Broadband Nonlinear Photoresponse of Monolayer $MoSe_2$

Zhonghui Nie[1], Edmund Kelleher[2], Kaihui Liu[3], Yongbing Xu[1], Fengqiu Wang[1*]

[1]School of Electronic Science and Engineering and Collaborative Innovation Center of Advanced Microstructures,
Nanjing University, Nanjing 210093, China
[2]Femtosecond Optics Group, Department of Physics, Imperial College London, SW7 2AZ, UK.
[3] State Key Laboratory of Surface Physics and Department of Physics, Collaborative Innovation Center of Advanced Microstructures,
Fudan University, Shanghai 200433, China

E-mail address: fwang@nju.edu.cn

Abstract: We report the first broadband nonlinear absorption characterization of CVD-grown intrinsic monolayer molybdenum diselenide ($MoSe_2$) from 720–810 nm. A constant modulation depth of ~80% is revealed across the lowest energy excitonic absorption feature.

OCIS codes: (190.4400) Nonlinear optics, materials; (300, 1030) Absorption; (300, 6420) Spectroscopy nonlinear

1. Introduction

Two-dimensional (2d) materials – beyond graphene – are receiving significant attention. In particular, transition metal dichalcogenide (TMDC) crystals have recently emerged as a highly desirable platform for studying the physics of 2d layered semiconductors, with broad applicability in nonlinear optics and optoelectronics [1, 2]. Recently, a number of fiber and solid-state lasers have been mode-locked by TMDCs, including MoS_2, WS_2 and $MoSe_2$. Although several nonlinear absorption characterizations have been reported, these are usually performed on TMDC nano-flake based dispersions or polymer composites [3-5]. Characterizing the highly crystalline intrinsic material is critical in mitigating effects from extrinsic factors such as electronic defects or morphological deforms. While such investigations have been performed on graphene, monolayer TMDCs are less well studied and their optical properties less understood.

Here, we address this issue, reporting the first direct measurements of the nonlinear optical absorption of monolayer $MoSe_2$ across a broad spectral range (720 nm–810 nm), covering the lowest energy exciton resonance of the material. In contrast to one-dimensional systems, such as carbon nanotubes, we observe a near-constant normalized modulation depth (~80%) both on- and off-resonance. A saturation intensity of ~2.5 MW/cm^2 is extracted from the measurements, approximately in agreement with previous studies on few-layer $MoSe_2$ nano-flake based composites at sub bandgap energy equivalent wavelengths [4, 5]. Our results provide new insight into the optical properties of TMDCs and provide updated design guidelines for in-band pumped TMDC-based nonlinear optical devices.

2. Experimental setup and measurement

Monolayer $MoSe_2$ is grown on a SiO_2/Si substrate by Chemical Vapor Deposition (CVD), then transferred to a silver mirror by a wet-transfer technique based on a sacrificial layer of poly-methyl-methacrylate (PMMA). Fig.1 (b) shows an optical micrograph highlighting the triangular islands of monolayer $MoSe_2$. The average lateral dimensions of these monolayers is approximately 30-40 μm, larger than typically achieved using e.g. mechanical exfoliation. Fig.2 (a) and Fig.2 (b) show the photoluminescence (PL), linear absorption and Raman spectra of the sample. The lowest energy peak of the absorption and PL spectrum is located at ~790 nm, in agreement with the absorption peak of the A exciton in $MoSe_2$ [6]. Two distinct peaks in the Raman spectrum at 240 cm^{-1} and 287 cm^{-1} correspond to the A_{1g} and E^1_{2g} vibration modes, as typically seen in high quality samples [6].

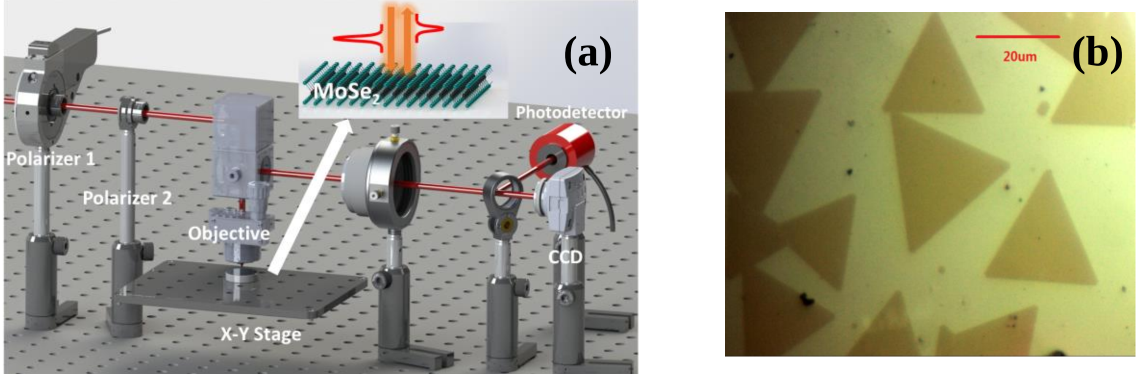

Figure 1 (a) A schematic of the measurement setup. (b) Optical micrograph of $MoSe_2$ on silver mirror (scale bar, 20 μm).

Experiments measuring the nonlinear optical absorption are performed using a Ti: sapphire laser, with a pulse duration of ~100 fs and a repetition rate of 76 MHz. A reflective objective is used to focus the laser output onto the sample, achieving a minimal spot diameter at focus of ~2 μm. A pair of linear polarizers allows the input power from the laser to be controllably varied, as illustrated in Fig.1 (a).

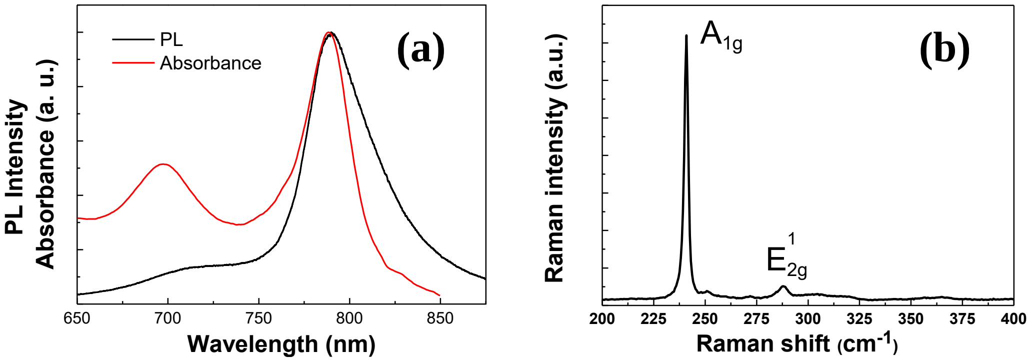

Figure 2 (a) Photoluminescence and linear absorption spectrum, and (b) Raman spectrum of the monolayer $MoSe_2$ flake.

3. Results and discussion

The nonlinear optical response of the $MoSe_2$ sample is recorded, while tuning the excitation wavelength through the materials lowest energy excitonic resonance, ~760-810 nm. Fig.3 (a) shows the intensity dependent reflectance of the sample (on mirror). It is observed that as the excitation wavelength moves through the resonance, an increasing change of reflectance is obtained. While the largest change in reflectance can reach 20% for 790 nm, this can be as low as 2.5% for the off-resonance wavelength, i.e. at 812 nm. This means that $MoSe_2$ can exhibit strong spectral modulation in its effective saturable absorption characteristics. When the photoresponse of the monolayer $MoSe_2$ is considered, we extract the absorption from the reflectance by using $\alpha=-log(R)$, where α and R denote absorbance and reflectance respectively. The normalized absorption spectra, in Fig. 3(b) presents a rather different physical picture. All curves overlap, revealing a modulation depth ~80% and a saturation intensity around 2.5 MW/cm^2. Such a response is different from other saturable absorbers, such as single-wall carbon nanotubes, where enhancement of modulation depth is observed for on-resonance wavelengths [7]. We interpret our results by considering the role of bandgap renormalization, where photogenerated carriers can dynamically alter the bandgap [8].

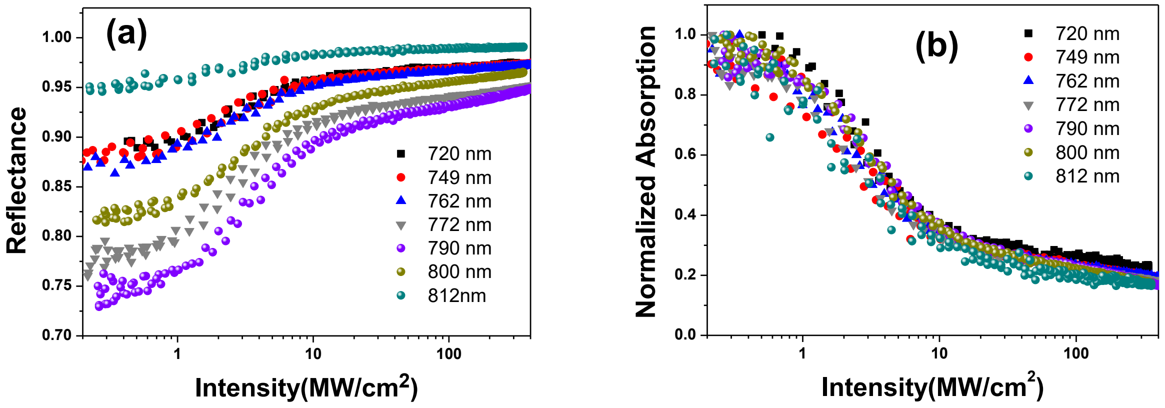

Figure 3 (a) Nonlinear reflectance ($MoSe_2$ on mirror), and (b) normalized absorption of $MoSe_2$ at various wavelengths.

4. Conclusion

In summary, we present the first broadband nonlinear absorption characterization of CVD-grown, highly crystalline monolayer $MoSe_2$. Surprisingly, our results show that the modulation depth and saturable intensity is approximately invariant across the low energy exciton resonance. Scheduled broadband pump-probe experiments will help elucidate this mechanism, and clarify the contribution of bandgap renormalization.

[1] X. Yin et al., “Edge Nonlinear Optics on a MoS2 Atomic Monolayer,” Science **344**, 488 (2014).

[2] Q. Wang et al., “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” Nature Nanotech **7**, 699 (2012).

[3] K. Wang et al., “Ultrafast Saturable Absorption of Two-Dimensional MoS_2 Nanosheets,” ACS Nano **7**, 9260 (2013).

[4] R. I. Woodward et al., “Wideband saturable absorption in few-layer molybdenum diselenide ($MoSe_2$) for Q-switching Yb-, Er- and Tm-doped fiber lasers,” Opt. Express **23**, 20051 (2015).

[5] Z. Luo et al., “Nonlinear optical absorption of few-layer molybdenum diselenide ($MoSe_2$) for passively mode-locked soliton fiber laser,” Photon. Res. **3**, A79 (2015).

[6] D. H. Kim et al., “Optical Second-harmonic Generation in Few-layer MoSe2,” J. Korean Phys. Soc. **66**, 816 (2015).

[7] G. N. Ostojic et al., “Interband Recombination Dynamics in Resonantly Excited Single-Walled Carbon Nanotubes,” PRL **92**, 117402 (2004).

[8] E. A. A. Pogna et al. "Photo-Induced Bandgap Renormalization Governs the Ultrafast Response of Single-Layer MoS_2," ACS Nano **10**, 1182 (2016).