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Abstract Vanadium diselenide (VSe$_2$), a typical metallic behaviour material among transition metal dichalcogenides (TMDCs) family, exhibits excellent photoelectric characteristics with a zero band gap, missing application in pulse generation. In this work, a high-quality VSe$_2$ saturable absorber (SA) was synthesized through a liquid-phase exfoliation method. The saturable absorption of obtained VSe$_2$-SA was characterized systematically. The measured modulation depth was 9.9%, and the saturated intensity was 533.8 µJ/cm$^2$. By incorporating this optical modulator into a ytterbium-doped fiber laser cavity, a stable passively Q-switched laser could be achieved. The pulse had the central wavelength of 1064.03 nm. As the pump power was increased, the repetition rate increased from 24.3 kHz to 35.6 kHz, and the pulse duration decreased from 7.21 µs to 5.27 µs. The output power had the maximum value of 28.55 mW. These results indicated that VSe$_2$ is an effective candidate to generate pulse laser due to its excellent nonlinear optical properties and universal photoelectric response, which may advance the applications of VSe$_2$-based nonlinear optics and photoelectric devices.

Keywords transition metal dichalcogenides, VSe$_2$, saturable absorber, pulse laser, fiber laser


1 Introduction

Since the foundation of pulsed fiber laser, due to the rapidly increasing demand for industrial material processing, bio-medicine sensing, high-speed communication and other fields [1–4], ultrashort pulse fiber lasers generation has attracted much attention. For the benefit of easy processing characteristics, desirable structure and tunable energy band, and excellent nonlinear optical properties, various novel two-dimensional (2D) materials have attracted considerable interest in the recent decade, since the graphene was first fabricated in 2004 [5]. Inspired by the outstanding performance of graphene [6–9], several different types of 2D materials, such as topological insulators (TIs) [10,11], black phosphorus (BP) [12,13], and transition metal dichalcogenides (TMDCs), have been extensively used in the field of pulsed fiber lasers. Especially, as novel 2D materials, various TMDCs (WS$_2$ [14, 15], MoS$_2$ [16, 17], WSe$_2$ [18], MoSe$_2$ [19], TiS$_2$ [20], TiSe$_2$ [21, 22], SnS$_2$ [23], etc.) have been widely studied as optical modulator at different

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† Wang T and Shi X Y have the same contribution to this work.
wavelengths due to their ultrafast recovery time, high nonlinearity, high damage threshold, and suitable band gaps. This group of TMDCs materials have a generic chemical formula of MX$_2$ (M = W, Mo, Nb, Sn, V, Ti, Zr, Hf, Ta, etc., and X = S, Se and Te) with a layered crystal structure. Furthermore, according to the various electronic properties, the TMDCs can be divided into semiconductors (WS$_2$, MoS$_2$, etc.), superconductors (NbSe$_2$, TaS$_2$, etc.), semimetals (MoTe$_2$, WTe$_2$, etc.) or true metals (VSe$_2$, NbS$_2$, etc.) [21]. Therefore, exploring the optoelectronic properties of TMDCs and their applications are a fundamentally and technologically interesting question.

There are few studies on the optical and electrical characteristics of metallic TMDCs compared with other TMDCs. Among the TMDCs family, vanadium diselenide (VSe$_2$) is a typical metallic member material aside graphene, which has a zero band gap [24]. VSe$_2$ is a typical layered compound, in which each layer is composed of metal V atoms sandwiched between two Se atoms, with Se-V-Se interlayers stacked together via weak van der Waals forces along the (001) direction [25]. Owing to its metallic property and high electrical conductivity (1000 Sm$^{-1}$) [26, 27], VSe$_2$ has been extensively investigated as an anode material for practical energy storage, such as potassium-ion and lithium-ion batteries [28–30], but has never been applied in the field of pulse fiber lasers. Compared to several other broadband saturable absorbers (SAs), such as MXene [31], PtTe$_2$ [32], and TiS$_2$ [33], VSe$_2$ possesses many advantages, including that the zero band gap makes VSe$_2$ have universal optical response, relatively large layer spacing of 6.1 Å [25, 34] and weak van der Waals interactions render it easy to be exfoliated from bulk crystals. It is expected that VSe$_2$ could be a promising broadband SA applied in pulsed laser field with these merits. However, the nonlinear optical saturated absorption properties of VSe$_2$ is sparse and remain unexplored, and its corresponding applications become an indispensable and challenging task.

To address this challenge, herein, the VSe$_2$ nanosheets was first prepared by a liquid-phase exfoliation (LPE) method. Then, the saturable absorption characteristics of the obtained sample were further characterized. The measured saturated intensity and modulation depth were 533.8 µJ/cm$^2$ and 9.9%, respectively. Then the VSe$_2$-SA was incorporated in a ytterbium-doped fiber laser, and a stable passively Q-switched pulse laser could be observed. The pulses had the maximum output power of 28.55 mW. The repetition rate increased from 24.3 kHz to 35.6 kHz with increasing pump power, but the pulse duration varied from 7.21 µs to 5.27 µs. It is the first time to achieve pulse output based on VSe$_2$-SA, to the best of our knowledge. These experimental results indicated that not only VSe$_2$ but also other metallic TMDCs could be alternative candidates for pulse lasers.

2 VSe$_2$-SA sample preparation and characterization

2.1 Crystal growth and preparation of a VSe$_2$ based SA

The high-quality VSe$_2$ crystals were synthesized via chemical vapor transport (CVT) method with iodine as a transport agent. The stoichiometric amount of vanadium powder (V, 99.9%, Aladdin), selenium (Se, 99.999%, Aladdin) with a total weight of 2 g and iodine (I$_2$, 5 mg/mL, 99.99%, Aladdin) was put in a quartz ampule (outer diameter: 20 mm; thickness: 2 mm; length: 150 mm). Then, the quartz ampule was sealed with an oxygen/hydrogen welding torch under high vacuum (less than 1 × 10$^{-3}$ Pa). After that, this ampule was heated at 800°C (T$_{H1}$) and 700°C (T$_{L}$) for at least one week, respectively. The heating rate and the cooling rate were both below 5°C/min to avoid the explosion. Finally, at the cold end of the ampule, the black hexagonal crystals with metallic luster were formed after the growth process was finished and cooled to room temperature.

The synthesized VSe$_2$ crystals were first soaked in ethanol for at least 2 h to wash away the transport agent I$_2$ from the surface. Then, clean VSe$_2$ crystals were put in about 20 mL ethanol again and then sonicated for more than 2 h. Finally, the solution of few-layer VSe$_2$ nanoflakes could be obtained and was dropped onto the end face of a clean fiber ferrule. This ferrule was connected to another one via a fiber flange. Thus, a VSe$_2$ based SA device was attained.
2.2 Apparatus and characterizations

As shown in Figure 1(a), VSe$_2$ belongs to a space group of P-3m1 (164) in the hexagonal crystal system and has a layered crystal structure with an atomic layer spacing of 6.1 Å. X-ray diffraction (XRD) pattern was further conducted by Bruker AXS X-ray scattering systems with Ni-filtered Cu K radiation to demonstrate the crystal structure of the obtained VSe$_2$ samples. All characteristic peaks, as shown in Figure 1(b), matches well with the standard JCPDS card of VSe$_2$ (No. 89-1641), indicating the purity of VSe$_2$ crystals. The (001) peak in the figure also shows a lattice periodicity along the c-direction, which could prove a layered crystal structure of VSe$_2$ crystals. Raman spectrum was performed in a LABRAM HR Evolution with visible laser light ($\lambda$ = 532 nm) and Figure 1(c) shows a typical Raman spectrum of a few-layer VSe$_2$ nanoflake on a Si substrate with 285 nm SiO$_2$ after the liquid-phase exfoliation. The obvious Raman shift peak observed at 207 cm$^{-1}$ was considered to $A_{1g}$ vibration mode of VSe$_2$, and the other peak over 500 cm$^{-1}$ was related to Si substrate, suggesting the thinness of the VSe$_2$ nanoflakes.

As presented in Figure 1(d), the transmission electron microscopy (TEM) image (Tecnai ® G2 F20) of VSe$_2$ nanoflakes shows relatively clean morphology and visible layered structure. Figure 1(e) depicts a high-resolution TEM image of the VSe$_2$ nanoflakes and the lattice fringes measured are about 3.2 Å and 2.6 Å, which are corresponding to (111) plane and (220) plane, respectively. As shown in Figure 1(f), the crystal characteristic of VSe$_2$ is also proved by the sharp and bright selected area electron diffraction (SAED) patterns, which coincides with its hexagonal crystal structure and shows high crystallinity.

Scanning electron microscopy (SEM, quanta FEG 250) was also utilized to watch the microscopic appearance and elemental composition of VSe$_2$ crystals, as shown in Figure 2(a). VSe$_2$ crystals show a conspicuous hexagonal edge of 120° and layered structure, which conform with the crystal structure. As depicted in Figure 2(b)–(d), the energy-dispersive X-ray (EDX) mappings and EDX spectrum prove that VSe$_2$ crystals have a uniform elemental composition and an accurate elemental ratio of 1:2 (vanadium: 33.38% and selenium: 66.62%). All of these characterizations certificate that high-quality VSe$_2$ crystals can be obtained via a CVT method. Before forming a VSe$_2$ based SA device, an atomic force microscope (AFM, dimension 3100) was used. Figure 2(e) presents a representative AFM image of VSe$_2$ nanoflakes after the liquid-phase exfoliation, showing clean surface and flat shape. The corresponding linear scan analysis of height and optical photograph are exhibited in Figure 2(f) with a thickness of around 30 nm.
Figure 2 (Color online) (a) A typical SEM image of a VSe$_2$ crystal with a hexagonal shape; (b)–(d) the corresponding EDX mappings and EDX spectrum with an atomic ratio of V and Se elements showed in (a); (e) an AFM image of few-layer VSe$_2$ nanoflakes on a Si substrate with 285 nm SiO$_2$; (f) the corresponding optical photograph ($\times$100) and a height graph of thickness around 30 nm.

Figure 3 (Color online) (a) the ultraviolet-visible absorption spectrum of VSe$_2$ nanosheets; (b) nonlinear SA curve of the VSe$_2$-SA at different light intensity.

Besides, the optical properties of VSe$_2$ were also studied. As illustrated in Figure 3(a), VSe$_2$ has similar absorption intensity over a broadband spectrum, corresponding to its zero band gap characteristics. The saturable absorption characteristics of VSe$_2$ were characterized with the power-dependent transmission technique, as reported previously in our studies [35, 36]. The laser source was a homemade ytterbium-doped mode-locked fiber laser (central wavelength of 1064 nm, repetition rate of 20.95 MHz). The measured nonlinear transmittance under different incident power intensity is presented in Figure 3(b). The fitting curve of saturable intensity, modulation depth, and nonsaturable loss are 533.8 µJ/cm$^2$, 9.9% and 48.9%, respectively.

3 Pulse laser generation setup and results

Figure 4 illuminates the diagram of VSe$_2$-based passively Q-switched fiber laser, where a 976 nm laser diode (LD) pumped 2 m ytterbium-doped fiber (YDF, dispersion coefficient 23 ps$^2$/km) as the gain medium. Meanwhile, a wavelength-division multiplexing (WDM) was applied to deliver the 976 nm pump light into the cavity. In order to achieve spectral filter at 1 µm wavelength, a band-pass filter (BPF) centered at 1064 nm with the bandwidth of 2 nm was connected after the YDF. A polarization-independent isolator (PI-ISO) and a polarization controller (PC) were employed to ensure the unidirectional light propagation and adjust the polarization states. A fiber-fused optical coupler (OC, 10:90) was adopted...
Figure 4 (Color online) Experimental setup for the VSe$_2$-based passively Q-switched fiber laser.

![Experimental setup diagram]

Figure 5 (Color online) Output pulse properties. (a) Output power; (b) the variation of repetition rate and pulse duration with different pump power; (c) pulse energy as a function of pump power; (d) peak power versus pump power.

Figure 4...
increased, the single pulse energy as well as peak power increased gradually, shown in Figure 5(c) and (d). The maximum value of pulse energy was 802 nJ and the maximum peak power was 152.1 mW.

At the pump power of 263.1 mW, the pulse properties were also observed in detail. The output spectrum centered at 1064.03 nm with a 3 dB bandwidth of 0.25 nm is presented in Figure 6(a). The pulse train has the repetition rate of 29.6 kHz, corresponding to the pulse interval of 33.78 µs, as shown in Figure 6(b). Figure 6(c) presents a single pulse envelope, which was fitted by a Gaussian function. As can be seen, the pulse duration is 5.66 µs. The temporal stability of output pulse was also characterized. The measured radio frequency (RF) spectrum locates at 29.6 kHz, having the signal to noise ratio (SNR) of 57.2 dB (over 520000 contrast), as shown in Figure 6(d). The RF spectrum over a wide range of 300 kHz with the bandwidth resolution of 200 Hz is shown in the inset. These results indicate that the obtained Q-switched pulse had excellent temporal stability.

The long-term stability of this VSe$_2$-based Q-switched pulse was also characterized every 5 min interval throughout 40 min continuously at the pump power of 321 mW. The spectrums were presented in Figure 7(a), which shows the Q-switched state was kept steadily and the central wavelengths did not have obvious change in 40 min. At the same pump power, the variations of bandwidth and output power are depicted in Figure 7(b) and (c), and the fluctuations from average were less than 0.8% and 1.5%, respectively. Fifteen days after the completion of the experiment, the passively Q-switched pulses could still be observed without any additional adjustments. The setup remained almost unchanged, and the VSe$_2$-SA was encapsulated between two fiber adaptors to avoid dust pollution in the past 15 days. These experimental results indicate that this VSe$_2$-based Q-switched pulse has excellent long-term stability.

In this work, the mode-locking operation was not achieved for several reasons. Firstly, the mode-locking operations require phase locking between many longitudinal modes. However, in this experiment, the bandwidth of BPF is 2 nm, which may be too small for mode-locking. In addition, the intra-cavity loss is too high to achieve the power threshold of mode-locking operation. Intra-cavity losses may come from fiber ferrules and optical devices. Besides, the thickness of the VSe$_2$-SA may affect the modulation depth.
Figure 7 (Color online) Q-switched pulse stability every 5 min for a total of 40 min. (a) Output spectrums; (b) bandwidth; (c) output power.

This is a key factor in determining the mode-locking operation. In the future work, the mode-locking operation could be expected by adopting a broadband BPF, reducing the cavity loss, and improving the thickness of VSe$_2$-SA.

4 Conclusion

In conclusion, a VSe$_2$-based passively Q-switched ytterbium-doped fiber laser was demonstrated for the first time. The high-quality VSe$_2$-SA was fabricated with the LPE method. The saturated intensity and modulation depth of VSe$_2$-SA were 533.8 µJ/cm$^2$ and 9.9%, respectively. When the pump power increased to 190.5 mW, the stable passively Q-switched laser could be observed. The pulse width varied from 7.21 µs to 5.27 µs with the repetition rate increasing from 24.3 kHz to 35.6 kHz. The obtained maximum output power was 28.55 mW. These experimental results exhibited that VSe$_2$ could be employed as a promising candidate for pulse lasers taking the advantages of its excellent nonlinear optical properties and universal photoelectric response, and may advance the applications of metallic TMDCs-based optoelectronic devices.

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References