Wideband saturable absorption in few-layer molybdenum diselenide (MoSe$_2$) for Q-switching Yb-, Er- and Tm-doped fiber lasers

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Abstract: We fabricate a free-standing molybdenum diselenide (MoSe$_2$) saturable absorber by embedding liquid-phase exfoliated few-layer MoSe$_2$ flakes into a polymer film. The MoSe$_2$-polymer composite is used to Q-switch fiber lasers based on ytterbium (Yb), erbium (Er) and thulium (Tm) gain fiber, producing trains of microsecond-duration pulses with kilohertz repetition rates at 1060 nm, 1566 nm and 1924 nm, respectively. Such operating wavelengths correspond to sub-bandgap saturable absorption in MoSe$_2$, which is explained in the context of edge-states, building upon studies of other semiconducting transition metal dichalcogenide (TMD)-based saturable absorbers. Our work adds few-layer MoSe$_2$ to the growing catalog of TMDs with remarkable optical properties, which offer new opportunities for photonic devices.

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References and links

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1. Introduction

Transition metal dichalcogenides (TMDs) are a family of more than 40 layered materials with general formula MX$_2$, where M is a transition metal, and X is a chalcogen (i.e. a group VI element such as sulfur or selenium) [1]. Their structure consists of quasi-2d layers weakly bound together by van der Waals forces. In each layer, a plane of transition metal atoms is covalently bonded between two planes of chalcogen atoms. TMDs have a diverse range of properties and include metallic (e.g. NbS$_2$), semiconducting (e.g. MoS$_2$) and insulating (e.g. HfS$_2$) materials [1].

Despite many fundamental studies of the structure and properties of TMDs in the 1960s and 70s [1–6], including reports of monolayer [5] and few-layer crystals [3], the lack of suitable processing and characterization techniques for such materials meant that their unique optical characteristics were not exploited for practical technologies. At present, semiconducting TMDs (MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$, MoTe$_2$ etc.) are experiencing renewed interest due to their remarkable layer-dependent optoelectronic properties, which hold great promise for future photonic devices [7]. These include a transition from an indirect to direct bandgap at visible / near-infrared wavelengths when moving from bulk to monolayer form, in addition to strong photoluminescence, high nonlinearity and ultrafast carrier dynamics for mono- and few-layer forms [7]. The direct bandgaps of monolayer semiconducting TMDs in the visible and near-infrared offer advantages over graphene, a zero-gap material, for many optoelectronic applications. Additionally, the layer- and size-dependent characteristics of these TMDs allow great flexibility for engineering their optical properties [7].

Molybdenum disulfide (MoS$_2$) is perhaps the most widely studied TMD to date [5–7, 9]. Recent work has demonstrated wideband saturable absorption in few-layer MoS$_2$ [10–13], suggesting that semiconducting TMDs could be a promising class of saturable absorber (SA) for short laser pulse generation [14]. Numerous studies have exploited this SA response, demonstrating mode-locked and Q-switched lasers (with both bulk and fiber gain media) from 1030 to 2100 nm [14, 25] either at discrete wavelengths or with broadband tunability [16, 18, 25]. It has been proposed that the ability of a single MoS$_2$ SA device to operate at numerous wavelengths, even in spectral regions corresponding to sub-bandgap photon energies, is due to edge-state absorption in the material [14, 18].

More recently, other sulfide-based TMDs such as tungsten disulfide (WS$_2$) have emerged as candidate materials for future saturable absorbers: WS$_2$ has recently been demonstrated to...
mode-lock and Q-switch fiber lasers [26-29]. However, selenide-based TMDs (MoSe₂, WSe₂, etc.) have yet to be fully explored and could offer advantages over sulfide TMDs for certain applications, for instance where a narrower gap semiconductor is required (heavier chalcogenide atoms lead to reduced bandgap energies [7]). Therefore, further investigation to understand the optical properties of few-layer transition metal selenides is required before they can be exploited in practical systems.

Few-layer molybdenum diselenide (MoSe₂) flakes have been fabricated by mechanical exfoliation [30], ultrasound-assisted liquid-phase exfoliation (UALPE) [31] and chemical vapor deposition (CVD) [32-34] techniques. Bulk MoSe₂ has a ∼1.1 eV (∼1128 nm) indirect bandgap, which increases to a ∼1.41 eV (∼879 nm) indirect gap for 8-layer MoSe₂ [35] and a direct ∼1.55 eV (∼800 nm) gap for monolayer MoSe₂ [30,35]. The nonlinear optical properties of few-layer MoSe₂ have been studied by Wang et al. [11], for UALPE MoSe₂ dispersed in cyclohexylpyrrolidone (CHP), and by Dong et al. [36] in N-methyl-pyrrolidone (NMP); both saturable absorption and optical limiting behavior were reported.

Here, we produce a few-layer MoSe₂-polyvinyl alcohol (PVA) composite SA for short-pulse generation. Fiber lasers based on ytterbium- (Yb), erbium- (Er) and thulium-doped (Tm) gain media are demonstrated, operating at 1060 nm, 1566 nm and 1924 nm, respectively, which generate stable trains of Q-switched pulses when the MoSe₂-PVA SA is integrated into the cavity.

2. Few-layer MoSe₂ fabrication and integration into a saturable absorber device

We use an ultrasound-assisted liquid phase exfoliation (UALPE) technique to produce few-layer MoSe₂ nanoflakes from their bulk crystals. UALPE exploits cavitation arising from high frequency pressure variation. These cavities subsequently collapse due to instability and pressure variation, resulting in high shear forces [37]. This exfoliates flakes from bulk crystals by overcoming the interlayer van der Waals forces.

In general, solvents matching the experimentally-determined Hansen solubility parame-
ters of layered materials support their exfoliation and stabilization. This offers a more refined understanding than considering only the surface energies or Hildebrand solubility parameters of the solvents and materials. Experimental evidence suggests that NMP and CHP are two of the more suitable solvents for TMDs. However, it is challenging to process these high boiling point (>200°C) solvents for the fabrication of SA composites. Low boiling point solvents, e.g. water, are thus more desirable to exfoliate MoSe₂, although large mismatch of Hansen solubility parameters of water with MoSe₂ (and other layered materials) dictates the use of surfactants for its exfoliation and stabilization in water.

For layered materials, the molecular structure of surfactants plays an important role. The most effective are bile salt surfactants (e.g. sodium cholate) due to their planar structure with a hydrophobic and a hydrophilic side. The hydrophobic side of the bile salt surfactant molecules adsorbs onto the flat surface of the layered materials, while the hydrophilic side creates an effective surface charge around the flake. The exfoliated layered materials are thus stabilized against re-aggregation by the Coulomb repulsion resulting from this surface charge. Among the different bile salt surfactants, we choose sodium deoxycholate (SDC) due to its high hydrophobic index. We prepare the MoSe₂ dispersion by sonicating 100 mg of MoSe₂ crystals with 70 mg SDC in 10 mL deionized water for 12 hours at 15°C. The resultant dispersion is centrifuged at 4000 rpm (∼1500 g) for 1 hour to sediment the unexfoliated large flakes. The upper 70% of the centrifuged dispersion, enriched with few layer MoSe₂ flakes, is decanted for characterization and composite fabrication.

The optical absorption spectrum of the MoSe₂ dispersion, diluted to 10% (v/v) to avoid scattering losses, shows two absorption peaks labeled as A (~800 nm) and B (~710 nm) [Fig. 1(a)]. These peaks correspond to the excitons from the two spin-orbit split transitions at the K point of the Brillouin zone. To estimate the concentration of the dispersed MoSe₂, we use the Beer-Lambert law, \( \alpha \lambda = \alpha_{\lambda} \cdot c \cdot l \), where \( \alpha_{\lambda} \) is the absorbance at wavelength \( \lambda \), \( \alpha_{\lambda} \) is the absorption coefficient at \( \lambda \), \( c \) is the concentration, and \( l \) is the optical path of incident light through the dispersion. First, we experimentally estimate \( \alpha_{710} \) for MoSe₂ at \( \lambda = 710 \) nm following the procedure developed in Ref. [24] for MoS₂. This gives \( \alpha_{710nm} = 615 \) Lg⁻¹m⁻¹, from which we estimate the concentration of the undiluted MoSe₂ as 0.78 gL⁻¹.

The thickness distribution of exfoliated MoSe₂ flake dimensions is measured via atomic force microscopy (AFM), shown in Fig. 1(b)–(d). Samples for AFM are prepared by diluting the MoSe₂ dispersion to 5% (v/v), drop-casting on to a Si/SiO₂ wafer and then rinsing with deionized water to remove the surfactant. The average flake thickness is 3.8 ± 0.1 nm, while 80% of the flakes have thickness ≤5 nm [Fig. 1(c)], corresponding to ≤6–7 layers for the majority of the flakes, assuming 0.9–1.0 nm measured thickness for a monolayer flake, and 0.65–0.7 nm increase for each additional layer. The average lateral dimension of the exfoliated flakes is 80 ± 5 nm, resulting in a high edge-to-surface area ratio [Fig. 1(d)].

The free-standing MoSe₂-polymer composite SA is fabricated by following a procedure commonly adopted for other layered material-based polymer composite SAs such as graphene.
temperature in a desiccator. Slow evaporation of water over several days forms a 2 mL 5 wt% aqueous PV A solution. The mixture is poured into a petri dish and dried at room temperature in a desiccator. Slow evaporation of water over several days forms a ~30 µm thick free-standing composite SA film [Fig. 2(a)]. An optical microscope image of the composite verifies the absence of aggregates and voids [Fig. 2(b)], which could otherwise increase the non-saturable scattering loss. For comparison, a ~30 µm thick pure PVA film is fabricated using a similar method, but without the MoSe₂ flakes.

The linear optical absorption profile of the MoSe₂-PVA film shows the characteristic MoSe₂ excitonic peaks (A & B) and a non-negligible absorbance throughout the near-infrared (>800 nm), as highlighted in Fig. 3(a). The MoSe₂-PVA film absorbs 7.5%, 8.1% and 7.6% more light than the pure PVA film at 1060 nm, 1566 nm and 1924 nm, respectively (the three operating wavelengths of the lasers in Section 3). The nonlinear optical response of the few-layer MoSe₂-PVA composite is measured using an open-aperture Z-scan technique [44]: the composite is swept through the focus of a beam of ultrashort pulses from a mode-locked fiber laser (750 fs pulse duration, 1566 nm wavelength, 7.5 MHz pulse repetition frequency) and the transmitted power is recorded as a function of incident intensity on the device (in addition to a reference power signal for normalization). Our few-layer MoSe₂ sample exhibits a strong saturable absorption response [Fig. 3(b)], well-fitted by the two-level SA model [45]. From this fit, the following SA parameters can be extracted: saturation intensity, \( I_{sat} \sim 3.4 \text{ MW/cm}^2 \); modulation depth, \( \alpha_s \sim 4.7\% \); and nonsaturable absorption, \( \alpha_{ns} \sim 6.6\% \). Such SA parameters are similar in magnitude to previously reported saturable absorbers based on few-layer MoSe₂ [14, 24]. We note that the Z-scan pulse source at 1566 nm corresponds to a photon energy of 0.79 eV, less than the energy required for single photon excitation of carriers across the bandgap of few-layer MoSe₂ [30]. A proposal for the mechanism of the observed sub-bandgap saturable absorption is discussed in Section 5.3.

3. Q-switched fiber lasers using few-layer MoSe₂ SA

The demonstrated sub-bandgap saturable absorption of our few-layer MoSe₂-PVA composite at 1566 nm indicates that the device could Q-switch an Er-doped fiber laser cavity to generate short optical pulses, which are needed for many applications such as fundamental research and industrial materials processing and micromachining. The MoSe₂-PVA SA is integrated into an Er-doped fiber laser, in addition to Yb- and Tm-doped fiber lasers to explore the potential of ex-
ploiting sub-bandgap saturable absorption for short-pulse generation at different near-infrared wavelengths, using a single MoSe$_2$ SA. For each laser cavity, a ring design is adopted, including a polarization-independent isolator, output coupler and polarization controller, in addition to the fiber amplifier [Figs. 4(a), 5(a) & 6(a)]. The Yb and Er amplifiers consist of double-clad Yb and Er fiber, respectively, pumped by a multimode 965 nm laser diode, whereas the single-mode Tm fiber amplifier is pumped by a 1550 nm continuous wave fiber laser. A 1 mm × 1 mm piece of the MoSe$_2$ SA film is integrated into the cavity by placing it between two fiber patch cords [Fig. 2(c)].

3.1. Q-switched Yb:fiber laser characterization

Self-starting Q-switching is observed from the Yb-doped fiber laser, generating a steady train of pulses [typical pulse characteristics shown in Fig. 4(b) & (c)], centered at 1060 nm [Fig. 7(a)]. By changing the pump power, the average output power can be varied from 6.26 mW (corresponding to the threshold for Q-switched emission; below this, the laser output is a continuous wave) to 8.72 mW. The steady-state output pulse properties depend on the cavity gain and absorber saturation dynamics, coupling the pump power to the pulse duration and repetition rate. With increasing power, the pulse repetition frequency is increased from 60.0 kHz to 74.9 kHz and the duration decreased from 4.6 µs to 2.8 µs [Fig. 8(a)]. At the maximum average output power, the pulse energy is 116 nJ.

3.2. Q-switched Er:fiber laser characterization

The Er-doped fiber laser incorporating the few-layer MoSe$_2$-PVA composite exhibits self-starting Q-switching at an average output power of 18.9 mW, operating at 1566 nm [Fig. 7(b)]. Typical output pulse train properties are shown in Fig. 5(b) & (c). By varying the pump power, the repetition rate could be changed from 26.5 kHz to 35.4 kHz and the duration decreased from 7.9 µs to 4.8 µs as the average output power increased from 18.9 mW to 29.2 mW [Fig. 8(b)]. At the highest output power, the pulse energy is 825 nJ.

Fig. 4. Yb:fiber Q-switched laser: (a) cavity schematic; (b) output pulse train at 65.0 kHz repetition rate; (c) pulse profile with 2.85 µs duration for 8.0 mW average output power.
3.3. Q-switched Tm:fiber laser characterization

Continuous-wave lasing at 1924 nm is initially observed as the pump power of the Tm-doped fiber laser is increased, until the Q-switching threshold is reached, corresponding to 0.13 mW average output power [Fig. 7(c)]. Beyond threshold, a steady train of Q-switched pulses is generated [Fig. 6(b) & (c)]. As the pump power is increased, the average output power increases and the Q-switched pulse duration reduces from 16.0 µs to 5.5 µs while the repetition rate increases from 14.0 kHz to 21.8 kHz [Fig. 8(c)]. The maximum pulse energy is 42 nJ.

3.4. Discussion

The MoSe$_2$-PV A composite enables Q-switched operation in fiber laser cavities at 1060 nm, 1566 nm and 1924 nm. The lasers were also operated with ∼30 µm-thick pure PV A film (fabricated in a similar way to the MoSe$_2$-PV A composite, but without MoSe$_2$ flake enrichment) sandwiched between the fiber patch cords, although in this case Q-switching was not observed at any power level or polarization controller position, confirming that the saturable absorption arises from the few-layer MoSe$_2$ material.

While bulk MoSe$_2$ has an indirect bandgap of ∼1.1 eV (∼1128 nm) [30, 35], a recent angle-resolved photoemission spectroscopy (ARPES) study on molecular beam epitaxy (MBE)-grown MoSe$_2$ samples demonstrated a transition from an indirect bandgap of ∼1.41 eV (∼880 nm) for 8-layer MoSe$_2$ to a direct bandgap of ∼1.58 eV (∼784 nm) for monolayer MoSe$_2$ [35].

AFM statistics, considering >400 flakes of our UALPE MoSe$_2$ samples, show that 80% of the flakes consists of ≤6–7 layers. Based on the above experimental data and ARPES study by Ref. [35], we estimate an indirect bandgap just above ∼1.41 eV for these flakes. Therefore, single-photon optical absorption from the MoSe$_2$ samples above 880 nm is not expected. However, our linear absorption measurement indicates ∼11% absorption at these near-infrared wavelengths (>880 nm), ∼8% of which is due to the addition of MoSe$_2$, compared to the pure PVA film [Fig. 2(a)]. While this measurement also takes into account scattering loss, the sub-
Fig. 6. Tm:fiber Q-switched laser: (a) cavity schematic; (b) output pulse train at 16.9 kHz repetition rate; (c) pulse profile with 7.11 µs duration for 0.79 mW average output power.

Fig. 7. Spectra for Q-switched operation of few-layer MoSe$_2$ Q-switched Yb- and Er- and Tm-doped fiber lasers; (a) and (b) were measured using an optical spectrum analyzer (0.02 nm resolution), while (c) was measured on a spectrometer (~0.1 nm resolution).

Fig. 8. Variation of pulse duration and repetition rate with average (av.) output power for (a) Yb-, (b) Er-, and (c) Tm-doped fiber lasers, Q-switched with few-layer MoSe$_2$ SA.
bandgap absorption observed in our UALPE MoSe$_2$ is verified by our Z-scan measurement at 1550 nm and demonstration of few-layer MoSe$_2$-based Q-switched lasers at 1060 nm (1.16 eV), 1566 nm (0.79 eV) and 1924 nm (0.64 eV). Indeed, similar observations of sub-bandgap saturable absorption have been reported for few-layer MoS$_2$ \cite{10,24} and WS$_2$ \cite{26-29}.

We recently proposed an explanation for this phenomenon based on edge-states (in the context of MoS$_2$ SA devices) \cite{14,18,24}. This mechanism is supported by early photothermal deflection spectroscopy studies of few-layer MoS$_2$ samples \cite{6}. By comparing MoS$_2$ samples with different microcrystal sizes and lithographically textured single crystals, Ref. \cite{6} demonstrated increased sub-bandgap absorption in samples with a greater amount of crystal edges. This suggests that states at the edges of the MoS$_2$ flakes play a significant role in defining the material band structure and enable absorption by exciting electrons to the edge-state levels within the material bandgap. This edge-induced sub-bandgap absorption can be saturated by Pauli blocking at high incident intensities, which enables the material to act as a Q-switch in a laser cavity \cite{14,18,24}. We note that Wang et al. have also proposed a complementary explanation for this phenomenon, supported by theoretical bandgap studies, based on crystallographic defect states \cite{15}.

Generalizing the above discussion to other semiconducting TMD materials, we propose that a high edge-to-surface area ratio can lead to sub-bandgap absorption in these materials. While this is not fully understood at present, crystallographic defects, dislocations, grain boundaries etc in semiconducting TMD samples may also contribute to sub-bandgap absorption. This could also explain observation of saturable absorption in CVD-grown MoS$_2$ samples \cite{22}, which, in general, are expected to have less edge-to-surface area ratio than those prepared by UALPE.

Our UALPE MoSe$_2$ flakes with average lateral dimensions of $80 \pm 5$ nm have a high edge-to-surface area ratio. We propose this high edge-to-surface area ratio to be the primary origin of the optical absorption below the material bandgap. While the direct visible bandgap of mono- and few-layer MoSe$_2$ suggests suitability for optical applications in the visible spectral region, the edge-state driven wideband absorption in the infrared highlights that few-layer MoSe$_2$ could be a very versatile material for developing future laser-based photonic technologies.

4. Conclusion

In summary, we have reported the production of few-layer MoSe$_2$ flakes by ultrasound-assisted liquid-phase exfoliation and the fabrication of a saturable absorber device by embedding these MoSe$_2$ flakes into PVA. For the first time, we have demonstrated that a selenide-based transition metal dichalcogenide is able to generate short laser pulses by Q-switching: we developed ytterbium-, erbium- and thulium-doped fiber lasers, Q-switched by few-layer MoSe$_2$, operating at 1060 nm, 1566 nm and 1924 nm, respectively. The wideband saturable absorption was explained in the context of sub-bandgap edge states, extending our existing proposed mechanism for this phenomenon to the wider class of semiconducting transition metal dichalcogenides. This adds few-layer MoSe$_2$ to the growing library of nanomaterials with exceptional optical properties and exciting opportunities for future photonic applications.

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