

Review

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Solution-processed two-dimensional materials for ultrafast fiber lasers (invited)

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Abstract: Since graphene was first reported as a saturable absorber to achieve ultrafast pulses in fiber lasers, many other two-dimensional (2D) materials, such as topological insulators, transition metal dichalcogenides, black phosphorus, and MXenes, have been widely investigated in fiber lasers due to their broadband operation, ultrafast recovery time, and controllable modulation depth. Recently, solution-processing methods for the fabrication of 2D materials have attracted considerable interest due to their advantages of low cost, easy fabrication, and scalability. Here, we review the various solution-processed methods for the preparation of different 2D materials. Then, the applications and performance of solution-processing-based 2D materials in fiber lasers are discussed. Finally, a perspective of the solution-processed methods and 2D material-based saturable absorbers are presented.

1 Introduction

Lasers able to generate pulses on a picosecond time scale or less have widespread applications in science and technology [1]. Among these, fiber lasers have advantages such as alignment-free operation, efficient heat dissipation, and compact designs, making them particularly attractive for applications requiring a stable operation [2, 3]. For example, in medicine, stable pulses operating at ~ 2 μm are required for surgery due to the water absorption at this wavelength [4, 5], while pulses operating in the ~ 1 – 1.5 μm range are required for imaging, to minimize photodamage and maximize penetration depth [6]. Owing to their high performance, design flexibility, and low maintenance costs [7, 8], fiber lasers have been particularly successful in applications such as medicine [9, 10], telecommunication [11], and sensing [12]. Optical pulses, as required by most applications, are generated by a mode-locking or Q-switching technique [13, 14], where an intensity-dependent saturable absorber (SA) is typically used [15]. SAs with high modulation depths (e.g. 41.2% and 51.3% [16, 17]) and low saturation intensity (e.g. 0.75 and 2.02 MW/cm^2 [18, 19]) are typically desired for mode locking of fiber lasers due to their higher gain and lower cavity losses compared with solid-state lasers [20]. To date, the most common SAs used in commercial fiber lasers are based on semiconductor SA mirrors (SESAMs) [21] and non-linear polarization evolution [22]. However, SESAMs generally have a limited bandwidth (~ 100 nm [21]), while non-linear polarization evolution-based SAs are sensitive to environmental parameters [22], resulting in stringent technological requirements needed to control their properties. These limitations are particularly detrimental for scientific research and technological development. For example, from a laser design perspective, SAs able to provide flexible parameters (e.g. low linear absorption

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and high modulation depth), and that can be easy to fabricate and integrate, are especially desirable [23, 24]. These requirements, driven by a growing number of scientific and industrial applications, motivate research on new materials, novel designs, and technologies [25–28].

Two-dimensional materials (2DMs) have emerged as promising SAs with a number of favorable properties for laser development [29, 30], such as broadband operation [31, 32], controllable modulation depth [33], and ultrafast recovery time [34, 35]. In addition, they can be solution processed by means of wet chemistry [36], making them easy to fabricate and integrate into all-fiber configurations. Since the first demonstration of a graphene SA produced by liquid-phase exfoliation (LPE) [37], a growing number of related 2DMs are being investigated due to their diverse properties and manufacturing flexibility [30]. Among these, SAs based on topological insulators (TIs) have been demonstrated with high (~95%) modulation depth [38], while transition metal dichalcogenides (TMDs) have better saturable absorption response (1.38 MW/cm² [39]) compared with graphene (e.g. 60 and 266 MW/cm² [40, 41]). Moreover, black phosphorus (BP) with a large span of bandgap and controllable band energy (0.3 eV for bulk BP and 2 eV for monolayer BP) that can be controlled by the number of layers has also proved to be a broadband SA up to the mid-infrared band [42].

Here, we review recent developments toward the implementation of solution-processed 2DMs to fiber lasers and present our outlook on this field. The exfoliation, stabilization, sorting, and MXene fabrication are discussed in Section 2. Then, the applications of solution-processed 2DM-based ultrafast fiber lasers are presented. Finally, a summary and outlook is given in Section 4.

2 Fabrication methods

The two main methods to produce 2DMs (i.e. crystalline materials with a layered structure) can be categorized into bottom-up and top-down [43]. For example, chemical vapor deposition (CVD) is a popular bottom-up method able to produce high-quality, large-area materials [44–46]. While CVD is used for applications such as integrated electronic devices [47, 48] or transparent electrodes, for other applications such as solar cells, fuel cells, thermoelectric devices, or optical sensing systems [49–52], it is preferable to have the 2DMs dispersed in a liquid, which would make them easier to process and manipulate [53, 54].

LPE of 2DMs is a typical top-down method where a bulk crystal or powder (of the starting material) is exfoliated

in a liquid medium by disrupting the forces keeping the layers together [43]. It can be achieved by using physical forces (e.g. ultrasound waves or shear forces [53, 55, 56]) or by chemically modifying the layers, e.g. by intercalation (e.g. insertion of ions or use of electrochemical actions [56]), or by oxidation [57, 58]. Compared to CVD, which requires high substrate temperatures followed by transfer to the target substrate, LPE has the advantages of scalability, room temperature processing, and high yield, and does not require any substrate [43]. Dispersions produced by LPE can be easily integrated into various systems like batteries or solar cells [49]. Here, we provide a brief overview of the main LPE methods used to achieve stable 2DM dispersions for ultrafast laser applications.

LPE is one of the most popular methods to produce 2DM-based SAs. From the SA perspective, a number of aspects need to be considered when evaluating an LPE method. For example, the yield of single or few layers, as well as their concentration, is important to maximize the modulation depth [59], while the dispersion stability (i.e. the ability to prevent reaggregation [53]) is crucial as aggregates could cause non-saturable scattering losses [60]. Other aspects such as cost and scalability are clearly important from a technology implementation standpoint [53, 61]. Regardless of the type of forces involved, there are three main steps in achieving stable dispersions: actual exfoliation, stabilization, and sorting. Herein, we summarize the typical LPE-based 2DM SAs, as shown in Table 1.

2.1 Exfoliation methods

Exfoliation is the process by which the layered structure of a 2DM is disrupted to form individual layers or few-layer structures [133–135]. The most popular exfoliation method used to fabricate SAs is ultrasonication, in which ultrasound waves are employed to disrupt the weak inter-layer van der Waals forces within the 2D crystal (Figure 1A, B). Ultrasonication has proved effective for most 2DM-based SAs, including graphene [36, 41, 62–67, 133], TIs [16, 59, 89, 91, 105, 107–111, 114, 136–138], TMDs [19, 39, 60, 74, 83–89, 91, 92, 96, 97, 99–104, 135, 139–142], and BP [42, 116–130, 143–145]. Its popularity arises from the ease of use, low cost, and immediate availability across most laboratories [55, 146, 147]. Conversely, scalability is an issue for such methods, as ultrasonication remains essentially a laboratory-based process [55].

Intercalation is another popular method used to exfoliate 2DMs for SA preparation. The intercalation process can occur by using intercalants (typically small ions like Li⁺) or by electrochemistry [56]. The process relies on the

Table 1: Summary of the typical LPE-based 2DM SAs.

Material	Exfoliation	Medium/stabilization	Integration	Ref.
Graphene	Ultrasonication	PVA	PVA composite	[62]
Graphene	Ultrasonication	Surfactant	PVA composite	[36, 41, 63–66]
Graphene	Ultrasonication	Surfactant or solvent (NMP or ODCB)	PVA or SMMA composite	[61]
Graphene	Ultrasonication	NMP	SMMA composite	[67]
Graphene	Electrochemistry	Sulfuric acid	Photonic crystal fiber	[68]
GO	Acid treatment	–	PPV composite	[69]
GO	Hummers	–	Optical deposition	[40]
GO	Hummers	–	PVA composite	[70–72]
GO	–	–	Photonic crystal fiber	[73]
GO	–	–	Spray	[74–76]
RGO	Hummers/hydrazine	–	Self-assembled membrane	[77]
RGO	Hummers/hydrazine	–	Optical deposition	[78–81]
GO and RGO	Hummers/benzylamine	–	Deposited on fused silica	[82]
MoS ₂	Ultrasonication	Surfactant	PVA composite	[19, 83, 84]
MoS ₂	Ultrasonication	DMF	PVA composite	[85–88]
MoS ₂	Ultrasonication	IPA	PVA composite	[89]
MoS ₂	Intercalation	Li-ion and ethylene glycol	Optical deposition	[90]
WS ₂	Ultrasonication	Surfactant	PVA composite	[39, 84, 91, 92]
WS ₂	Ultrasonication	NMP	PVA composite	[88]
WS ₂	Intercalation	Hydrazine and Na-ion	Optical deposition on tapered fiber	[93]
WS ₂	Intercalation	Li-ion in ethanol	Spin coating on side polished fiber	[94]
WS ₂	Intercalation	Li-ion and butyl-lithium in hexane	PVA composite	[95]
WS ₂ /MoSe ₂	Ultrasonication	Surfactant	PVA composite	[96]
WS ₂	Ultrasonication	Water and ethanol	Optical deposition or PVA composite	[97]
MoSe ₂	Ultrasonication	Surfactant	PVA composite	[60, 84]
MoSe ₂	Intercalation	Hydrazine and Na-ion	Optical deposition	[98]
WSe ₂	Ultrasonication	Surfactant	PVA composite	[84, 99]
TiS ₂	Ultrasonication	NMP	Optical deposition	[100]
SnS ₂	Ultrasonication	Alcohol	PVA composite	[101, 102]
ReS ₂	Ultrasonication	NMP	PVA composite	[103]
PtTe ₂	Ultrasonication	IPA	PVA composite	[104]
Bi ₂ Te ₃	Ultrasonication	Surfactant	PVA composite	[91]
Bi ₂ Te ₃	Ultrasonication	NMP	PVA composite	[105]
Bi ₂ Te ₃	Intercalation	Li-ion and ethylene glycol	Drop cast on CaF ₂ lens	[17]
Bi ₂ Te ₃	Intercalation	Li-ion and ethylene glycol	Solution-filled photonic crystal fiber	[106]
Bi ₂ Se ₃	Ultrasonication	NMP	Optical deposition	[59]
Bi ₂ Se ₃	Ultrasonication	NMP	PVA composite	[105, 107–109]
Bi ₂ Se ₃	Ultrasonication	IPA	Drop-cast on quartz plate	[110]
Bi ₂ Se ₃	Ultrasonication	IPA	Transfer onto fiber end facet	[111]
Bi ₂ Se ₃	Intercalation	Li-ion and ethylene glycol	Optical deposition	[112, 113]
Bi ₂ Te ₃	Ultrasonication	NMP	Solution-filled photonic crystal fiber	[114]
Sb ₂ Te ₃	Stirring	Water and chitosan	Drop-cast on side-polished fiber	[115]
BP	Ultrasonication	IPA	Optical deposition	[116–118]
BP	Ultrasonication	NMP	Optical deposition	[119–124]
BP	Ultrasonication	NMP	PVA composite	[125–128]
BP	Ultrasonication	NMP	Deposited on Au mirror	[116, 117]
BP	Ultrasonication	NMP	Inkjet printing	[129]
BP	Ultrasonication	Surfactant	PVA composite	[130]
BP	Electrochemistry	Tetra- <i>n</i> -butyl-ammonium bisulfate	Transfer onto fiber adapter	[131]
BP	Electrochemistry	Tetra- <i>n</i> -butyl-ammonium bisulfate	Sandwiched freestanding film	[132]

PVA, polyvinyl alcohol; SMMA, styrene methylmethacrylate; NMP, *N*-methyl-2-pyrrolidone; ODCB, ortho-dichlorobenzene; PPV, poly-phenylene vinylene; DMF, dimethyl formamide; IPA, isopropyl alcohol.

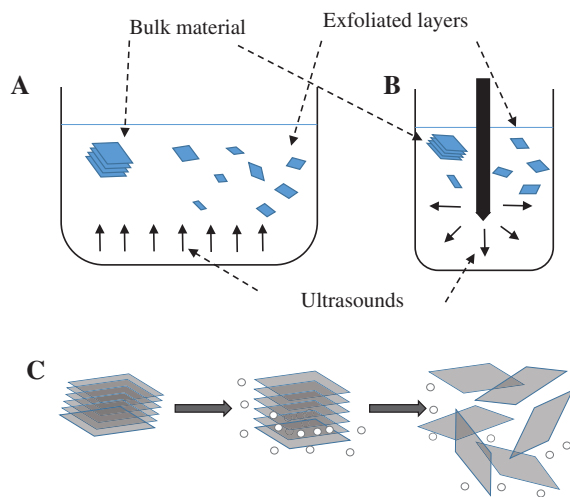


Figure 1: Schematics of the main exfoliation methods. (A) Bath ultrasonication. (B) Tip ultrasonication. (C) Intercalation.

insertion of an ion or a molecule into a 2DM structure to disrupt its inter-layer forces (Figure 1C). For SA fabrication, intercalating ions have been used for TMDs [90, 93–95] and TIs [17, 38, 106, 112, 113, 148–155]. Lithium ions (Li^+) were first used to produce MoS_2 monolayers using a chemical reaction with *n*-butyl lithium [156]. In this case, such reaction produced molecular hydrogen (H_2), which released forced layers to detach and migrate in solution [157]. Indeed, Li-ion-based intercalation is the most popular intercalation method used to produce SAs based on MoS_2 [90], WS_2 [94, 95], Bi_2Te_3 [17, 38, 106, 148–155], and Bi_2Se_3 [112, 113]. Sodium ions can also be used in a process involving hydrazine initially, which releases ammonia (NH_3), H_2 , and nitrogen (N_2) gases while intercalating the TMD layers, then an Na-naphthalenide solution is added in a second step [93, 158]. Intercalation by electrochemistry is an exfoliation process in which the layered material acts as an electrode in an electrochemical setup [56], which has also been used to produce SAs. For example, graphite can be used as anode with platinum (Pt) as cathode in an electrolyte solution to produce graphene monolayers [159–161, 68]. In such experiments, sulfuric acid or sulfate salts were used and sulfate was the intercalated ion. A similar process was used to produce BP-based SAs, with the crystal used as cathode (with a Pt foil anode) with tetra-*n*-butyl-ammonium bisulfate as electrolyte in anhydrous deoxygenated propylene carbonate [131, 132].

A chemical modification of the layers has proved to be a very popular method to exfoliate graphene in water, avoiding the use of surfactants. The material obtained has oxygen-containing functional groups [58], making it

easily soluble in water, and is so called graphene oxide (GO), which is different from the graphene obtained in the liquid phase by other methods discussed above. This is usually carried out using the Hummers method, consisting of treatment in sulfuric acid and potassium permanganate [57]. Other oxidization routes include nitric acid or other oxidizing agents like potassium chlorate [58]. GO can be used as such to make SAs [18, 40, 69–76, 82, 162]. GO can be reduced back to graphene by hydrazine [163]. As reduction is never complete, this material is known as reduced GO (RGO), to distinguish from pristine graphene, which can also be used to make SAs [77–82].

2.2 Stabilization methods

Once exfoliated, 2DMs need to be stabilized in the liquid phase to avoid reaggregation. Stabilization methods are 2DM dependent and can involve the use of a suitable solvent, surfactants, or polymers, to minimize the exfoliation energy cost [55]. Organic solvents like *N*-methyl-2-pyrrolidone (NMP) and dimethyl formamide (DMF) have successfully been employed for the liquid-based exfoliation of a number of 2DMs, like graphene [133], TMDs [135, 164], and BP [165–167]. It has been proposed that exfoliation in a solvent is successful as long as some solubility parameters, like surface tension and Hildebrandt or Hansen parameters, are very close for the solvent and the material [55, 133, 135, 146]. This enhances the compatibility between the material and the solvent, and increases the material concentration in solution [55, 133, 135, 146]. Other solvents used for graphene were ortho-dichlorobenzene [168] and perfluorinated aromatic solvents [169]. Among the solvents used for fabricating SAs, NMP is the most popular [61, 67, 88, 103, 116, 117, 119–129, 144, 145], while other solvents used are DMF [85–88] and isopropyl alcohol (IPA) [42, 89, 104, 116–118]. While the main advantage of using solvents is the high purity of the final material, there are also several drawbacks. Indeed, NMP and DMF are toxic and their high boiling point prevents an easy removal [55]. Also, solvents may not be compatible with further steps of a process [55]. While other solvents with lower boiling points have been proposed, like acetone, acetonitrile, 1-propanol, or IPA, their solubility parameters were not as good as those for NMP and DMF and their use was not as successful [170–174]. Despite this, there are a number of reports on SAs made from IPA-based 2DM solutions, particularly MoS_2 [89], PtTe [104], Bi_2Se_3 [16, 89, 110, 111, 137, 138], and BP [42, 116–118].

The use of surfactants (i.e. cationic, anionic, or non-ionic molecules with a long non-polar tail and a polar or

charged head) in water provides a viable alternative to exfoliation in organic solvents [55, 56]. In this approach, the long non-polar tail of the surfactant adsorbs on the layered material, also non-polar. The polar or ionic head is instead exposed to water, also polar, thus stabilizing the solution and also preventing aggregation by electrostatic or steric repulsion [55]. This method has been mainly adopted for graphene, using sodium dodecylbenzene sulfonate, sodium cholate, sodium deoxycholate, cetyltrimethylammonium bromide, and tetracyanoquinodimethane [61, 134, 175–177]. TMDs have also been dispersed in water using SC [178].

Due to the convenience of operating in aqueous environment, surfactants have been widely used in processes for fabricating SAs [19, 36, 39, 41, 60, 61, 63–66, 83, 84, 91, 92, 96, 99, 130]. While the use of water as a solvent makes the processing environmentally friendly and harmless, as well as potentially compatible with subsequent steps, the final material is not pure and may require a further processing step in case the surfactant causes interference with the designated application. When 2DMs are to be used as SAs, absorption of the surfactants in the laser region should be taken into account. Surfactants are usually transparent in the visible range but may give some optical absorption in the near-infrared region, where they may then cause non-saturable losses in the laser cavity. Hence, for fiber laser applications, they must be chosen carefully depending on the output wavelength or removed from the final SA material. Beyond the specific SA applications, surfactants must also be removed if, for example, graphene dispersions are to be used for making transparent conductive films. In this case, surfactant molecules prevent efficient contact between flakes, thus increasing junction resistance, impeding efficient carrier hopping from flake to flake and ultimately increasing the overall film resistance [179]. However, an easy solution is just washing the surfactant away with water to minimize junction and the overall sheet resistance [179]. Hence, surfactants are potentially detrimental not just for optical applications but also for electrical ones.

The use of polymers is also a valid approach to the stabilization of 2DMs in both water and organic solvents. In general, polymers are partially adsorbed onto the material's surface, leaving segments protruding into the liquid and preventing reaggregation by steric repulsion [55, 180]. However, this approach has found only limited applications for SA fabrication, as only in one case has polyvinyl alcohol (PVA) been reported as both a stabilizing polymer and polymer matrix for fiber laser integration [62].

2.3 Sorting methods

Regardless of the exfoliation and stabilization method, a final sorting step is always needed to enrich the solution of single- or few-layer material with the desired flake size. The universal sorting technique is centrifugation. Standard centrifugation can also be referred to as sediment-based separation. During this process, the fragmented 2DMs separate according to their size and thickness. Thick and large flakes sediment faster and are thus found in the bottom at the end of the process [55].

Standard centrifugation is the only sorting method used within SA fabrication. However, variations of the standard centrifugation exist. Density gradient ultracentrifugation allows a more precise control on the number of layers and lateral size [181–183], where flakes separate according to their density through a density gradient. However, this process is time consuming and has a very low yield, and thus is not useful for practical applications, including SAs.

A centrifugation method with good size and thickness control as well as higher yield than density gradient ultracentrifugation is liquid cascade centrifugation [184], which has been developed for TMDs but can be used in principle for any 2DMs. In this method, a solution containing the exfoliated and stabilized material is subjected to subsequent centrifugation steps, where the sediment is separated and redispersed and the supernatant is centrifuged again at a higher speed. This is repeated multiple times with speeds that can be tuned according to the desired size and thickness distribution [184]. This is a recently developed method that has not found application in SA fabrication yet; however, we cannot rule out its application in the near future.

2.4 MXene fabrication

MXenes are not typically produced by the common LPE methods. These are carbides or nitrides (or carbonitrides) of early transition metals, of which the most popular is titanium [185]. MXenes are obtained from the so-called MAX phases, also containing a layer of a group IIIA element, normally Al. Such MAX phases can be treated with hydrofluoric acid (HF) to etch the Al layer and leave the exfoliated MXene sheets in solution [185]. MXenes can be prepared by top-down or bottom-up methods such as aqueous acid etching (AAE), high-temperature etching, and CVD method, of which AAE is the most commonly used method in the preparation of high-quality MXenes

[186]. AAE is the etching of element A in the MAX phase by using acid solution, while MXenes are usually exfoliated by an ultrasonic method [187]. In this process, HF solution is the most attractive etchant for researchers due to its advantages of mature process, high practicability, and low cost [188]. For example, Wu et al. and Jhon et al. obtained $Ti_3C_2T_x$ and Ti_3CNT_x by etching Al layers from different MAX phases in 40% and 30% HF acid, respectively [189, 190]. Because intercalation cations such as NH_4^+ and K^+ can facilitate etching and exfoliation, fluorohydrides (e.g. NH_4HF_2 and KHF_2) are also popular etchants for fabricating MXenes [191].

2.5 Fabrication summary

Table 1 shows a summary of fabrication methods for SAs. Notably, ultrasonication maintains its popularity as an exfoliation method; however, intercalation is still significantly used to fabricate SAs. The intercalation process relies on chemistry (or electrochemistry) to produce exfoliated layers, and as such may cause their chemical modification and ultimately an alteration of the electronic and optical properties, which is an effect that should be taken into account when fabricating an SA. Conversely, ultrasonication only relies on physical forces and maintains the layer structure intact [53, 55, 56]. We thus believe that this is a preferable exfoliation method. When ultrasonication is used, we notice that the applications of surfactant and solvents are roughly evenly split. This is because both have their own distinct advantages and disadvantages, as mentioned above. When intercalation is used, the most popular option is based on lithium ions.

3 Solution-processed 2DM-based ultrafast fiber lasers

Fiber lasers are attractive platforms for ultrafast pulse generation due to their advantages of high pulse quality, flexibility, and compactness [1, 2]. Meanwhile, the use of SAs is a preferred method for the generation of pulses in fiber lasers [30]. Particularly, 2DM-based SAs are more attractive in terms of their broadband operation and engineerable properties [23]. Indeed, solution-processed 2DMs have been widely exploited in fiber lasers, as evident from Table 2. Here, we summarize the common 2DMs used and the current trends.

3.1 Graphene

Since the first demonstration of graphene-mode-locked fiber lasers based on solution processing [37], solution-processing-based graphene has been widely used for mode locking fiber lasers in the 1- μm [62], 1.5- μm [36, 41], and 2- μm regions [66]. For example, Hasan et al. obtained 630-fs pulse at 1.56 μm by LPE of graphite [61]. Besides, polymer composites are a common carrier that is used to integrate graphene into fiber lasers [18]. In 2010, Sun et al. reported a wavelength-tunable (1525–1559 nm) fiber laser based on graphene PVA composite [41]. Popa et al. obtained 173-fs pulse from a dispersion-managed Er-doped fiber laser mode-locked by graphene PVA composite [63]. Apart from PVA [36, 41, 62–66, 69], some other polymers have also been exploited to fabricate graphene-based films. In 2009, Zhang et al. demonstrated mode-locked Er-doped fiber lasers based on graphene polyvinylidene fluoride polymer membrane [18]. In 2011, Gui et al. reported a self-assembled graphene membrane as an ultrafast mode locker in an Er-doped fiber laser [77]. In 2016, Torrisi et al. proposed graphene-styrene methylmethacrylate composite for ultrafast lasers [67]. The method of optical deposition is also used to transfer graphene to the fiber in laser cavity [78–81, 162]. For instance, Fu et al. reported a graphene-mode-locked Er-doped fiber laser based on optical deposition, where a fiber connector for physical contact (FC/PC) was immersed in graphene solution. After alcohol evaporation, a graphene film was obtained at the center of the fiber core on the FC/PC tip, as shown in the inset of Figure 2A. They obtained the bound states of solitons and harmonic mode locking (HML) with orders from 1st to 26th [81]. Figure 2B shows a spectrum of HML (inset, pulse profile). Similar to optical deposition, Lin et al. embedded graphene nanoparticles into photonic crystal fiber (PCF), which achieves the evanescent wave mode locking in an Er-doped fiber laser [68].

As a graphene derivative, GO has been widely investigated as a broadband SA candidate because of its ultrafast recovery time, flat saturable absorption, low cost, and easy preparation [40, 200]. In 2010, GO-based fiber laser was first reported by Bonaccorso et al., who achieved an ~ 743 -fs pulse in an Er-doped fiber laser [201]. PVA as a polymer matrix was also popular in GO-based ultrafast fiber lasers [70–72]. Besides, Liu et al. demonstrated a nanosecond pulse by using few-layered GO SA, where a hollow core PCF was filled with GO solution [73]. Xu et al. obtained 200-fs pulses in a dispersion-managed fiber laser, where a thin GO membrane was formed on the broadband reflective mirror [40]. Jung et al. achieved a mode-locked fiber laser at 2- μm band by spraying GO onto the flat side of

Table 2: Summary of the typical ultrafast fiber lasers enabled by solution-processed 2DMs.

Material type	Fabrication method ^a	Incorporation method ^b	Laser type ^c	α_s (%)	I_{sat} (MW/cm ²)	λ (nm)	τ (s)	f_{rep} (Hz)	SNR (dB)	Energy (mW/fJ)	Ref.
Graphene	LPE	PVA	EDFL	4.5	266	1523–1559	1 p	8 M	80	1/125 p	[41]
Graphene	RGO	PVDF	EDFL	28.3	0.75	1589.68	694 f	6.95 M	65	20.85/3 n	[18]
Graphene	LPE	PVA	EDFL	5	266	1562	970 f	19.9 M	–	–/–	[61]
Graphene	LPE	SMMA	EDFL	0.9	140 μ J/cm ²	1550	502 f	–	–	–/–	[67]
Graphene	RGO	OD	EDFL	7.6	2.675 GW/cm ²	1562.26	950 f	502.84 M	50	2.3/4.6 p	[80]
Graphene	RGO	OD	EDFL	6.6	–	1558	950 f	15.75 M	70	0.18/11.2 p	[81]
GO	GO	SAM	EDFL	2.6	60	1556.9	600 f	25.6 M	50	3.3, 5.8	[40]
						1560	200 f	22.9 M	60	0.13 n, 0.25 n	
GO	GO	Filling PCF	EDFL	8	3.5 mW	1561.2	4.85 n	7.68 M	81	4.3/0.56 n	[73]
GO	GO	DSF	TDFL	–	–	1910	1.3 p	15.9 M	47	–	[75]
GO	GO	DSF	THDFL	7.1	14.83 W	1950	578 f	33.25 M	50	–/4.3 n	[74]
GO	GO	SAM	EDFL	2.6	60	1531	11 p	19.5 M	65	23.3/1.2 n	[192]
Bi ₂ Se ₃	LPE	OD	YDFL	3.8	53	1067.66	1.95–8.3 μ	8.3–29.1 k	48	0.46/17.9 n	[136]
Bi ₂ Se ₃	LPE	NMP	EDFL	3.8	53	1530.3	4.9–24 μ	6.2–40.1 k	50	1.6/39.8 n	[59]
Bi ₂ Se ₃	PM	PVA	EDFL	~3.9	12	1557.5	660 f	12.5 M	55	1.8/0.144 n	[89]
Bi ₂ Se ₃	LPE	PVA	Pr-doped ZBLAN	3.7	41	604	497–748 n	86.2–187.4 k	40	7.7/3.1 n	[109]
Bi ₂ Se ₃	PM	OD	EDFL	41.20	101.8	1565.14	13.4–36 μ	4.508–12.88 k	55	112 μ W/13.3 n	[16]
Bi ₂ Se ₃	LPE	OD	TM-DCFL	3.7	41	1980	4.18 μ	8.4–26.8 k	43	8.4/313 n	[193]
Bi ₂ Se ₃	PM	IPA	YDFL	5.2	70 μ J/cm ²	1031.7	46 p	44.6 M	58	33.7/0.756 n	[111]
Bi ₂ Se ₃	PM	PVA	YDFL	11.05	17.4	1036	7.2–11.6 μ	86.2–137.8 k	35 dBm	4.6, 1.88	[138]
						1554.56	507 p	17.7 M	44 dBm	34.2 n, 0.1 n	
Bi ₂ Se ₃	HIE	CaF ₂ substrate	Ho-doped ZBLAN	51.3	2.12	2979.9	1.37–4.83 μ	46.20–81.96 k	37.4	327.38/3.99 μ	[17]
Bi ₂ Te ₃	HIE	PVA	EDFL	2	180	1557	1.08 p	8.635 M	60	0.25/29.0 p	[151]
Bi ₂ Te ₃	LPE	OD	EDFL	22	57	1510.9–1589.1	13–49 μ	2.154–12.82 k	36.4	238.5/1.525 μ	[153]
Bi ₂ Te ₃	HIE	Filling PCF	YDFL	19.1	14.9	1064.47	960 p	1.11 M	60	–/–	[106]
Sb ₂ Te ₃	LPE	DSF	EDFL	3.9	106	1556	449 f	22.13 M	74	0.9/39.6 p	[115]
MoS ₂	HIE	EF	EDFL	2.82	–	1556.86	–	6.77 M	–	65 μ W/9.6 p	[98]
MoS ₂	HIE	PVA	EDFL	4.3	34	1569.5	710 f	12.09 M	60	1.78/0.147 n	[194]
MoS ₂	LPE	PVA	EDFL	10.69	2.02	1535–1565	0.96–7.1 p	12.99 M	55	0.844/65 p	[19]
MoS ₂	HIE	EF	YDFL	10.47	0.88 mW	1042.6	656 p	6.74 M	59	2.37/0.352 n	[93]
MoS ₂ /WS ₂	LPE	DMF	Pr-doped ZBLAN	–	–	604	602–1955 n	50.8–118.4 k	39	0.6, 0.7	[88]
MoS ₂	LPE	PVA	YDFL	1.6	13	1066.5	5.8 μ	67.3–132.2 k	41	5.5 n, 6.4 n	[87]
						1565	23.3–5.4 μ	6.4–28.9 k	44.6	0.9, 1.7, 47.3	
						2032	1.76 μ	6.5–27.0 k	54.5	/32.6 n, 63.2 n	
MoSe ₂	LPE	PVA	TDFL	4.4	25.7 W	1912.6	920 f	33.6–48.1 k	54.6	1 μ	[141]
MoSe ₂	Bath type sonication	DSF	EDFL	5.4	24	1557.3	737–798 f	15.38 M–3.27 G	61.9	0.23–22.8	[142]

Table 2 (continued)

Material type	Fabrication method ^a	Incorporation method ^b	Laser type ^c	α_s (%)	I_{sat} (MW/cm ²)	λ (nm)	τ (s)	f_{rep} (Hz)	SNR (dB)	Energy (mW/f)	Ref.
WS ₂	LPE	DSF	THDFL	4.2	43 W	1941	1.3 p	34.8 M	72	5.9–14.6 p	[195]
WS ₂	LPE	PVA	YDFL	10.9	1.9 W	1030	3.2–6.4 μ	24.9–36.7 k	53	0.6/17.2 p	[39]
			EDFL	3.1	1.38	1558	1.1–3.4 μ	79–97 k	44	0.5, 16.4	
WS ₂	Thermal decomposition	Fluorine mica film	YDFL	4.9	3.83	1053	713 p	23.26 M	55	13.6 n, 179.6 n	[196]
			EDFL	5.8	–					–/–	
WSe ₂	LPE	PVA	EDFL	3.5	103.9	1560	3.1–7.9 μ	4.5–49.6 k	46.7	1.23/33.2 n	[99]
TiS ₂	LPE	EF	EDFL	8.3	1.2 mW	1563.3	812 f	22.7 M	60	0.574/25.3 p	[100]
SnS ₂	LPE	PVA	YDFL	0.76	78	1062.66	656 p	39.33 M	53	2.23/0.057 n	[101]
SnS ₂	LPE	PVA	EDFL	4.6	125	1562.01	623 f	29.33 M	45	1.2/0.041 n	[102]
ReS ₂	LPE	PVA	EDFL	0.12	74	1557.3	5.496–23 μ	12.6–19 k	46	1.2/62.8 μ	[103]
PtTe ₂	LPE	PVA	YDFL	–	–	1066	5.2–13.6 μ	23.0–33.5 k	35	2.48/74 n	[104]
BP	LPE	CHP	EDFL	3.45	–50	1555	1.06 p	37.8 M	80	–/–	[197]
BP	LPE	Au mirror	HDFL	41.2	3.767	2970.3	2.41 μ	62.5 k	37.7	308.7, 87.8	[116]
			HPDFL			2866.7	8.6 p	13.987 M	56	4.93 μ , 6.28 n	
BP	LPE	PVA	EDFL	8.3	7.9	1565.3–1567.8	1.365–3.39 μ	64.51–82.64 k	>75	12.03/148.63 n	[127]
BP	LPE	SAM	Er-doped ZBLAN	15	9 μ /cm ²	2779	1.18–2.1 μ	39–63 k	35	485/7.7 μ	[117]
BP	LPE	EF	EDFL	10.1	9.27	1549–1575	280 f	60.5 M	68	–/–	[118]
BP	LPE	Inkjet-printed	EDFL	~10.03	~14.98	1555	102 f	23.9 M	>60	1.7/71 p	[129]
BP	LPE	PVA	EDFL	–0.35	–	~1558	~700 f	~20.82 M	>60	~1.5/–0.07 n	[128]
BPOQDs	LPE	EF	EDFL	8.1	1.69 mW	1561.7	882 f	5.47 M	~67	135 μ W/24.7 p	[119]
BPOQDs	LPE	EF	EDFL	9.0	1.5	1562.8	291 f	10.36 M	>50	–/–	[120]
BPOQDs	Solvothetmal	PVDF	EDFL	36	3.3 GW/cm ²	1567.5	1.08 p	15.22 M	64.3	–/–	[198]
Ti ₃ CNT _x	AAE	DSF	EDFL	1.7	45 W	1557	660 f	15.4 M	60	0.05/3.25 p	[190]
Ti ₃ C ₂ T _x	AAE	DSF	YDFL	38.3	69.3 GW/cm ²	1065.89	480 p	18.96	56	9, 3	[186]
			EDFL	2.0, –	37.5 GW/cm ²	1555.01	159 f	7.28 M	62	0.47 n, 0.41 n	
Ti ₃ C ₂ T _x	AAE	EF	EDFL 1	11.3	1.94 mW	1564.24	597.8	17.9	55.2	0.283, 1.3	[189]
			EDFL 2			1550	104 f	20.03 M	62.4	15.8 n, 64.9 p	
Ti ₃ C ₂ T _x	AAE	OD	EDFL	2.8	191	1565	1.37–3.19 μ	99.6–131.1 k	61	40/305 n	[188]
Ti ₂ CT _x	AAE	Film deposition	YDFL	23.1	4.2	1051.08	164.4 p	11.2 M	57.1	80/0.81 μ	[199]
			EDFL	15.7	5.1	1565.4	5.3 p	8.25 M	62		
			Er-doped ZBLAN			2798	730 n	44.1 k	33.1		
							–1.83 μ	–99.5			

α_s , modulation depth; I_{sat} , saturation intensity; λ , wavelength; τ , pulse width; f_{rep} , repetition frequency; SNR, signal-to-noise ratio.

^aFabrication method: liquid-phase exfoliation (LPE), polyol method (PM), hydrothermal intercalation/exfoliation (HIE), aqueous acid etching (AAE).

^bIncorporation method: saturable absorber mirror (SAM), polyvinylidene fluoride (PVDF), styrene methacrylate (SMMA), optical deposition (OD), photonic crystal fiber (PCF), D-shaped fiber (DSF), *N*-methyl-2-pyrrolidone (NMP), isopropyl alcohol (IPA), evanescent field (EF), dimethyl formamide (DMF), cyclohexyl pyrrolidone (CHP).

^cLaser type: Yb-doped fiber laser (YDFL), Er-doped fiber laser (EDFL), Tm-doped fiber laser (TDFL), Ho-doped fiber laser (HDFL), Ho, Pr-codoped fiber laser (HPDFL), Tm-doped double-clad fiber laser (TM-DCFL).

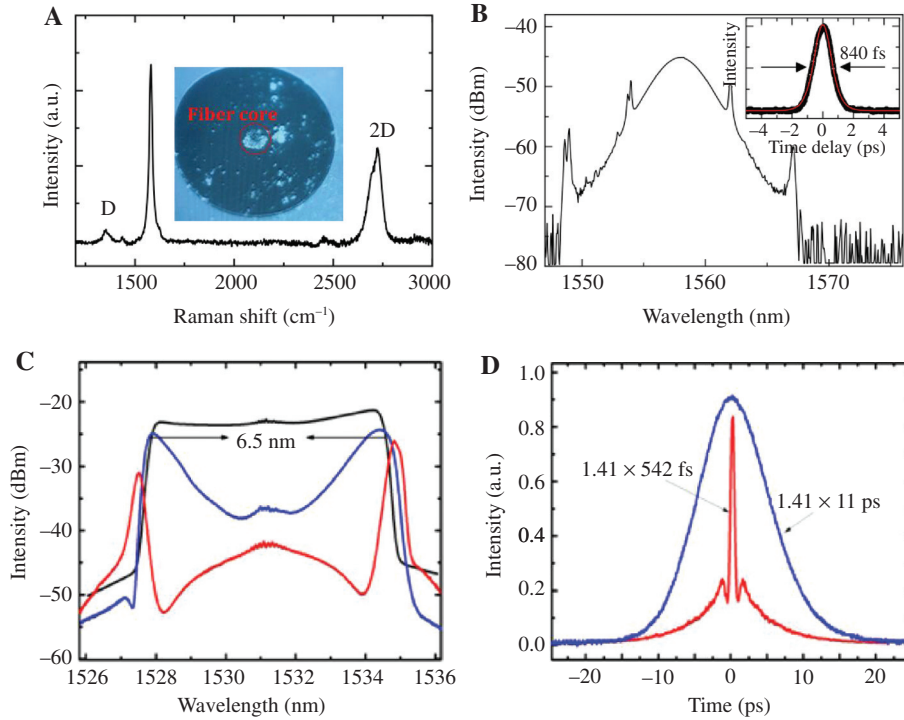


Figure 2: Mode-locked results enabled by graphene and GO.

(A) Raman spectrum of the graphene (inset: graphene optically deposited on fiber tip). (B) HML spectrum (inset: the autocorrelation trace of the 26th harmonic). (C) Spectra: before pulse compression (black curve), after 50-m single-mode fiber (blue curve), and after 75-m single-mode fiber (red curve). (D) Autocorrelation trace of chirped (blue curve) and dechirped pulses (red curve). (A) and (B) are reproduced with permission from Ref. [81]. Copyright 2019 CLP Publishing. (C) and (D) are reproduced with permission from Ref. [192]. Copyright 2012 OSA Publishing.

a D-shaped fiber [74, 75]. Xu et al. reported dissipative soliton generated from a GO-mode-locked fiber laser, in which a broadband reflective mirror was immersed into the GO hydrosol for 48 h [192]. Figure 2C shows the spectra before pulse compression (black curve), after 50-m single-mode fiber (blue curve) and after 75-m single-mode fiber (red curve). Figure 2D shows the autocorrelation trace of chirped (blue curve) and dechirped pulses (red curve). Lee et al. reported a Q-switched mode-locked fiber laser by depositing GO to a D-shaped fiber [76]. Sobon et al. compared the properties of GO with RGO as SAs in Er-doped mode-locked fiber laser, and showed that GO could be an efficient SA without reduction to RGO [82].

Although the modulation depth of single-layer graphene is ~2.3% or less [33, 36, 67], it can be easily enhanced by increasing the number of layers [33]. Furthermore, broadband operation is another remarkable property of graphene [41]. For example, Fu et al. achieved a broadband mode-locked fiber laser by using a single graphene SA at different wavelengths, where the span of the wavelength covers from Yb-doped (1 μ m), Er-doped (1.5 μ m), and Tm-doped (2 μ m) (up to 1000 nm) [31]. Graphene started a new beginning for 2DM-based ultrafast

photonics, paving the way for the research and development of ultrafast lasers enabled by 2DMs [20].

3.2 Topological insulators

Similar to graphene, TIs such as Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃ belong to the Dirac materials [202]. In 2012, TI-based SA was first reported in an Er-doped fiber laser [38]. Panels A and B of Figure 3 show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the Bi₂Te₃ nanosheets fabricated by the method of hydrothermal intercalation/exfoliation. The mode-locked spectrum and corresponding autocorrelation trace are shown in Figure 3C and D, respectively. Since then, hydrothermal intercalation/exfoliation has been widely used to produce TIs [17, 38, 112, 148–150]. For example, Wu et al. reported on 635-nm visible Q-switched Pr-doped ZBLAN fiber lasers with Bi₂Se₃ and Bi₂Te₃ SAs [105]. Li et al. experimentally demonstrated a 212-kHz-linewidth transform-limited pulse from a single-frequency Q-switched fiber laser based on a few-layer Bi₂Se₃ SA [107]. For TI integration into the laser cavities, polymer matrices

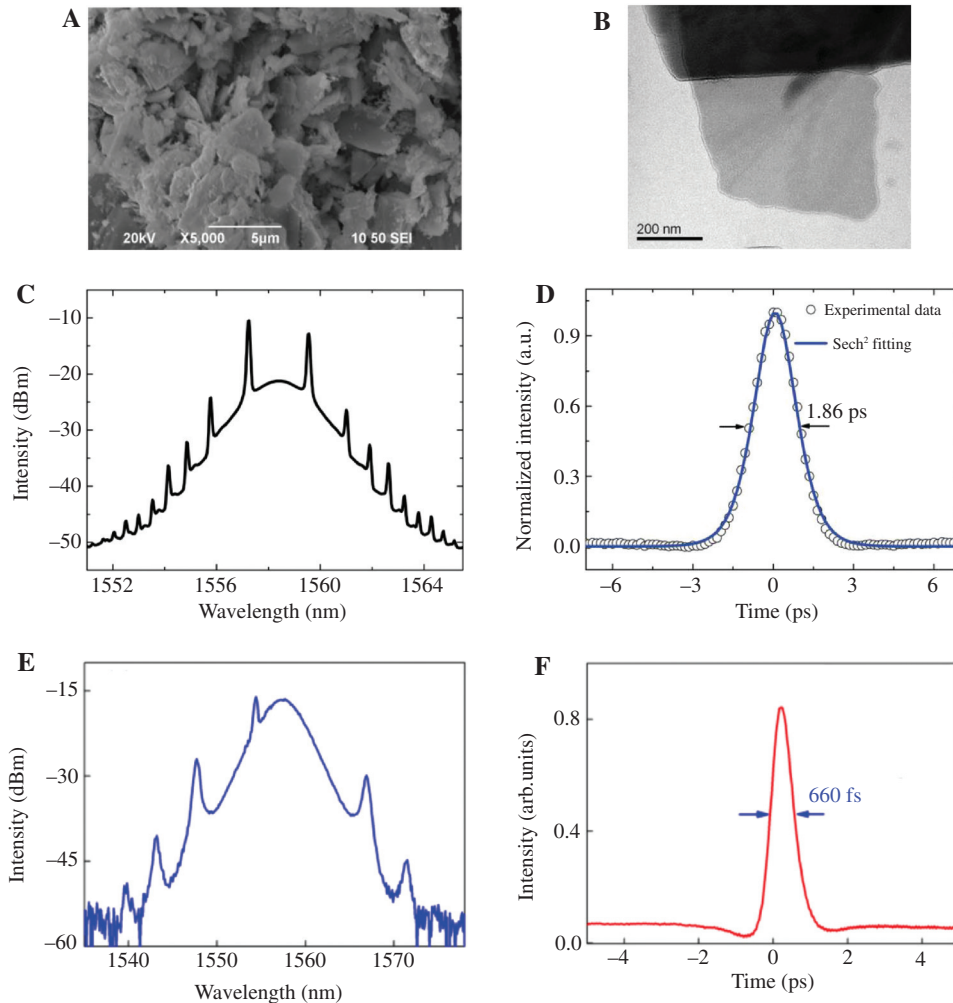


Figure 3: Mode-locked results enabled by Bi₂Te₃ and Bi₂Se₃.

(A) SEM and (B) TEM images of the Bi₂Te₃ nanosheets prepared by hydrothermal intercalation/exfoliation. (C) Spectrum and (D) autocorrelation trace. (E) Spectrum and (F) autocorrelation trace of mode-locked fiber laser based on Bi₂Se₃. (A)–(D) are reproduced with permission from Ref. [38]. Copyright 2012 AIP Publishing. (E) and (F) are reproduced with permission from Ref. [89]. Copyright 2014 OSA Publishing.

such as PVA were frequently utilized in the preparation of TI-based SAs [89, 108, 109, 137, 151]. In 2014, Liu et al. obtained 660-fs pulses generated in an Er-doped fiber laser enabled by Bi₂Se₃ nanosheets [89]. The spectrum and autocorrelation trace are shown in Figure 3E and F, respectively. In 2015, Mao et al. integrated Bi₂Te₃-PVA films into an Er-doped fiber laser and obtained mode-locked pulses at a low pump power of ~13 mW [151]. Optical deposition is also suitable for transferring TIs to the fiber tips in laser cavity [16, 113, 152–155, 193, 203]. In 2013, Chen et al. proposed a self-assembled Bi₂Se₃-based membrane as an SA, which achieved dual-wavelength Q-switched pulses in Er-doped fiber laser [16]. In 2014, Liu et al. obtained dual-wavelength harmonic-mode-locked pulses with Bi₂Te₃-based microfiber [154]. In 2018, Jin et al. reported on 3.125-GHz harmonics realized by Bi₂Te₃-based tapered fiber

by optical deposition [155]. In addition, polyol method was also used to prepare TIs as SAs in fiber lasers [110, 111, 138]. For example, Zhao et al. reported a wavelength-tunable picosecond soliton pulse generated in a Bi₂Se₃ mode-locked fiber laser [110]. Dou et al. exploited Bi₂Se₃ as SA to achieve mode locking in a Yb-doped fiber laser [111]. Lin et al. obtained Q-switched pulses in a Yb-doped fiber laser by Bi₂Se₃ [138]. Besides, some other methods such as TI-based solution filled in PCF were also used to achieve mode locking in fiber lasers [106, 114].

TIs have a broad non-linear response and a large modulation depth [23]; however, the mode-locking stability is, to some extent, lower than graphene. Sometimes, the signal-to-noise ratio of the mode-locked fiber lasers based on TIs SAs are <60 dB [89, 108, 111, 137]. In addition, TI-based SAs tend to obtain Q-switched pulses with pulse width

in the order of nanoseconds or microseconds [16, 109], which is undesirable as it is usually preferred to achieve ultrashort pulses (picoseconds or sub-picoseconds) for applications in optical communications and material processing [89, 114]. Therefore, it is of vital importance to make TI-based SAs with better performance in order to further optimize the mode-locking properties.

3.3 Transition metal dichalcogenides

TMDs, such as MoS_2 , MoSe_2 , WS_2 , and WSe_2 , have a layer-dependent bandgap that allows them to be used as broadband SAs in ultrafast fiber lasers [90]. Since Zhang et al. first demonstrated MoS_2 as an SA in passively mode-locked fiber laser by optical deposition [90], ultrafast fiber lasers enabled by TMD-based SAs have been extensively investigated. Several techniques were used for the preparation of TMDs as SAs in fiber lasers [194, 195, 204]. In 2013, Wang et al. revealed the ultrafast saturable absorption of 2D MoS_2 nanosheets by using the LPE technique, indicating that MoS_2 is a potential SA for achieving ultrafast fiber lasers [34]. In 2014, Luo et al. reported Q-switched fiber lasers operated at 1, 1.5, and 2 μm by sandwiching the

MoS_2 PVA film between two fiber ferrules, which shows the broadband properties of MoS_2 as an SA for ultrafast photonics [87]. In 2015, Woodward et al. obtained stable Q-switched pulses at 1060, 1566, and 1924 nm in Yb-, Er-, and Tm-doped fiber lasers, respectively, by embedding liquid-phase exfoliated few-layer MoSe_2 flakes into a polymer film [60]. Mao et al. reported on WS_2 -mode-locked fiber lasers, where WS_2 nanosheets were deposited on a D-shaped fiber and WS_2 PVA film was sandwiched into the facet of the fiber connector [97]. Li et al. proposed a WS_2 -based SA fabricated by the thermal decomposition method, which achieves sub-nanosecond mode-locked pulses in Yb-doped fiber laser [196]. Chen et al. obtained Q-switched pulses based on four kinds of TMD PVA materials (MoS_2 , MoSe_2 , WS_2 , and WSe_2) with the same cavity configurations [84]. Panels A–D of Figure 4 show the spectra of MoS_2 , MoSe_2 , WS_2 , and WSe_2 , respectively. In fact, while several TMDs have been obtained by solution processing [135], researchers are devoting significant effort to explore such new TMDs for applications in ultrafast photonics [35, 91, 100–104, 205]. In 2017, Mao et al. reported on a passively Q-switched and mode-locked fiber laser based on a film-type ReS_2 PVA, demonstrating that ReS_2 has similar saturable absorption property to MoS_2

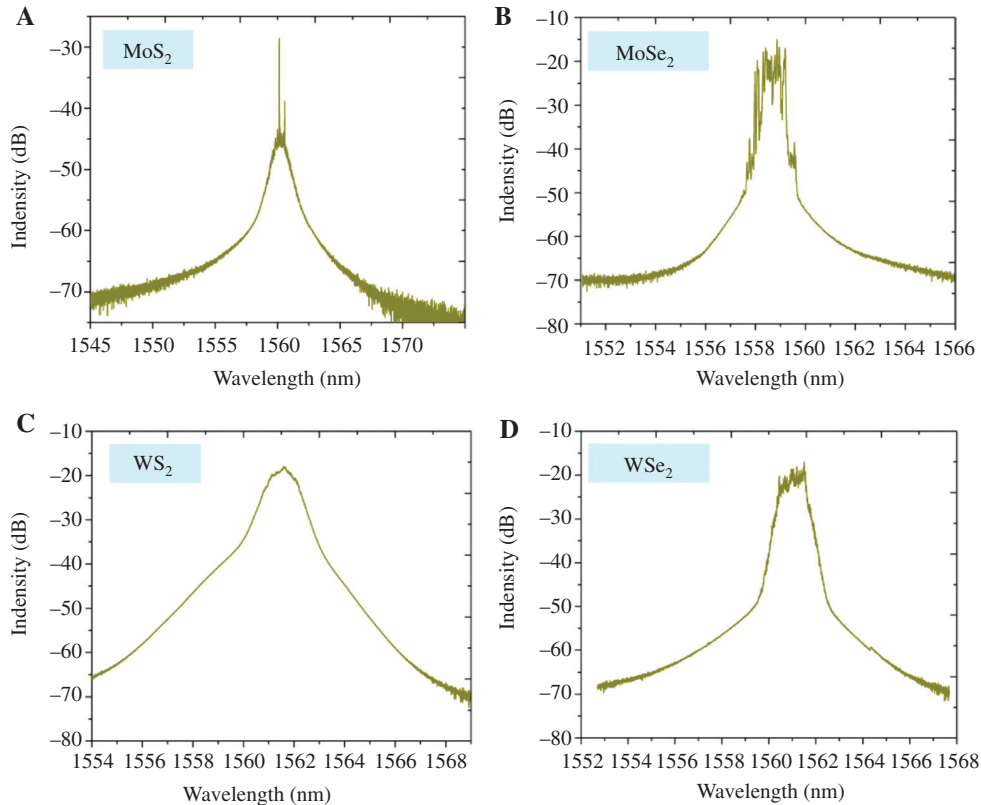


Figure 4: Q-switched spectra enabled by TMD-based SAs.

(A) MoS_2 , (B) MoSe_2 , (C) WS_2 , and (D) WSe_2 . Reproduced with permission from Ref. [84]. Copyright 2015 OSA Publishing.

and WS_2 [103]. In 2018, Tian et al. reported a femtosecond mode-locked fiber laser with TiS_2 based on LPE, indicating that non-equilibrium electrons could promote TiS_2 -based SA to be an ultrafast switch for ultrafast pulse output [35]. In 2018, Niu et al. reported a passively mode-locked Er-doped fiber laser based on SnS_2 PVA film, where a long-time and stable mode locking was achieved [102]. Wang et al. reported that a high-energy passively Q-switched Er-doped fiber laser enabled $Mo_{0.5}W_{0.5}S_2$ -based SA, where the $Mo_{0.5}W_{0.5}S_2$ -alcohol solution was injected into the quartz tube in order to deposit it onto the taper fiber [91]. In 2019, Cheng et al. suggested a multilayer $PtTe_2$ PVA composite thin film as an SA, achieving Q-switched pulses in a Yb-doped fiber laser [104].

A variety of TMD materials have been discovered, where MoS_2 and WS_2 are the most common SAs that were used to achieve ultrashort pulses. PVA composites usually serve as carriers for transferring TMDs to the laser cavity. Meanwhile, the method of evanescent field is an alternative way to accomplish the interaction between lasers and TMDs. Similar to TIs, TMD-based SAs also easily produce Q-switched pulses. Thus, it is important to fabricate better TMD materials to improve the performance of lasers.

3.4 Black phosphorus

In 2014, BP joined the family of 2DMs [206]. The bandgap of BP ranges from 0.3 eV (bulk) to 2.0 eV (monolayer) and the energy bandgap depends on its thickness [207]. The broadband non-linear optical response of BP was confirmed by the wideband open-aperture Z-scan measurement technique from the visible to mid-infrared region [208]. Since the first demonstration of BP-based passively mode-locked fiber lasers [209], BP has been used to mode lock fiber lasers in the 1- μm [42, 131], 1.5- μm [119–121, 125, 197], and 2- μm regions [122, 144] by the solution-processing method, as well as to Q-switch fiber lasers [116, 123, 126, 127, 130, 132, 210]. For example, Qin et al. reported on BP fabricated by LPE for the Q-switched Er:ZBLAN fiber laser at 2.8 μm , where the maximum average power of 485 mW with pulse energy of 7.7 μJ was achieved [117]. Luo et al. proposed a lateral interaction mechanism based on BP-based microfibers by the LPE in an Er-doped fiber laser [124]. They believed that this mechanism not only increases the damage threshold of several layers of BP as SA but also increases the interaction between light and matter [124]. Chen et al. reported on sub-300-fs tunable fiber laser with all-anomalous dispersion mode locked by BP, in which the multi-layer BP was deposited on the tapered fiber by the method of evanescent field interaction [118]. Jin et al. obtained a long-term stable

ultrashort pulse (~ 100 fs) generated in a BP mode-locked fiber laser by a scalable and highly controllable inkjet printing technology [129]. Song et al. achieved a vector soliton fiber laser by incorporating BP nanoflake-based SA into an Er-doped fiber laser, indicating that nanoflake-based BP SAs were polarization independent and suitable for vector soliton fiber laser [145]. Panels E and F of Figure 5 show the spectra and autocorrelation trace of vector soliton fiber laser mode locked by BP. Furthermore, Yun reported a dual-wavelength polarization-locked vector soliton in an Er-doped fiber laser enabled by BP-based PVA film [128]. Xu et al. exploited black phosphorene quantum dots (BPQDs) as a mode-locker in an Er-doped fiber laser, indicating that BPQDs have potential applications for ultrafast photonics [198]. Figure 5A shows the TEM of BPQDs prepared by a solvothermal method in NMP solution, and the absorption trace is shown in Figure 5B. Panels C and D of Figure 5 show the spectrum and autocorrelation trace, respectively. It is worth noting that BPQDs as SAs demonstrated better performance than BP nanosheets due to quantum confinement effects [198].

PVA composites and evanescent field interaction are the typical methods to incorporate BP to the laser cavity. BP has a low saturation intensity and the ability of broadband operation up to the ~ 3 - μm band [120, 208]. BP-based SAs such as BPQDs and black phosphorene nanoparticles have also been exploited to achieve ultrashort pulses in fiber lasers [119–121]. However, BP is not stable enough and easily oxidized in the air. Different preparation methods have been studied to obtain the BP-based SAs with the best performance. For example, Hu et al. proposed a printed BP ink in order to improve the long-term stability (~ 30 days) of the BP devices [211]. For now, the fabrication of BP with higher stability and quality is still a big challenge.

3.5 MXenes

Recently, MXenes (2D transition metal carbides, carbonitrides, or nitrides [20]) have attracted more attention because of their outstanding optoelectronic and optical properties [185, 212, 213]. In 2017, John et al. reported $Ti_3C_2NT_x$ -based SA by solution processing in an Er-doped fiber laser, where the stacked $Ti_3C_2NT_x$ monolayers were transferred to a side-polished fiber, and obtained stable pulses as short as 660 fs at a repetition rate of 15.4 MHz and a wavelength of 1557 nm [190]. In 2018, Jiang et al. investigated the broadband non-linear photonics of $Ti_3C_2T_x$ by depositing $Ti_3C_2T_x$ solution onto a side-polished fiber [186], where stable mode locking was achieved in Yb- and Er-doped fiber lasers, respectively, as shown in Figure 6.

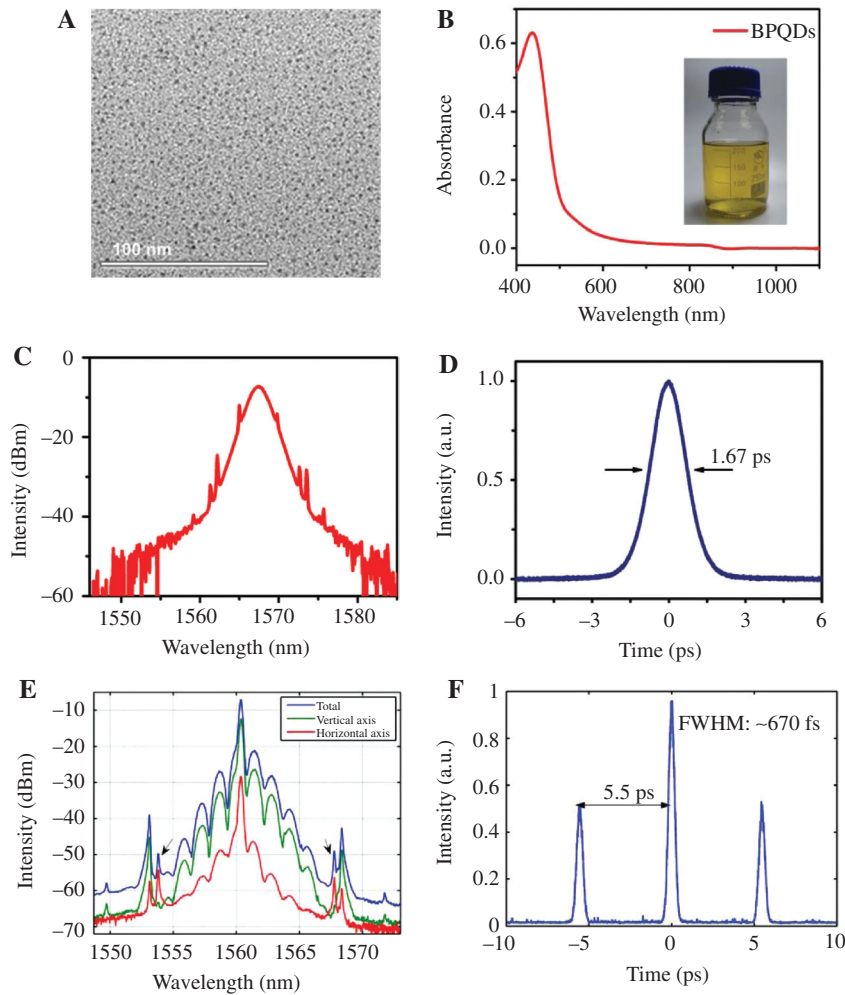


Figure 5: Mode-locked results enabled by BP-based SAs.

(A) TEM image and (B) absorption trace (inset: NMP solution) of BPQDs, (C) spectrum, and (D) autocorrelation trace of mode-locked fiber lasers based on BPQDs. (E) Spectra and (F) autocorrelation trace of vector soliton fiber laser mode-locked by BP. (A)–(D) are reproduced with permission from Ref. [198]. Copyright 2016 Wiley-VCH Publishing. (E) and (F) are reproduced with permission from Ref. [145]. Copyright 2016 OSA Publishing.

In 2019, Zhang et al. obtained an ultrashort pulse (104 fs) in a dispersion-managed fiber laser by depositing $\text{Ti}_3\text{C}_2\text{T}_x$ onto a microfiber [189]. The spectrum and the autocorrelation trace are shown in Figure 6E and F, respectively. Wang et al. reported a high-energy pulse (~ 305 nJ) realized in a Q-switched fiber laser based on $\text{Ti}_3\text{C}_2\text{T}_x$ by optical deposition [188], which shows that $\text{Ti}_3\text{C}_2\text{T}_x$ could be applied as an SA for high-energy pulse generation. Yi et al. demonstrated the solution processing Ti_2CT_x operated in three different fiber lasers (1-, 1.5-, and 2.8- μm bands) [199], indicating the excellent non-linear absorption performance of Ti_2CT_x in the mid-infrared regime.

As a kind of emerging new 2DM, some MXene-based SAs possess high modulation depth, which is beneficial to obtain ultrafast pulses ($\sim 38\%$) [186]. Besides, MXenes can also be operated as broadband SAs from the near- to

mid-infrared band [199]. It can be expected that MXene-based SAs will bring more surprises to the research and development of ultrafast photonics in lasers.

4 Perspective

The development of 2DM-based fiber lasers has brought great convenience to industry because of their compactness, flexibility, broadband operation, and high pulse quality. 2DM-based SAs are being developed rapidly and attracting substantial attention [214–217]. Graphene has excellent broadband operation and an adjustable modulation depth that depends on its layer number [33]. Graphene-based 2DMs have also been used to achieve single-frequency Q-switching [218], singly polarized

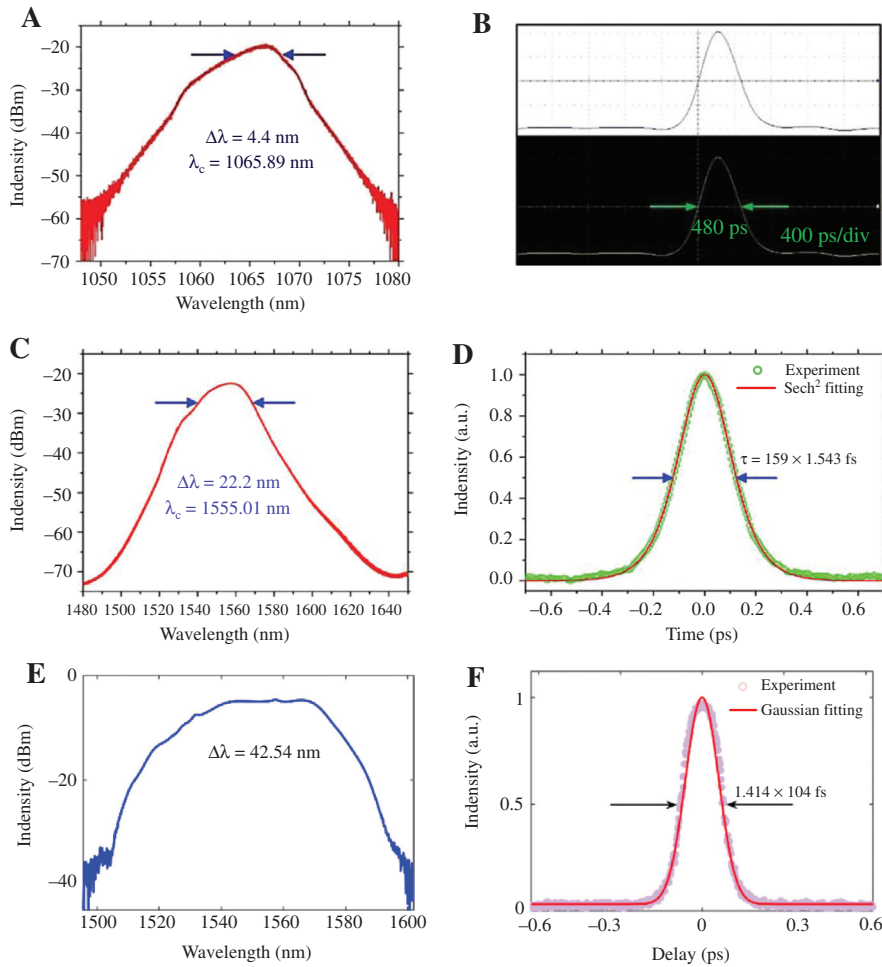


Figure 6: Mode-locked results enabled by MXene-based SAs.

(A) Spectrum and (B) pulse profile in Yb-doped fiber laser. (C) Spectrum and (D) autocorrelation trace in Er-doped fiber laser. (E) Spectrum and (F) autocorrelation trace in a dispersion-managed fiber laser. (A)–(D) are reproduced with permission from Ref. [186]. Copyright 2016 Wiley-VCH Publishing. (E) and (F) are reproduced with permission from Ref. [189]. Copyright 2019 OSA Publishing.

pulse generation [219], optical frequency comb [220], and broadband gate-tunable terahertz plasmons [221]. TIs can achieve a high modulation depth, and TMDs have better saturable absorption compared with graphene; however, the mode-locked stability of TIs and TMDs still needs to be improved. Although BP is easily oxidized in the air, it can be operated in the mid-infrared band [211]. Besides, BP as a platform of nanomedicine has also been used for biomedical diagnosis [222–224]. As a new family member of 2DMs, MXenes have many desirable properties, such as high modulation depth and broadband operation [190, 199]. However, the existing 2DM-based SAs also have their own shortcomings. In order to overcome the existing shortcomings of 2DMs and achieve wide applications in industry, some other mono-elemental 2D materials, such as antimonene and bismuthene, have attracted more attention [225–233]. In 2017, Song et al. experimentally investigated

the broadband non-linear optical response of few-layer antimonene as SA, and obtained ~ 550 -fs pulses in an Er-doped fiber laser [225]. In 2018, Lu et al. obtained 652-fs pulses in a bismuthene-based mode-locked fiber laser [226]. In addition, Ge et al. exploited few-layer selenium-doped BP nanosheets as SA to achieve mode-locked pulses in an Er-doped fiber laser, indicating that selenium-doped BP is an excellent SA candidate for ultrafast photonics [234]. To date, there have been various attempts to avoid their drawbacks. Different preparation methods have been studied to obtain SAs with better performance [235–237].

From a processing standpoint, while ultrasonication and intercalation potentially suffer from poor scalability, other exfoliation methods have been demonstrated as effective LPE techniques. These include ball milling and shear exfoliation. Ball milling is an exfoliation technique that has been demonstrated for graphene and MoS_2 [238, 239]. It uses

collisions and shear forces to disrupt the layer-to-layer interactions. Originally being an industrial process, it is intrinsically scalable. Shear exfoliation is based on the action of a rotor/stator or a rotating blade [240–243]. Exfoliation occurs by shear forces and produces large flakes of single- and few-layer material [240]. This is also a simple industrial process and thus intrinsically scalable, as it allows processing of much larger volumes than ultrasonication and higher production rates, thus reducing the potential cost. While ball milling and shear exfoliation are still batch processes, a continuous process has recently been developed for the exfoliation of graphite into graphene that uses turbulent flow and high pressure and does not require a centrifugation step afterwards [244]. Such methods, to our knowledge, have not been used thus far to produce SAs. However, they seem to be very promising methods to achieve 2DM dispersions suitable for SA fabrication at a lower cost and on a larger scale than ultrasonication or intercalation, and may thus find applications in this field in the near future.

5 Conclusion

We have reviewed solution-processed 2D materials for ultrafast fiber lasers. Exfoliation, stabilization, sorting, and MXene fabrication are introduced in this review. The applications of 2DM-based SAs such as graphene, TIs, TMDs, BP, and MXenes in ultrafast fiber lasers have been discussed. In addition, a summary and outlook has been presented in perspective. We believe that the exploration of 2DMs for ultrafast photonics will never stop, and we look forward to seeing the better combination of 2DMs and fiber lasers in the near future.

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