



Preparation of ultrathin ReS₂ nanosheets and their application to Q-switched Er-doped fiber lasers^{*}

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Abstract: We study the exfoliation of ultrathin ReS₂ nanosheets from the prepared ReS₂ powder and their application to Q-switched Er-doped fiber laser. XRD, Raman, and XPS spectra confirm the successful preparation of the layered ReS₂. SEM images show that the obtained ReS₂ sheets have lateral size below 200 nm. The thickness of the ReS₂ nanosheets is smaller than 5 nm according to the AFM results. ReS₂/PVA film is applied as a saturable absorber in an Er-doped Q-switched fiber laser, and a minimum pulse duration of 2.4 μs and an output power of 1.25 mW are obtained, indicating the potential application to Q-switched lasers.

Key words: Rhenium disulfide; Saturable absorber; Two-dimensional materials; Q-switched fiber laser
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1 Introduction

Optical modulation is an important area for fundamental research and has specific applications (Xing et al., 2017; Guo J et al., 2019). In recent years, two-dimensional (2D) materials, including graphene, black phosphorus (BP), transition metal dichalco-

genides (TMDs), and topological insulators (TIs), have attracted significant attention due to their unique electrical, optical, and photoelectrical properties (Huang X et al., 2011; Wang QH et al., 2012; Manzeli et al., 2017; Tao et al., 2018; Zeng et al., 2018, 2019; He et al., 2019; Huang WC et al., 2020). Among them, TMDs represent a large family and include MoS₂, WS₂, MoSe₂, and WSe₂. The bandgaps of MoS₂, WS₂, MoSe₂, and WSe₂ depend greatly on the number of layers and change from direct to indirect semiconductors from monolayer to bulk layers (Tongay et al., 2012; Du J et al., 2014; Liu H et al., 2014; Wang SX et al., 2014; Zhang Y et al., 2014). As is commonly known, for most semiconducting devices, semiconductors with direct bandgaps are preferred for their better performance (Mak et al., 2010; Chen et al., 2015). Therefore, monolayer MoS₂, WS₂, MoSe₂, and

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WSe₂ with large size are required for many applications, but the technology for preparing large-area monolayer TMDs is immature, thus hindering their application.

Recently, ReS₂ has attracted much attention from researchers (Qin et al., 2018; Guo ZL et al., 2019; Liu F et al., 2019; Liu Y et al., 2019). In contrast to the above mentioned TMDs, the monolayer ReS₂, few-layer ReS₂, and bulk ReS₂ are all direct semiconductors (Cui et al., 2017; Su et al., 2017). Moreover, the bandgaps of monolayer and bulk ReS₂ are 1.44 and 1.35 eV, respectively, showing a small bandgap difference (Cui et al., 2017). The physical properties of ReS₂ have little dependence on the layer number, showing a great chance of being used in practical applications.

To date, there have been several reports on Q-switched lasers based on ReS₂. For example, Su et al. (2017) reported few-layer ReS₂ as a saturable absorber (SA) for a 2.8- μm solid state laser. Lin et al. (2019) realized a 1.3- μm Q-switched solid-state laser based on a few-layer ReS₂ SA. Mao et al. (2018) reported Q-switched Er-doped fiber lasers based on ReS₂. However, almost without exception, the raw materials used are ReS₂ single crystals with high purity, which are expensive and inappropriate for large-scale applications (Mao et al., 2018; Xu et al., 2018). In this study, ReS₂ powder is first prepared using low-cost rhenium and sulfur powder as raw materials, and then ReS₂ nanosheets are obtained through liquid exfoliation of the prepared powder. ReS₂/PVA film is used as an SA in a fiber laser, showing good modulation performance for converting a continuous wave (CW) laser into a pulsed Q-switched laser. The obtained minimum pulse width is 2.4 μs , which is comparable to results realized using ReS₂ single crystals as the raw materials, indicating that the prepared ReS₂ has potential application to Er-doped Q-switched fiber lasers.

2 Experiments

ReS₂ powder was prepared in a tube furnace with an argon protective gas using rhenium and sulfur powder as raw materials. A quartz boat filled with rhenium was placed in the center of the tube furnace, while another quartz boat filled with sulfur powder was placed on the upstream side with a low temper-

ature. The temperature of the furnace reached 750 °C in 30 min and maintained for 10 min. Then, the furnace was cooled to room temperature naturally, and thus ReS₂ powder was obtained. ReS₂ nanosheets were prepared through liquid exfoliation and centrifugal separation. In detail, 0.1 g ReS₂ powder was dispersed in a solvent, composed of the mixture of ethanol (30 mL) and deionized water (10 mL). The ReS₂ dispersion was exfoliated in an ultrasound cleaner for 12 h at a power of 400 mW. Then, the mixture was centrifuged at a speed of 5000 revolution per minute for 10 min to remove thick ReS₂. The obtained supernatant was the dispersion containing ultrathin ReS₂. Furthermore, the ReS₂ dispersion and 0.0417 g/mL PVA solution were mixed at a volume ratio of 2:3. Then, the mixture was put into an ultrasonic cleaner for 3 h and poured into an appropriate container for drying. Finally, flexible ReS₂ nanosheets/PVA film was successfully prepared.

The crystalline structure was examined by X-ray diffraction (XRD, D/MAX-Ultima IV, RigakuSmartLab, Japan) using a RigakuSmartLab X-ray diffractometer. The Raman spectra were detected using a Raman spectrometer (NOST, FEX, NOST, Korea) with a 532-nm argon ion excitation laser. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific, USA) was used to confirm the elementary composition and bonding of the prepared sample. The morphology and chemical composition were investigated using a scanning electron microscope (SEM, JSM-6490, JEOL Model, Japan) equipped with an energy dispersive spectrometer (EDS). Information on the thickness of the nanosheets was obtained through an atomic force microscopy (AFM, VeecoNanoscope V, Veeco, USA).

3 Results and discussion

Fig. 1a shows the XRD pattern of the prepared ReS₂ powder. A strong diffraction peak was detected at $2\theta=14.58^\circ$, corresponding to the (001) crystal plane of ReS₂ (Jariwala et al., 2016), confirming the layer-by-layer structure along the *c*-axis. Fig. 1b presents the Raman spectra of the ReS₂ powder, nanosheets, and nanosheets/PVA film. The two low-frequency peaks located at 129.61 and 138.25 cm^{-1} are attributed to A_g modes, corresponding to the out-of-

plane vibration modes of rhenium atoms. The peaks located at 146.85, 157.18, 206.92, and 232.52 cm^{-1} are E_g modes, corresponding to the in-plane vibration modes of rhenium atoms. Other peaks located at higher frequencies come from the vibrations of lighter sulfur atoms (Feng et al., 2015; Hafeez et al., 2016). These strong vibration peaks indicate good crystallinity of the prepared ReS_2 . In addition, the Raman characteristic peaks of different forms of ReS_2 do not change, except their intensity. The high-resolution XPS spectra of rhenium and sulfur are shown in Figs. 1c and 1d, respectively. The two peaks located at 41.8 and 44.2 eV correspond to $4f^{7/2}$ and $4f^{5/2}$ of rhenium, respectively. In Fig. 1d, the two peaks are fitted to be 162.25 and 163.5 eV, corresponding to $2p^{3/2}$ and $2p^{1/2}$ of sulfur, respectively. These results strongly agree with other reported XPS spectra of ReS_2 , confirming the successful preparation of ReS_2 (Hafeez et al., 2016).

Figs. 2a–2c are the SEM images obtained at different magnifications, showing that the prepared ReS_2 are thin nanosheets with lateral size below 200 nm. Fig. 2d shows the EDX spectrum of the sample, confirming that the component elements are rhenium and sulfur, and that the ratio of Re:S is 0.5731:1, which is close to the ratio of Re:S in ReS_2 . To determine the thickness of the ReS_2 nanosheets, AFM characterization was carried out (Figs. 2e and 2f). The AFM image (Fig. 2e) indicates that the ReS_2 sheets are nanosized and ultrathin. The height profiles of some randomly selected ReS_2 nanosheets are given in Fig. 2f, showing that all the thicknesses of the nanosheets are below 5 nm. As the interlayer spacing of the few-layer ReS_2 is 0.7 nm (Liu EF et al., 2016), the number of layers of the prepared ReS_2 nanosheets is estimated to be less than 7.

Fig. 3 shows the experimental setup of the Q-switched Er-doped fiber laser based on the ReS_2

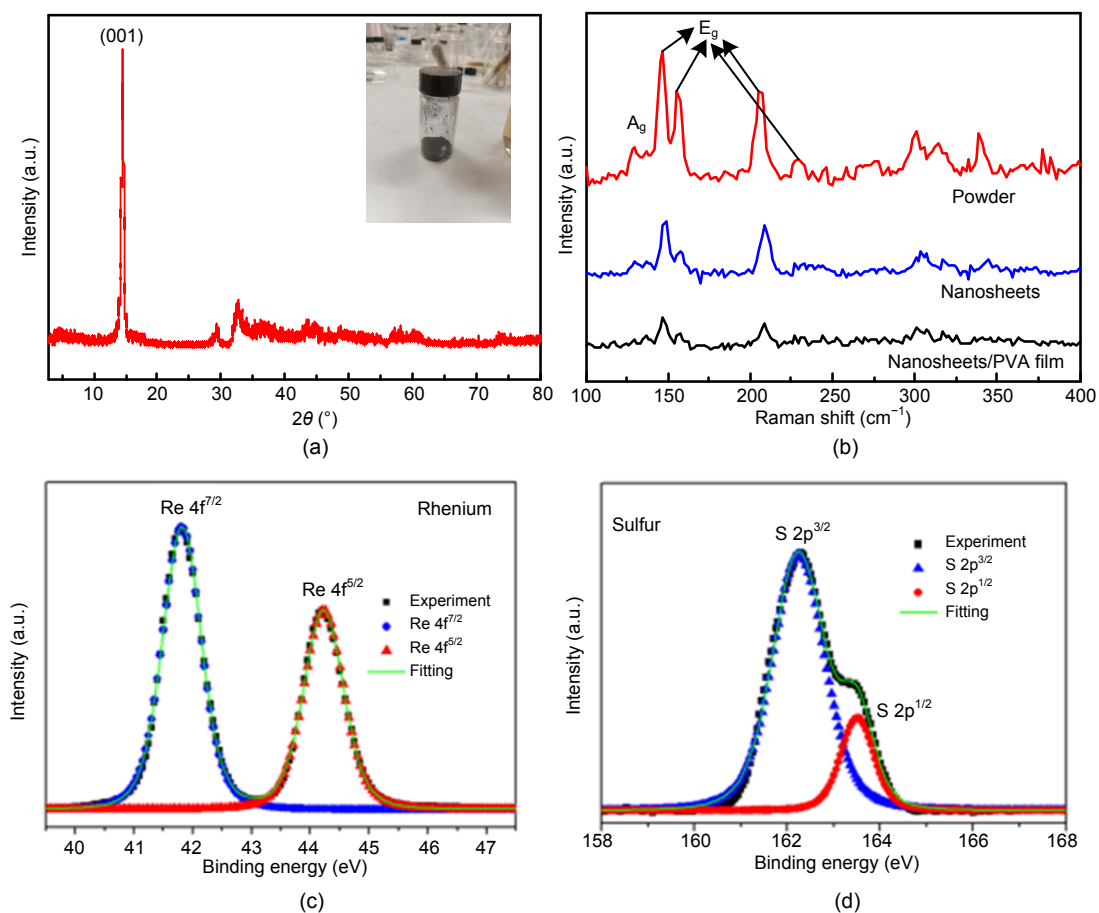


Fig. 1 (a) XRD pattern of the prepared ReS_2 powder (inset is a photograph of the powder); (b) Raman spectra of the ReS_2 powder, nanosheets, and nanosheets/PVA film; (c) high resolution XPS spectra of Re 4f; (d) high resolution XPS spectra of S 2p

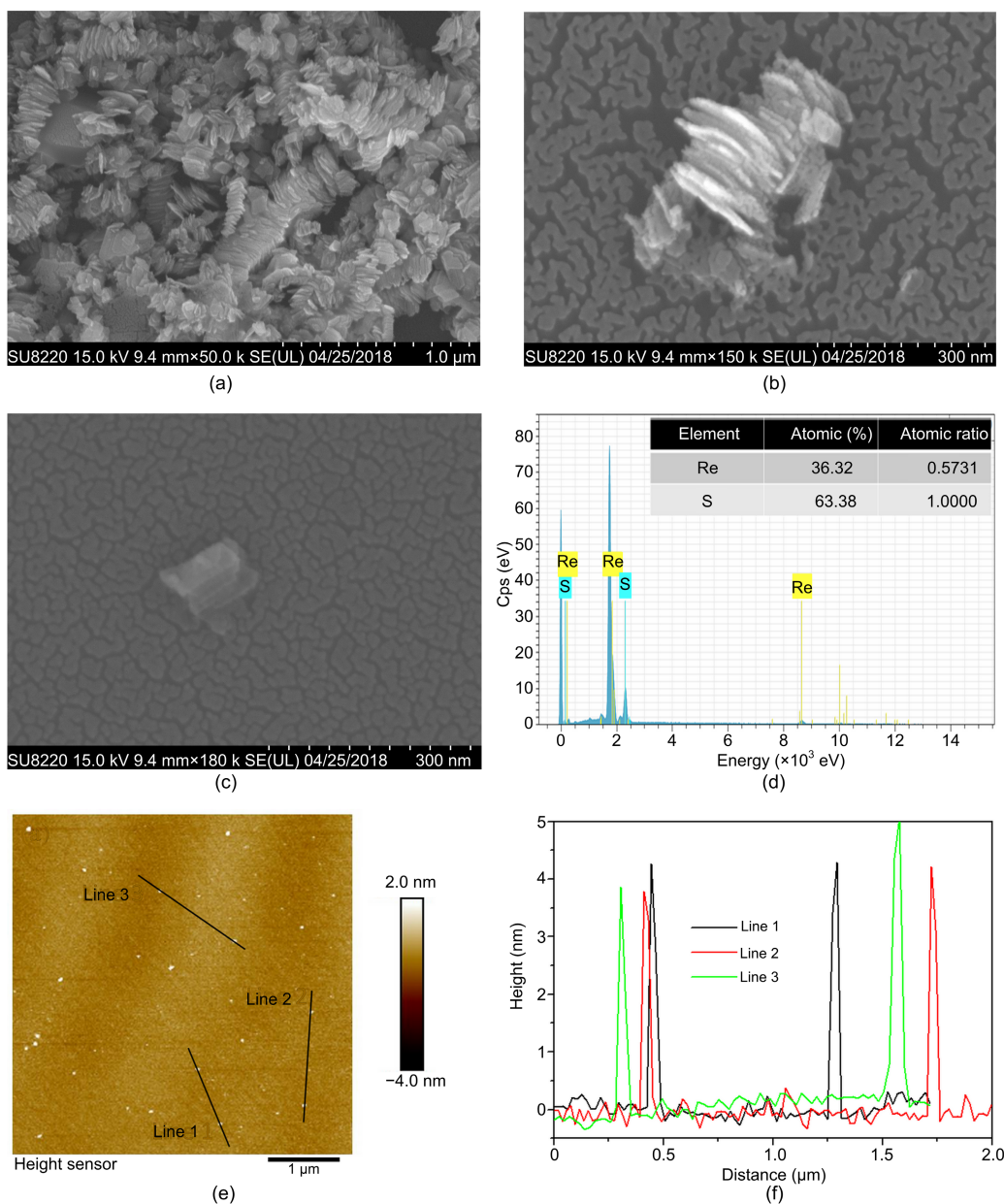


Fig. 2 (a–c) SEM images; (d) EDX spectrum; (e) AFM image; (f) height profile of the ReS₂ nanosheets marked in (e) (References to color refer to the online version of this figure)

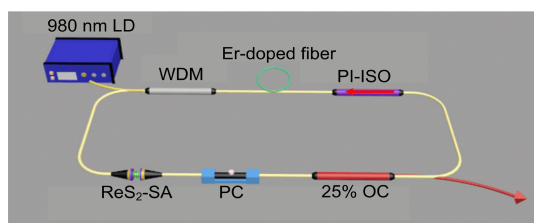


Fig. 3 Experimental setup of the Q-switched Er-doped fiber laser based on ReS₂ saturable absorber (SA)

LD: laser diode; WDM: wavelength division multiplexer; PI-ISO: polarization-independent isolator; PC: polarization controller; OC: output coupler

SA. A laser diode (LD) centered at the wavelength of 976 nm with the maximum power of 500 mW was used as the pump source. The pump energy was delivered into a piece of 2 m-long Er-doped fiber via a 980/1064 wavelength division multiplexer (WDM). A polarization-independent isolator (PI-ISO) was connected to ensure the unidirectional signal propagation in the cavity. A 75:25 output coupler (OC) was used to extract the output signal. The total length of the cavity was 8.4 m.

In this experiment, we first inserted a pure PVA film into the laser cavity and increased the pump power. Even when the pump power was up to 400 mW or the PC was constantly adjusted, the laser worked only in a CW mode. Then, the ReS₂/PVA film was inserted into the laser cavity, and a Q-switching signal was obtained when the pump power was increased to about 120 mW. Fig. 4a shows the pulse trains with a pulse duration of 2.8 μ s of the Q-switched Er-doped fiber laser based on ReS₂ SA obtained at a pump power of 160 mW. Fig. 4b demonstrates the evolution of the repetition rate and

pulse duration with an increasing pump power. The repetition rate became higher, from 56.8 to 66.52 kHz, and the pulse duration narrowed from 9.74 to 2.4 μ s with an increasing pump power, showing the typical characteristics of a Q-switched laser. Fig. 4c shows the average output power and single pulse energy vs. pump power. The maximum output power and single pulse energy were 1.25 mW and 18.88 nJ, respectively. Performance comparison of Q-switched Er-doped fiber lasers based on different TMDs is summarized in Table 1, indicating that the performance of the Q-switched Er-doped fiber laser based

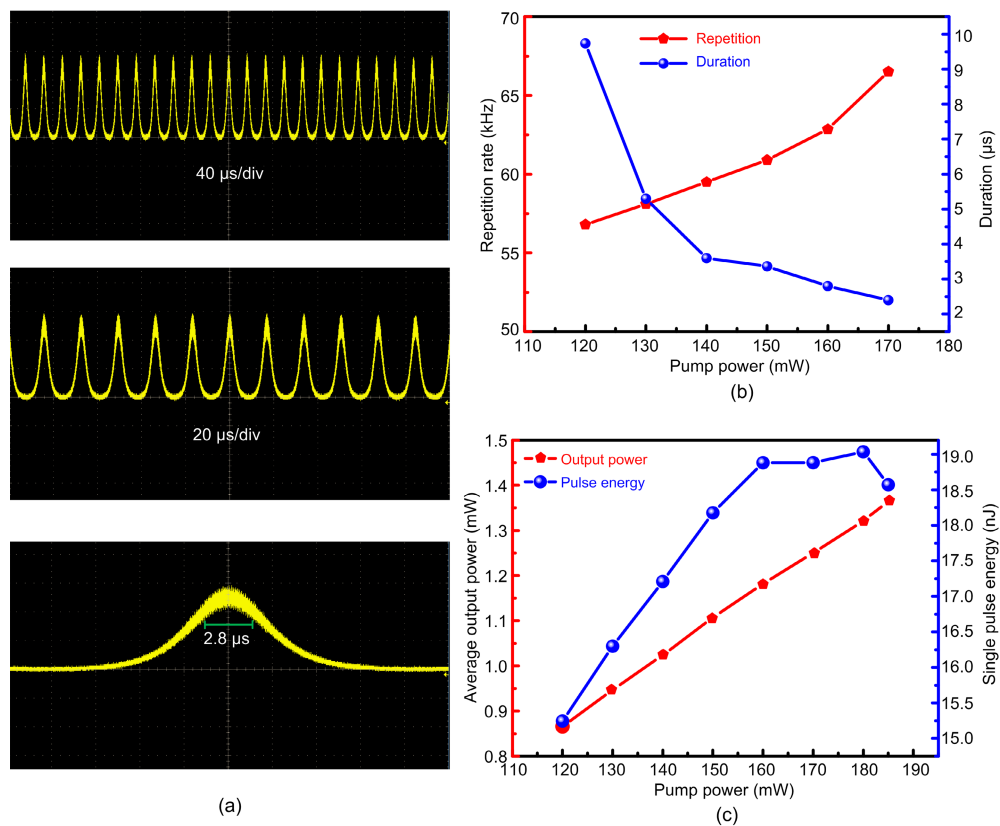


Fig. 4 (a) Q-switched pulse trains in different scales obtained at a pump power of 160 mW; (b) repetition rate and pulse duration vs. pump power; (c) average output power and single pulse energy vs. pump power

Table 1 Performance comparison of Q-switched Er-doped fiber lasers based on different TMDs

Material	Pulse duration (μ s)	Maximum output power (mW)	Repetition rate (kHz)	Maximum pulse energy (nJ)	Reference
MoS ₂	23.3–5.4	1.70	6.5–27	63.20	Luo et al. (2014)
WS ₂	3.4–1.1	16.40	79–97	179.60	Zhang M et al. (2015)
ReSe ₂	16.5–4.98	0.76	6.64–21.04	36.00	Du L et al. (2018)
PtSe ₂	4.6–0.9	11.34	20.5–79.2	143.20	Zhang K et al. (2018)
PtS ₂	9.6–4.2	1.10	18.1–24.6	45.60	Wang XY et al. (2018)
ReS ₂	7.4–2.1	2.48	43–64	38.00	Xu et al. (2018)
ReS ₂	23–5.496	1.20	12.6–19	62.80	Mao et al. (2018)
ReS ₂	9.74–2.4	1.25	56.8–66.52	18.88	This work

on ReS₂ in this research is comparable to those of other reported ones. However, it is noteworthy that the ReS₂ nanosheets prepared in this work were exfoliated from low-cost powder, while the raw material used in other work was ReS₂ single crystal, purchased at high expenses.

4 Conclusions

We have studied a Q-switched Er-doped fiber laser based on ultrathin ReS₂ nanosheets exfoliated from the prepared low-cost ReS₂ powder. XRD pattern, Raman spectrum, XPS spectra, and EDX results indicated the successful preparation of ReS₂. The thickness of the ReS₂ nanosheets was below 5 nm according to the AFM results. The realized Q-switched Er-doped fiber laser based on ReS₂ had a minimum pulse duration of 2.4 μs with a repetition of 66.52 kHz, indicating that the prepared ultrathin ReS₂ nanosheets have potential application as saturable absorbers to Q-switched fiber lasers.

Contributors

Lili TAO and Bo ZHOU designed the research. Junshan HE, Guohua ZENG, Shaoxian LIU, and Haiming LU conducted the experiments and processed the data. Junshan HE drafted the manuscript. Ruixian XIE and Jingjing QI helped organize the manuscript. Lili TAO and Bo ZHOU revised and finalized the paper.

Compliance with ethics guidelines

Junshan HE, Guohua ZENG, Shaoxian LIU, Haiming LU, Ruixian XIE, Jingjing QI, Lili TAO, and Bo ZHOU declare that they have no conflict of interest.

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