Research Article | Vol. 26, No. 10 | 14 May 2018 | OPTICS EXPRESS 13055
Optics EXPRESS

Laser Q-switching with PtS_2 microflakes saturable absorber

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Abstract: Numerous studies have been conducted to explore the performance of two-dimensional (2D) layered nano-materials based saturable absorber (SA) for pulsed laser applications. However, fabricating materials in nanoscale requires complicated preparation processes, high energy consumption, and high expertise. Hence, the study of pulsed laser performance based on the saturable absorber prepared by layered materials with bulk-micro size have gained a great attention. Platinum disulfide (PtS_2), which is newly developed group 10 2D layered materials, offers great potential for the laser photonic applications owing to its high carrier mobility, broadly tunable natural bandgap energy, and stability. In this work, the first passively Q-switched Erbium (Er) doped fiber laser is demonstrated with an operational wavelength of 1568.8 nm by using PtS_2 microflakes saturable absorber, fabricated by a simple liquid exfoliation in N-Methyl-2-pyrrolidone (NMP) and then incorporated into polyvinyl alcohol (PVA) polymer thin film. A stable Q-switched laser operation is achieved by using this PtS_2-SA within a fiber laser ring cavity. The maximum average output power is obtained as 1.1 mW, corresponding to the repetition rate of 24.6 kHz, the pulse duration of 4.2 μs, and single pulse energy of 45.6 nJ. These results open up new applications of this novel PtS_2 layered material.

OCIS codes: (140.3540) Lasers, Q-switched; (140.3500) Lasers, erbium.

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#326638 https://doi.org/10.1364/OE.26.013055
Journal © 2018 Received 23 Mar 2018; revised 26 Apr 2018; accepted 29 Apr 2018; published 7 May 2018

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1. Introduction

Attribute to the low repetition rate and corresponding high pulse energy and peak power [1], Q-switched laser is one of the most popular types of laser, which is widely being applied in laser materials processing, microfabrication, remote sensing, range finding, skin treatment, tattoos removal, pumping source for nonlinear frequency conversion devices, and medical surgery [2,3]. Drifted by the strong commercial interests, the Q-switched laser has gained a considerable attention within the modern industry and science communities. Unlike the costly, complex, and bulkiness of active electro- or acousto- optic modulators which can be utilized within the laser cavity to generate Q-switched laser pulses [4]. The passive Q-switching technique with saturable absorber (SA) offers a simple, low cost, compact and reliable alternative way to produce Q-switching pulses. Furthermore, the low energy

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consumption and lightweight properties have made it more suitable for the practical applications of some portable devices e.g. range finder.

Usually, doped crystal, e.g. Co:MALO [5], Cr:YAG [6] etc. are used for the fabrication of commercially produced passive Q-switching systems. However, these crystal-based Q-switchers require expensive crystal growth process and doping techniques [7]. Hence, simple fabrication methods with novel saturable absorber materials are quite encouraging. In the past decade, numerous studies have been carried out implementing carbon-based nano-materials e.g. graphene [8,9], graphene oxide [10,11], and carbon nanotube [12] saturable absorber to generate Q-switching pulses. Graphene-based SA exhibits zero or small bandgap energy, offering a broad response wavelength ranging from UV to mid-infrared. However, the weak layer absorption significantly limits the light modulation ability [7]. Recently, the research interest of graphene has been extended to other two-dimensional (2D) layered materials with nature bandgap, stronger layer absorption, and modulation depth. Black phosphorus (BP) has shown strong layer dependent bandgap energy [13], which has also been used to fabricate SA for Q-switching pulse generation [14]. Transition metal dichalcogenides (TMDs) compounds, a different type of 2D layered materials, have demonstrated excellent properties based on the atomic ratio [15] and d-electron number of the transition metal [16]. TMDs has the stoichiometry of MX_2. Each layer is composed of a single plane hexagonally arranged with groups 4–10 transition metal atoms sandwiched between two of chalcogen atoms (S, Se, or Te) [7]. The demonstration of group 6 TMDs materials as SA e.g. MoS_2 [17,18], $MoSe_2$ [19], WS_2 [20–22], and WSe_2 [21] for Q-switching or mode locking laser systems have also recently been achieved. These 2D materials have gained huge interest due to their unique electrical and optical properties, which can be further tailored for the laser pulse generation and according to the application needs.

The newly discovered group 10 TMDs layered materials such as platinum diselenide ($PtSe_2$) and platinum disulfide (PtS_2) have recently attracted great attention, which have been demonstrated to be capable of enabling high performance optoelectronic devices due to their high carrier mobility and broadband light absorption [23–25]. The potential applications of layered PtX_2 have already been demonstrated in photocatalyst [23] and field-effect transistors [24,26]. PtS_2 exhibits a layer dependent tunable and indirect bandgap behavior ranging from 1.6 eV for monolayer to a bandgap of 0.25 eV for bulk materials [27]. Such a broad bandgap range of the material allows to utilize it as a SA from mid to near infrared region of the wavelength spectrum. Hence, the inherent properties of noble PtS_2 material system open up new doors to study the nonlinear absorption properties. So far, chemical vapor deposition (CVD) [27] and molecular beam epitaxy (MBE) [23,24] techniques have been used for fabricating few layered group 10 TMDs materials. However, the costly and complicated preparation process of CVD and MBE techniques prevent the realization of making PtS_2 films. Nevertheless, the use of micro-size bulk-structured WTe_2 has been demonstrated as a promising approach to fabricate SA in generating ultrafast mode locking pulses in a fiber laser cavity [28]. The approach has also gained a lot of attention as a cost-effective technique for mass production of bulk-like materials by crashing the materials mechanically or exfoliated with the help of ultrasound in liquid. In this study, the possibility to use the microflakes of the novel PtS_2 2D material in Q-switching laser application will be explored [28]. A low-cost ultrasound liquid exfoliation method will be employed to produce micro-size PtS_2, which is used for fabricating saturable absorber. The fabricated PtS_2 based saturable absorber will be used to study a passively Q-switched Erbium (Er)-doped fiber laser operating at 1569 nm.

2. PtS_2 saturable absorber fabrication and characterizations

The PtS_2 microflakes are fabricated via liquid exfoliation to separate layered materials from the bulk counterparts. N-Methyl-2-pyrrolidone (NMP) was chosen as solvent for conducting liquid exfoliation due to its great compatibility of surface energy with TMDs materials. 50 mg

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bulk PtS_2 powder (Alfa Aesar) was added into 250ml NMP solvent followed by probe sonication using SCIENTZ-1200E (Ningbo Scientz Biotechnology Co., Ltd). The sonication was conducted under the power of 1200 W with 20 kHz below 27°C for 3 h, with an ultrasound probe time of 2 s at an interval of 4 s. The as-prepared PtS_2 microflakes solution was centrifuged in the ambient environment at 1500 rpm for 5 min to precipitate the large bulks that are not sufficiently separated. Then the supernatant liquor was taken for further characterizations. The sample was prepared by drop casting the PtS_2 supernatant solution on the surface of the quartz substrate and then drying in glove box with nitrogen atmosphere to prevent it from oxidization. A 15.0 g of polyvinyl alcohol (PVA) was dissolved in 85 g of NMP to give a 15 wt. % gel-like solution. Then, 0.4 g of this solution was mixed with 2.0 g as-prepared PtS_2 supernatant liquor and stirred for 30 min to produce the saturable absorber. The mixture was dried under 60°C for 48 h in the oven, yielding PtS_2/PVA composite film.

The dominant PtS_2 samples with similar dimensions were observed by field emission scanning electron microscope (FESEM, S-4800, Hitachi – Science & Technology), as shown in Fig. 1(a). The statics of size distribution among 170 flakes represents that an average dimension along the short-axis is 1.35 μm roughly and an approximately 2.40 μm size for long-axis, as shown in Figs. 1(b) and 1(c), respectively. The atomic force microscopy (AFM, Bruker Nanoscope 8) was carried out to measure the thickness of the exfoliated PtS_2 samples. Topology graph of a typical sample and associated height variations along the marked lines are depicted in Figs. 2(a) and 2(b). The lateral dimensions of 3.16 μm for long-axis and 1.59 μm for short-axis agree with the statics of SEM distribution. The thickness was measured to be around 0.35 μm which explains that it is far beyond the nano-regime. Combining the thickness with SEM analysis, those dimensions indicate that the ultrasound energy is not high enough to weaken the Van der Waals forces between each interlayer, resulting in uniform micro-size flakes.

One of the PtS_2 micro-flakes was identified by the field emission transmission electron microscopy (FETEM, JEM-2100F) as shown in Fig. 2(c). A high resolution of the FETEM image of the micro-flake is shown in Fig. 2(d), which illustrates a clear lattice fringe with an interplanar space of 0.303 nm. This is indicating an in-plane lattice constant of $\alpha = 0.350$ nm, which is very close to the DFT value of 0.358 nm as reported in a recent literature [24].

Chemical compositions were characterized by X-ray photoelectron spectra (XPS, ESCALAB 250Xi, Thermo Fisher Scientific) with achromatic 200W Al Kα as the X-ray source and the resolution of 0.10 eV. XPS spectra of core level Pt4f region and the core level regions for S2p are depicted in Figs. 3(a) and 3(b), respectively. The predominant Pt state is identified to be Pt(II) at 72.58 eV and 75.92 eV. Peaks at 163.73 eV and 165.14 eV correspond to S2p3/2 and S2p1/2, respectively. Atomic percentages for Pt4f, S2p, and C1s are recorded as 15.01%, 26.05%, and 58.93%, respectively. The chalcogen-to-metal ratios are calculated to be 1.74, indicating a partial oxidization occurs on the surface of the sample. Oxidation may also appear during liquid exfoliation when bubbles meet the heated surfaces that are induced by violent vibration caused by sonication. The presence of considerable sulphate series in XPS spectrum of S2p leads to a major contribution of Pt(II) at the localized oxidation of the sample.

3. Laser experiment and results discussion

In order to test the nonlinear property of the fabricated PtS_2-SA, an Er-doped fiber laser with ring cavity was constructed. The cavity consists of a 0.7 m long Er-doped single mode fiber (LIEKKI Er110-4/125), a polarization-independent isolator, a 10% output coupler, and a polarization controller. The total cavity length is about 11.5 m. The 1 mm x 1 mm size PtS_2-SA was integrated into the cavity by sandwiching between the two FC/APC connectors as shown in Fig. 4. The utilization of FC/APC connector instead of FC/PC was to eliminate the parasitic reflection and to maintain the stability of the Q-switched system operation. A pure PVA thin film with the same thickness as the PtS_2-SA was integrated into the fiber laser

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system as shown in Fig. 4 to serve it as a control experiment. In this setting, various pump power level and the polarization direction were adjusted to confirm that no mode locking pulse is observed by using the pure PVA sample.

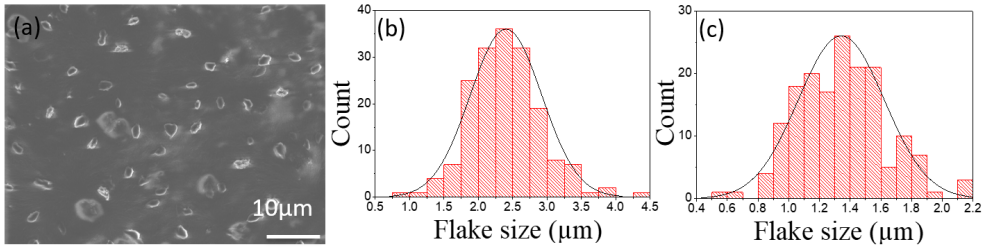

Fig. 1. (a) SEM image of PtS_2 microflakes; and statics of SEM distribution of 170 flakes along the lateral dimensions for the (b) short axis and (c) long axis.

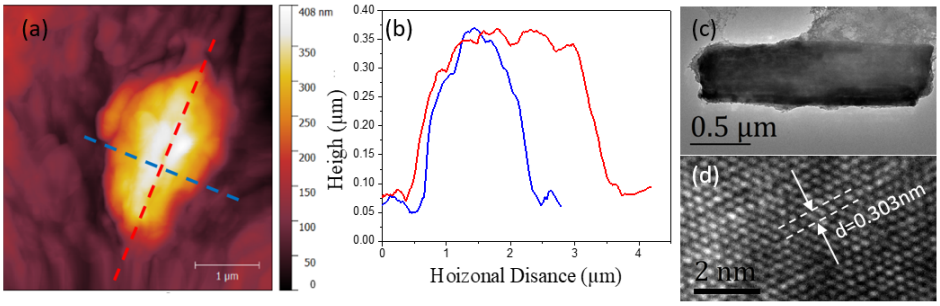

Fig. 2. (a) Atomic force microscopy image of the prepared PtS_2 micro-flake on a quartz substrate. (b) The height profile measured along the blue and red lines shown in (a). (c) FETEM image of a PtS_2 microflake, (d) High resolution TEM image of (c)

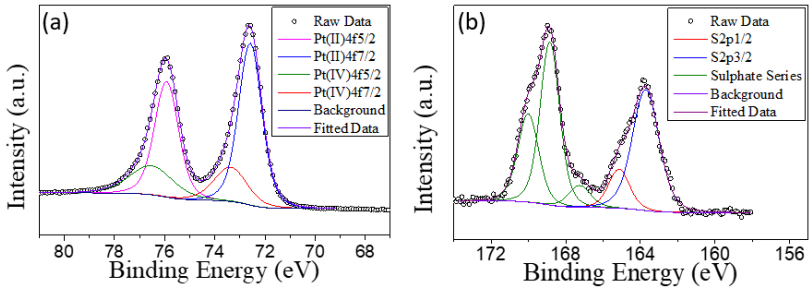

Fig. 3. High resolution X-ray photoelectron spectra of the respective chalcogen for (a) PtS_2 (Pt4f region) and (b) PtS_2 (S2p region)

Then the pure PVA thin film in between the connector junctions was replaced by the fabricated PtS_2-SA. In this case, a stable pulse train was detected, when the pump power was scaled beyond 53 mW. The modulation range of the repetition rate and the full width at half maximum (FWHM) of the pulse duration were observed as 18.1 kHz - 24.6 kHz and 9.6 μs - 4.2 μs, respectively, by changing the pump and the output power as shown in Fig. 5(a). The pulse duration can be further minimized by shortening the total cavity length [4] and enhancing the modulation depth of the PtS_2-SA.

The maximum achieved single pulse energy is 45.6 nJ with respect to 84 mW pumping power. The achieved pulse energy is comparable to those reported in Q-switched Er-doped fiber laser by using other 2D TMDs-SA such as WS_2 (46.3 nJ) [20] and MoS_2 (63.2 nJ) [29]. The corresponding pulse train, single pulse profile, and wavelength spectrum are shown in Figs. 5(b)-6(d), respectively. Beyond this pumping power, the Q-switched operation became

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unstable and eventually vanished. This phenomenon may be due to the oversaturation of the PtS_2 saturable absorber and the instability of laser cavity in the high pump power [30]. A further modification of the cavity setting may further improve the stability of the laser and thus enhance the obtained maximum pulse energy and the peak power.

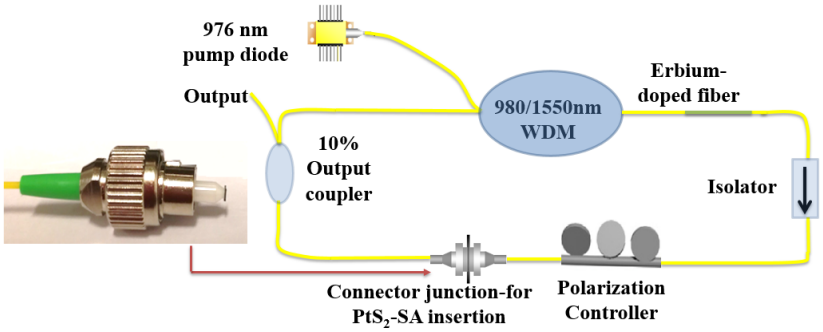

Fig. 4. Schematic experimental set-up of the Q-switched Er doped fiber laser ring cavity.

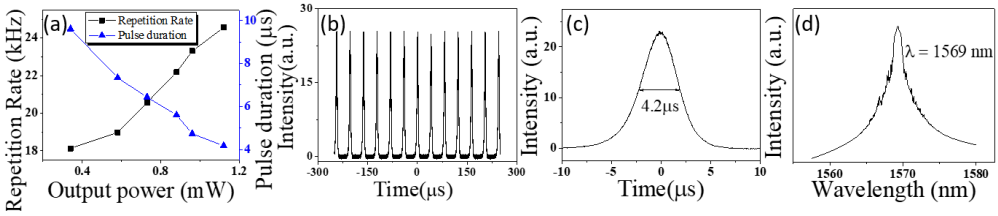

Fig. 5. Q-switched laser characteristics: (a) Variation of repetition frequency and pulse duration with respect to different output power. (b) Pulse train, (c) Single pulse profile, and (d) Output spectrum of the output pulse energy of 45.6 nJ.

4. Conclusion

In this study, for the first time a Q-switched laser based on PtS_2 microflakes saturable absorber fabricated by low cost ultrasonic liquid exfoliation method was demonstrated. Stable 1569 nm Q-switching pulses were obtained from the laser system. The demonstrated pump power depending on the repetition rate and the pulse duration range are 18.1 to 24.6 kHz and 9.6 to 4.2 μs, respectively, with respect to pump power ranging from 53 mW to 84 mW. The maximum output power is about 1.1 mW. This work proves the potential of newly developed layered PtS_2 microflakes saturable absorber fabricated by low-cost ultrasound techniques for laser Q-switching applications.

Funding

National Natural Science Foundation of China (61575167); Shenzhen Science and Technology Innovation Commission (JCYJ20170303160136888); The Research Grants Council of Hong Kong, China (GRF 152109/16E PolyU B-Q52T).