

Review article

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Recent progress of pulsed fiber lasers based on transition-metal dichalcogenides and black phosphorus saturable absorbers

<https://doi.org/10.1515/nanoph-2019-0566>

Received December 30, 2019; revised February 4, 2020; accepted February 4, 2020

Abstract: Transition-metal dichalcogenides (TMDCs) and black phosphorus (BP) are typical 2D materials with layer-dependent bandgaps, which are emerging as promising saturable absorption materials for pulsed fiber lasers. In this review, we discuss the nonlinear saturable absorption properties of TMDCs and BP, and summarize the recent progress of saturable absorbers from fabrication methods to incorporation strategies. The performances of saturable absorbers and the properties of Q-switched/mode-locked fiber lasers at different wavelengths are summarized and compared to give a comprehensive insight to optical modulators based on TMDCs/BP, and to promote their practical applications in nonlinear optics.

Keywords: transition-metal dichalcogenides; black phosphorus; saturable absorber; mode-locked fiber laser; Q-switched fiber laser.

1 Introduction

Attributed to their unique properties of compact structure, good flexibility, and low cost, pulsed fiber lasers are excellent light sources for various applications, such as optical communications [1, 2], biological photonics [3, 4],

laser micromachining [5, 6], etc. Passive Q-switching and mode-locking techniques are two common methods for generating pulsed lasers, with the key component of a saturable absorber (SA). Several types of techniques or elements, including a semiconductor SA mirror (SESAM) [7, 8], nonlinear polarization rotation [9, 10], carbon nanotubes [11, 12], and a nonlinear optical loop mirror (NOLM) [13, 14] have been developed to shorten the pulse for generating Q-switched or mode-locked lasers.

In the past several decades, the most famous SA, SESAM, has been widely used in commercial laser systems. However, SESAMs also suffer from a narrow operating bandwidth, low damage threshold, and complex preparation process. Those limitations motivate researchers to search for new types of SAs for pulsed lasers. Recently, 2D materials revolutionized the study from nonlinear optics [15], optoelectronics [16–21], medical treatment [22–24], and energy storage [25–27] attributing to their remarkable physical properties and the unique dimensionality effect [28, 29]. These 2D materials usually exhibit layered structures in which weak Van der Waals forces stabilize the stacking of layers and strong covalent bonds join together atoms in-plane. As a result, they can be exfoliated into single-layer or few-layer nanosheets that have the advantages of a fast recovery time, ease of preparation and integration to a fiber system. The most well-known 2D material is graphene, which was demonstrated by Novoselov et al. [30] using the mechanical exfoliation (ME) approach. Single-layer graphene is composed of a single-atom layer of carbon forming a 2D honeycomb lattice. Bao et al. [31] and Hasan et al. [32] have demonstrated mode-locked erbium-doped fiber lasers (EDFLs) based on a few-layer graphene SA.

Motivated by the progress of a graphene SA, researchers have developed a host of graphene-like materials and explored their applications in pulsed fiber lasers from visible, near-infrared to mid-infrared wavelength [33–35]. A topological insulator [36–38] is a new state of quantum matter that has an insulating bulky gap, and a gapless edge state or surface state. Several types of topological

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insulators such as Bi_2Te_3 , Sb_2Te_3 and Bi_2Se_3 have been proved to exhibit a broadband saturable absorption property [39] and Q-switched or mode-locked fiber lasers have been reported at 1.06 μm [40, 41], 1.55 μm [42, 43], and 2 μm [44, 45].

After that, another type of 2D material, transition-metal dichalcogenides (TMDCs) [46–49], has attracted rising attention due to the layer-dependent bandgap and high nonlinear optical response. TMDCs are a family of anisotropic semiconductor materials with the common chemical formula of MX_2 , in which X is a group VI element (i.e. S, Se, Te) and M is a transition metal (i.e. Mo, W). By using single-layer or few-layer TMDCs as a nonlinear medium, several typical nonlinear phenomena have been reported, such as second harmonic generation [50, 51], saturable absorption [52–54], and two-photon absorption [55, 56]. The bandgap and stability of TMDCs decrease as the mass of the chalcogen atom increases from S, Se to Te [57]. However, the bandgap of typical TMDCs is still higher than 0.7 eV, which is still far away for the mid-infrared waveband [58–60].

In recent years, some 2D monoelemental materials such as phosphorene [61], arsenene [62], antimonene [63], and bismuthene [64] have also attracted great interest owing to their extraordinary physical properties. Especially, black phosphorus (BP) [65–69], the most thermodynamically stable allotrope of the element phosphorus, has a layer-dependent bandgap from 0.3 eV (bulk) to 2.0 eV (monolayer) [70, 71], which covers the vacancy between zero-bandgap graphene and large-bandgap TMDCs (e.g. 1.29–1.8 eV for MoS_2) [72]. Thus, BP is a promising nonlinear optical material at the mid-infrared range that is beyond the absorption wavelength of TMDCs [66, 73–78]. In addition to these famous 2D materials, several new materials such as tin sulfide [79, 80] and perovskite [81–83], were also found to exhibit a saturable absorption property.

As aforementioned, graphene and topological insulators can be categorized as Dirac materials that have zero bandgaps [84–86]. The preparation of graphene and topological insulators, as well as their applications in pulsed lasers, have been discussed and summarized by several exhaustive reviews and articles [37, 39, 87–91]. Unlike zero-bandgap materials, TMDCs and BP benefit from the layer-dependent bandgap, and their nonlinear optical properties are more complex and interesting [15, 66, 92, 93]. Here, we review these important advances of pulsed fiber lasers based on TMDCs and BP SAs. The nonlinear optical properties and fabrication methods of two types of SA are discussed and compared to give a comprehensive insight to optical modulators based on 2D materials.

The performances of Q-switched and mode-locked fiber lasers at different wavelengths are also summarized in this review.

2 Fabrication and characterization of TMDCs and BP SAs

2.1 Fabrication methods

As illustrated in Figure 1, there are two main methods for preparing 2D materials: the top-down method [94] and the bottom-up method [95]. The top-down method includes ME and liquid-phase exfoliation (LPE) [96, 97] by destroying the van der Waals forces to fabricate single-layer or few-layer 2D materials. The bottom-up method grows nanomaterials on a molecular level utilizing chemical or physical reactions, such as chemical vapor deposition (CVD) [98, 99], molecular beam epitaxy [100, 101], hydrothermal synthesis [102, 103], pulse magnetron sputtering [104, 105], pulsed laser deposition [106, 107], etc. Here, we give a simple introduction to ME, LPE and CVD, which are three widely used methods for preparing 2D materials including TMDCs and BP.

The ME method has been widely used to fabricate 2D nanomaterials since the first successful exfoliation of graphene in 2004 by Novoselov et al. [30]. After that, few-layer or single-layer topological insulators, TMDCs, and BP were obtained by using a similar approach. In the ME process, adhesive tape is used to exfoliate bulk layered crystals down to monolayer and few-layer nanosheets. The ME method can produce high-quality 2D nanomaterials for fundamental research, but the efficiency is extremely low, which limits its realistic applications.

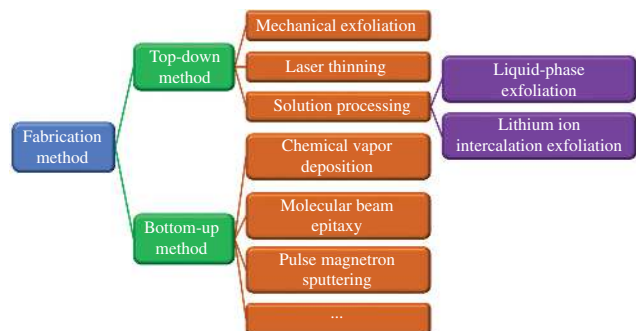


Figure 1: Typical fabrication methods of 2D materials including transition-metal dichalcogenides (TMDCs) and black phosphorus (BP).

LPE is another physical method that employs high-intensity ultrasound to generate microbubbles to continuously destroy the van der Waals forces between the layers [108, 109]. By selecting proper solvents or surfactant solutions, the LPE method can produce mass dispersions of mono-layer and few-layer nanosheets from pristine bulk material under ambient conditions. This method is quite simple and cost-effective, but can only produce small-size nanosheets and the layer number is difficult to precisely control.

CVD is a common approach for the synthesis of large-scale high-quality 2D materials [110, 111]. Generally, gaseous or pulverized reactants are sent to the reaction chamber under a high temperature to produce 2D materials on a substrate. Unlike the ME and LPE techniques, the defects and the layer number of 2D materials prepared by CVD can be controlled by reaction parameters. The CVD method is expected to be used for commercial productions, while the fabrication process is rather complicated and still requires further development. Unlike zero-bandgap graphene, few-layer Mo/WTe₂ and BP tend to be oxidized in air and need additional protection devices during fabrication and application.

2.2 Saturable absorption properties

Various nonlinear optical phenomena have been observed from 2D materials, such as high-order harmonic generation [112], four-wave mixing [113], and the Kerr effect [114]. Saturable absorption is a typical third-order nonlinear effect that the optical absorbance reduces with the increase of light intensity and becomes saturated at a certain threshold. Actually, the real part of third-order Kerr nonlinearity $\chi^{(3)}$ is related to the nonlinearity refractive index n_2 while

the imaginary part of $\chi^{(3)}$ is responsible for the saturable absorption property.

SAs are frequently used in fiber lasers to generate passively Q-switched pulses or mode-locked pulses. The parameters of SAs include modulation depth (α_s), non-saturable loss (α_{ns}), and saturable intensity (I_{sat}). A broad operation bandwidth and high damage threshold are usually required for practical applications. The absorption coefficient $\alpha(I)$ and optical intensity I follow the equation [115]:

$$\alpha(I) = \alpha_{ns} + \frac{\alpha_s}{1 + I/I_{sat}}$$

The Z-scan technique is a common technique for characterizing the nonlinear absorption of materials [116–118]. The Z-scan setup is shown in Figure 2A, and is used to measure the intensity-dependent nonlinear susceptibility of materials. In the measurement arm, the sample is moved in the Z-direction along the axis of a focused laser beam and the far field intensity is measured as a function of the sample position. In the reference arm, detector 2 is used for monitoring the incident light intensity. The magnitude of the nonlinear index can be calculated from the dependence of the detector signal on the sample position.

The total absorption $\alpha(I) = \alpha_0 + \alpha_{NL}I$, where α_0 is the linear absorption coefficient, and nonlinear coefficient α_{NL} can be calculated by the data of the Z-scan curves based on the nonlinear propagation equation $dI/dz = -(\alpha_0 + \alpha_{NL}I)I$. The imaginary part of the third-order nonlinear optical susceptibility $\text{Im}\chi^{(3)}$ is related to the nonlinear coefficient by $\text{Im}\chi^{(3)} = [10^{-7}c\lambda n^2/96\pi^2]\alpha_{NL}$, where c is the speed of light in a vacuum, λ is the laser wavelength, and n is the refractive index [119]. The saturable intensity I_{sat} can be obtained from the equation of

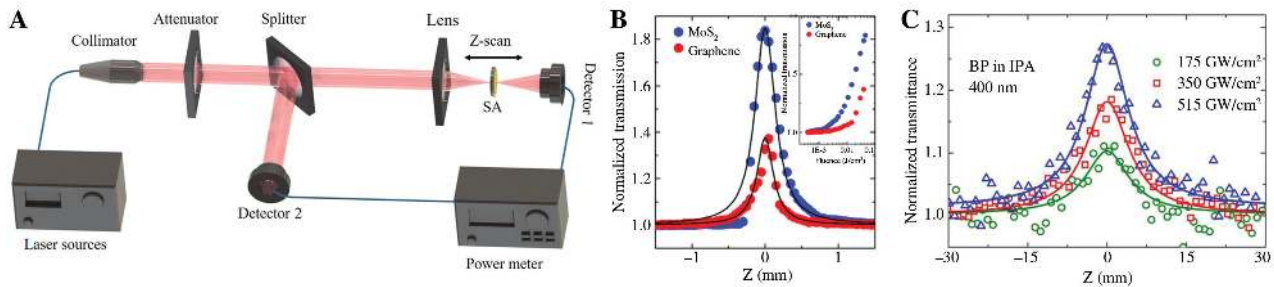


Figure 2: (A) Schematic of the Z-scan. (B) Comparison of nonlinear performance of MoS₂ (T = 34.4%) and graphene (T = 16.5%) dispersions, where MoS₂ shows a higher modulation depth. Inset: normalized transmission as a function of fluence. Reproduced with permission [116]. Copyright 2013, ACS Publishing. (C) Z-scan measurements of black phosphorus (BP) dispersions under different intensities at 400 nm. Reproduced with permission [76]. Copyright 2015, The Optical Society.

$dI/dz = -\alpha_o I / (1 + I/I_{\text{sat}})$, and the normalized transmittance can be expressed as [120–122]:

$$T(z) = \sum_{m=0}^{\infty} \left\{ \left[\frac{-\alpha(I)I_0 L_{\text{eff}}}{1 + z^2/z_0^2} \right]^m / (m+1)^{3/2} \right\}$$

where $L_{\text{eff}} = (1 - e^{-\alpha_o L}) / \alpha_o$, L is the sample length, I_0 is the on-axis peak intensity at the focus, z_0 is the Rayleigh diffraction length, and z is the longitudinal displacement of the sample.

The saturable absorption properties of TMDCs have been extensively studied by researchers in recent years [123–125]. Wang et al. [116] reported the ultrafast saturable absorption in MoS_2 dispersions produced by LPE under femtosecond laser excitation at 800 nm. It is shown that MoS_2 exhibits a higher saturable absorption than that of graphene under the same experimental conditions, as illustrated in Figure 2B. Zhang et al. [126] revealed the broadband saturable absorption property of few-layered MoS_2 nanosheets utilizing the open-aperture Z-scan technique, and further demonstrated the passively Q-switched and mode-locked fiber lasers at wavelengths of 1.06 μm , 1.55 μm and 2.1 μm using the MoS_2 SA [127]. The broadband saturable absorption properties of TMDCs may arise from the defect-induced decrease of the bandgap [37]. The layered TMDCs display features of high third-order susceptibility ($\sim 10^{-19} \text{ m}^2/\text{V}^2$), acceptable saturation intensity, and tunable bandgap by varying the layer numbers of the material. The layer-dependent absorption wavelength and broadband saturable absorption property enables them to be used in optoelectronic and photonic applications [126, 128, 129].

Due to its layer-dependent bandgap, similar to TMDCs, the nonlinear optical response of BP can be tuned over a broad range from visible to mid-infrared wavelengths [130].

BP nanosheets with a thickness of 52 nm (104 layers) were prepared by the ultrasonicated method, which has a bandgap of 0.357 eV, corresponding to a wavelength of 3.48 μm [131]. The broadband saturable

absorption (400–2799 nm) has been demonstrated using BP nanosheets exfoliated by the LPE method [76, 132, 133], as shown in Figure 2C. The wavelength-dependent relaxation times of BP nanosheets were determined to be 360 fs to 1.36 ps with photon energies from 1.55 eV to 0.61 eV. In a comparative study with graphene, it was found that BP has a faster carrier relaxation in near-infrared and mid-infrared wavelengths [132]. Compared with graphene, the few-layer BP is less stable because the P atom can easily react with oxygen and water, resulting in its rapid degradation in air. Thus, long-term stability is a key parameter for BP SAs.

The nonlinear optical properties of TMDCs and BP measured by the Z-scan method are summarized in Table 1. TMDCs and BP materials are found to exhibit a normalized transmittance higher than 30%, and the saturation intensity ranges from tens of GW/cm^2 to several hundreds of GW/cm^2 .

2.3 Incorporation methods

Several schemes based on mirrors or fibers have been proposed to actualize TMDCs and BP SAs. The first type of SA is prepared by spin-coating nanomaterials on mirrors or quartz, as shown in Figure 3A. Such an SA is mainly used in solid-state lasers, and requires a complex coupling system for fiber laser applications. The second SA is prepared by mixing the 2D material nanosheets with composite materials, such as polyvinyl alcohol (PVA) and polymethyl methacrylate. Then, the film-type SA is sandwiched between two fiber facets with a connector (Figure 3B). Although the sandwich structure can be easily incorporated with fiber lasers, the low damage threshold and poor stability limit its further applications in high-power pulsed fiber lasers. The third type of SA is based on a nonlinear interaction between nanomaterials and the evanescent field of D-shaped fibers (DSFs) and tapered fibers, as shown in Figure 3C and D. Due to the weak evanescent field and long interaction length, the laser-induced

Table 1: Summarization of nonlinear optical properties of transition-metal dichalcogenides (TMDCs) and black phosphorus (BP).

| 2D Mater. | Laser parameters | T (%) | I_s (GW/cm^2) | α_o (cm^{-1}) | α_{NL} (cm/GW) | $\text{Im}\chi^{(3)}$ (esu) | Ref. |
|-----------------|-----------------------|----------------|-----------------------------------|---------------------------------|---|------------------------------------|-------|
| MoS_2 | 800 nm, 1 KHz, 100 fs | 32.6 | 381 ± 346 | 11.22 | $-(2.42 \pm 0.8) \times 10^{-2}$ | $-(1.38 \pm 0.45) \times 10^{-14}$ | [116] |
| MoSe_2 | 800 nm, 1 KHz, 100 fs | 45.3 | 590 ± 225 | 7.93 | $-(2.54 \pm 0.6) \times 10^{-2}$ | $-(1.45 \pm 0.34) \times 10^{-15}$ | [134] |
| MoTe_2 | 800 nm, 1 KHz, 40 fs | 86.3 | 217 ± 11 | 1.47 | $-(3.7 \pm 1.2) \times 10^{-2}$ | $-(2.13 \pm 0.66) \times 10^{-15}$ | [126] |
| BP | 400 nm, 1 KHz, 100 fs | 70.5 | 455.3 ± 55 | 3.49 | $-(1.62 \pm 0.28) \times 10^{-2}$ | – | [76] |
| BP | 800 nm, 1 KHz, 100 fs | 85.6 | 334.6 ± 43 | 1.55 | $-(6.17 \pm 0.19) \times 10^{-3}$ | – | [76] |
| BP | 1330 nm, 50 kHz, fs | 45.9 ± 2.2 | 382 ± 60 | 7.8 ± 0.5 | $-(1.9 \pm 0.3) \times 10^{-2}$ | $-(1.83 \pm 0.29) \times 10^{-14}$ | [132] |
| BP | 1550 nm, 50 kHz, fs | 59.1 ± 0.1 | 398 ± 163 | 5.3 ± 0.1 | $-(1.8 \pm 0.9) \times 10^{-2}$ | $-(1.98 \pm 0.95) \times 10^{-14}$ | [132] |
| BP | 2100 nm, 50 kHz, fs | 60.6 ± 0.5 | 71.3 ± 28.2 | 5 ± 0.1 | $-(5.7 \pm 1.4) \times 10^{-2}$ | $-(8.49 \pm 2.1) \times 10^{-14}$ | [132] |

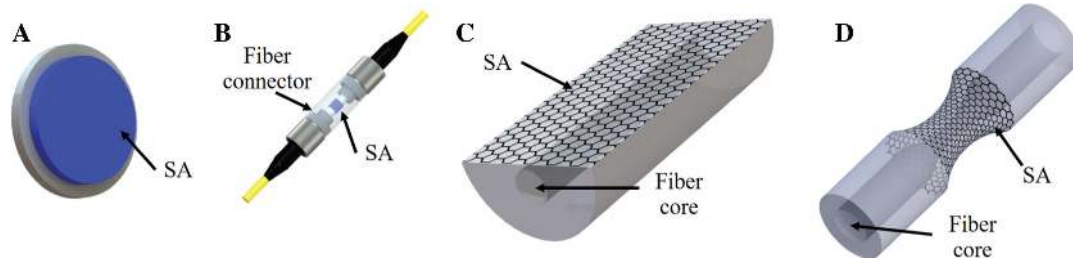


Figure 3: Incorporation methods.

(A) Spin coating 2D materials on mirrors or quartz. (B) Sandwiched structure. Transferring saturable absorber (SA) on (C) D-shaped fibers and (D) tapered fibers.

heating in DSFs and tapered fibers can be rapidly dispersed, and thus the SAs have a high damage threshold. However, the DSFs are polarization sensitive elements, and tapered fibers have a slight nonuniformity during the fabrication. When such components are inserted into the cavity, a nonlinear polarization rotation effect may occur and result in Q-switched or mode-locked operations.

Since graphene was first successfully applied as an SA, more and more 2D material-based SAs have been used in passively mode-locked and Q-switched fiber lasers. The broadband saturable absorption of TMDCs and BP enable them to be universal SAs for generating mode-locked and Q-switched pulses in ytterbium-doped fiber lasers (YDFLs), EDFLs, and thulium-doped fiber lasers, etc. In the following section, we discuss recent advances of pulsed fiber lasers at different wavelengths based on TMDCs and BP SAs.

3 Passively mode-locked fiber lasers based on TMDCs and BP SAs

3.1 Mode-locked fiber lasers at 1.06 μm

YDFLs usually work at 1.06 μm and have a large normal dispersion [135]. To realize the mode locking operation, the modulation depth of the SA must be large enough

to compensate the dispersion-induced stretching of the pulse [28, 136]. Zhang et al. [129] demonstrated the first YDFL passively mode locked by an MoS_2 SA, and obtained 800 ps pulses at a wavelength of 1054 nm. The studies also revealed that the modulation depth of the MoS_2 SA is 10% at 400-nm excitation and 34% at 800-nm excitation, and the absorption wavelength spans from the visible band to the near-infrared band. Subsequently, we also realized dissipative soliton mode locking in an YDFL by using a WS_2 -DSF SA, as illustrated in Figure 4A–C [137]. The modulation depth of the SA is about 2.9%, and the output pulse has a duration of 630 ps with a 3-dB spectral width of 0.77 nm. Single-pulse mode locking can be maintained at a pump power of 610 mW, and the maximum pulse energy is 13.6 nJ. It is demonstrated that the WS_2 -DSF SA is capable of working at a high-power regime without damage. The strongly chirped dissipative solitons can be amplified external to the cavity to generate high-intensity pulses after compression. These progresses have greatly promoted the development of TMDC SAs and their applications in mode-locked fiber lasers at 1.06 μm [138, 139].

After that, few-layer BP has been prepared using the LPE method, and a fiber-based BP SA was achieved using the laser deposition method. With the proposed SA, Song et al. [140] reported dissipative soliton mode locking at 1030 nm in a YDFL, with a pulse duration of 400 ps and an output power of 32.5 mW. Hisyam et al. [141]

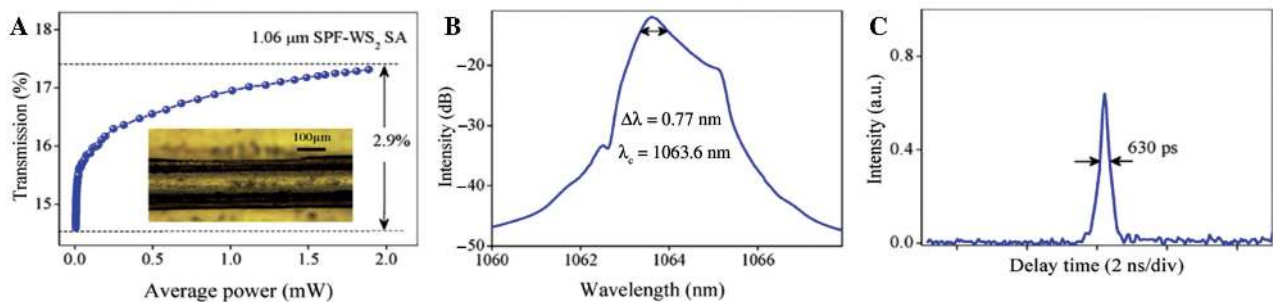


Figure 4: Mode-locked ytterbium-doped fiber lasers (YDFLs) based on WS_2 -D-shaped fiber (DSF) saturable absorber (SA).

(A) Nonlinear transmission of the SA. (B) Spectrum. (C) Pulse profile. Reproduced with permission [137]. Copyright 2015, The Optical Society.

also reported a YDFL passively mode-locked by a BP SA, delivering an optical pulse train with a repetition rate of 13.5 MHz at a wavelength of 1085.58 nm. The maximum pulse energy is 5.93 nJ at a pump power of 1322 mW. The properties of mode-locked fiber lasers using TMDCs and BP SAs are summarized in Table 2. Although TMDCs and BP have much lower optical damage thresholds than that of graphene, the lateral interaction between the evanescent field and these 2D materials allows them to survive with a high incident power, which guarantees the reliable nonlinear effect against thermal damage for the dissipative soliton mode locking [26]. Based on TMDCs and BP SAs, dissipative solitons with a maximum pulse energy of 30 mW [139] and a shortest pulse duration of 7.54 ps [141] have been reported.

3.2 Mode-locked fiber lasers at 1.55 μm

EDFLs are the most important light source at 1.55 μm , and also provide a perfect platform to study the nonlinear properties of SAs. The fiber components are available from commercial optical communication systems, and it is easy to build all-fiber resonators without free-space bulk components. Xia et al. [142] achieved ultrafast pulses in an EDFL mode locked by a CVD-grown MoS_2 SA; the output pulses have a central wavelength, pulse duration, and repetition rate of 1568.9 nm, 1.28 ps, and 8.288 MHz, respectively. Zhang et al. [143] demonstrated a tunable mode-locked EDFL based on an MoS_2 -PVA SA, in which the central wavelength is tunable from 1535 nm to 1565 nm. Similar to MoS_2 , few-layer WS_2 also has remarkable saturable absorption properties and a high optical damage threshold [126]. Based on a WS_2 -DSF SA, we have achieved soliton mode locking in an anomalous-dispersion EDFL [144] and dissipative soliton mode locking in a normal-dispersion EDFL [137].

A pulse with duration of 67 fs has also been reported in a mode-locked EDFL with the combination of fiber-taper WS_2 SA and the nonlinear polarization rotation technique [145].

With the assistance of the high-damage threshold SA, passively harmonic mode locking (HML) fiber lasers can also be obtained at the high pump regime. The principle of HML is that multiple pulses rearrange themselves in a regular position and the pulse repetition rate is the multiple of the fundamental repetition rate. By using an MoS_2 -DSF SA, we have observed HML of bound-state pulses in an EDFL, as illustrated in Figure 5A–D. At a pump power of 600 mW, bound-state pulses with a separation of 3.4 ps are distributed equally in the cavity. The repetition rate of the bound-state pulses is 125 MHz, corresponding to 14th harmonic of fundamental cavity repetition rate [146]. Zhang et al. [147] also reported the 369th HML in an EDFL using a microfiber-based MoS_2 SA. A 2.5 GHz repetition rate pulse could be obtained at a pump power of 181 mW. So far, HML up to 3.25 GHz [148] and 3.27 GHz [149] has also been realized from EDFLs using WSe_2 and MoSe_2 SAs, respectively.

After that, many studies have demonstrated that other layered TMDCs and their derivatives including WSe_2 [148], MoSe_2 [150], WTe_2 [151], SnS_2 [138], ReS_2 [125] etc. could be used to prepare SAs for generating ultrafast mode-locked pulses in fiber lasers. We demonstrated soliton mode-locked fiber lasers utilizing two types of MoTe_2 / WTe_2 -based SAs, one of which is prepared by depositing the nanosheets on DSF, while the other is fabricated by mixing the nanosheets with PVA [152]. Yan et al. [104] achieved a mode-locked pulse with a duration of 229 fs and an average output power of 57 mW in an EDFL using a MoTe_2 SA that is fabricated by the magnetron sputtering deposition method.

In 2015, Zhang et al. [76] found that BP nanosheets have a saturable absorption property at 400 nm,

Table 2: Summarization of mode-locked fiber laser at 1.06 μm based transition-metal dichalcogenides (TMDCs) and black phosphorus (BP) saturable absorbers (SAs).

| 2D-Mater. | Fabrication method | Incorporation method | Laser performance | | | | Ref. |
|----------------|--------------------------|-------------------------|-------------------|---------------|---------|----------|-------|
| | | | λ (nm) | Duration (ps) | Energy | RF (MHz) | |
| MoS_2 | Hydrothermal exfoliation | DSF | 1054.3 | 800 | 9.3 mW | 7 | [129] |
| WS_2 | LPE | DSF | 1063.6 | 630 | 13.6 nJ | 5.57 | [137] |
| WS_2 | Thermal decomposition | Fluorine mica substrate | 1052.45 | 288 | 30 mW | 23.26 | [139] |
| SnS_2 | LPE | Sandwiched | 1062.66 | 656 | 2.23 mW | 39.33 | [138] |
| BP | LPE | Sandwiched | 1030.6 | 400 | 0.70 nJ | 46.3 | [140] |
| BP | ME | Sandwiched | 1085.5 | 7.54 | 5.93 nJ | 13.5 | [141] |

DSF, D-shaped fibers; LPE, liquid-phase exfoliation; ME, mechanical exfoliation; RF, repetition frequency.

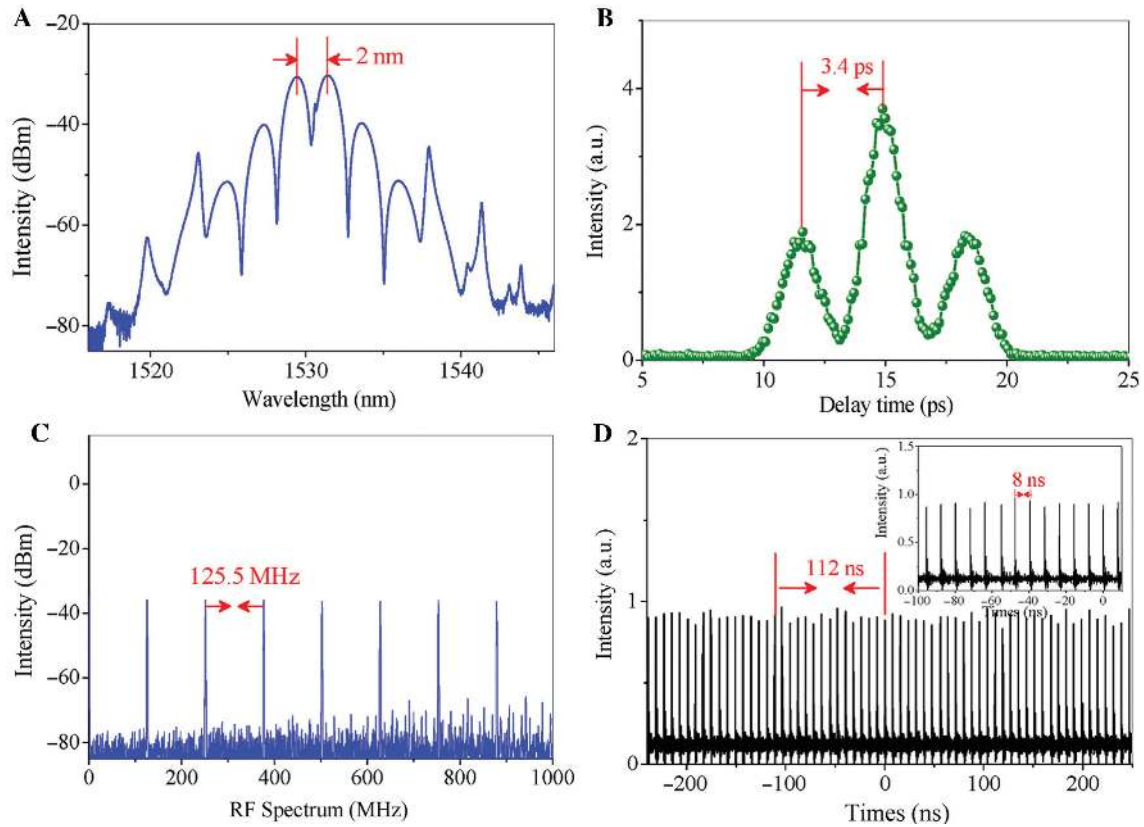


Figure 5: (A) Spectrum, (B) auto-correlation trace, (C) radiofrequency spectrum, and (D) oscilloscope trace of harmonic mode locking (HML) pulses based on MoS₂-D-shaped fiber (DSF) saturable absorber (SA). Reproduced with permission. Copyright 2015 The Optical Society.

800 nm, 1563 nm and 1930 nm using the Z-scan method. After that, various BP SAs have been fabricated and applied in fiber lasers to generate ultrafast pulses. Chen et al. [153] demonstrated a mode-locked EDFL by using the mechanically exfoliated BP as an SA, and obtained 946 fs transform limited pulses at a wavelength of 1571.45 nm, as depicted in Figure 6A–C. It is worth mentioning that Sotor et al. [74] and Sun et al. [155] reported that the mechanically exfoliated BP has a polarization-dependent absorption property, which is different from other 2D material SAs (i.e. graphene SAs, topological insulator SAs). The polarization-sensitive saturable absorption induces a polarization selection effect to the laser cavity and prevents the formation of the vector soliton. However, Zhang et al. [156] observed vector solitons in a mode-locked EDFL, in which the SA is based on BP nanosheets exfoliated by the LPE method. The generation of vector soliton can be understood by noting that BP nanosheets are distributed randomly in all orientations and the interaction area of the SA is much larger than the size of the nanosheets [157].

Various methods have been proposed to improve the stability of BP in air [158, 159]. For example, Jin et al. [154] demonstrated a self-starting mode-locking operation stable for >10 days without any noticeable performance degradation utilizing an inkjet-printed BP-SA, and obtained 102 fs pulses with 40 nm spectral width, as shown in Figure 6D–F. We have obtained anti-oxidized BP nanosheets based on the liquid exfoliation approach, using aqueous poly dimethyldiallyl ammonium chloride as a dispersion fluid. Based on the BP-polymer SA, passive mode-locking operations are realized in an EDFL, delivering a train of pulses with a duration of 1.2 ps at 1557.8 nm [160]. The properties of mode-locked EDFLs using TMDCs and BP SAs are summarized in Table 3. Up to now, to our knowledge, the shortest pulse duration of 67 fs has been achieved in an EDFL with the combination of the fiber-taper WS₂ SA and the nonlinear polarization rotation technique [145], the highest pulse repetition rate (3.27 GHz) has been reported by using an MoSe₂ SA in the HML [149], and the maximum output power of 57 mW has been obtained by using the MoTe₂ SA prepared by the magnetron-sputtering deposition method [104].

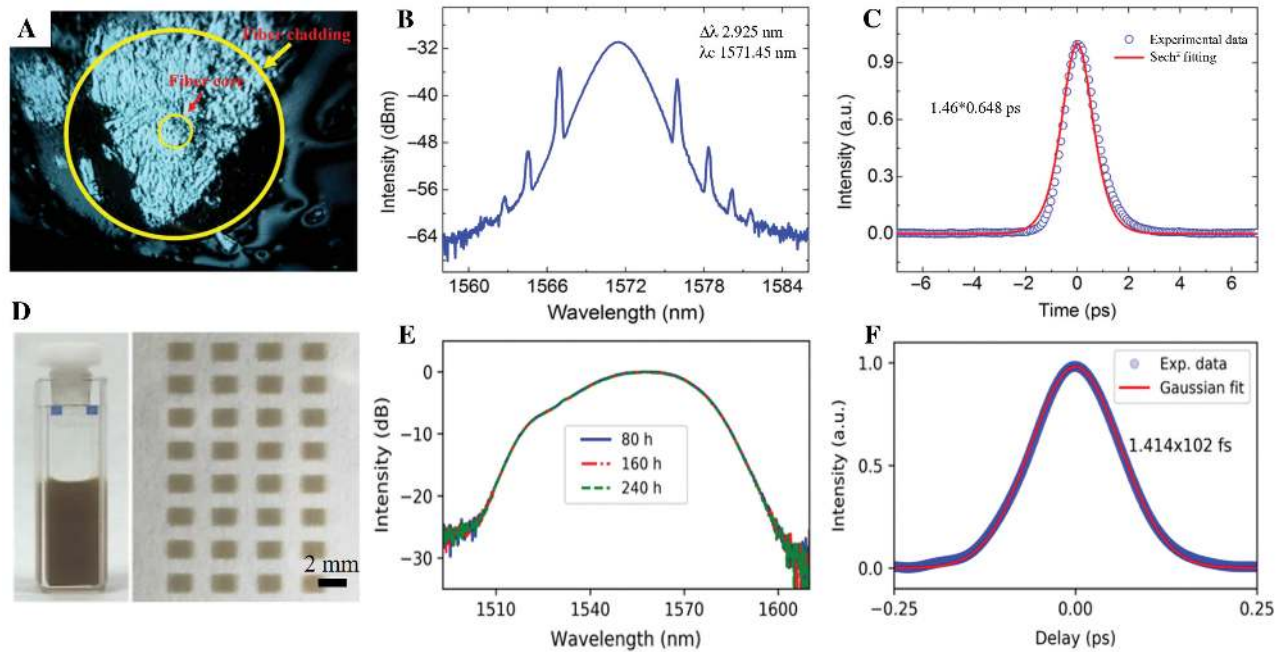


Figure 6: Typical mode-locked erbium-doped fiber lasers (EDFLs) by black phosphorus (BP) saturable absorbers (SAs). (A) Optical image of BP on fiber facet. (B) Pulse spectrum. (C) Autocorrelation traces. Reproduced with permission [153]. Copyright 2015, The Optical Society. (D) Photograph of BP dispersion and inkjet-printed BP SA arrays. (E) Spectra of mode-locked pulse acquired after 80 h, 160 h and 240 h. (F) Autocorrelation traces. Reproduced with permission [154]. Copyright 2018, The Optical Society.

Table 3: Summarization of mode-locked erbium-doped fiber lasers (EDFLs) based on transition-metal dichalcogenides (TMDCs) and black phosphorus (BP) saturable absorbers (SAs) at 1.55 μm .

| 2D-Mater. | Fabrication method | Incorporation method | Laser performance | | | | Ref. |
|-------------------|--------------------|----------------------|-------------------|---------------|----------|----------|-------|
| | | | λ (nm) | Duration (fs) | Energy | RF (MHz) | |
| MoS ₂ | CVD | Sandwiched | 1568.9 | 1280 | – | 8.288 | [142] |
| MoS ₂ | LPE | PVA film | 1535–1565 | ps | 65 pJ | 12.99 | [143] |
| WS ₂ | LPE | PVA-film | 1557 | 1320 | 0.248 nJ | 8.86 | [144] |
| WS ₂ | PLD | Tapered fiber | 1540 | 67 | – | 135 | [145] |
| MoS ₂ | LPE | DSF | 1530.4 | 1210 | – | 125 | [146] |
| MoS ₂ | LPE | DSF | 1556.86 | 3000 | – | 2.5 GHz | [147] |
| MoS ₂ | CVD | DSF | 1568 | 4980 | – | 26.02 | [161] |
| MoS ₂ | LPE | PVA film | 1569.5 | 710 | 22 mW | 12.09 | [162] |
| WS ₂ | Solution | DSF | 1557 | 660 | – | 10.2 | [163] |
| WS ₂ | LPE | Tapered fiber | 1561 | 369 | 1.93 mW | 24.93 | [164] |
| WS ₂ | PLD | Tapered fiber | 1561 | 246 | 18 mW | 101.4 | [165] |
| MoTe ₂ | MSD | Tapered fiber | 1559.57 | 229 | 57 mW | 26.601 | [104] |
| MoSe ₂ | CVD | Tapered fiber | 1552 | 207 | – | 64.56 | [150] |
| WTe ₂ | LPE | DSF | 1556.2 | 770 | – | 13.98 | [151] |
| SnS ₂ | LPE | PVA film | 1562.01 | 623 | 1.2 mW | 29.33 | [138] |
| ReS ₂ | LPE | PVA film | 1558.6 | 1600 | 0.4 mW | 5.48 | [125] |
| BP | ME | Sandwiched | 1571.45 | 946 | – | 5.96 | [153] |
| BP | ME | Sandwiched | 1559.5 | 670 | – | 8.77 | [156] |
| BP | ME | Sandwiched | 1558.7 | 786 | 0.11 nJ | 14.7 | [155] |
| BP | LPE | Sandwiched | 1555 | 102 | 0.071 nJ | 23.9 | [154] |
| BP | LPE | PVA film | 1557.8 | 1200 | – | 6.317 | [160] |
| BP | ME | Sandwiched | 1560.5 | 946 | – | 5.96 | [153] |

CVD, chemical vapor deposition; DSF, D-shaped fibers; LPE, liquid-phase exfoliation; ME, mechanical exfoliation; MSD, magnetron sputtering deposition; PLD, pulsed laser deposition; RF, repetition frequency; PVA, polyvinyl alcohol.

3.3 Mode-locked fiber lasers at mid-infrared wavelengths

Ultrafast fiber lasers operating from 2 μm to 20 μm wavelength are one of the most important branches of laser technology [166–169]. Mid-infrared fiber lasers are experiencing intense development due to their important applications in remote sensing [170], spectroscopy [171, 172], environmental monitoring [173, 174], materials processing [175], etc. In the mid-infrared region, the study of ultrafast fiber lasers started in the 1990s since Nelson et al. [176] demonstrated a mode-locked Tm^{3+} -doped fiber laser that produced sub-500 fs pulses. After that, ultrafast fiber lasers developed rapidly in this waveband, and a number of mode-locked Tm^{3+} -, Ho^{3+} -, and $\text{Ho}^{3+}/\text{Pr}^{3+}$ -doped fiber lasers have been reported [177–180]. Simultaneously, the booming advances of low-dimensional nanomaterials over the past decade have triggered an increasing interest in nanomaterial-based SAs at mid-infrared wavelengths [181–184]. Up to now, 2 μm mode-locked fiber lasers have been achieved with the assistance of layered materials. In 2017, Jung et al. [185] reported mode locking in $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped fiber lasers by a WS_2 -DSF SA, and achieved stable mode-locked pulses with a width of ~ 1.3 ps at a repetition rate of 34.8 MHz at 1941 nm, as shown in Figure 7A–C.

Stimulated by the applications in atmospheric remote sensing [187], the wavelengths of fiber lasers have been extended beyond the 3 μm regime. However, TMDCs such as MoS_2 and WS_2 generally have large bandgaps (1–2 eV), which limits their applications in the mid-infrared wavelength >3 μm . Depending on the number of layers [23], BP has a tunable direct energy bandgap from 0.3 eV to 2 eV, which makes it an ideal saturable absorption material, especially in the mid-infrared wavelength region.

The first BP mode-locked operation at 3 μm was reported by Li et al. [188] in an $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped fluoride fiber laser, where BP was fabricated using the LPE method and then integrated with a mirror. The pulse duration, repetition rate, and output power are 8.6 ps, 13.987 MHz, and 6.28 nJ, respectively. Qin et al. reported a passively mode-locked Er: ZBLAN fiber laser by transferring the thickness of ~ 143 nm BP nanosheets onto the gold-coated mirror to serve as a BP SA. The mode-locked mid-infrared laser at 2783 nm generated a pulse with an average output power of 613 mW, a pulse duration of 42 ps and a repetition rate of 24 MHz, as shown in Figure 7D and E [186]. Qin et al. [131] reported a mode-locked Er-doped ZBLAN fiber laser at 3.48 μm by transferring 52 nm BP flakes onto an Au-coated mirror as the SA, producing picosecond pulses with an average power of 40 mW and a repetition rate of

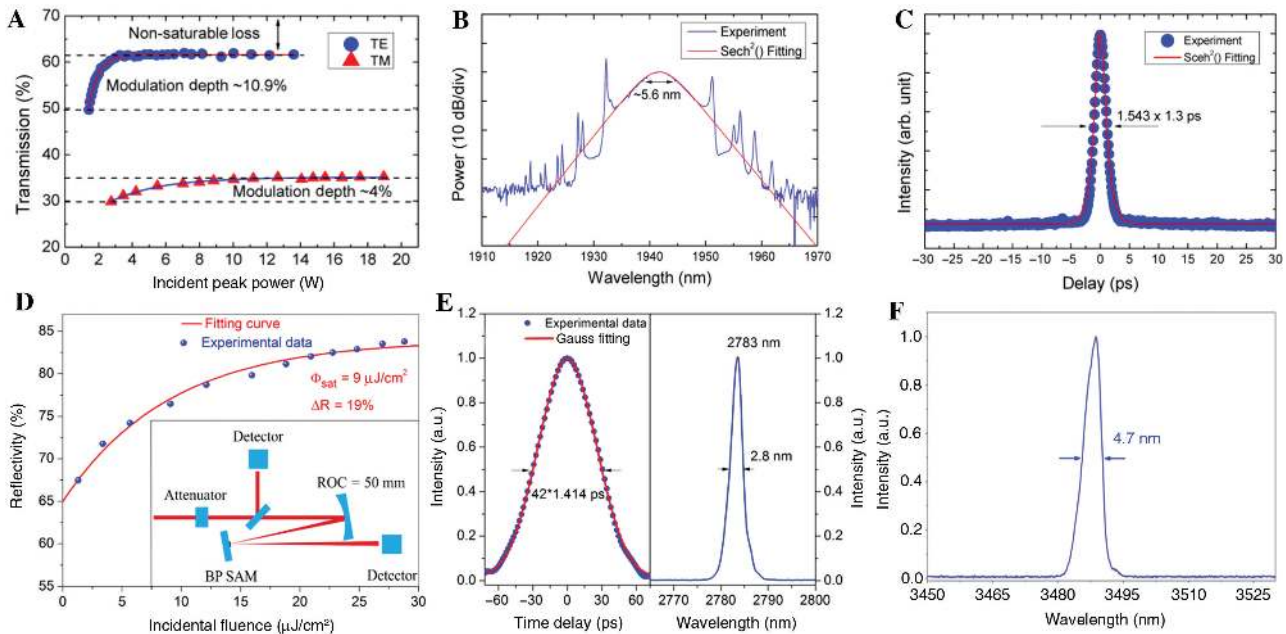


Figure 7: Mode-locked fiber lasers using WS_2 saturable absorber (SA).

(A) Nonlinear transmission curves at 1925 nm. (B) Spectrum. (C) Autocorrelation traces. Reproduced with permission [185]. Copyright 2015, The Optical Society. Mode-locked Er: ZBLAN fiber laser at 2.8 μm and 3.5 μm . (D) Saturable absorption of black phosphorus (BP) SA at 2.8 μm . (E) Autocorrelation trace and spectrum at 2.8 μm . Reproduced with permission [186]. Copyright 2016, The Optical Society. (F) Spectrum at 3.5 μm . Reproduced with permission [131]. Copyright 2018, The Optical Society.

Table 4: Summarization of mode-locked fiber lasers with transition-metal dichalcogenides (TMDCs) and black phosphorus (BP) saturable absorbers (SAs) at mid-infrared wavelengths.

| 2D-Mater. | Fabrication method | Incorporation method | Laser performance | | | | | Ref. |
|-------------------|--------------------|----------------------|------------------------------------|----------------|---------------|----------|---------|-------|
| | | | Laser type | λ (nm) | Duration (ps) | Energy | RF(MHz) | |
| WS ₂ | LPE | DSF | Tm/Ho | 1941 | 1.3 | 17.2 pJ | 34.8 | [185] |
| MoSe ₂ | LPE | DSF | Tm/Ho | 1912 | 920 | 4.3 mW | 18.21 | [190] |
| WTe ₂ | MSD | Microfiber | Tm | 1915.5 | 1.25 | 39.9 mW | 18.72 | [189] |
| BP | ME | Fiber end facet | Tm | 1910 | 739 | 0.047 nJ | 36.8 | [74] |
| BP | LPE | SA mirror | Ho ³⁺ /Pr ³⁺ | 2866.7 | 8.6 | 6.28 nJ | 13.987 | [188] |
| BP | ME | SA mirror | Er: ZBLAN | 2783 | 42 | 613 mW | 24 | [186] |
| BP | Sonication | SA mirror | Er: ZBLAN | 3489 | – | 40 mW | 28.91 | [131] |

DSF, D-shaped fibers; LPE, liquid-phase exfoliation; ME, mechanical exfoliation; MSD, magnetron sputtering deposition; RF, repetition frequency.

28.91 MHz, as illustrated in Figure 7F. Besides the BP SA, by introducing defects in MoS₂ [180], WS₂ [185], WTe₂ [189], MoSe₂ [190], mode-locked Tm³⁺, Ho³⁺, Ho³⁺/Pr³⁺, ZBLAN-doped fiber lasers have been reported using TMDC SAs. Table 4 summarizes these important achievements of mode-locked fiber lasers with TMDCs and BP SAs at mid-infrared wavelengths.

4 Passively Q-switched fiber lasers based on TMDCs and BP SAs

Passive Q-switching is another important technique for generating pulsed lasers, which have nanosecond/microsecond pulse duration and a large pulse energy at the kHz repetition rate [191]. Attributed to their remarkable high pulse energy, Q-switched fiber lasers can be applied in many fields, such as industrial laser engraving, metal cutting, and laser surgery. Compared with mode-locked fiber lasers that require a careful design of the cavity to balance the dispersion and nonlinearity, Q-switched fiber lasers are quite easy for implementation by modulating the loss of a laser oscillator. An SESAM was generally used to achieve passively Q-switched operation in previous commercial laser systems. However, the fabrication of an SESAM usually requires expensive and complicated fabrication systems and the SAs have bandwidths less than 50 nm. Thus, a low-cost high-performance Q-switcher is quite urgent for practical applications. Benefiting from the broadband property of TMDCs and BP SAs, the wavelength of passively Q-switched fiber lasers can range from the visible to mid-infrared range [192–197].

Li et al. [198] have generated 604 nm Q-switched pulses in Pr³⁺-doped fiber lasers utilizing filmy WS₂ and MoS₂ SA. For WS₂ (MoS₂) SAs, the pulse has a repetition

rate of 67.3–132.2 kHz (50.8–118.4 kHz) with a minimum duration of 435 ns (602 ns). Woodward et al. [199] have demonstrated a passively Q-switched YDFL tunable from 1030 nm to 1070 nm based on an MoS₂-PVA SA. Luo et al. [200] also demonstrated passively Q-switched fiber lasers at 1 μ m, 1.5 μ m, and 2 μ m by exploiting a few-layer MoS₂-polymer SA. Jiang et al. [201] achieved a passively Q-switched thulium/holmium-doped fiber laser at 2 μ m by a BP-SA that is fabricated by the optical deposition method. The Q-switched pulse has a minimum duration of ~731 ns, a maximum pulse energy of 632.4 nJ, and a repetition rate of 69.4–113.3 kHz. Qin et al. [131] reported a Q-switched Er: ZBLAN fiber laser at 3462 nm by transferring BP flakes onto an Au-coated mirror. The output power, pulse width, and repetition rate are 120 mW, 2.05 μ s, and 66.33 kHz, respectively. Table 5 summarizes these important progresses of Q-switched fiber lasers based on TMDCs and BP SAs.

5 Summary and outlook

TMDCs and BP are two typical layered 2D nanomaterials that have a large third-order nonlinearity and layer-dependent bandgap. In this review, we have discussed nonlinear optical properties and fabrication methods of TMDCs and BP nanosheets, and summarized typical approaches of incorporating nanosheets with fibers to achieve fiber-based SAs. In the main part, we have also highlighted the recent progresses of mode-locked and Q-switched fiber lasers from the visible to mid-infrared regime. The pure TMDCs exhibit comparatively large bandgaps in the visible or near-infrared wavelength region (~1.8 eV for MoS₂, ~2.1 eV for WS₂, ~0.8 eV for WTe₂). Although their bandgaps can be controlled by changing the layer numbers or introducing atomic defects, the

Table 5: Summarization of Q-switched fiber lasers based on transition-metal dichalcogenides (TMDCs) and black phosphorus (BP) saturable absorbers (SAs).

| 2D-Mater. | Fabrication method | Incorporation method | Laser performance | | | | | Ref. |
|-------------------|---------------------|----------------------|------------------------|----------------|------------------|--------------|---------------|-------|
| | | | Laser type | λ (nm) | Duration | Energy | RF (KHz) | |
| MoS ₂ | LPE | SA mirror | Pr ³⁺ ZBLAN | 604 | 602 ns | 5.5 nJ | 50.8–118.4 | [198] |
| MoS ₂ | LPE | Sandwiched | Yb | 1030–1070 | 2.88 μ s | 126 nJ | 65.3–89 | [199] |
| MoS ₂ | Hydrothermal | PVA | Er | 1560 | 3.2–5.1 μ s | 17.16 nJ | 36.8–91.7 | [202] |
| MoS ₂ | Thermal evaporation | Sandwiched | Er | 1550–1575 | 6–35 μ s | 150 nJ | 22 | [203] |
| MoS ₂ | CVD | Sandwiched | Er | 1529.8–1570.1 | 1.92 μ s | 8.2 nJ | 28.6–114.8 | [204] |
| MoS ₂ | LPE | Sandwiched | Er | 1519.6–1567.7 | 3.3 μ s | 160 nJ | 8.77–43.47 | [205] |
| MoS ₂ | PLD | SA mirror | Er | 1549.8 | 660 ns | 152 nJ | 116–131 | [206] |
| MoS ₂ | LPE | Sandwiched | Tm | 2030 | 1.76 μ s | 1 μ J | 33.6–48.1 | [200] |
| WS ₂ | LPE | SA mirror | Pr ³⁺ ZBLAN | 604 | 435 ns | 6.4 nJ | 67.3–132.2 | [198] |
| WS ₂ | CVD | PVA | Yb | 1027–1065 | 1.65 μ s | – | 60.2–97 | [207] |
| WS ₂ | LPE | Sandwiched | Er | 1547.5 | 985 ns | 44 nJ | 80–120 | [208] |
| WS ₂ | LPE | Sandwiched | Er | 1550 | 4.04 μ s | 369.5 nJ | 60.724–66.847 | [197] |
| MoSe ₂ | LPE | Sandwiched | Tm | 1924 | 5.5 μ s | 42 nJ | 14–21.8 | [209] |
| TiSe ₂ | PMS/CVD | SA mirror | Er | 1530 | 1.126 μ s | 11.5 mW | 70–154 | [210] |
| BP | LPE | Sandwiched | Pr ³⁺ ZBLAN | 635 | 383–1560 ns | 27.6 nJ | 108.8–409.8 | [211] |
| BP | ME | Microfiber | Yb | 1064.7 | 2.0–5.5 μ s | 17.8 nJ | 26–76 | [212] |
| BP | ME | Sandwiched | Er | 1561.9 | 2.96 μ s | 194 nJ | 7.86–34.32 | [213] |
| BP | Solution | Sandwiched | Tm/Ho | 1912 | 731 μ s | 632.4 nJ | 69.4–113.3 | [201] |
| BP | LPE | SA mirror | Er: ZBLAN | 2800 | 1.18–2.1 μ s | 7.7 μ J | 39–63 | [214] |
| BP | Sonication | SA mirror | Er: ZBLAN | 3462 | 2.05 μ s | 1.83 μ J | 66.33 | [131] |

CVD, chemical vapor deposition; LPE, liquid-phase exfoliation; ME, mechanical exfoliation; PLD, pulsed laser deposition; PMS, pulse magnetron sputtering; PVA, polyvinyl alcohol; RF, repetition frequency.

absorption is relatively weak in the mid-infrared wavelength. Thus, the TMDC-based SAs are difficult to apply in mid-infrared lasers. In contrast to TMDCs, the bandgap of BP can be tuned from 0.3 eV to 2 eV (corresponding to the wavelength from 4 μ m to 0.6 μ m) depending on the layer number. Thus, BP SAs are more attractive for pulsed fiber lasers at mid-infrared wavelengths.

In addition to their widespread applications in fiber lasers [65, 215], these 2D materials have also been used as SAs to realize mode-locked/Q-switched operations in solid-state lasers [216, 217] and waveguide lasers [218, 219] from visible to mid-infrared wavelengths. Although many breakthroughs of these studies have been achieved in recent years, there are still many challenges. For instance, the high nonsaturable loss of 2D material SAs limits the efficiency of fiber lasers. The pulsed fiber laser based on the TMDCs and BP SAs can be further optimized by changing the cavity design and growing high-quality 2D materials. Fiber lasers can be further extended to shorter or longer wavelengths using new fibers and a gain medium. More importantly, how to transfer the laboratory technology for commercial applications is the key direction in the future.

For perspective, the TMDCs and BP SAs can be further developed from several aspects, such as reducing the nonsaturable loss, improving the stability, and controlling the modulation depth. With the development of mid-infrared fiber components, we expect that BP can be used as an SA in mid-infrared fiber lasers beyond 4 μ m. Moreover, TMDCs and BP SAs can be used in few-mode fiber lasers or multi-mode fiber lasers to generate spatial-temporal mode-locked pulses [135]. The growing interest of exploring TMDCs and BP encourages researchers to look for new physics and technology breakthroughs, and also further exploit practical applications, including not only SAs, but also photodetectors, optical modulators and light-emitting devices.

Acknowledgements: This work was supported by the National Key R&D Program of China (2017YFA0303800); National Natural Science Foundation of China (11874300, Funder Id: <http://dx.doi.org/10.13039/501100001809,61575162>); the Fundamental Research Funds for the Central Universities (3102017AX009, 3102019PY002, 3102019JC008); the Natural Science Foundation of Shanxi Province (2018JM6013).

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