Characteristics of saturable absorption of MoS$_2$ films in the visible to near-infrared range

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Abstract: MoS$_2$ films consisting mainly of few-layer MoS$_2$ nanoplatelets are fabricated. Tunable Z-scan measurement reveals strong saturable absorption (~70% modulation depth) around 500 nm, demonstrating the potential of MoS$_2$ for visible laser mode-locking and optical switching.

OCIS codes: (320.7080) Ultrafast devices; (320.7090) Ultrafast lasers; (140.4050) Mode-locked lasers

1. Introduction

Saturable Absorbers (SAs) are key enabling elements for mode-locked lasers which are finding ever wide-ranging applications in fields such as optical communication, spectroscopy, biomedical diagnosis and precision material processing. Key requirements for SAs include wide operation wavelength range, large nonlinear response (or modulation depth), ultrafast carrier relaxation time, compactness as well as the ease of tailoring the relevant optical parameters. Carbon nanomaterials including carbon nanotubes and graphene have proved to be excellent saturable absorbers for fiber and solid-state lasers [1-5]. They have become important alternative to the more established SESAM technology, especially at longer wavelength range, i.e. mid infrared. Although both graphene and carbon nanotubes exhibit broadband saturable absorption, their applications in ultrafast photonics have so far been confined in the near-infrared to mid-infrared range [3-7]. Employing the $E_{2g}$ transition in nanotubes is a feasible way to extend carbon nanotubes' nonlinear absorption edge towards shorter wavelength, though it leads to higher saturation intensity and no characterization of nonlinear absorption in the visible range has been reported so far [8].

Molybdenum disulfide (MoS$_2$) is subject to intense research efforts because of its unusual electronic and optical properties. While few-layer and bulk MoS$_2$ is a semiconductor with an indirect bandgap of ~1.3 eV, monolayer MoS$_2$ has a direct bandgap of ~1.8 eV [9]. Recently, saturable absorption has been reported for MoS$_2$ dispersions [10,11], and mode-locked lasers at ~1 µm has also been reported [11,12], suggesting a broad nonlinear absorption bandwidth. However, thus far there has been no report that systematically studies the wavelength dependence of the broadband nonlinear absorption of MoS$_2$, especially for a solid-state form of MoS$_2$. In this paper, we have fabricated MoS$_2$ films using a vacuum filtration technique. The film can be easily transferred to other optical surfaces, such as an optical fiber ferrule, and its linear and nonlinear absorptions can be readily tuned by controlling the film thickness. Investigation in the nonlinear optical properties by Z-scan measurement employing ~100 fs pulses tunable across visible to near infrared is carried out. Our results show that few-layer MoS$_2$ nanoplatelets exhibit strong saturable absorption (~70% modulation depth) in the visible range and the modulation depth (in transmittance) diminishes with the increase of exciting wavelength. Our results show that MoS$_2$ films may be an excellent SA material for ultrafast pulse generation and optical switching in the visible range where no competent SA technology exists yet.

2. MoS$_2$ film fabrication

Two-dimensional (2D) MoS$_2$ dispersions were prepared by liquid exfoliation using ionic surfactant sodium cholate as a stabilizer [13]. First of all, 200 mg of MoS$_2$ powders (Sigma-Aldrich) were dispersed in 40 mL of 1.5 mg/mL sodium cholate (SC) (Sigma-Aldrich) aqueous solution, followed by sonication for 1 hour with high intensity ultrasonic liquid processor. Then, the obtained MoS$_2$ suspensions were centrifuged at 3000 r/min for 90 minutes. The top 3/4 of the dispersion was collected by pipette for later use. 2 mL of the above prepared 2D MoS$_2$ dispersion was taken and diluted into 50 mL with a bath sonication for 1 hour. The diluted MoS$_2$ dispersion was vacuum-filtrated using a mixed cellulose ester membrane with 200 nm pores (Millipore). The film was then transferred onto a quartz substrate and heated at 60 °C for 6 hours. To remove the cellulose ester membrane, the MoS$_2$ films were immersed in acetone for several times. Fig. 1(a) shows the absorption spectrum of the MoS$_2$ film. Four typical peaks can be observed in the range of 300 ~ 800 nm, which correspond to the transition of excitons of A, B, C, D, respectively.

Fig.1(b) shows the Raman spectrum of the MoS$_2$ film. While the mean difference for $E_{1g}^1$ and $A_{1g}$ mode is similar to the bulk MoS$_2$ value of ~25.2 cm$^{-1}$, the broadening of the linewidths of the $E_{1g}^1$ band (2.9 cm$^{-1}$) and the $A_{1g}$ band
(3.5 cm⁻¹) in comparison with those of the bulk MoS₂ (i.e. ~1.4 cm⁻¹ and ~3.2 cm⁻¹ respectively) verifies the significant reduction of the flake thickness from the bulk MoS₂[10]. Fig.1(c) shows a photograph of an as-fabricated MoS₂ film (on a quartz substrate). The typical thickness of the film is 100-300 nm.

3. Wavelength tunable Z-scan characterizations

To gain insights into the broadband nonlinear optical properties of MoS₂, we employ an open-aperture Z-scan setup to characterize the nonlinear absorption of MoS₂ nanoplatelets. The pump source consists of a Coherent Libra-HE amplifier system with a OPERA-SOLO Optical parametric amplifier (OPA). Specifically, we have chosen the wavelength 500 nm, 650 nm, 800 nm, 950 nm and 1100 nm to illustrate the trends of the wideband nonlinear absorption. The excitation pulse duration is ~ 100 fs (with a 1 kHz repetition rate) and a neutral density filter is employed to set the incident optical power. A power meter with a pair of photodiode detectors (Ophir PD300-IR) is used to record the incident and transmitted power through the samples. At each excitation wavelength, we have attempted to investigate the full range of the available pump power from the OPA. However, to avoid laser damage caused by either high peak intensity or thermal effects, we have limited our excitation power to a range within which Z-scan curves are readily reproducible without change in linear transmittance of the samples [11]. It should be noticed that two-photon absorption (TPA) threshold is found to be higher than the stability range of excitation power, that is why we concern ourselves only with saturable absorption in this experiment.

Fig.2 illustrates the Z-scan results for a set of excitation wavelengths from 500 nm - 1100 nm (with a 150 nm interval). The Z-scan curves under different excitation intensities indicate a large nonlinear response up to a modulation depth of ~70% at 500nm. With the increase of the excitation wavelength, we observe continuous decrease of the modulation depth.
4. Conclusion

We have for the first time systematically investigated the characteristics of wideband saturable absorption of MoS$_2$ nanoplatelets (in the form of a thin film) in the visible and near-infrared range. Using an open-aperture Z-scan technique, the MoS$_2$ sample is found to exhibit strong and wideband nonlinear optical properties, with the best signals obtained at a wavelength \(\sim 500\) nm. The modulation depth at \(\sim 500\) nm are measured to be \(\sim 70\%\). Our results show that MoS$_2$ has great potential in visible laser mode-locking/Q-switching and optical switching applications.

