{-7} \text{ mV}^{-1} \)) [92,93], implying huge potential of these materials for various applications (e.g., ultrafast pulse characterization [126], telecom wavelength conversion [127,128]).

3.2.1 Second-harmonic generation

The lack of inversion symmetry in a material can give rise to a strong SHG signal under an intense optical pump. The observation of SHG in monolayer MoS₂ with ~800 nm excitation wavelength was reported in References [20,22,129]. It demonstrated that SHG in monolayer MoS₂ is orders of magnitude larger than that of bilayer or bulk MoS₂, as expected from their crystal symmetry properties [129]. Note that SHG signal also has been observed in monolayer graphene [91,130], even-number layered MoS₂ [131] and WSe₂ [132] flakes, and spiral WS₂ nanosheets [133] by symmetry breaking. In addition to the NLO response at the wavelength of ~800 nm, another interesting wavelength range is ~1550 nm, commonly used for optical telecommunication related applications. With the fundamental wavelength close to 1550 nm, the reported \( \chi^{(2)} \) values (i.e., in the range of few pmV⁻¹ for MoS₂ [97,134,135] and MoSe₂ [109,110]) are clearly lower than that measured with 800 nm lasers. The difference between measured results at 800 nm and 1550 nm was attributed by the exciton resonant enhancement [109].
The effects of strongly bound excitons on the SHG in monolayer TMDs have attracted much attention. Reference [20] tuned the excitation wavelength from ~680 to 1080 nm to study the wavelength dependence of the SHG in monolayer MoS₂. It was found that the SHG intensity is significantly enhanced when the SHG wavelength overlaps with the energy of the C exciton (~2.8 eV), as shown in Figure 3.3(a). Second-order sheet susceptibility value of \(\sim 8 \times 10^4 \text{pm}^2 \text{V}^{-1}\) was reported, when the SHG is in resonance with the C exciton.[20] The C exciton was further indicated as the band nesting region with singularities of the joint density of states.[94] For comparison purposes, an effective bulk-like second-order NLO susceptibility is typically obtained by dividing the sheet susceptibility with the thickness of the monolayer (e.g., 0.65 nm for MoS₂) yielding an effective bulk-like second-order susceptibility of ~0.1 nm V⁻¹.[20] Roughly similar values were also reported for MoS₂ in other studies [129,137] as well as for WS₂[105] and WSe₂[103] at the same wavelength range. The SHG has also been found in the symmetry materials by exciting the electric-quadrupole term of second-order susceptibility. For example, graphene has been found with strong SHG by optical dressing an in-plane photon wave vector and proper carrier doping.[58] In addition, by stacking graphene into twisted bilayer graphene, the inversion symmetry is broken at typical angel and a strong SHG has been observed, which introduces a new way of symmetry engineering for SHG process.

Figure 3.3. Harmonic generation in 2D materials: (a) Measured absorption (solid lines) and second-order susceptibility (circles) of MoS₂. Data shown on blue is from monolayer and green is from tri-layer MoS₂. Exciton peaks (i.e., A, B and C) are also indicated. [20] (b) SHG, THG and FHG in monolayer MoS₂. Inset: THG image of a MoS₂ flake.[134] (c) HHG in monolayer graphene with different polarized light excitations.[51] (d) HHG in monolayer MoS₂.[138]
In monolayer TMDs, the two polarization components of SHG depend on the crystal orientation as [129]: $I_\parallel = I_0 \cos^2(3\theta)$ and $I_\perp = I_0 \sin^2(3\theta)$, where $\theta$ is the angle between the mirror plane and the input light polarization, $I_0$ is the maximum intensity of the SHG [129], and $I_\parallel$ and $I_\perp$ are the SHG intensity components parallel and perpendicular to the input light polarization, respectively. Therefore, SHG can be efficiently utilized to probe the crystallographic orientation of 2D materials, by measuring the SHG intensity parallel or perpendicular with the excitation polarization direction.

### 3.2.2 Third-harmonic generation

In contrast to SHG, THG can be possibly observed in materials regardless of symmetry selection rules. References [44-46] reported on the observation of THG in graphene. For instance, Reference [46] obtained a $\chi^{(3)}$ value of graphene by comparing the THG signal from graphene to that of SiO$_2$ based substrates (e.g., fused silica), reporting that $\chi^{(3)}$ of graphene ($\sim 10^{-19}$ m$^2$ V$^{-2}$) is nearly 3 orders of magnitude larger than that of fused silica ($\sim 2.5 \times 10^{-22}$ m$^2$ V$^{-2}$).[88,89] Note that the reported $\chi^{(3)}$ values of graphene measured with various excitation wavelengths range from $\sim 10^{-15}$ m$^2$ V$^{-2}$ [19,44] to $\sim 10^{-19}$ m$^2$ V$^{-2}$ [97,139]. Such a large deviation between the measured values reflects the challenge in accurate measurement of optical nonlinearity of nanomaterials. On the other hand, the large deviation of the measured $\chi^{(3)}$ values in graphene also highlights that the optical nonlinearity in graphene and other 2D materials can be very sensitive to various parameters (e.g., substrates [140-142], defects [143], doping [141], strain [144], chemical treatment [98]). Despite these deviations, it is clear that 2D materials possess large third-order susceptibilities potentially for a wide range of applications. Other 2D materials (e.g., MoS$_2$ [97,98,134] in Figure 3.3(b), BP [100-102], and GaSe [111]) have also been shown to possess $\chi^{(3)}$ in the same range as graphene for relatively large THG. In addition, it has been demonstrated that THG can be used as a rapid and large-area characterization method for determining the crystallographic orientations of exfoliated BP [100] and the grain boundaries of chemical vapor deposited TMDs[98].

### 3.2.3 High-harmonic generation

High-harmonic generation (HHG) can provide an alternative light source in the deep ultraviolet or even the X-ray spectral range, which has been widely used to produce pulses with attosecond [145] (or even zeptosecond [146]) durations for various fundamental research experiments (e.g., monitoring electronic motion inside materials). Traditionally, HHG is observed from atomic gases [147,148] and more recently from various bulk crystals (e.g., ZnO [149], and GaSe [150]). However, the underlying mechanism of HHG in bulk solids is still under debate.[138]

HHGs that were experimentally observed in graphene [51] and MoS$_2$[138] might provide some indications for the behind mechanism. Reference [51] studied the 5$^{th}$, 7$^{th}$, and 9$^{th}$ harmonics in graphene, and observed that HHG signal in graphene is dramatically enhanced under elliptically polarized excitation.
Nonlinear optics in 2D materials (Figure 3.3(c)), in which the ratio between the bandgap and Rabi frequency in graphene strongly affects the HHG performance.[51]

MoS₂ with a finite bandgap is different from zero-gap graphene.[51] Reference [138] studied the HHG in MoS₂ with an intense mid-IR excitation (0.3 eV), as shown in Figure 3.3(d). It reveals that generated harmonics up to the 13th order emerge in the visible range, where the odd-order harmonic efficiency per layer exhibits significant enhancement compared to the bulk, which is attributed by the electronic correlation effects.[138] Furthermore, the band nesting effect has been found to contribute the strong even-order HHG, which further indicates contribution of the interband transitions.[151] These key findings of these proof-of-principle HHG results observed in monolayer [51,138,152,153] and thick-layer [154] materials suggest that much more research efforts are likely to come in the near future, which would fully discover the potential mechanisms behind the HHG.

Figure 3.4. (a) FWM spectra of a graphene flake excited with pump pulses at different wavelengths. The dashed line represents the wavelength dependence predicted by nonlinear quantum response theory.[19] (b) Schematic illustration of FWM-based wavelength conversion in a BP-deposited integrated fiber device. Inset: bandgap of BP.[155] (c) NLO absorption of graphene at different wavelengths.[31] (d) A typical configuration of 2D materials based ultrafast fibre lasers. Inset: an optical image of a BP (marked by pink dotted line) integrated fiber device. The red dot indicates the optical fibre core. PC: polarization controller; LD: laser diode; WDM: wavelength division multiplexer; EDF: Erbium-doped fiber; ISO: isolator.[156]

3.3 Four-wave mixing

Four-wave mixing (FWM) is widely employed for various applications, such as wavelength conversion, optical signal amplification, imaging, and many other
light manipulation applications. Graphene-based FWM was first reported in the near-infrared region. Figure 3.4(a) shows the measured NLO response of monolayer graphene as a function of the emission wavelength for several combinations of pump wavelength $\lambda_1$ and $\lambda_2$, where the large FWM signal is usually attributed to the coherence of NLO processes with the strong interband electron transitions. By integrating 2D materials with various photonic structures (e.g., photonic crystal cavities, micro-ring resonators, microfibers), FWM based NLO devices have been realized. For example, high $Q$-factor silicon photonic crystal microcavity has been used to demonstrate cavity-enhanced FWM in graphene. The conversion efficiencies were observed up to $10^{-3}$ at a cavity $Q$-value of 7500 with a low pump power of 600 $\mu$W. Another example is to integrate BP into microfiber to achieve ultrafast optical switching with FWM, as shown in Figure 3.4(b). FWM induced wavelength conversion was enhanced by depositing BP on a D-shaped optical fiber, with an estimated conversion efficiency of $\sim 10^{-7}$, indicating that BP could provide a good platform for ultrafast optical switching at high speed up to 20 GHz.

### 3.4 Saturable absorption

Saturable absorption effect in 2D materials has been widely used in ultrafast fiber lasers. These lasers with output pulse duration in picosecond or femtosecond timescale can be constructed by placing a saturable absorber inside a laser cavity. While the real part of the third-order NLO susceptibility (i.e., $\text{Re}(\chi^{(3)})$) is responsible for typical third-order NLO processes (e.g., FWM and THG), the imaginary part (i.e., $\text{Im}(\chi^{(3)})$) dominates the nonlinear absorption such as multi-photon absorption, optical limiting, and SA property. Note that higher-order susceptibility (e.g., $\text{Im}(\chi^{(5)})$) can also contribute to SA.

In the past decade, the demonstration of graphene based saturable absorbers has created a new paradigm for building ultrafast pulsed lasers. Figure 3.4(c) shows a graphene SA at different pump wavelengths, which indicates its broadband operation property. A typical 2D material integrated fiber laser is shown in Figure 3.4(d). More recently, other 2D materials have also been demonstrated for saturable absorbers (e.g., MoS$_2$, WS$_2$, WSe$_2$, ReS$_2$, BP) in Figure 3.4(d)). Thus far, 2D materials have been integrated in various lasers (such as solid-state, waveguide, fiber, and semiconductor lasers) to generate ultrashort optical pulses.

### 3.5 Difference-frequency generation

Difference-frequency generation (DFG) is of great significance a large range of applications. It plays the main role for generating coherent light at longer wavelengths and acts as the base for other second-order nonlinear parametric interactions such as optical parametric generation (OPG), amplification (OPA) and oscillation (OPO), which enable to produce tunable light sources across
different spectral regions for a large variety of applications including material characterizations, laser spectroscopy, and molecular sensing.[195]

Along with SHG, SFG, the exploration of DFG, a frequency down-conversion process in 2DMs would extend the application range of nonlinear optics. Thus far, DFG in graphene has been observed in terahertz region.[196] With symmetry broken, the DFG in TMDs has been observed within single layer thickness. Figure 3.5(a) plots the spectra of DFG process: an idler output under the excitation of pump and signal pulses. The idler power shows the linear relationship with the pump and signal power (Figure 3.5(b, c)). The generated idler power indicates an effective second-order nonlinear susceptibility $\chi^{(2)} \approx 1.8 \times 10^{-8}$ m/V, comparable to other reported values.[20] The maximum quantum conversion efficiency from the pump to the idler in this DFG process is calculated as $\approx 2 \times 10^{-4}$.

![Figure 3.1. DFG process in monolayer MoS$_2$. (a) The generated DFG spectrum; (b) DFG power of the idler at 595 nm as a function of the pump power with the signal power fixed at $\approx 2.5 \mu W$; (c) The DFG idler power dependence on the signal power with the fixed pump power at $\approx 0.9 \mu W$. Adapted from Publication 1.](image)

The single-layer thick TMDs physically limits the light–matter interaction length. By employing the thicker sample such as 3R-type bulk MoS$_2$ with broken inversion symmetry, the higher DFG conversion efficiency would be realized.[197] On the other hand, with external cavities (such as photonic-crystal nanocavity, micro–ring resonator, whispering-gallery cavity and metallic plasmon), or waveguides (including microfibers, on-chip waveguides) is also promising for further improvements. With these methods, the possible observable OPA is expectable. Further, with proper assistance of the cavities, OPO operation with 2D materials could be achieved.[198]
3.6 Engineering nonlinear optical responses

Active and efficient control of optical responses is the major function for optical signal processing, which is intrinsically connected to the nonlinear optics. In 1962, electrically tunable SHG have been achieved at the surface of calcite crystal by inducing a third-order optical nonlinearity with a DC electric field.[199] In 2D materials, tunable nonlinear optical responses have been largely developed, mainly depending on the tunable resonant optical transitions. Figure 3.6(a) shows a structure with monolayer MoS$_2$ to electrical tune optical nonlinearity. With the device, FWM signals at A, B excitons have been electrically tuned with around 80% depth, while that without exciton assistance remains unchanged (Figure 3.6(b)). The electrically tunable SHG with similar structure has also been demonstrated in WSe$_2$.[136] On the other hand, the tunable THG and FWM have been reported in graphene with help of Fermi level and hot carriers [63,64], of which the linear dispersion of Dirac fermions promises a wide-band optical tunability. The gate dependent nonlinear optical responses can be further developed into waveguide integrated devices [65,200] and ultrafast fiber lasers [66]. Tunable nonlinearities in 2D materials offer many advantages, such as fast speed and compact footprint, for the future optoelectronic applications.

Figure 3.2. (a) An illustration of a MoS$_2$ tunable nonlinear optical device. (b) Gate tunable FWM at A (~650 nm), B (~610 nm) excitonic states and off-resonance (~700 nm). (c) An illustration of enhanced FWM from a hybrid MoS$_2$-plasmonic structures. Inset: simulated electric field enhancement in the plasmonic structure. (d) Experimental FWM signals at different wavelengths from the hybrid MoS$_2$-plasmonic structure (coloured curves) and bare MoS$_2$ (gray curves). Figures (a) and (b) are adapted from Publication 8. Figures (c) and (d) are adapted from Publication 9.

However, the atomic thickness of 2D material limits the length of its nonlinear interaction with light. The absolute conversion efficiency is still low, typically around $10^{-10}$. Further development to enhance the nonlinear optical interaction
Nonlinear optics in 2D materials is necessary. In fact, various platforms, such as optical cavity [47,201], plasmons [202], metasurface [203] have been explored to enhance the optical nonlinearities.[204] Figure 3.6(c) gives an example of bowtie based plasmons enhanced FWM. The enhancement of FWM signals with such structure can be achieved with one order of magnitude, as shown in Figure 3.6(d). The equivalent third-order nonlinearity of the hybrid MoS$_2$-plasmonic structure is in the order of $10^{-17}$ m$^2$/V$^2$, superior ($\sim$10–100-time larger) to the widely used conventional bulk materials (e.g., LiNbO$_3$, BBO) and nanomaterials (e.g., gold nanofilms).

Although the nonlinearities including second- and third-order susceptibility in 2D materials have been significantly increased via various advanced methods (e.g. cavities, plasmonic, and waveguides), the current development of 2D materials for the practical applications remains elusive. Nevertheless, further investigations on physics and characterizations in 2D materials could deepen the understanding of the nonlinear optical phenomena and potentially pave a way for advanced applications in the field of optoelectronics and nanophononics.
Nonlinear optics in 2D materials
4. Transient linear and nonlinear absorption in monolayer MoS$_2$

The topic of light–matter interaction in semiconductors has raised a remarkable interest for various photonic and optoelectronic applications, which is intrinsically determined by the bandgap of the materials involved. To extend the applications beyond the bandgap limit, it is important to study the light–matter interaction below the material bandgap. In this chapter, we study ultrafast optical absorption of monolayer MoS$_2$ in its sub-bandgap region from ~0.86 μm to 1.4 μm under the ultrafast pump light excitation. Our objective would elucidate the fundamental understanding regarding the optical properties, excited carrier states, and carrier dynamics in the technologically important near-infrared region, which potentially lead to various photonic and optoelectronic applications (e.g., excited-state-based photodetectors and modulators) of two-dimensional materials and their heterostructures beyond their intrinsic bandgap limitations.

4.1 Linear optical properties in monolayer MoS$_2$

![Figure 4.1. Optical characterization of monolayer MoS$_2$. (a) Microscope image, (b) Raman spectrum, where $\Delta$ is the difference between two Raman peaks. (c) Linear reflection (black) and photoluminescence (red) spectra. The blue and violet curves are the Lorentz fitting corresponding to the A, B excitonic resonances. Adapted from Publication 1.](image)
We use monolayer MoS$_2$ as a typical representative of TMDs. Monolayer MoS$_2$ is grown on a SiO$_2$/Si substrate (the thickness of SiO$_2$: 285 nm) via vapor-liquid-solid method. First, $\sim$2 mg/mL Na$_2$MoO$_4$ aqueous solution was spin-coated on the substrate at 6000 rpm for 30 seconds. Then, the Na$_2$MoO$_4$ coating is sulfurized in sulphur vapor to obtain monolayer MoS$_2$ at $750^\circ$C for 5 min.[205,206]

As shown in Figure 4.1(a), the MoS$_2$ flake has a triangle shape. The Raman measurement (Figure 4.1(b)) is performed with peaks of an in-plane mode ($E_{2g}$) located at $\sim$384 cm$^{-1}$, and an out-of-plane mode ($A_{1g}$) at $\sim$402 cm$^{-1}$. The difference between these two modes is around $\sim$18 cm$^{-1}$, indicating the monolayer structure.[207] Further, the monolayer MoS$_2$ flake is characterized by linear optical reflection and photoluminescence measurement. As shown in Figure 4.1(c), the three dips at $\sim$421 nm, 604 nm, 650 nm, appear in the reflection spectrum (black curve), corresponding to the C, B, A excitons. In the meantime, the photoluminescence spectrum (red curve) is also plotted in Figure 4.1(c). Two photoluminescence peaks ($\sim$619 nm and $\sim$673 nm, corresponding to B, A excitons) are obtained by Lorentz fitting, shown as the violet and blue curves. The peak positions are slightly red-shifted comparing with the dips of the reflection spectrum, due to large binding energy in the confined structure. Thus, the experiments indicate that our CVD-grown MoS$_2$ flakes are typically monolayer with relatively high quality.

### 4.2 Pump-probe optical setup

![Figure 4.2. Pump-probe setup. BS: beamsplitter, DM: dichroic mirror, PMT: photomultiplier tube. Adapted from Publication 1.](image)

To perform the transient optical interaction, we built an experimental setup as shown in Figure 4.2. Femtosecond ($\sim$220 fs) pulses from an amplified Ti:sapphire laser system at the wavelength of $\sim$812 nm with a repetition rate of 2 kHz are employed as a light source. The output beam is first divided into two beams, one is applied for the generation of pump pulses at $\sim$400 nm via frequency doubling with a BiBO crystal and the other for generating the tunable near-infrared pulses ($\sim$1300 to 1550 nm) by pumping a TOPAS system (Light conversion). The
pump and idler beams are combined by a dichroic mirror (DM) and then focused by an objective (40×, NA, 0.75) on the target sample. The full width at half maximum of the pump and idler beam spots is ~2.5 μm. A delay line is employed to synchronize pump and probe pulses. The probe is then collected with the same objective lens by a reflection configuration and finally focused into a monochromator followed by a photomultiplier tube (PMT). Colour filters are used in order to remove the residual pump light before the monochromator. A microscopy is installed in the system (not displayed here) with a white light illumination and a CCD camera to check the sample. This system is also used for the experiments carried in chapters 5 and 6 after minor modification.

4.3 Transient optical absorption

Ultrafast transient absorption (TA) properties of ML-MoS\(_2\) flakes are explored in the NIR region from ~0.86 to 1.4 μm wavelength and investigated with its ultrafast carrier dynamics when excited by the pump light at 400 nm in a reflection geometry. The normalized time-resolved absorption modulation (Δ\(A\)) mapping is shown in Figure 4.3(a), with an average probe power \(P_s\)~1.5 μW and average pump power \(P_p\)~0.3 μW. The zero-delay position is indicated by a black solid line, which is determined by the difference-frequency generation between the pump and probe pulses. Due to the presence of the pump, it clearly shows that the absorption of the probe beam in monolayer MoS\(_2\) changes across the whole probe spectrum range. As shown in Figure 4.3(b), the time-resolved absorption modulation (Δ\(A=A_1-A_0\)) at the probe wavelength of ~1.13 μm is displayed, where \(A_1\) and \(A_0\) are the absorptions with and without the presence of pump light. The delay time \(\Delta \tau\) is the relative time difference between the pump and probe pulses on the sample.

![Figure 4.3. Broad transient absorption in the NIR region.](image)

(a) Mapping of normalized absorption modulation (Δ\(A\)) over the probe spectrum range from ~0.86 to 1.4 μm. Average pump power \(P_p\) (intensity \(I_p\)) is ~0.3 μW (~4.53 GW/cm\(^2\)) and average probe power \(P_s\) (intensity \(I_s\)) is ~1.5 μW (~28.93 GW/cm\(^2\)). (b) The time-resolved absorption modulation when the probe is at 1.13 μm. An illustration of rise time (\(\tau_0\)), fast recovery (\(\tau_1\)), and slow recovery (\(\tau_2\)) time constants are labelled. The rising and decay curve fit with the single and bi-exponential function, respectively. Adapted from Publication 7.
The results clearly show TA modulation, which first rises and then decays. The rising of $\Delta A$ (marked in purple color) from zero to its maximum value is very fast. With the presence of pump light $\Delta A$ is immediately increased with a single-exponential rising time constant ($\tau_0 = \sim 538$ fs). Once absorption modulation $\Delta A$ reaches its highest level, it starts to recover. At the beginning of the decay, the intensity of $\Delta A$ drops down to a certain level very quickly (marked in magenta color) and then decays slowly (marked in green color). Therefore, the decay dynamics can be fitted (red curve) by two exponential time constants (i.e., fast ($\tau_1$) and slow recovery ($\tau_2$) constants). At the probe wavelength 1.13 $\mu$m, the fitted $\tau_1$ and $\tau_2$ are $\sim 1.02$ ps and $\sim 80.5$ ps respectively. It is evident that the carrier dynamics is pretty independent of both pump and probe powers. Since the carrier dynamics did not exhibit a strong dependency on pump and probe fluence, therefore we can rule out exciton-exciton annihilation processes.

We therefore conclude that the enhancement of absorption in this wavelength range of our experiments ($\sim 1\mu$m) is due to the formation of the exciton, where the rising time constant $\tau_0$ of $\sim 477\pm 80$ fs is close to the time constant for exciton formation in ML-MoS$_2$ as reported in [208,209]. After ultrafast thermalization and formation and excited states, the hot carriers relax via a two-step process, which indicates the decay dynamics. The initial fast recovery is happening within the time range of $\sim 1.05\pm 0.39$ ps, which is very well matched with the process of fast carrier capture due to defects as reported by Wang et al. [210]. The invariant TA dynamics over pump power and linear increment of absorption modulation $\Delta A$ (Figure 4a) further ensure this process. The slow recovery component has a time constant of tens of picoseconds ($\sim 93.9\pm 14$ ps) corresponds to the carrier-phonon scattering.[41,211-213]

**Figure 4.4.** Power dependent of transient absorption ($\Delta A_{\text{max}}$). $\Delta A_{\text{max}}$ at few selective probe light wavelengths w.r.t (a) pump and (b) probe light power with a fixed probe light power of 1 $\mu$W and pump light power of 0.3 $\mu$W respectively. Adapted from Publication 7.
Further, we studied both $P_p(I_p)$ and $P_s(I_s)$ dependent $\Delta A_{\text{max}}$ by keeping $P_s(I_s)$ and $P_p(I_p)$ constant successively with an appropriate delay time $\Delta \tau$ where $\Delta A$ is maximum. The dependency of $\Delta A_{\text{max}}$ on $P_p(I_p)$ by keeping $P_s(I_s)$ fixed at $\sim 1 \mu W$ ($\sim 19.29$ GW/cm$^2$) is shown in Figure 4.4(a) for a few selective probe wavelengths. There is a linear relationship between $\Delta A_{\text{max}}$ and $P_p$ at the beginning. When $P_p(I_p)$ reached $\sim 0.5 \mu W$ ($\sim 7.55$ GW/cm$^2$) and beyond, $\Delta A$ become saturated and has no observable change within the error limit. The linear dependence of $\Delta A$ on $P_p$ (i.e., $\Delta A_{\text{max}} \propto P_p$), indicates one-photon excitation and contribution process (i.e., one absorbed pump photon creates one excited carrier, and presents excited-state introduced absorption at the probe wavelength). Additionally, the saturation of absorption modulation $\Delta A_{\text{max}}$ for the pump beam power can be attributed to the deficiency of photo-excited carriers after the power crosses a certain threshold. The saturation can be caused by Pauli blocking, which explains the recently reported saturable absorption in TMDs and their applications in ultrafast pulse generation.[167]

Similarly, the influence of $P_s(I_s)$ on $\Delta A_{\text{max}}$ has been studied with a fixed $P_p(I_p)$ of $0.3 \mu W$ (4.53 GW/cm$^2$) at different probe wavelengths as depicted in Figure 4.4(b). The observed maximum value of $\Delta A_{\text{max}}$ is as high as $\sim 4.2\%$ of the 1.13 $\mu$m probe wavelength. Here we observe nonlinear relation between $P_s$ and $\Delta A_{\text{max}}$ at the beginning till to the saturation effect at high $P_s(I_s)$. The power dependence before saturation can be fitted with at $\Delta A_{\text{max}} \propto P_s^\alpha$ at fixed $P_p$, where $\alpha$ is the power-law coefficient. The value of $\alpha$ at different probe wavelengths is shown in the inset of Figure 4.4(b). Dependency of $\Delta A$ on $P_s$ (i.e., $\Delta A_{\text{max}} \propto P_s^\alpha$) is nonlinear which signifies that two-photon absorption (TPA) phenomena at the probe wavelength takes place before it hits the saturation region. The value of $\alpha$ has a tendency to decrease with the increase of probe wavelength which indicates that the two-photon absorption is more dominant at the shorter probe wavelengths and becoming linear at the longer wavelength range. This is possibly due to the enhanced intraband absorption at a longer wavelength of the excited carriers, which is expected to be linear. Here, the saturation of absorption modulation $\Delta A_{\text{max}}$ for the probe beam power also can be attributed the Pauli blocking effect.
Dynamic control of light-matter interaction is of significant importance for the generation, modulation, and detection of optical signals. Besides the linear absorption control in chapter 4, it is extremely fascinating to all-optically modulate nonlinear optical responses of materials for a large range of applications, such as optical data processing, optical communications[9], optical frequency comb generation, and quantum optics[214]. The efficient strategies to all-optically control the SHG process have still remained elusive, while it has been reported previously with metals[11] and semiconductors [12,13,15,215]. Novel all-optical modulation methods with new materials are thus of great significance for various emerging and future applications (e.g., on-chip nonlinear photonics).

In this chapter, we report a giant, ultrafast, and broadband modulation of second harmonic generation with excitons in monolayer MoS₂. Optically excited dark exciton states can significantly modulate SHG in MoS₂ with weak control light. Thanks to the strong excitonic effect, a giant enhancement factor of up to ~400 times is achieved at room temperature, one order of magnitude larger than the current state-of-the-art methods using metallic or semiconducting nanostructures. Moreover, the modulation amplitude and sign of SHG variation can be adjusted with various intra-excitonic dynamics, such as transitions associated with dark (e.g., 2p, 3p) and bright (e.g., 1s, 2s) states. Our results not only present a complementary method to the currently widely used linear absorption-based pump-probe spectroscopy for providing insights into the intriguing exciton dynamics of 2D materials, but also offer a new scheme for all-optical nonlinear photonic and optoelectronic based on excitons.

5.1 Second-harmonic generation

We first investigate SHG in monolayer MoS₂. The monolayer MoS₂ is grown on a SiO₂/Si substrate by using the chemical vapor deposition method with a ~10 mg sulphur (at 170 °C) and ~0.5/15 mg NaCl/MoO₃ mixture (at 750 °C) for 5 minutes in high purity Argon (same method in chapter 4). Figure 5.1(a) shows the typical optical image of MoS₂. The SHG is observed with a centre wavelength at 530 nm and bandwidth of 8.4 nm (Lorentz fitting) when the MoS₂ is illuminated with the femtosecond pulsed laser at 1060 nm (Figure 5.1(b)). Figure
Transient second-harmonic generation in monolayer TMDs. The measured SHG signal scales quadratically (~1.95) with the fundamental pump intensity, confirming the second-order nonlinear optical process.

Figure 5.1. Second-harmonic generation in monolayer MoS$_2$. (a) Optical image of monolayer CVD MoS$_2$. (b) SHG spectrum at 530 nm. (c) Power dependence of SHG. (d) Polarization dependence of SHG. Adapted from Publication 3.

Since SHG is very sensitive to crystal symmetry, the polarization-resolved SHG offers crystallographic features of MoS$_2$. The monolayer MoS$_2$ has the D$_{3h}$ point-group symmetry, the second-order susceptibility tensor has nonzero elements with $\chi^{(2)}_{xyx} = -\chi^{(2)}_{yyx} = -\chi^{(2)}_{yxy}$, where x, y, z are crystalline coordinates. And x axis is along with the armchair direction, 30° with zigzag direction, where the mirror symmetry is broken. We have measured the polarization-dependent SHG by employing the linear polarized excitation pulses and the SHG is detected after a polarizer parallel to that of the incident polarization by rotating the sample step by step. Figure 5.1(d) shows the polarization dependent SHG. It displays a clear sixfold pattern, confirming D$_{3h}$ symmetry with the relation of $P_x \sim \sin^2 3\theta$. Similarly, the relation of y element ($P_y \sim \cos^2 3\theta$) can be obtained when the polarizer is set perpendicular to the polarization of incident light.

The SHG process in monolayer TMDs with D$_{3h}$ symmetry requires total angular momentum conservation during light–matter interactions, therefore exhibiting the valley-exciton locked selection rule.[216] For example, during the SHG process, the transition from the ground state to the exciton state at a K valley requires two $\sigma^+$ fundamental photons and emits a $\sigma^-$ SH photon. While in the $\bar{K}$ valley, the situation is opposite, i.e. with $\sigma^-$ incident photons and emitted $\sigma^+$ SH photon. To observe this phenomenon, we use a $\sigma^-$ polarized incident light to excite the SHG. As shown in Figure 5.2, the SHG spectral components shows a
strong emission with $\sigma^+$ polarization and almost zero of $\sigma^-$ polarization. The helicity contrast ($I^{\sigma^+}/I^{\sigma^-}$) is calculated as ~96%, confirming the valley selection rule from the $D_{3h}$ crystal symmetry.

![Figure 5.2. Generated spectra of $\sigma^+$ SHG and $\sigma^-$ SHG when the incident fundamental light is 1060 nm with polarization of $\sigma^-$. Adapted from Publication 3.](image)

We further explore the wavelength-dependent SHG and uncover the C exciton enhanced SHG, similar to the previously published results.[20] By tuning the incident pulses with a wavelength range from 880 nm to 1160 nm and fixing the incident power at 2 $\mu$W, the broadband SHG is obtained as shown in Figure 5.3. Clearly, the strong enhancement of SHG is observed at 450 nm corresponding to the C exciton by comparing the linear reflection spectrum in Figure 4.1(c). And the largest enhancement is calculated with a ratio of 65 times with comparing maximum to minimum SHG. The C exciton is originated from the band nesting effect that occurs when conduction and valence bands are approximately equi-spaced over regions in the Brillouin zone. The band nesting region has singularities of the joint density of states and therefore results in a strongly enhanced optical response including linear and nonlinear effects.
5.2 Transient second-harmonic generation in MoS$_2$

Figure 5.4(a) shows our simplified characterization setup, by which we study the SHG produced by seed light pulses as a function of delay time $\Delta \tau$ with respect to control light pulses in monolayer MoS$_2$ (Detail in Figure 4.2). We present a typical SHG modulation result in Figure 5.4(b), similar to the previously results.[217-224] A readily available control light of photon energy $h\omega_c \approx 3.1$ eV ($\lambda_c \approx 400$ nm wavelength) above the C-exciton peak is chosen. The SHG signal at $h\omega_{SHG} \approx 2.36$ eV ($\lambda_{SHG} \approx 525$ nm) generated by the seed light at $h\omega_s \approx 1.18$ eV ($\lambda_s \approx 1050$ nm) is immediately enhanced by the control light with a single-exponential rising time constant ($\tau_0 \approx 600$ fs, orange fitted line). After $\Delta \tau \approx 1.3$ ps, the SH intensity starts to decay, exhibiting two exponential time constants ($\tau_1 \approx 4.4$ ps and $\tau_2 \approx 33$ ps, red fitted line). The SH spectra at $\Delta \tau = -1$ and 1.3 ps are shown in Figure 5.4(c), which indicates strong SHG enhancement produced by the control light.

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**Figure 5.4.** Giant SHG enhancement in MoS$_2$ (a), Sketch of the experimental setup. The inset shows an optical image of the MoS$_2$ flakes. (b), Normalized SHG intensity as a function of delay time $\Delta \tau$. The average power of the control and seed light is $\sim 0.5$ and $\sim 2$ $\mu$W, respectively. The pulse duration is $\sim 230$ fs. The inset shows a semi-log rendering of the same data. (c), SH spectra before and after the control light excitation. (d), SHG enhancement factor $\gamma$ as a function of input power/peak-intensity of the control ($P_c, I_c$) and seed ($P_s, I_s$) light. (e), $\gamma$ as a function of the control light power/intensity for $P_s = 2 \mu$W (data along the white dashed line in d). (f), Polar plot of the circular-polarized SHG measured after passing a quarter-wave plate with and without the control light using $\sigma^-$ seed light. In (b)-(e), $h\omega_c \approx 3.1$ eV. In (d)-(f), $\Delta \tau = 1.3$ ps. In (b)-(f), $h\omega_{SHG} \approx 2.36$ eV. Adapted from Publication 3.
Figure 5.4(d) shows the enhancement factor $\gamma$ at $\Delta \tau = 1.3$ ps as a function of the control and seed light powers. The value of $\gamma$ is defined as $\gamma = P_w/P_{wo}$, where $P_w$ and $P_{wo}$ are SHG powers with and without the control light, respectively. We find that $\gamma$ is highly dependent on incident light power. Figure 5.4(e) represents $\gamma$ as a function of control light power when the average seed light power (peak intensity) is $\sim 2 \mu W$ ($\sim 21.9$ GW/cm$^2$). We find that $\gamma$ increases linearly with the control light power ($P_c$) and is slightly saturated when $P_c$ is $> 0.4 \mu W$ (corresponding to a light intensity of $\sim 3.43$ GW/cm$^2$, equivalent to an electron-hole (e-h) pair density of $\sim 5.7 \times 10^{14}$ cm$^{-2}$ considering the measured absorption of $\sim 7.1\%$ at $\sim 3.1$ eV). In Figure 5.4(e), $\gamma$ reaches a maximum of 386 (with a corresponding enhancement of $\sim 19$ times in second-order nonlinear optical susceptibility). Similar enhancement phenomena are observed when the control light energy is changed to $\sim 1.55$ eV ($\lambda_c = 800$ nm) due to two-photon excitations.

Furthermore, we characterize the valley selection rule with and without control light. When switching on and off the control light, the polarization directions of SHG after passing a quarter-wave plate are almost the same (fitted parameters, Figure 5.4(f)), indicating that only $\sigma^+$ polarized SHG is enhanced. This proves that symmetry remains conserved with control light excitation.

To explore the modulation mechanism, we measure the temporally and spectrally resolved SH fractional power changes ($\Delta P_{SHG} = (P_w-P_{wo})/P_{wo}$) at different seed energies ($\hbar \omega_s$ from 0.92 to 1.44 eV) with a fixed control light energy of 1.55 eV. Figure 5.5(a) shows an overview of the broadband wavelength-dependent SHG modulation dynamics. The SHG is enhanced (i.e., $\Delta P_{SHG} > 0$) by the control light when $\hbar \omega_{SHG}$ ranges from $\sim 2.07$ to 2.56 eV ($\sim 598$ - 485 nm). We name this spectral range as the “enhancement region”. A representative result when $\hbar \omega_{SHG} \approx 2.27$ eV is plotted in Figure 5.5(b), showing a dynamic similar to that in Figure 5.4(b). When $\hbar \omega_{SHG}$ ranges from $\sim 2.64$ to 2.88 eV (i.e., $\sim 470$ - 430 nm) or from 1.84 to 2.07 eV (i.e., $\sim 675$ - 598 nm), the SHG is suppressed (i.e., $\Delta P_{SHG} \leq 0$) with the control light. We mark this spectral range as the “suppression region”. A representative result is shown in Figure 5.5(c) when $\hbar \omega_{SHG} \approx 2.85$ eV. In the suppression region, $\Delta P_{SHG}$ drops sharply in the presence of the control light and reaches its minimum within $\Delta \tau \approx 150$ fs, faster than our measured temporal resolution (220 fs). Then, $\Delta P_{SHG}$ recovers with bi-exponential time constants $\tau_1 \approx 590$ fs and $\tau_2 \approx 96$ ps. Between the above-mentioned enhancement and suppression regions in Figure 5.5(a) (i.e., $\sim 2.56$ - 2.64 eV), the results typically show an extremely fast decay ($\Delta \tau \approx 150$ fs) followed by fast recovery with a single-exponential time constant of $\sim 600$ fs. An example of this behaviour with $\hbar \omega_{SHG} \approx 2.58$ eV is plotted in Figure 5.5(d). We denote this spectral region as the “transition region”.


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Figure 5.5. Broadband all-optical SHG modulation dynamics in MoS2. (a), Normalized SHG change $\Delta P_{\text{SHG}}$ as a function of time delay and SHG photon wavelength/energy. The vertical black dashed line indicates $\Delta \tau = 0$ ps position. (b)-(d), $\Delta P_{\text{SHG}}$ response for $\hbar \omega_{\text{SHG}} \approx 2.27, 2.85,$ and $2.58$ eV, respectively. Blue and orange dashed lines mark $\Delta \tau = 0$ and $1.3$ ps. We use $I_c \approx 17.42$ GW/cm$^2$, $\hbar \omega_c \approx 1.55$ eV, and $I_s \approx 32.85$ GW/cm$^2$. Adapted from Publication 3.

In our measurements (Figure 5.5), the time-resolved dynamics are almost independent of the seed and control light powers, whereas the relative SHG change ($\Delta P_{\text{SHG}}$) is linearly related with the control light power in all three regions using the $3.1$-eV control light. Therefore, we can rule out an exciton-exciton interaction effect (e.g., exciton-exciton annihilation and Auger recombination), which commonly exhibit a nonlinear excitation power dependence. We thus can attribute the SHG modulation effects (i.e., enhancement and suppression) to various excitonic transition processes (e.g., scattering, transition, and recombination) in monolayer MoS2.

Figure 5.6. Maximum SHG modulation $\Delta P_{\text{SHG}}$ and optical absorption in monolayer MoS2. (a) SHG change $\Delta P_{\text{SHG}}$ in monolayer MoS2 when $\Delta \tau = 1.3$ ps, $\hbar \omega_c \approx 1.55$ eV, $I_c$
To gain further understanding, we plot $P_{\text{SHG}}$ as a function of the SHG photon energy (Figure 5.6(a)) for fixed seed and control light intensities with a delay $\Delta \tau \approx 1.3$ ps, where the maximum enhancement is achieved. We find that the minimum dip positions in the suppression region are well correlated with the energies of $1s$ bright exciton states (e.g., $1s_A$, $1s_B$, and $1s_C$, where the subscript denotes the exciton species) in the linear absorption spectrum of monolayer MoS$_2$ (Figure 5.6(b)). We thus attribute the observed suppression of SHG to optical bleaching of bright excitons: the control light excites carriers from the ground state into quasi-continuum states with a single-photon excitation process at 3.1 eV (two-photon excitation at 1.55 eV), and the ground state becomes consequently depleted. The depletion suppresses the formation of bright excitons, blocks the typically observed bright excitonic resonance enhancement effect of SHG, and thus reduces the SHG signal.\[20\] The bleaching process is typically fast (normally <100 fs) [208,225], which fits well with the dynamics in the suppression region (Figure 5.6(b)). The subsequent bi-exponential recovery process in the suppression region can be correlated with different carrier relaxation processes, which gradually relax to the ground carrier states: an initial period of fast recovery with characteristic time $\tau_1 \approx 590$ fs can be attributed to carrier cooling dynamics and formation of bright excitons; a slow recovery with a time constant $\tau_2 \approx 96$ ps can be attributed to carrier-phonon scattering and nonradiative carrier recombination. This bi-exponential recovery process is similar to what has been previously reported in linear-absorption-based pump-probe measurements on bright excitons.

Additionally, there are two strong enhancement peaks at ~2.27 and 2.36 eV in Figure 5.6(a), which are far away from the A and B excitons. We verify that these two enhancement peaks are not featured in either the linear inter-band absorption spectrum (Figure 5.6(b)) and the wavelength dependent SHG spectrum (Figure 5.3). Furthermore, as shown in the time-resolved results of Figure 5.5(a), the initial rise time of SHG modulation in the enhancement region ($\tau_0 \approx 600$ fs) is much longer than that in the suppression region (typically ~150 fs). This indicates a completely different carrier dynamics, which excludes various simultaneous or ultrafast nonlinear effects, including ultrafast optical bleaching and optical parametric interactions.
To understand the observed optically-driven SHG enhancement, we elaborate a theoretical interpretation of our experimental results in monolayer MoS$_2$ based on first-principles calculations combined with a phenomenological treatment of optical pumping. We start by producing accurate calculations of the electronic band structure, as well as the exciton energies and wave functions. We then introduce optical pumping through an effective depletion of electrons within an energy interval $\Delta$ at the top of the valence band, accompanied by the corresponding filling near the bottom of the conduction band (Figure 5.7(a)). The optical transition strengths associated with the excitons are then modified by this redistribution of band occupations, which we directly introduce in the electron-hole-pair decomposition of their wave functions. This allows us to produce a map of exciton transition strengths resolved in photon energy and band depletion energy $\Delta$ (Figure 5.7(b)). Spectral variations for selected values of $\Delta$ are shown in Figure 5.7(c) after introducing a spectral broadening to facilitate comparison to the experiment. As the depletion energy increases, we find that the allowed excitations vary considerably: dark excitons with originally low oscillator strength increase their strength and dominate the optical spectrum, while bright excitons become weaker, in qualitative agreement with the experimental observations. We identify four dominant dark excitons in this process (D1-D4), whose real-space wave functions are plotted in Figure 5.7(d). In addition, assuming that all of the energy absorbed by the material from the control light is invested in producing a depletion $\Delta$, we find that the required light intensities are a factor of ~3 lower than those used in the experiments (Figure 5.7(b), right scale), which is reasonable in view of the fact that part of that energy
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can be lost in other dissipative processes (e.g., by spreading the energy among carriers away from the K point).

Table 5.1  Comparison of exciton energies in monolayer MoS2.

<table>
<thead>
<tr>
<th>Exciton</th>
<th>Ref. [225] (eV)</th>
<th>$\Delta P_{\text{SHG}}$ (eV)*</th>
<th>Linear reflection (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s_A$</td>
<td>1.86</td>
<td>1.89</td>
<td>1.9</td>
</tr>
<tr>
<td>$3p_A$</td>
<td>2.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1s_B$</td>
<td>2.01</td>
<td>2.0</td>
<td>2.05</td>
</tr>
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<td>2.22</td>
<td>2.27</td>
<td>-</td>
</tr>
<tr>
<td>$3p_B$</td>
<td>2.37</td>
<td>2.36</td>
<td>-</td>
</tr>
<tr>
<td>$1s_C$</td>
<td>-</td>
<td>2.9</td>
<td>2.93</td>
</tr>
</tbody>
</table>

*This work

Supported by these theoretical calculations, we attribute the SHG enhancement to the modified exciton oscillation strength created by a redistribution of excited carrier. In the enhancement region, we propose that some of the carriers in the quasi-continuum state excited by the control light scatter into low energy bands and modify the e-h composition of the excited dark excitonic states, which acquire a substantial transition strength, thus becoming bright and playing a leading role in SHG (Figure 5.5(b)). In consequence, we attribute the rise time (e.g., $\tau_0 = \sim 600 \text{ fs}$ in Figure 5.4(b)) to the remorphing of the e-h pair composition of dark excitons. The enhancement decreases due to decay of the excited carrier states with a relatively slow bi-exponential behaviour (e.g., $\tau_1 = \sim 2.9 \text{ ps}$ and $\tau_2 = \sim 325 \text{ ps}$ at $2.27 \text{ eV}$). We attribute the fast decay to cooling dynamics of the excited dark excitons, while the slow recovery can be related to carrier-phonon scattering and nonradiative carrier recombination. Note that the decay time in the enhancement region is typically $\sim 10$ times longer than the bi-exponential recovery components in the suppression region induced by bright excitons, which fits well with the results of excited exciton dynamics observed in previous experiments.[226] The leading role of dark excitons can be further confirmed by comparing the enhancement peak positions with calculated dark exciton results [77] and mid-infrared intra-band absorption measurements (details in Table 5.1).[225] We find that the two enhancement peaks at $2.27$ and $2.36 \text{ eV}$ are likely associated with the $2p$ and $3p$ excitonic states, respectively.

To explain the dynamics in the transition region, we plot time-resolved SHG modulation at different time delays in the $2.5$ to $2.6 \text{ eV}$ spectral range as shown in Figure 5.8(a). The results confirm that the time-resolved SHG dynamics is governed by the contributions from the suppression and enhancement effects at different time scales: fast suppression process ($< 150 \text{ fs}$) in the transition region is initially dominated by bright exciton suppression, similar to the suppression region; then, a relatively slow ($\sim 1 \text{ ps}$) enhancement process takes over, similar to the initial response in the enhancement region. Such ultrashort response time allows ultrafast optical modulation. The response time can be measured with 20% to 80% of modulation with a rise (dropout) time of $80 \text{ fs}$ ($900 \text{ fs}$), as shown in Figure 5.8(b). It corresponds to a modulation speed of $\sim \text{THz}$, which is much faster than state-of-the-art electro-optic modulators.[227] And the modulation depth is linearly dependent on the $P_c$ and can be achieved as high as 62% when
$P_c = 1.6 \, \mu W$. The power consumption of $P_c$ is calculated as 800 fJ, indicating a very low power consumption and high efficiency.

![Figure 5.8. Ultrafast optical modulation. (a) $\Delta P_{\text{SHG}}$ spectra at different delays \(\Delta \tau\). (b) $\Delta P_{\text{SHG}}$ with time delay when $h_{\text{SHG}} = 2.58$ eV and $P_c = 0.4 \, \mu W$. (c) Power dependence of $\Delta P_{\text{SHG}}$ when $\Delta \tau = 0.15$ ps. Adapted from Publication 3.]

5.3 Transient second-harmonic generation in WS$_2$

We also carry out the SHG modulation in monolayer WS$_2$ with the same system to the one used for MoS$_2$ by using control light of 400 nm wavelength (3.1-eV photon energy). Monolayer WS$_2$ is grown by the CVD method similar to that with MoS$_2$.\[228\] Figure 5.9(a) shows the optical image of monolayer WS$_2$, exhibiting a typical triangular structure. The photoluminescence centred at 627 nm (1.98 eV) is measured by a 488-nm continuous laser, indicating the strong A exciton resonance (Figure 5.9(b)). And the reflection contrast measured by white light gives clear exciton states of A, B, C excitons at 627 nm (1.98 eV), 519 nm (2.39 eV), 394 nm (3.14 eV), as shown in Figure 5.9(c). Figure 5.9(d) gives the typical Raman shifts of WS$_2$, further confirming the good quality of the sample.

![Figure 5.9. CVD WS$_2$ sample characterization. (a) Optical image. (b) Photoluminescence spectrum. (c) Optical reflectance. (d) Raman spectrum with an excitation wavelength of 488 nm. Inset: Raman map with the 336 cm$^{-1}$ shift peak. Adapted from Publication 3.]

Figure 5.10(a) shows the SHG power dependence on control light and seed light (1170 nm, 1.05 eV). The SHG enhancement factor $\gamma$ increases with increasing control light power, whereas it decreases with increasing seed light power. Figure 5.10(b) shows $\gamma$ as a function of control light power when the seed light power is 1 $\mu$W. It shows that $\gamma$ can be as high as $\sim$76 when the control light power is 0.3 $\mu$W.

The normalized $\Delta P_{\text{SHG}}$ is shown in Figure 5.11(a) as a function of time delay at different seed light wavelengths. The incident average powers of the seed light and control light are $\sim$3 $\mu$W and 0.3 $\mu$W, respectively. As shown in Figure 5.11(a), the time-resolved $\Delta P_{\text{SHG}}$ dynamics with various SHG energies clearly show suppression, transition, and enhancement regions. The SHG modulation results represented in Fig 5.11(b-e) show very similar dynamics when comparing the results of MoS$_2$ at different regions.

Figure 5.11. All-optical modulation dynamics in monolayer WS$_2$. (a) Normalized SHG power change $\Delta P_{\text{SHG}}$ as a function of time delay and SHG photon wavelength/energy. The breaking region signals the overlap between difference frequency generation and SHG. (b)-(e) $\Delta P_{\text{SHG}}$ dynamics when $h\omega_{\text{SHG}} = 1.9$, 2.13, 2.48, and 2.75 eV, respectively. Adapted from Publication 3.
Figure 5.12(a) shows $\Delta P_{\text{SHG}}$ results at a delay time of 2.8 ps. Comparing with the optical absorption results in Figure 5.12(b), we assign the dip at $\sim 1.98$ eV in the suppression region as the bright $1s_A$ state, which also matches well with the PL measurements. On the other hand, the enhancement region in the $\Delta P_{\text{SHG}}$ spectrum ranging from $\sim 2.0$ eV to $2.67$ eV has a strong peak at $\sim 2.11$ eV and two small peaks at $\sim 2.43$ eV and $\sim 2.58$ eV, all of which are not visible in the linear inter-band absorption spectrum.

![Figure 5.12](image)

**Table 5.2.** Comparison of exciton energies in monolayer WS$_2$.

<table>
<thead>
<tr>
<th>Unit: eV</th>
<th>$1s_A$</th>
<th>$2p$</th>
<th>$1s_B$</th>
<th>$3p$</th>
<th>$4p$</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference [78]</td>
<td>2.04</td>
<td>2.28</td>
<td>2.45</td>
<td>2.48</td>
<td></td>
<td>10k</td>
</tr>
<tr>
<td>Reference [229]</td>
<td>2.12</td>
<td>*</td>
<td>2.50</td>
<td>*</td>
<td>*</td>
<td>10k</td>
</tr>
<tr>
<td>Reference [229]</td>
<td>2.02</td>
<td>*</td>
<td>2.40</td>
<td>2.45</td>
<td>2.58</td>
<td>300k</td>
</tr>
<tr>
<td>Linear</td>
<td>1.98</td>
<td>*</td>
<td>2.39</td>
<td>*</td>
<td>*</td>
<td>300k</td>
</tr>
<tr>
<td>$\Delta P_{\text{SHG}}$</td>
<td>1.98</td>
<td>2.11</td>
<td>*</td>
<td>2.43</td>
<td>2.58</td>
<td>300k</td>
</tr>
</tbody>
</table>

* unmeasured point.

The generality of the dark-exciton mechanism and the dynamics unveiled here is also supported by the SHG experiments with monolayer WS$_2$ (Figure 5.12). We could assign those peaks in the enhancement region as $2p$, $3p$, and $4p$ dark states, respectively, by comparing energies of dark states from reference [78,229]. Table 5.2 shows the comparison results. This suggests that all-optical modulation of SHG is indeed applicable to other TMDs as well as their heterostructures. We also note that similar modulation effects are possible in other nonlinear optical responses (e.g., third-harmonic generation, optical-comb generation, and high-harmonic generation), some of which will be discussed in the next chapter.
Nonlinear optical spectroscopy has been widely utilized for the exploration of physical properties in various materials, such as semiconductors, metals, and bio-tissues. Besides SHG discussed in the last chapter, higher-order harmonic generations (HOHG), for example, THG in monolayer MoS$_2$ has been observed with relatively high conversion efficiency.[96,97,134,230] The strong nonlinear responses are contributed from vividly resonance enhancement, which can study electronic properties and thus play a complementary role in linear optical spectroscopy. The relation between HOHG and prominent carrier states (such as A, B, C excitons of monolayer TMDs) has been rarely studied.

In this chapter, we first demonstrate a broadband third-harmonic spectroscopy (THS) and transient THS ranging from ~1.77 to 3.10 eV in monolayer MoS$_2$ to explore prominent fingerprints of various electronic states and realize the efficient THG modulation with an optical method. The carrier dynamics at various states characterized by transient THS could offer a clear sign of carrier trajectories with exciton formation, electron-phonon interaction, and recombination in monolayer MoS$_2$. Further, we investigate the optical control of HHG in monolayer MoS$_2$ and achieve highly efficient HHG modulation at the atomic thickness.

6.1 Broadband third-harmonic generation

To observe the THG of monolayer MoS$_2$, we employ 150-fs laser pulses with the photon energy ranging from ~0.56 to 1.03 eV generated by an optical parametric amplifier (TOPAS) pumped with an 800-nm Ti:sapphire femtosecond laser. The fundamental pulses at $\hbar\omega_0$ are tightly focused on the sample by an objective lens (40×, 0.75 NA.), and the generated third-harmonic pulses at $\hbar\omega_{THG}$ are collected by the same objective, then reflected by a beam-splitter to the spectrometer. The full width at the half maximum of the excitation beam diameter on the sample is ~2.5 μm. Various polarizer and optical filters are used during the measurements. All the incident powers at different wavelengths are calibrated by a power meter behind the objective. All the experiments are performed at room temperature.

Figure 6.1(a) shows the diagram of THG in monolayer MoS$_2$ samples. Strong optical pulses with a photon energy of $\hbar\omega_0$ are incident onto the MoS$_2$ flake, generating pulses with a photon energy of $\hbar\omega_{THG}$ through the third-order optical
Transient higher-order harmonic spectroscopy in MoS₂. A schematic plot of THG is shown in the up-right side of Figure 6.1(a). We tune the pulsed laser at ~0.79 eV with an average power of ~10 μW as the excitation source. The TH signal of monolayer MoS₂ on the sapphire substrate can be found around ~2.38 eV as shown in Figure 6.1(b). When gradually increasing the excitation power, the TH intensity grows with a power dependence of a slope of ~2.7 (Figure 6.1(c)). The dependence of THG on input/output polarization is uniform by rotating the azimuthal angle of the sample, which agrees with the structural symmetry of MoS₂, as shown in Figure 6.1(d). Note that all results here are measured under ambient conditions, and we do not observe the TH signal from the sapphire substrate under the same experimental conditions. This indicates that the third-order nonlinear susceptibility element $\chi^{(3)}$ of MoS₂ is responsible for the TH signal.

\[ |\chi_{\text{eff}}^{(3)}| = \frac{4\varepsilon_0 c^2}{3\omega d} \sqrt{n_{3\omega}^3 n_{3\omega} I_{3\omega}^3 I_{\omega}^3} \]  

where $\varepsilon_0$ and $c$ are the permittivity and speed of light in the vacuum, respectively. And $\omega$, $n_\omega$, $I_\omega$ and $3\omega$, $n_{3\omega}$, $I_{3\omega}$ are the frequency, refractive index, the peak
Transient higher-order harmonic spectroscopy in MoS2 intensity of fundamental and TH pulses, respectively; \(d \approx 0.65 \text{ nm}\) is the thickness of monolayer MoS2. Here we use the value of \(n_0 = 3.5, n_3 \approx 4.6\) for the refractive indices at a photon energy of ~0.79 and ~2.38 eV.[231] When the excitation pulses is ~10 \(\mu\text{W}\) (peak power: ~141 GW/cm\(^2\)), the power of TH signal is ~16 fW. Thus, we can obtain the value of \(|\chi^{(3)}| \approx 5 \times 10^{-19} \text{ m}^2/\text{V}^2\), similar to the previously measured third-order nonlinear susceptibilities (~10\(^{-19}\) m\(^2\)/V\(^2\) [98,134,230]).

\[\chi^{(3)}\]

**Figure 6.2.** THS of monolayer MoS\(_2\). (a) THG powers and (b) experimentally evaluated \(|\chi^{(3)}|\) as a function of THG photon energy, and (c) second-order linear reflectance derivation of monolayer MoS2. Series peaks in (b) are labelled as P1-P7 by stars. Series electronic states (including exciton states) are labelled in (c). Adapted from Publication 4.

In order to carry out the broadband THS of monolayer MoS\(_2\), ~150-fs incident fundamental pulses with photon energies (\(\hbar \omega_0\)) tunable from ~0.59 to 1.02 eV (\(\lambda_0: ~1210\) to 2080 nm) are used to generate third-harmonic pulses. Figure 6.2(a) shows THG results at different incident wavelengths in monolayer MoS\(_2\) with a fixed incident average power of ~10 \(\mu\text{W}\) (peak power: ~141 GW/cm\(^2\)). The results show that THG signals are highly dependent on the incident fundamental wavelength. When \(\hbar \omega_0\) is ~0.79 eV (\(\lambda_0 \approx 1560\) nm), the THG (\(\hbar \omega_{\text{THG}} \approx 2.37\) eV) efficiency is the highest compared to those at other incident photon energies. The variation of THG intensity efficiencies can reach ~800 times between ~1.79 eV and 3.08 eV, which shows remarkable THG enhancement at specific photon energies.[96]

To further understand the resonance peaks, we calculate the effective third-order nonlinear susceptibility \(|\chi^{(3)}|\) at different THG energies (the grey dots in Figure 6.2(b)). In Figure 6.2(b), the seven-resonant peaks (P1-P7) can be well fitted with the Lorentz function, where P1-P7 are located at ~1.84, 2.03, 2.16,
Transient higher-order harmonic spectroscopy in MoS\(_2\)

In order to assign the observed peaks in the THS results, we extract the linear reflection spectrum into the second-order contrast derivative (Figure 6.2(c)). Seven dips have been observed, with photon energies of ~1.85, 2.00, 2.17, 2.38, 2.55, 2.84, and 3.05 eV, respectively. Interestingly, the THG peaks nicely match with the dips in the reflectance derivation spectrum, which gives strong evidence for the three-photon resonance of THG with electronic states. Among them, three dips in Figure 2(c) at ~1.85 eV, 2.00 eV, 2.84 eV obviously correspond to the A, B, C excitons with 1s series, matching THS peaks at P1, P2, P6 in Figure 6.2(b), respectively. This is similar to previously reported exciton enhanced SHG results in monolayer TMDs.[20,21] Then, we assign the dip at ~2.17 eV in Figure 6.2(c) and the corresponding peak P3 (Figure 6.2(b)) to the 2s exciton.[83] The dip at ~2.38 eV in Figure 6.2(c), matching peak P4 in Figure 6.2(b), possibly corresponds to the 3s exciton.[83] Meanwhile, P5 in Figure 6.2(b) and the corresponding weak dip at 2.55 eV in Figure 6.2(c) remain unknown to our current knowledge. The well-known band-nest effect contributes to the linear absorption at ~2.84 (1s\(_c\)), and 3.05 eV (1s\(_D\)), matching Peaks P6 and P7 in Figure 6.2(b). Thus far, all 7 electronic states of monolayer MoS\(_2\) are nicely matching between linear absorption spectrum and THS (Table 6.1). With comparison with the linear reflection spectroscopy (Figure 6.2(c)), we can conclude that our THG method has advantages with high contrast (up to 800 times).

Still, there are two concerns that remained. One is that the THG at ~2.38 eV (P4) is extremely strong, in contrast to the weaker oscillation at high-order exciton states.[232] Also, the fitted FWHM width of peak P4 in Figure 2(b) is ~0.14 eV, slightly larger than the other six peaks with a typical FWHM of ~0.11 eV. The substantial enhancement and broaden bandwidth possibly indicate additional resonance contribution to Peak P4, besides the 3s excitonic state. On the other hand, we find that the enhancement of the band-nesting (P6 and P7) on THG, is one order of magnitude smaller than that in linear and SHG responses.[20]

6.2 Transient third-harmonic generation

After gaining the knowledge of resonant enhanced THG, we carry out transient THS to study the carrier dynamics associated with the THG process, which is highly important for electronics and optoelectronics. Figure 6.3(a) shows the experimental setup of transient THS, which is similar to the transient SHG in Chapter 5. With the excitation of pump pulses at higher photon energy, carriers are excited to higher states and then relax to lower states (Figure 6.3(b)), resulting in the bleaching and then recovering of THG, offering a good way to identify the electronic states and relaxation dynamics. In our experiment, a pump light at ~3.1 eV is used with a delay line to adjust the time delay (\(\Delta \tau\)) between the
Transient higher-order harmonic spectroscopy in MoS2

Figure 6.3(c) shows the transient THG ($\Delta P_{\text{THG}}$) at the generated photon energy of $\sim0.218$ eV. The $\Delta P_{\text{THG}}$ is defined by the equation of $\Delta P_{\text{THG}} = (P_w - P_0) / P_w$, where $P_w$ is the THG intensity with the pump excitation and $P_0$ is the THG intensity without the pump excitation. In Figure 6.3(c), when the pump pulses arrive, the THG intensity decreases quasi-instantaneously within $\sim100$ fs and reaches the lowest value of $-88\%$ at $\Delta t = -0.3$ ps. In the measurements, the pump excited carriers bleach the corresponding multi-photon transitions of THG, and thus decrease the THG efficiency. Then, it begins to recover with a typical bi-exponential trajectory (the fitted time constants: a fast time constant of $\tau_1 = -1.3$ ps and a slow time constant of $\tau_2 = -46.4$ ps). It indicates two processes of carrier dynamics in the crystal lattice: i) fast relaxation process: The pump excited carriers would decay from the continuum band to lower electronic states. Due to the relaxation of the hot carriers, the bleaching state steadily recovers. In this case, the multi-photon transition at exciton state is gradually built and the THG efficiency thus is recovered with the enhancement of exciton oscillations. This process usually happens within several picoseconds and is identified with a fast recovery time $\tau_1$. ii) Slow relaxation process. During this process, the interaction between the excited electron and phonon could play a key role, while other interactions from defect effects, charge trapping could also happen.

Figure 6.3. Transient THS of monolayer MoS2. (a) Schematic illustration of transient THS; (b) illustration of carrier relaxation during transient THG process interacting with various electronic states, i.e., excitons. (c) Transient $\Delta P_{\text{THG}}$ when the seed and pump light powers are $\sim10$ and $1 \mu$W. The decay process is fitted by bi-exponential function (yellow
Transient higher-order harmonic spectroscopy in MoS2

By fixing the delay time (Δτ) at ~0.3 ps and gradually increasing the pump power, we observe that ΔP_{THG} continuously decreases to ~94% until the average pump power reaches ~1.8 μW (Figure 6.3(d)). The nonlinear behaviour of the power dependence could be explained by carrier depletion. The inset of Figure 6.3(d) shows the ΔP_{THG} as a function of the pump light polarization, indicating that the THG modulation is independent of the pump polarization.

Figure 6.4. Transient THS at different ħω_{THG} from ~1.9 to 2.7 eV; Right panel is the ΔP_{THG} at a delay time of ~0.2 ps. Adapted from Publication 4.

To find the relationship between electronic states and ΔP_{THG}, we collect the ΔP_{THG} by scanning the excitation seed energies from ~0.62 eV to ~0.89 eV (average seed light power: 10 μW) with ~1-μW pump pulses at ~3.1 eV (Figure 6.4). The results show that THG intensities decrease in the whole spectral region. Specifically, we extract the ΔP_{THG} response at the delay time Δτ = ~0.2 ps as shown in the right panel of Figure 6.4. It clearly shows five dips at ~1.87, 2.00, 2.18, 2.40, 2.55 eV respectively, which nicely agrees with the THS results (i.e., P1-P5) in Figure 6.2(b) and the reflectance spectrum in Figure 6.2(c) (Table 6.1). The ΔP_{THG} at C exciton (~2.8 eV) does not exhibit due to the weak THG signal. We find that the 2s state enhanced THG at Peak P3 enables the highest modulation depth, while that of the 3s state at Peak P4 is relatively weak. It possibly indicates that the electronic bandgap contribution to the THG enhancement at Peak P4, besides the higher-level excitonic states.
Finally, we plot the fitted decay time constants as a function of the THG photon energy (Figure 6.5(a) and (b)). The fast time constant $\tau_1$ decreases almost linearly with the THG photon energies from ~2.47 ps at ~1.88 eV to ~0.1 ps at ~2.64 eV. It is reasonable that it takes a longer time for lower energy exciton.[238] The slow time constant $\tau_2$ does not show a clear linear relationship with THG photon energies, while it increases when the THG photon energy is close to the resonance states (i.e., $1s_B$ (P2), $2s$ (P3), $3s$ (P4)), as shown in Figure 6.5(b). This indicates that the bounded excitons have a longer lifetime.[239] With transient THS, various carrier dynamics can be monitored with high modulation depth (~90% in Figure 6.3(d)) and high resolution (<0.1ps in Figure 6.5(b)). Such a method could also be used for other TMDs and heterostructures to explore the dynamics of interlayer electronic states, such as moiré excitons.[240,241]

### Table 6.1. Comparison of series of excitonic states.

<table>
<thead>
<tr>
<th>Unit: eV</th>
<th>$1s_A$</th>
<th>$1s_B$</th>
<th>$2s$</th>
<th>$3s$</th>
<th>Electronic band</th>
<th>$1s_C$</th>
<th>$1s_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectance</td>
<td>1.85</td>
<td>2.00</td>
<td>2.17</td>
<td>2.38</td>
<td>*</td>
<td>2.84</td>
<td>3.05</td>
</tr>
<tr>
<td>THG</td>
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<td>2.03</td>
<td>2.16</td>
<td>2.39</td>
<td>2.55</td>
<td>2.81</td>
<td>3.05</td>
</tr>
<tr>
<td>Transient THG</td>
<td>1.87</td>
<td>2.00</td>
<td>2.18</td>
<td>2.40</td>
<td>2.55</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

### 6.3 Optical control of high-harmonic generation

High-harmonic generation (HHG) in solid materials [242], has attracted significant interest in the field of strong-field and attosecond physics. Since firstly observed in a bulk ZnO crystal in 2010 [149], solid-state HHG has been investigated with a wide range of materials, including large bandgap dielectrics [243] [244], semiconductors [151,245-247], semimetals [51], and topological insulators [248]. Along with optically modulated SHG and THG, the active control of the extreme nonlinear process would make a step forward to those potential applications. In this session, we investigate an optically controlled HHG in atomically thin 2D materials. The 2D materials with the advantages of strong optical nonlinearity and phase-matching-free have been found to motivate the essential
Transient higher-order harmonic spectroscopy in MoS$_2$ flake employed in this experiment is the same with the previous sample grown by chemical vapor deposition (CVD) and its quality is confirmed by inspecting the photoluminescence and Raman spectroscopies (See Figure 4.1 in chapter 4). The nonlinear optical responses in monolayer MoS$_2$ are analysed at room temperature when illuminated with femtosecond seed pulses (~200 fs, 2 kHz, photon energy ~0.57 eV, See Figure 4.2). To control the nonlinear optical responses, we employ a control light with photon energy $\hbar \omega_c$ at ~3.1 eV. By tuning the delay time ($\Delta \tau$) between the control and seed pulses with a homemade delay line, the time-resolved HHG can be achieved.

Figure 7.1. (a-c) Transient 3$^{\text{rd}}$-, 4$^{\text{th}}$-, 5$^{\text{th}}$-HG signal in monolayer MoS$_2$ when the pump light energy is 3.1 eV with the average power 300 nW. The seed light photon energy is ~0.57 eV with an average power ~80 µW. Red curves are the bi-exponential fitting.

Figure 7.1 shows the $\Delta P_{\text{signal}}$ at the 3$^{\text{rd}}$-, 4$^{\text{th}}$-, 5$^{\text{th}}$-harmonic photon energy as a function of delay time between the control and seed lights. In contrast to the previous results of transient THG, the 3$^{\text{rd}}$-HG (i.e. THG) signal at 1.71 eV remains unchanged when the pump light arises. Note that the photon energy of 3$^{\text{rd}}$-HG is lower than the energy of the optical bandgap (~1.8 eV). Thus, it is reasonable that there is no observable modulation at the 3$^{\text{rd}}$-HG due to no resonance states. Whereas the 4$^{\text{th}}$-HG at ~2.28 eV and 5$^{\text{th}}$-HG at ~2.85 eV that are above the bandgap show efficient modulation with the pump light. For the 4$^{\text{th}}$-HG, the $\Delta P_{\text{4th}}$ first decreases within ~100 fs due to the quasi-instantaneous optical bleaching, then the $\Delta P_{\text{4th}}$ starts to recover back. The bi-exponential fitting of the recovery trace gives a fast time constant of $\tau_1$ ~2.2 ps and a slow time constant of $\tau_2$ ~57.6 ps. The $\Delta P_{\text{5th}}$ behaves similarly to $\Delta P_{\text{4th}}$, first decreasing
sharply within 100 fs and then recovering with bi-exponential time constants \( \tau_1 = \sim 1.7 \text{ ps}, \ \tau_2 = \sim 143.2 \text{ ps} \). The underlying mechanism of solid-state HHG is generally described as an integration of interband transition and intraband oscillations.\cite{7} Especially, when the photon energy of HHG is above the bandgap, the solid-state HHG operating with a significant overlap of atomic orbitals gives a rise of probability for the interband transition, which is applicable for explaining our experimental results.
In this thesis, we have systemically studied the light induced linear and nonlinear optical changes in 2D materials, specifically transient linear absorption, and harmonic generations with different order nonlinearities. During these processes, the excited carriers associated optical effects, such as exciton bleaching, formation, electron-phonon scattering, have been observed with an ultrafast time scale.

In chapter 4, we have studied the transient absorption of ML-MoS₂ in the NIR region from 0.86 to 1.4 μm and the achieved enhancement of absorption can be up to 4.2%. The time-resolved carrier dynamics with hundreds of femtosecond resolution provide detailed views of the relaxation time of the carriers. Furthermore, we observed that the absorption modulation amplitude is highly dependent on pump and probe intensities, due to the presence of excited carrier states with both one-photon and two-photon absorption processes.

In chapter 5, we have demonstrated giant all-optical modulation of SHG mediated by excitons in monolayer TMDs. The transient dynamics of excitonic dark and bright states in monolayer MoS₂ have been determined to be the origin of the observed SHG modulation. Thanks to a redistribution of charge carriers produced by a control light beam, excited states acquired a substantial transition strength that contributes to enhancing SHG by a factor as large as 386 in our measurements.

In chapter 6, we have demonstrated the high-contrast third-harmonic spectroscopy in monolayer MoS₂ and uncovered the various electronic states such as s series excitons and interlayer band-to-band transition effect. Furthermore, the carrier dynamics in monolayer MoS₂ have been vividly observed by highly sensitive transient THS with modulation depth up to 95%. Secondly, we have achieved the active controls of high-harmonic generation with the optical method in TMDs, indicating that the electronic state can also support the higher-order optical nonlinearity. Our optically controlled optical nonlinearity would pave a new route for the nonlinear optical engineering toward on-chip all-optical devices.

All in all, our results on all-optical modulations of linear absorption and harmonic generations provide a basis for exploiting the unique exciton-photon interactions in 2D materials, while they enable the development of emerging all-optical linear and nonlinear optoelectronic applications. For example, the modulation amplitude, sign, and response time in transient SHG can be adjusted
over a broad spectral range spanning a few eV’s, which potentially enable versatile photonic devices with different functionalities. In particular, at a transition region, the large fractional SHG change $|\Delta P_{\text{SHG}}|$ (up to 62%) with the ultrafast rise (80 fs) and drop (~900 fs) response times could be used for ultrafast all-optical photonic devices, such as all-optical nonlinear modulators. Furthermore, the broadband transient linear and nonlinear responses provide a useful platform to explore the bright and dark excitons and related ultrafast dynamics. Benefited from all the features of 2DLMs, we believe that 2DLM-based nonlinear optics will pave the way for a wide variety of novel applications in various cross-disciplinary fields.

Thanks to the great progresses on nonlinear optics of 2D materials in the last decade [204], the basic nonlinear behaviours have been investigated in 2D materials and some methods of tunable nonlinear optics have been achieved. There still are plenty of opportunities to investigate fundamental physics and optoelectronic applications in 2D materials. For example, with atomic thickness, the nonlinear optical phenomena in 2D materials wouldn’t be hindered by the phase matching and propagation effects such as self-phase modulation of excitation pulses, thus exhibits their intrinsic features. One possible scheme is that the investigation of HHG in 2D materials would give a better understanding to the debate about the physical mechanism of HHG.[7]

In addition, the twisted heterostructure has been investigated in the last decade, with amazing optoelectronic features of single-layer 2D materials.[252] Indeed, in 2018, Prof. Pablo Jarillo-Herrero’s group has found that twisted bilayer graphene stacked at magic angle 1.1° shows flat bands near-zero Fermi energy and exhibits superconductivity at 1.7 K.[253] The moiré excitons were then observed in van der Waals TMD heterostructures.[240,241,254,255] These discoveries give rise to the research on twistronics and launching a new study subject (e.g., linear and nonlinear optical behavior from moiré excitons) from 2D to 3D.[256-259]
References

References

References

References


Since the first reported second-harmonic generation (SHG) in 1961, harmonic generations (HGs) play an increasingly important role in various technologies, especially in our modern information society. However, nonlinear optical effects normally have relatively low efficiency to be controlled. Therefore, reinforcing and controlling the efficiency of HGs are of importance for numerous applications of nonlinear optics.

Thanks to the recent discovery and development of two-dimensional (2D) materials with excellent physical properties, this thesis studies the transient linear and nonlinear optical processes in 2D materials, offering a way to control and enhance nonlinear optical responses in nanoscale. Our results have revealed that 2D materials are promising for actively engineered nonlinear optics in nanophotonics and nanoelectronics.