



Research article

Huanian Zhang^{a,*}, Pengfei Ma^a, Mingxiao Zhu, Wenfei Zhang, Guomei Wang and Shenggui Fu^{*}

Palladium selenide as a broadband saturable absorber for ultra-fast photonics

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Abstract: Air-stable broadband saturable absorbers (SAs) exhibit a promising application potential, and their preparations are also full of challenges. Palladium selenide (PdSe₂), as a novel two-dimensional (2D) layered material, exhibits competitive optical properties including wide tunable bandgap, unique pentagonal atomic structure, excellent air stability, and so on, which are significant in designing air-stable broadband SAs. In our work, theoretical calculation of the electronic band structures and bandgap characteristics of PdSe₂ are studied first. Additionally, PdSe₂ nanosheets are synthesized and used for designing broadband SAs. Based on the PdSe₂ SA, ultra-fast mode-locked operations in 1- and 1.5- μm spectral regions are generated successfully. For the mode-locked Er-doped operations, the central wavelength, pulse width, and pulse repetition rate are 1561.77 nm, 323.7 fs, and 20.37 MHz, respectively. Meanwhile, in all normal dispersion regions, mode-locked Yb-doped fiber laser with 767.7-ps pulse width and 15.6-mW maximum average output power is also generated successfully. Our results fully reveal the capacity of PdSe₂ as a broadband SA and provide new opportunities for designing air-stable broadband ultra-fast photonic devices.

^a**Huanian Zhang and Pengfei Ma:** These authors equally contributed to this work.

***Corresponding authors: Huanian Zhang,** School of Physics and Optoelectronic Engineering, Shandong University of Technology, Zibo 255049, China; and Shandong Normal University, Jinan 250358, China, e-mail: huanian_zhang@163.com. <https://orcid.org/0000-0001-7369-3379>; and **Shenggui Fu,** School of Physics and Optoelectronic Engineering, Shandong University of Technology, Zibo 255049, China, e-mail: fushenggui@sdu.edu.cn

Pengfei Ma: State Key Laboratory of Luminescent Materials and Devices and Institute of Optical Communication Materials, South China University of Technology, Guangzhou 510640, China

Mingxiao Zhu, Wenfei Zhang and Guomei Wang: School of Physics and Optoelectronic Engineering, Shandong University of Technology, Zibo 255049, China

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1 Introduction

The emergency of two-dimensional (2D) layered materials provided exciting opportunities for the development of novel opto-electric, bio-medical, and energy devices [1–13]. Recently, novel ultra-fast optical devices such as Q-switchers, mode-lockers, optical switchers, and so on have been investigated extensively due to their excellent opto-electric characteristics including wide-absorption band, ultra-fast recovery time, high-damage threshold, etc. [1–5]. Especially, 2D material-based mode lockers were widely employed for proposing ultra-fast pulsed fiber lasers, which have important applications in the fields of medicine, optical spectroscopy, chemical and biomedical researches, and so on [1–3, 14–20]. In addition, 2D material-based mode-locked fiber lasers were also regarded as excellent test platforms for the research of various kinds of soliton phenomena, promoting the rapid progress of 2D ultra-fast device-based soliton research [21].

Graphene was the pioneer in exploring ultra-fast applications of 2D materials and exhibited excellent performance in demonstrating pulsed fiber laser operating from visible to mid infrared bands [22–29]. As is known, the zero-band-gap structure of graphene also brought great obstacles to its optoelectronic device applications. Since then, inspired by graphene, various 2D layered materials including multi-elemental (transition metal dichalcogenides (TMDs) [30–41], topological insulator (TIs) [42–47], ferromagnetic insulator (FIs) [48–50], metal chalcogenide [51, 52], MXenes [53–56], etc.) and mono-elemental (Xenes (phosphorene [57–66], graphdiyne [67], antimonene [68], bismuthene [69–71], tellurene [72, 73]) and selenene [74]) were prepared as mode lockers for obtaining pulsed fiber lasers extensively. Among which, black phosphorus (BP) was regarded as an ideal saturable absorption material due to its obvious advantages of a tunable bandgap value of 0.3–1.5 eV [57–59], high nonlinear coefficient, and so on. However, the air-unstable property of

BP also limited its wide in-deep photoelectric applications. In general, exploring air-stable materials with wide tunable bandgap value is of great significance in promoting the practical optical device applications of 2D materials.

In our contribution, PdSe₂ was selected as the base material for designing wide absorption-band ultra-fast optical devices. Reported results have proven that PdSe₂ exhibited several competitive excellent properties. Most importantly, PdSe₂ exhibits a thickness-dependent wide-tunable bandgap value, which can be narrowed from 1.3 eV for the monolayer to 0 eV for bulk [75–81]. Moreover, as is known that the thickness-dependent bandgap is not a unique property of PdSe₂ [82, 83], the thickness-dependent bandgap is regarded as a commonality of two-dimensional materials. However, in comparison with PdSe₂, the bandgaps of commonly reported TMDs (MoS₂, WS₂, SnS₂, etc.) always vary between 1 and 2 eV. In other words, 2D materials with such a widely tunable band gap as PdSe₂ were rarely reported before. Such a competitive wide optical bandwidth coverage is the most unique advantages of PdSe₂ compared with other types of 2D materials, indicating that PdSe₂ is a promising material for preparing wide absorption band photoelectric devices. Second, in comparison to other isotropic TMDCs, PdSe₂ has another unique property of pentagonal atomic structure in which Pd atoms coordinate with four Se atoms, forming a square backbone lattice (Figure 1A and B). The waved Pd–Se layers are held together by van der Waals force with a distance of about 0.4 nm (Figure 1C) [77–81]. Owing to the unique pentagonal atomic structure, in comparison with commonly used TMDs, PdSe₂ devices present a unique anisotropic response to external stimulations, which will provide opportunities for designing anisotropic photoelectric devices. Especially, PdSe₂ also has the essential basic properties used as the optoelectronic device: excellent air stability [80]. Besides, high-quality PdSe₂ nanosheets can be easily prepared by the cost-effective liquid-phase exfoliation (LPE) method. All the mentioned

properties indicate that PdSe₂ is an excellent air-stable low-cost nonlinear absorption material with wide absorption bandgap. Previously, the nonlinear absorption applications of PdSe₂ have been investigated within solid state lasers preliminarily [84, 85]. Besides that, the thickness-dependent wide-band ultra-fast optical applications of PdSe₂ are still far from thoroughly investigated. Exploring the wide-band absorption applications of PdSe₂ and designing PdSe₂-based broadband optical devices are meaningful for promoting the practical development of 2D-based ultra-fast optical devices.

In this work, first, based on the density function theory, the electronic band structures and bandgap characteristics are calculated. The calculated results prove that PdSe₂ exhibits a wide tunable indirect bandgap of 0–1.3 eV, which is suitable for designing broadband ultra-fast optical devices. In addition, PdSe₂ nanosheets with 15- to 16-layer thickness are prepared and employed for proposing as a saturable absorber (SA) successfully. Based on the PdSe₂ SA, within all anomalous dispersion regions, a mode-locked Er-doped fiber laser with a 323.7-fs pulse width under a pulse repetition rate of 22.7 MHz is obtained. Meanwhile, within all normal dispersion regions, a mode-locked Yb-doped fiber laser with a 767.7-ps pulse width and 15.6-mW maximum average output power is also generated successfully. The excellent wide-band absorption performance of PdSe₂ presents that PdSe₂ exhibits great potential and capacity in designing wide absorption band ultra-fast optical devices.

2 Density function theory (DFT) calculation

In our work, the Vienna ab initio simulation package (VASP, University of Vienna) was employed to optimize crystal structures and calculate electronic structures with

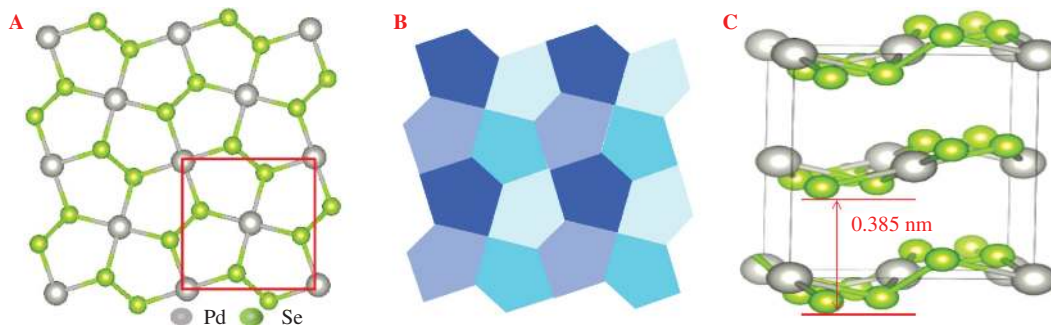


Figure 1: Atomic structures of PdSe₂.

(A) Top view of a $2 \times 2 \times 1$ supercell of the single-layer PdSe₂. (B) A sketch of the Cairo tessellation formed from pentagons. (C) Side view of the three-layer PdSe₂.

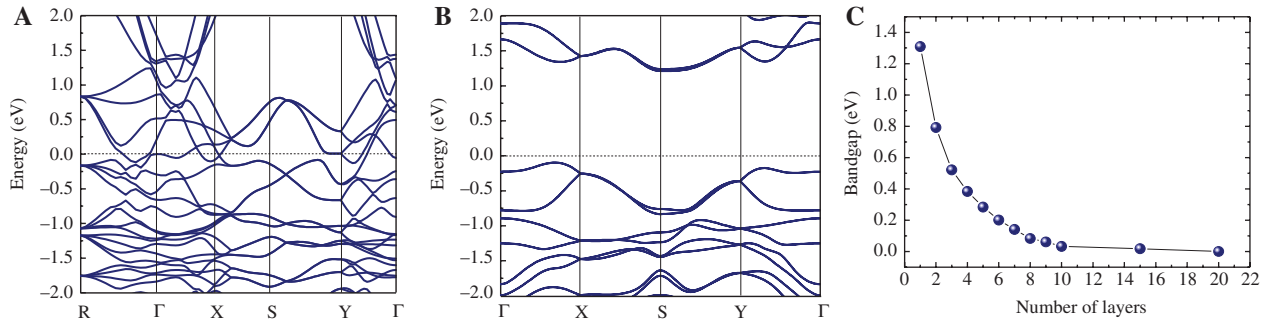


Figure 2: Calculated results of the electronic band structures and bandgap values.

Electronic band structures of (A) bulk PdSe₂ and (B) single-layered PdSe₂. (C) Relationship between the bandgap value and layer number.

the framework of density functional theory [86, 87]. We tested several functionals implemented in VASP, including PBE [88], optPBE [89], optB88 [89], PBE-D2 [90], PBE-D3 [91], and PBE-TS [92]. It is found that the functional of optPBE yields reasonable results for structural and electronic and properties. The energy cutoff for the plane-wave basis was set to 500 eV for all calculations and the k-point spacing of the reciprocal space was fixed to 0.02 Å⁻¹. All atoms were relaxed until the residual forces were below 0.001 eV/Å. For the 2D slab calculations (monolayer and few-layer PdSe₂ systems), a vacuum region of at least 20 Å in the out-of-plane direction was used to avoid spurious interactions with periodic images.

The calculated electronic band structures of bulk and single-layer PdSe₂ are provided in Figure 2A and B, respectively. For the bulk PdSe₂, no bandgap is recorded. Meanwhile, the single-layered PdSe₂ exhibits an obvious indirect bandgap of about 1.31 eV, which is close to its direct bandgap of 1.43 eV. The relationship between the bandgap value and layer number is also calculated and shown in Figure 2C. As is shown, when the layer number increases from 1 to 15, the bandgap value decreases from 1.31 to 0.02 eV. In addition, the bandgap values for 20 layers and bulk PdSe₂ are 0 and -0.01 eV, respectively, which also proves that bulk PdSe₂ exhibits no bandgap. Especially, such a large tunable bandgap is of great significance for designing broadband opto-electronic devices.

3 Preparation and characteristics of the PdSe₂

Because PdSe₂ exhibits excellent air stability, thus, in our work, PdSe₂ nanosheets were prepared by the commonly used low-cost LPE method. The preparation process is provided in Figure 3 (progress 1) and described as follows: 10 mg PdSe₂ powder is added into 100 ml of ethanol for soaking for

about 96 h. The soaked soliton is kept under ice-bath sonication for 24 h. The sonication is beneficial for stripping a few layers of the PdSe₂ nanosheets. After that, the suspension is centrifuged for 30 min at 5000 rpm to obtain few-layered PdSe₂ nanosheet dispersion. Finally, the dispersed PdSe₂ nanosheets is mixed with 100 ml of 5 wt% polyvinyl alcohol (PVA) solution and placed in the ultrasonic cleaner for another 6 h to obtain a uniform PdSe₂-PVA solution. In preparing the 2D material-based PdSe₂-PVA SA with good stability characteristics, a novel preparation method for isolating the oxygen and the materials, reported in our previous work [37], is employed. The preparation process is also provided in Figure 3 (progress 2) and described as follows: first, a thin liquid glass film is spin coated on the sapphire substrate. After solidification of the liquid glass, a thin PdSe₂-PVA film is spin coated on the surface of the liquid glass. Then, another liquid glass film is spin coated on the 2D materials to isolate the oxygen. In addition, another sapphire is coated on the liquid glass resulting in a five-layer sandwich structure. Finally, the sapphire substrates on both sides are removed, and the remaining structure is polished and cut to 1×1 mm² for proposing as SA, which is under the protection of the two outer glass films. In our experiment, the prepared three-layer glass-PdSe₂-glass material was inserted between two fiber ferrules so as to be easily integrated into the fiber laser cavity acting as a mode locker.

Figure 4 depicts the characterized results including Raman, transmission electron microscope (TEM), and atomic force microscope (AFM), which are beneficial in understanding the layered structure and saturable absorption characteristics of the PdSe₂ nanosheets. Figure 4A gives the Raman spectrum of the PdSe₂ powder recorded by a Raman spectrometer (Horiba HR Evolution). Four obvious Raman peaks located at 143.6, 205.3, 220.8, and 255.7 cm⁻¹ are presented, which correspond to the A_g¹, A_g², B_{1g}, and A_g³ Raman active modes of PdSe₂ [78–80]. In general, the Raman characteristics of the PdSe₂ nanosheets should be studied as a comparison. However,

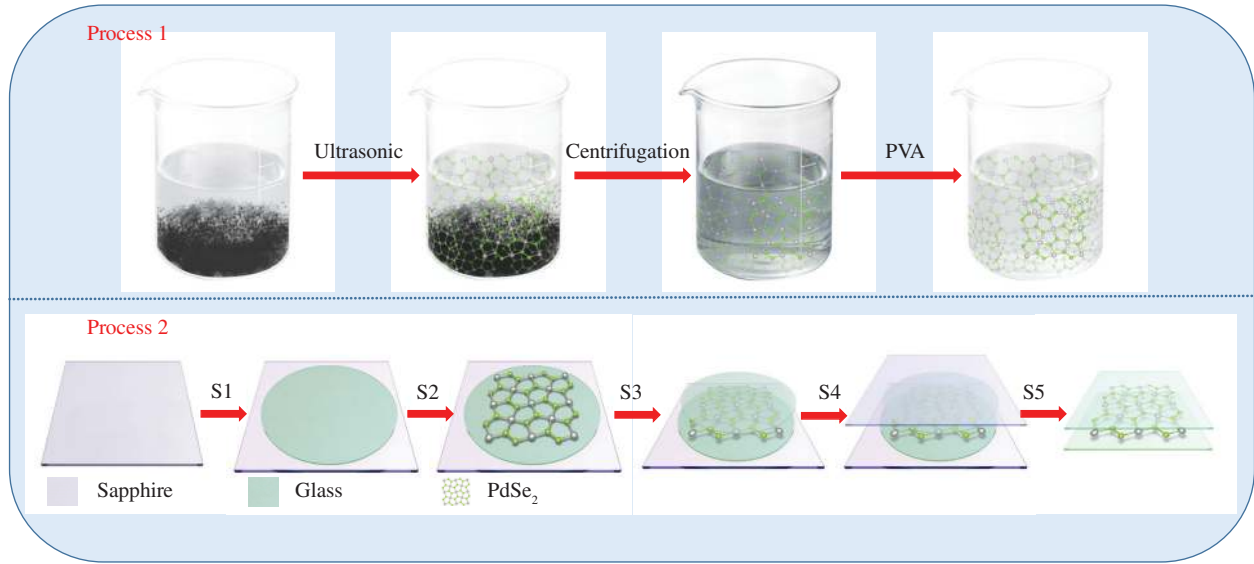


Figure 3: Preparation process of PdSe₂ nanosheets and PdSe₂-PVA SA.

in our experiment, after centrifugation, the concentration of PdSe₂ nanosheets in the solution is too dilute for testing their Raman characteristics. Therefore, for the further detailed characterization of the layered structure characteristics of the PdSe₂ nanosheets, their structure characteristics of PdSe₂ nanosheets are further characterized by TEM and AFM. The TEM and high-resolution TEM (HRTEM) images are shown in Figure 4B–D. As shown in Figure 4B, the PdSe₂ nanosheets exhibit an obvious layered structure. Clear crystal lattices with a d-spacing of ~0.4 nm are depicted in Figure 4C and D, indicating that the prepared PdSe₂ nanosheets possess excellent layered structure and crystallinity properties. After the preparation progress including soaking, ultrasonic, and centrifugation, the maintained layered structure and crystallinity indicates that the PdSe₂ material exhibits excellent air-stable properties. As is mentioned, PdSe₂ exhibits a wide tunable thickness-dependent bandgap and corresponding nonlinear optical properties. Thus, the thickness characteristics have great significance in designing PdSe₂-based broadband devices. Based on an atomic force microscope (AFM, Bruker Multimode 8, Bruker, Karlsruhe, Germany), the thickness characteristics are recorded and shown in Figure 4E and its inset. As is shown, the prepared PdSe₂ nanosheets exhibit uniform thickness and flat surface. In addition, overlapping phenomenon also occurs between the nanosheets (the inset in Figure 4E). The corresponding thicknesses of the marked areas of Figure 4E are provided in Figure 4F. The thicknesses of the PdSe₂ are about 6 nm, corresponding to ~15–16 layers [80], presenting a small fluctuation of thickness. The AFM results prove that

PdSe₂ nanosheets with uniform thickness characteristics were prepared successfully.

For an SA, its nonlinear optical properties including saturation intensity, modulation depth, and nonsaturable loss are basic and important for evaluating its nonlinear absorption performance. In our experiment, based on a commonly used power-dependent transmission technique, the nonlinear optical properties of the PdSe₂ SA were investigated experimentally. The experimental setup is shown in the inset of Figure 5A. As is shown, pulsed laser is employed as the pump source. In the experiment, homemade mode-locked Yb-doped and Er-doped fiber lasers are used as the pump source for testing the nonlinear optical properties of PdSe₂ SA within 1 and 1.5 μm regions, respectively. A variable optical attenuator (VOA) is used for adjusting the pump intensity continuously. The pump intensity is divided into two parts through a 50:50 output coupler (OC). One part is used for testing the SA and recorded by a power meter (PM2) and another part is recorded by PM1 directly as a comparison. Thus, the experimental transmission data can be calculated by the results recorded by PM1 and PM2. Calculated transmission results of the PdSe₂ SA are shown in Figure 5A and B. Additionally, the experiment results can be fitted according to a simple two-level model as follows [1–3]:

$$T(I) = 1 - \Delta T \cdot \exp\left(-\frac{I}{I_{\text{sat}}}\right) - T_{\text{ns}}$$

where $T(I)$, ΔT , I , I_{sat} , and T_{ns} are the transmission, modulation depth, input pulse energy, saturation intensity,

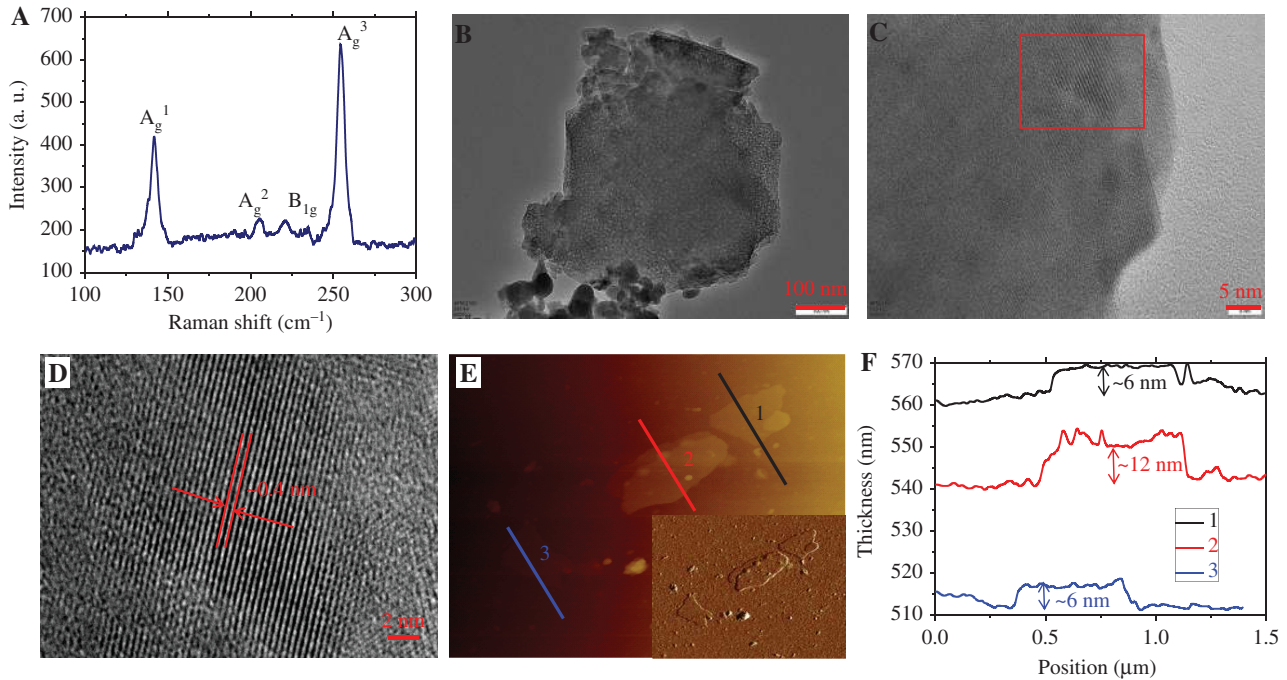


Figure 4: Characterized results of the PdSe₂. (A) Raman spectrum of the PdSe₂ powder. (B) TEM image of the PdSe₂ nanosheets. (C, D) HRTEM images of the PdSe₂ nanosheets. (E) AFM image of the prepared PdSe₂ nanosheets. (E) Inset: The corresponding morphology of the PdSe₂ nanosheets recorded with the AFM. (F) The corresponding thickness characteristics.

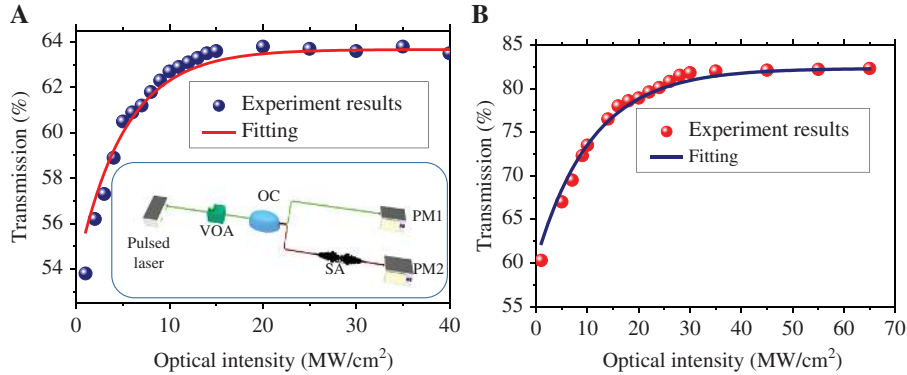


Figure 5: Nonlinear optical absorption properties of the PdSe₂-SA. (A) Within 1- μ m region. (B) Within 1.5- μ m region. (A) Inset: The experimental setup used for testing nonlinear optical properties.

and non-saturable loss, respectively. Finally, the saturation intensity, modulation depth, and the saturable loss of the PdSe₂ SA at 1064 nm are 5.01 MW/cm², 9.7%, and 36.2%, respectively. Meanwhile, at 1550 nm, the corresponding data are 15.63 MW/cm², 22.1%, and 17.9%, respectively.

As a typical 2D material, the saturable absorption mechanism can be explained by the Pauli blocking principle [70, 73]. The progress of the absorption is shown in Figure 6. First, under low excitation intensity, linear

absorption will occur. As is shown, when the energy of the incident light is larger than the bandgap value of the PdSe₂, electrons distributed in the valence band can absorb the energy of the incident light and be excited into the conduction band. After that, the hot electrons cooled almost immediately and led to the formation of a hot Fermi-Dirac distribution. Under this condition, the newly created electron-hole pairs will block the originally potential interband optical transitions around the Fermi energy ($-E/2$) and the absorption of photons. Finally,

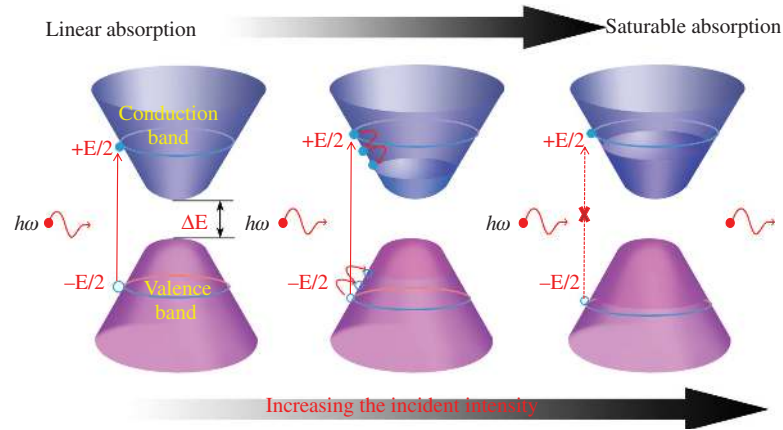


Figure 6: Saturable absorption mechanism of PdSe₂.

electrons and holes recombine and reach to an equilibrium distribution state due to the intraband phonon scattering. However, under a higher excitation intensity, the concentration of photocarriers increase instantaneously, and the energy states near the edge of the conduction and valence band will be filled. The absorption will be blocked due to the fact that no two electrons can reach the same state defined by the Pauli blocking principle. Thus, specific frequency photons transmit the material without absorption. As is described, the bandgap value is of great significance in designing ultra-fast photonics devices. Combined with the characterized results shown in Figure 4F and the simulation results provided in Figure 2C, the thickness of the PdSe₂ nanosheets used in our experiment is about 15–16 layers, corresponding to a narrow bandgap width of about 0.02 eV (6.2×10^4 nm). Thus, by adjusting the layer numbers, PdSe₂-based ultra-fast photonics devices with an expectant bandgap can be easily prepared. Besides, such a narrow bandgap value indicates that PdSe₂ is also an excellent candidate for developing wide-absorption band photonics devices covering almost the entire optical band.

4 Results and discussion

4.1 Mode-locked Er-doped operation

The absorption performance of the PdSe₂-PVA SA was tested within an Er-doped fiber laser for the first time. The experimental setup of the PdSe₂-PVA-based mode-locked Er-doped fiber laser is depicted in Figure 7A. A commonly used ring laser cavity consisting of a 980/1550 wavelength division multiplexer (WDM), a 0.23-m-long high

doping concentration Er-doped fiber (EDF; Liekki, Er-110, 4/125), a polarization-independent isolator (PI-ISO), two polarization controllers (PCs), a 20/80 output coupler (OC), and the prepared PdSe₂-PVA SA is demonstrated. A 400-mW/976-nm laser diode, acting as the pump source, is injected into the laser cavity through the WDM. The PCs, OC PI-ISO, and PdSe₂-PVA are used for adjusting the polarization states, outputting the energy, ensuring the unidirectional transmission, and acting as a mode locker within the ring laser cavity, respectively. The total length of the laser cavity is 10.09 m including 0.23 m of EDF and 9.86 m of single-mode fiber (SMF). The dispersion value of the EDF and SMF are -9 and 18 ps/nm/km [17], respectively. Thus, the net dispersion value of the cavity is calculated to be about -0.22 ps². The output characteristics of the mode-locked laser operation are tested by an optical spectrum analyzer (OSA; AQ6317B, Yokogawa, Tokyo, Japan), a 3-GHz photo-detector, a digital oscilloscope (DPO4054, Tektronix, Beaverton, OR, USA), a spectrum analyzer (R&S FPC1000, Jena, Germany), an auto-correlator (FR-103XL, Femtochrome, Berkeley, CA, USA), and a power meter (PM100D-S122C, Thorlabs, Newton, NJ, USA).

In the experiment, when the pump power was higher than 89 mW, mode-locked operation can be recorded by adjusting the PCs carefully and maintained to be stable with the pump power increasing from 89 to 356 mW, the maximum average output power was 3.66 mW, corresponding to an optical-to-optical conversion efficiency of 1.03%. The emission optical spectrum is provided in Figure 7B. Obvious Kelly sidebands are depicted in the spectrum, indicating that the mode-locked operation corresponds to the traditional soliton (TS) region. The central wavelength (λ_c) and the spectral full width at half maximum (FWHM) are 1561.77 and 9.33 nm, respectively. The pulse train of the mode-locked operation is shown in Figure 7C. The

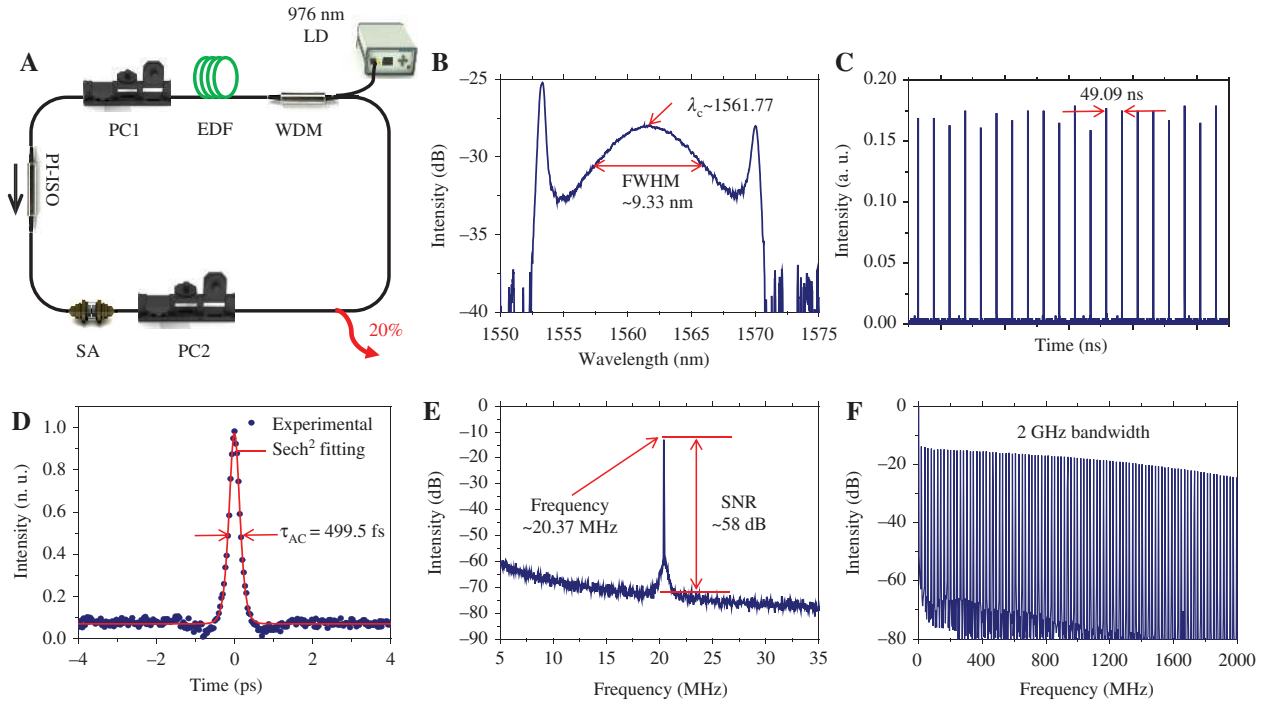


Figure 7: Experimental setup and output characteristics of the PdSe₂-based mode-locked Er-doped fiber laser. (A) Experimental setup. (B) Emission optical spectrum. (C) The recorded pulse train. (D) The measured auto-correlation trace. (E) RF spectrum located at 20.37 MHz. (F) RF spectrum recorded under 2 GHz bandwidth.

pulse-to-pulse time is 49.09 ns, corresponding to a pulse repetition rate of 20.37 MHz, which is in agreement with the cavity-length value ($f = c/nl$, where f , c , n , and l are the pulse repetition rate, velocity of light, refractive index, and the length of the cavity, respectively). Besides, it is obvious that the pulse trains are not uniform. In addition, no period doubling or periodicity phenomenon reported in previous works [93, 94] was recorded in the experiment, indicating that the fluctuation of the pulses can be further eliminated. The measured auto-correlation trace is provided in Figure 7D. As is shown, the FWHM of the pulse is about 499.5 fs, assuming a sech² temporal profile calculation for TS operation. The real pulse duration is about 323.7 fs (499.5×0.648 fs). Thus, combined with the mentioned 9.33-nm spectrum width, the time-bandwidth product (TBP) is about 0.37, which is slightly larger than the theoretical transform limit value (0.315) and indicates that the soliton pulse is a little chirped. For the mode-locked operation, its stability characteristics are tested by the spectrum analyzer. Radio frequency (RF) spectrum recorded within 30-MHz width is provided in Figure 7E, the central frequency is located at 20.37 MHz, and the signal-to-noise ratio (SNR) is as high as 58 dB, indicating that the mode-locked operation exhibits excellent stability characteristics. The RF spectrum within 2-GHz width is also depicted in Figure 7F for further revelation of its high stability characteristics.

4.2 Mode-locked Yb-doped operation

For future testing of the broadband absorption performance of the PdSe₂ SA, a mode-locked Yb-doped fiber (YDF) laser was also demonstrated in our work. An almost identical experimental setup as provided in Figure 7A is employed and shown in Figure 8A. Under this condition, the laser gain medium is a 0.36-m YDF (Liekki, Yb-1200, 4/125). The total length is about 60.97 m including 0.36 m YDF and 60.61 m SMF (Hi-1060) used for adjusting the dispersion value of the laser cavity. The dispersion value of the YDF and SMF are -43 and -42 ps/nm km, respectively. Thus, the net dispersion value of the cavity is calculated to be about 1.54 ps². Mode-locked pulses are delivered out the cavity through a 10% port of a 10/90 OC.

Stable mode-locked pulses were recorded when the pump power is higher than 135 mW by adjusting the polarization state carefully. In the experiment, the mode-locked state was maintained to be stable with the pump power increasing from 135 to 338 mW. The maximum average output power was as high as 15.6 mW, corresponding to an optical-to-optical conversion efficiency of 4.6%. The output characteristics of the PdSe₂-based mode-locked YDF laser are provided in Figure 8. The emission spectrum locates at the central wavelength of 1067.37 nm

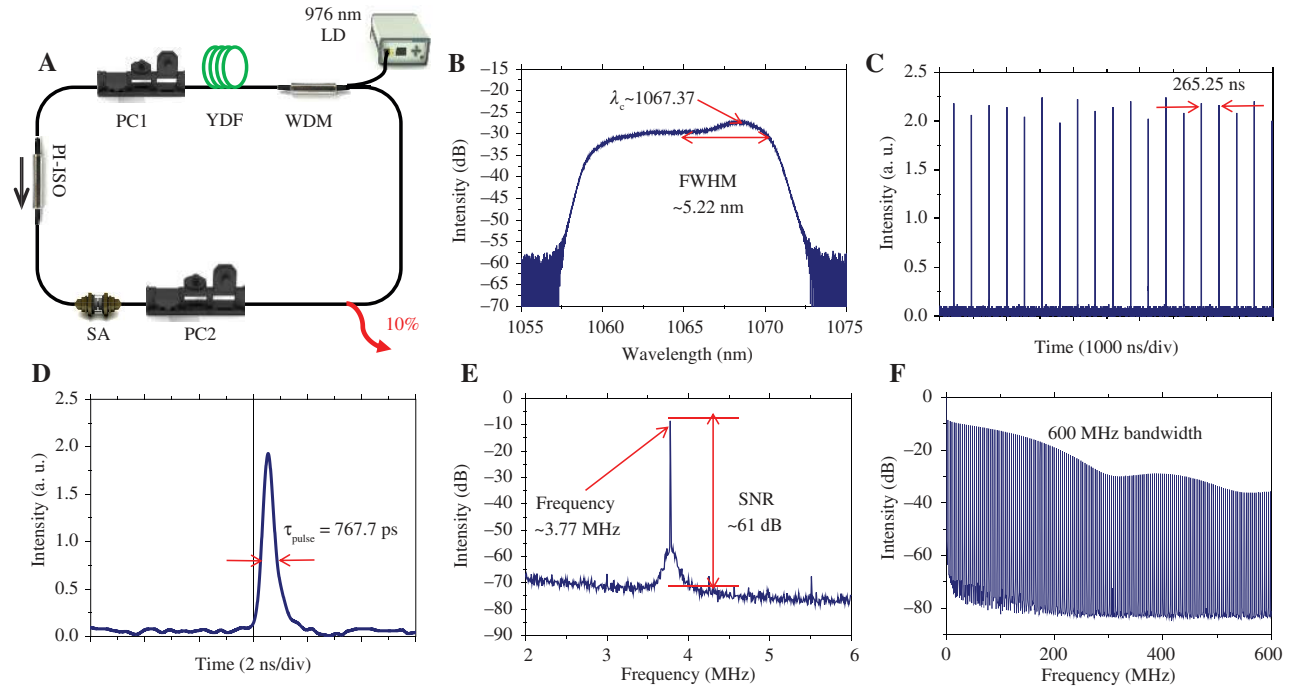


Figure 8: Experimental setup and output characteristics of the PdSe₂-based mode-locked Yb-doped fiber laser.

(A) Experimental setup. (B) Emission optical spectrum. (C) The recorded pulse train. (D) The single pulse shape. (E) RF spectrum located at 3.77 MHz. (F) RF spectrum recorded under 600 MHz bandwidth.

with an FWHM of 5.22 nm (Figure 8B). Figure 8C gives the typical pulse train of the mode-locked laser. The pulse-to-pulse time is 265.25 ns, corresponding to a pulse repetition rate of 3.77 MHz, which also matches well with the cavity length. Fluctuation of the mode-locked pulses is also recorded as described in the mode-locked Er-doped laser. The single-pulse shape is provided in Figure 8D, the pulse width is about 767.7 ps. However, due to lack of a higher speed oscilloscope with shorter rise time, the real width of the pulse is not recorded. In addition, the pulse width characteristics were also checked by the auto-correlator; however, no pulse peaks were tested, indicating that the pulse width is wider than 90 ps. As mentioned, the spectrum width was 5.22 nm, corresponding to a theoretical pulse width of ~ 0.33 ps. All the results prove that the mode-locked pulses are highly chirped due to the large dispersion value. The RF spectra are also recorded for examining the stability characteristics of the mode-locked operations. The results are described in Figure 8E and F. As is shown in Figure 8E, the central frequency locates at 3.77 MHz, and the SNR is as high as 61 dB. The wideband RF spectrum (Figure 8F) also proves that the mode-locked operations exhibit excellent stability properties. Additionally, it needs to be emphasized that, in our experiment, it takes about 1 month from the preparation and nonlinear characterization of the PdSe₂ SA to its

ultrafast laser applications. During the long-period investigation, PdSe₂ SA is preserved at normal temperature. As described above, it still exhibited good saturable absorption performance, proving that the PdSe₂ SA has excellent air stability.

In conclusion, the electronic band structures and bandgap characteristics of PdSe₂ are calculated theoretically. The bandgap value of PdSe₂ is calculated to be 0–1.3 eV, indicating that PdSe₂ was a promising material for designing broadband optical devices. In the experiment, PdSe₂ nanosheets were prepared with the LPE method and used for designing a new structure SA. Its broadband nonlinear absorption performance was characterized within Er- and Yb-doped fiber laser, respectively. The experiment results present PdSe₂ as exhibiting good performance in demonstrating ultra-fast pulsed lasers and great significance in designing broadband ultra-fast optical devices, which provide meaningful reference for designing air-stable broadband ultra-fast photonic devices.

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Conflict of interest: The authors declare no conflicts of interest.

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