2D Black Phosphorus Saturable Absorbers for Ultrafast Photonics

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2D nanomaterials are emerging as a promising platform for ultrashort-pulse fiber laser technology. This review presents a catalog of the factors affecting the nonlinear optical properties of 2D nanomaterials and the recent progress in processing and integration strategies into saturable absorber devices as versatile, wideband ultrafast optical switches for fiber-based-laser short-pulse generation. Particular focus is on black phosphorus, and a summary of the current status of black-phosphorus-based pulsed lasers is given, which provide new potential efficacy for this and other 2D nanomaterials in ultrafast photonic technology.

1. Introduction

Advances in ultrafast light sources have been applied as essential tools in a wide range of fields, such as laser physics, nanotechnology, and medicine. Progress in ultrafast science has always hinged on the availability of ultrashort light sources.[1–4] The use of ultrashort optical pulse techniques developed significantly after the realization of mode-locking from Ti:sapphire in the early 1990s.[3] Although these lasers offer a remarkable combination of spectroscopic and material properties, which in turn produce powerful lasers and amplifiers, they come at a large cost and are complicated to operate. More compact, user-friendly and turn-key operation instruments will be needed if ultrashort-pulsed light sources proliferate outside of laboratory environments and find use in multiused facilities.

In recent years, growing interest has been focused on the development of fiber-based pulsed light sources due to their practical advantages including alignment-free, environmental robustness, and low cost. The passive approach using a saturable absorber (SA) device attracts tremendous interest since it has the advantages of simple structure, low-cost and shorter achievable pulse durations.[2]

There are two types of SA devices[6–11]: real SAs including semiconductor saturable absorber mirrors (SESAM) and low-dimensional nanomaterials etc.—the materials themselves possess light intensity dependent nonlinear absorption; and artificial SAs,[12–15] such as Kerr lens effect and nonlinear polarization rotation etc.—the devices use the nonlinear refractive index or birefringent properties to induce an intensity dependent nonlinear absorption, mimicking the response of real SAs. Considering the growing interests and achievements that have been made in materials science, we mainly focus on the real SAs with a particular emphasis on 2D nanomaterials in this review.

The early work of using SA devices as an ultrafast optical switch were demonstrated four years after the first laser emission reported by Maiman, where a colored glass filter[4] and a reversibly bleachable dye[5] were applied in Q-switched bulk lasers for short-pulse generation. Since then, SA technology has witnessed rapid progress in developing various SA candidates with remarkable optical properties. The current dominant saturable absorber technologies for ultrashort-pulse generation are summarized in Figure 1. While SESAMs have been successfully applied in fiber-based light sources for mode-locked or Q-switched pulse generation, they have their own drawbacks, e.g., narrowband operation, complexity, costly fabrication and packing issues, and limited response time (=picosecond) without postprocessing. Therefore, novel SA candidates with more versatile properties are highly desired in the research community. Advances in material manipulation technology at the nanoscale enable new possibilities in the fabrication of novel 1D and 2D nanomaterials. These nanomaterials present remarkable photonic and optoelectronic properties by virtue of their low-dimensionality structure, and thus attract enormous research interest.[2,11,16–18]
As great interests have been paid to explore the optical properties of low-dimensional nanomaterials, such as strong nonlinear absorption and fast relaxation time, 1D carbon nanotubes (CNTs)\cite{11,18–20} and 2D graphene\cite{17,20–29} have been demonstrated as promising nanomaterial SAs. Graphene, a type of one-atom thick layered graphite, has attracted considerable attention as a potential alternative SA candidate\cite{23–50} in ultrafast fiber lasers due to its wide bandwidth operation property (gapless linear dispersion of Dirac electrons), fast carrier dynamics, and ease of fabrication (bandgap engineering or chirality control is not required for optimizing the performance). A variety of lasers exploiting the nonlinear absorption property of graphene have been reported since 2009, with ultrashort-pulse generation in fiber-based,\cite{25,26,28} solid-state,\cite{27,29,30} waveguide,\cite{31} and semiconductor lasers.\cite{32}

Beyond graphene, there is a much wider class of 2D nanomaterials\cite{51–76} with different properties, including quasi-2D topological insulators, transition metal dichalcogenides (TMD) and very recently, black phosphorous (BP). TMDs\cite{53–75} have a chemical formula of $\text{MX}_2$ (where $X = \text{S, Se, Te, etc.}$, and $M = \text{Mo, W, Nb, etc.}$) and may behave as metallic, semiconducting or insulating. While the covalent bond strongly holds the atoms within the material layer, weak van der Waals forces exist between layers, enabling the single- and few-layer formats to be exfoliated from the bulk material. It is found that the optical and electronic characteristics of such semiconducting TMD (s-TMD) flakes highly depend on the number of layers. For instance, the monolayer s-TMDs exhibit distinct property variation to bulk forms (indirect bandgap). There are a number of demonstrations showing that s-TMDs possess optical saturable absorption under strong illumination in a wide spectral range, even below their fundamental bandgaps because of the sub-bandgap saturable absorption in these materials owing to the existence of edge states.$^{[2,53,57–65]}$ However, S-TMDs possess limitations in a number of practical applications for optoelectronics devices because their intrinsic energy bandgap is in $1–2 \text{ eV}$.\cite{57–59}

Recently, BP has triggered rapid growing interests in both academic research and potential applications due to its remarkable properties. As a member in group V of the periodic table, phosphorus (P) accounts for $\approx 0.1\%$ of the earth’s crust volume and exists in the form of four major allotropes such as white phosphorus (WP), red phosphorus (RP), violet phosphorus (VP), and BP (with the monolayer form of phosphorene, shown in Figure 2a, a high pressure allotrope of phosphorus with a layered structure\cite{27}), in which BP is known as the most thermodynamically stable allotrope of the element compared to other phosphorus allotropes (e.g., white, red and violet phosphorus). BP has been thoroughly investigated as a new 2D nanomaterial since early 2014 as it possesses high charge carrier mobility, controllable direct bandgap characteristic and unique in-plane anisotropic structure.$^{[51–54,76,78–107]}$ While experimental research into the photonics properties of such material remains at an early stage, it has offered new opportunities for photonic and optoelectronic applications in compact ultrafast light sources.

Few layer BP presents layer-count-dependent properties, which is a typical feature for 2D nanomaterials.$^{[78–107]}$ Much progress has been made on investigating the electronic
bandgap of BP as a function of layer numbers. For instance, it has been shown that the extraordinary layer-dependent electronic structure in phosphorene that arises from layer–layer interactions.\(^{[79]}\) This leads to a direct optical bandgap evolving from 1.73 eV in monolayer, 1.15 eV in bilayer, and 0.83 eV in trilayer phosphorene to ultimately 0.35 eV in the bulk, along with its high intrinsic electron mobility (Figure 2b). The bandgap increases as the number of layers decreases. Unlike the in-plane center symmetry of graphene and s-TMDs, the puckered structure of BP results in anisotropic in-plane conductivity and photoconductivity. Therefore, the light absorption and photoluminescence in BP have a high degree of anisotropy. The bandgap property of BP, bridging the gap between the zero-bandgap graphene and large bandgap s-TMDs, prompts the extensive investigation of this novel material, enabling its fabrication into versatile photonic and optoelectronic devices for desirable applications.

In this review, we summarize the current state-of-art of BP-based photonics devices, including their fabrication and integration process, and applications as SA devices for BP-based ultrashort-pulsed lasers. Based on these advances, a conclusion and outlook of new potential opportunities of BP-based and

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**Figure 1.** Current dominant saturable absorber technologies for ultrashort-pulse generation.

**Figure 2.** a) Visualization of single-layer BP. b) Bandgaps of BP, where the solid squares and the empty squares respectively represent the observed optical resonance energy and the interband optical transitions predicted by the tight-binding model that fall outside the measurement range, and the solid curves correspond to the prediction by the phenomenological 1D tight-binding model. The lower and upper limits of the measurement range in the reference are marked by horizontal dashed lines. Reproduced with permission.\(^{[79]}\) Copyright 2017, Springer Nature.
other 2D-material-based devices in future optoelectronic and ultrafast photonic technologies are highlighted.

2. Processing and Device Integration

2.1. Mono- and Few-Layer BP Fabrication

Tremendous research interest has been paid to BP since its mono- or few-layer form was successfully exfoliated in 2014. BP crystal is composed of puckered-honeycomb layers stacked by weak van der Waals interactions, giving the possibility of preparing phosphorene via mechanical or sonication exfoliation methods. Similar to the fabrication procedures of other 2D nanomaterials, such as graphene\(^{25-50}\) and s-TMDs\(^{2,53,57-65,107}\) the most commonly used fabrication techniques for fabricating BP\(^{108-110}\) material are liquid phase exfoliation (LPE)\(^{111-123}\) and mechanical exfoliation (ME).\(^{124-127}\)

ME is usually realized by utilizing sticky tapes, where monolayer or few layer nanomaterial can be obtained by quickly tearing the tape from bulk crystals. The main advantage of ME lies in its simplicity and reliability, without involving any chemical methods and expensive equipment throughout the fabrication process. Currently, ME is the most commonly used method to obtain BP in the field of scientific research. For all fiber-based applications, the key issue of using ME technique is to transfer the material to the fiber device. In order to obtain ultrathin BP flakes with higher optical transmittance for laser applications, the flakes are repeatedly pressed and adhered to the scotch tape, and subsequently transferred to fiber-based devices, e.g., fiber end-facet\(^{128}\) (Figure 3; a typical image of BP flakes deposited on the fiber end-facet). However, there are several drawbacks of this technology such as low extensibility and uncontrollable yield, limiting ME to further applications in industrial manufacture.\(^{61,129}\)

Instead, solution processing is applicable to produce high quality few-layer 2D nanomaterial in a solvent\(^{61,130}\) providing the potential for massive fabrication of thin films and composites under ambient condition.\(^{110,114,131-140}\) This processing technology has been demonstrated for successfully fabricating electrodes of batteries and supercapacitors with distinct surface activity. As for ultrafast optics, the optical properties of the material-based devices are dependent on the flake size. This enables the LPE technique suitable for manufacturing materials with different sizes in a convenient and cost-effective way.

An example of a general concept in LPE fabrication process is shown in Figure 4, following a more comprehensive procedure reported in ref. \(^{131}\). The details in the processing procedure are described as follows

- **Ion Intercalation:** Ions, presented by orange globes in Figure 4a, are intercalated into the interspace between the layers, which diminish the interlayer constraint between layers. The exfoliated dispersion can be obtained through agitation (e.g., ultrasonication).
• **Ion Exchange:** Ions included in the interlayer of the compounds play a part in neutralizing the electric charge, which is distributed on the surface of the layers. As presented by blue globes in Figure 4b, ions are replaced in liquid and then exfoliated dispersions can be attained by agitation.

• **Sonication Assisted Exfoliation:** Ultrasonic concussion enables the layered crystal separated into solvent as nanosheet forms (Figure 4c). These nanosheets can withhold reaggregation with suitable surface energy in solvents and maintain stable, resistant to sedimentation and reaggregation.

Similar to other layered nanomaterials, BP has been reported to be dispersed into the selected solvents via LPE since the chemical bonds between the layers are weak compared to the force within a single layer, allowing the material to be processed into flakes that can be micrometers wide and nanometer (or less) thick.[144] For instance, ultrasonic energy can be used to exfoliate bulk BP, breaking it down into mono- or few-layers, and form well-defined triangle-shaped layered crystals (Figure 5). Figure 6 shows typical images of SEM and TEM of BP flakes. Ultrasound-assisted liquid phase exfoliation (UALPE)[142,143] is an important method because the exfoliated materials can be categorized in order of size and thickness to produce uniform dispersion with suitable surface energy in solvents and maintain stable, resistant to sedimentation and reaggregation.

2.2. Device Integration

Many deposition techniques exist for transferring the mono- and few-layer BP material onto fiber-based devices, which have evolved from other 2D material device integration strategies (Figure 7). These include transforming the materials directly on optical devices, e.g., fiber end-facets, microfiber (or D-shape fiber) or mirrors, by using light-induced deposition method and embedding the few-layer BP in transparent polymer films using different methods such as spin-coating, and inkjet printing.

An example illustrating the process of depositing material on the fiber end-facet is shown in Figure 7a, b. Figure 7a shows the fiber immersed in a cuvette and fixed upward. In Figure 7b, the material dispersion is dropped onto the fiber facet through a pipette. A 980 nm continuous wave laser (typically with an optical power up to 100 mW) is then coupled into the fiber and the light-induced deposition process starts. The light source used in the deposition process eliminates the influence of material precipitation on the deposition efficiency and shortens the evaporation time of the deposition process.

The nonlinear response of the microfiber or D-shape fiber based SA devices fabricated by optical deposition process is realized by the nonlinear interaction between the evanescent field and processed material on the surface of the fiber device for ultrashort-pulse emission. In this approach, the light interacts with the layered material deposited on the surface of the tapered region, leading to an enhancement of the nonlinear optical response due to a longer interaction length and a higher optical damage threshold. The saturable absorption effect, along with the large refractive index property of the 2D materials, is of great importance to the pulse-shaping process in mode-locked fiber lasers. Table 1 summarizes the most commonly used approaches for fabricating microfibers. In general, the microfiber could be fabricated by polishing a single-mode fiber after holding with an arcuate block. The distance between the fiber core to the polished surface can be monitored utilizing an optical power meter. The parameters of the microfiber, i.e., waist diameter, polished length, insertion loss etc., are characterized before the deposition process starts. As shown in Figure 7c, the material dispersion is dropped on the cross section of the microfiber which is fixed on a quartz plate. To start the disposition process, a light is induced from a continuous wave source. The light propagates through the microfiber device and the power is collected to monitor the deposition depth in real time. This process can also be used for transferring the layer material onto a side-polished fiber.

Considering beyond the light-induced deposition option, other solutions to obtain high quality devices for photonic applications exist, e.g., printing processes, including inkjet, and
roll-to-roll gravure printing, enabling the large-scale, low-cost production of packaging materials. Recently, the adaptation of functional materials to perform as active pigments within ink formulations has drawn increasing attention since this approach takes advantages of well-established print production processes for functional device fabrication.

The first printed 2D material application was reported in 2012, when graphene from LPE was inkjet-printed to fabricate field-effect transistors. Since this demonstration, the field of research has witnessed growing interests in ink formulation and device fabrication. Beyond graphene, various 2D nanomaterials have been investigated as active pigments, such as TMDs and BP. While the first generation of 2D nanomaterial inks was not optimized for the relevant printing processes, new 2D nanomaterial functional ink formulations are now emerging. Recent progress has reported a solvent exchange process to formulate BP ink processed via UALPE and a binary solvent carrier of isopropyl alcohol (IPA) and 2-butanol. The inkjet ink of BP is free from binders, and allows stable single-droplet jetting. Its surface tension allows wetting of untreated substrates, including Si/SiO₂, PET, and glass. The appropriate solvent is of great importance for effective material exfoliation and dispersion stabilization since the enthalpy of mixing should reduce sufficiently for UALPE. Suitable solvents are typically determined empirically by correlating the concentration of exfoliated material with the solvent surface tension. In recent reports, organic solvents with a high boiling point including CHP and NMP are found to be appropriate choices to produce BP via UALPE, which can promote exfoliation due to their suitable value of surface tension and withhold reaggregation. However, the composition and proportion of organic chemical solvents are required to be optimized to reduce the inconsistency of the ink caused by complex fluidic effects. A recent report on BP-based photonic device fabrication has shown that the number of layers and the thickness of the device can be precisely controlled through the inkjet printing process, leading to a wide direct bandgap from the visible light to near-infrared spectrum region.

![Figure 7. Integration schemes to form nanomaterial-based photonic devices.](image)

| Table 1. Microfiber fabrication approaches. |
|-------------------------------------------|
| Preparation of microfiber | Diameter max [nm] | Loss max [dB mm⁻¹] | Comparison |
|---------------------------|------------------|-------------------|-------------|
| A two-step drawing process    | 50               | Diameter 800 nm, 633 nm wavelength light input: 0.008 dB mm⁻¹ | Simplicity and high efficiency |
| Directly drawing from bulk glasses    | 50               | Diameter 550 nm, 633 nm wavelength light input: 0.01 dB mm⁻¹ | Versatility on the refractive index of microfibers |
| CO₂ laser heating drawing | 3000–4000        | Diameter 3000 nm, 980 nm wavelength light input: 0.006 dB mm⁻¹ | Avoid alcohol lamp heating caused by the disturbance |
| Electrode heating drawing    | 900              | Diameter 900 nm, 532 nm wavelength light input: 0.01 dB mm⁻¹ | Ease of fabricating long-length microfibers |
3.1. Nonlinear Optical Properties

For typical SA devices, incident light with higher intensity possesses larger transmittance (i.e., nonlinear optical absorption). This phenomenon can be explained by the Pauli exclusion principle: the electrons in the valence band will be excited to the conduction band by absorbing photon energy under a lower light power. With the increasing pump power, the upper states are gradually occupied by the electrons from the valence band until no more places for the electrons, and the final state is known as saturable absorption.

There are two main methods to measure the nonlinear optical absorption profile of the SA devices: open-aperture I-scan (known as the balanced twin-detector technique) and Z-scan, depending on the material integration approach. In the I-scan technique setup (shown in Figure 8a), a variable average-power ultra-short fiber light source (or a fixed input pulse fiber source through an attenuator) is split through a fused fiber coupler and sent down a test and reference arm, each output collected at separate power meters, allowing the calibration and characterization of the nonlinear optical response of sample as a function of the input average-power. To perform an open-aperture Z-scan measurement, a bulk...
configuration is adopted. An ultrashort pump source operated at the measured wavelength is split using a fused fiber coupler, where an output is used to monitor the power as a reference. The SA device is swept through the focus of a beam of the test arm and the transmitted power is recorded as a function of the incident intensity.

A number of theoretical models have been set up to gain a further insight into the phenomenon of nonlinear saturable absorption. For practical SAs, a model based on electron transition theory and two-level energy bands becomes widely accepted. In the measurement, the parameters of saturable absorption can be calculated by fitting the data utilizing the theoretical value of 0.6 nm for single-layer phosphorus.

Figure 8b presents an example of the microscope images of the microfiber-based BP quantum dots (BPQD) SA devices, with the upward images of the microfiber coated with BPQDs at a magnification of 500 times and the downward image and the inset of the device injecting a 650 nm He-Ne laser source at a magnification of 500 and 1000 fold respectively. Saturable absorption properties of the integrated BPQD-SA is shown in Figure 8c, which is measured by using an ultrashort fiber source at 1560 nm (500 fs pulse duration, 20 MHz repetition rate). The saturable average power and normalized modulation depth of the device are 1.69 mW and 8.1%, respectively.

A typical optical absorption profile of the printed BP on PET obtained at a magnification of 500 and 1000 fold respectively. Saturable absorption properties of the material composite. A typical optical absorption profile of the printed BPQD-SA devices is shown in Figure 9, where the pump source is a 150 fs pulse duration at repetition frequency of 10 MHz fiber laser operating at 1562 nm. From the fit, the linear absorption, the nonsaturable loss and the saturation intensity can be determined as 8.71%, 5.05%, and 7.5 MW cm\(^{-2}\) respectively.

There are increasing demands in the applications (e.g., spectroscopy and remote sensing) requiring mid-infrared ultrafast sources operating at 2 \(\mu\)m and thus, prompting research in seeking nonlinear materials with strong saturable absorption in mid-infrared spectral window.

### Table 2. Layered BP flakes integrated to form SA device for mode-locked Lasers.

| Fabrication method | Integration platform | Layers in BP flakes | Nonlinear characterization | Laser type | Laser properties | Stable time | Ref. |
|-------------------|----------------------|---------------------|---------------------------|------------|-----------------|------------|-----|
| ME                | Fiber facet          | 15                  |                           | Er:Fiber   | 1571.45         | 946       | 0.328 | ≥28 | [100] |
| LPE               | Microfiber           | 1–3                 | ≈4.5 mW                   | Er:Fiber   | 1532–1570       | 940       | 0.38  | ≥20 | [99]  |
| ME                | Fiber facet          | ≈500\(h\)          | –                         | Er:Fiber   | 1560.3          | 272       | 0.34  | –   | [77]  |
| LPE               | Side-polished Fiber  | ≈20                 | ≈12.5                     | Er:Fiber   | 1558.14         | 2.18 ps   | 0.336 | –   | [189] |
| ME                | Fiber facet          | ≈33–1833\(h\)      | –                         | Er:Fiber   | 1558.7          | ≈786     | 0.6   | –   | [88]  |
| LPE               | Fiber facet          | ≈3–41\(h\)         | 3.41                      | Er:Fiber   | 1568.19         | 117.6 ns  | –     | –   | [92]  |
| ME                | Fiber facet          | 5–8                 | 0.35                      | Er:Fiber   | 1085.3          | 7.54 ps   | 0.441 | –   | [190] |
| LPE               | Microfiber           | 25–33               | 10.1                      | Er:Fiber   | 1569.2          | 280       | 0.32  | ≥24 | [191] |
| ME                | Fiber facet          | 5–8                 | –                         | Er:Fiber   | 1561            | 2.66 ps   | 0.32  | ≥24 | [192] |
| LPE               | Quartz               | ≈8                  | 1.35                      | Nd:FVO\(_4\) | 1064.1        | 6.1 ps    | 0.646 | –   | [127] |
| LPE               | Fiber facet          | 14–29               | 182 GW cm\(^{-2}\)        | Er:Fiber   | 1562            | 635       | 0.351 | –   | [193] |
| LPE               | Fiber facet          | 13–20               | 123 GW cm\(^{-2}\)        | Er:Fiber   | 1562            | 635       | 0.351 | –   | [193] |
| LPE               | Fiber facet          | 13–15               | 6 GW cm\(^{-2}\)          | Er:Fiber   | 1562            | 635       | 0.351 | –   | [193] |
| LPE               | Microfiber           | 50                  | 1.5                       | Er:Fiber   | 1562.8          | 291       | 0.382 | ≥10 | [194] |
| LPE               | Fiber facet          | ≈4                  | 240 GW cm\(^{-2}\)        | Er:Fiber   | 1579.4          | 686       | 0.478 | –   | [101] |
| LPE               | Fiber facet          | 8–25\(h\)          | 2.95 MW cm\(^{-2}\)       | Yb:Fiber   | 1030.6          | 400 ps    | –     | ≥20 | [195] |
| EE                | Fiber facet          | 3.25 ± 1.25\(h\)   | 0.69 ± 0.03               | Er:Fiber   | 1567.6          | 1.07 ps   | 0.444 | –   | [196] |
| LPE               | Nonpassivation       | ≈60                 | –                         | Er:Fiber   | 1564.6 ± 2.8    | 690 ± 550 | 0.404 | ≥9  | [197] |
| LPE               | PDMS Passivation     | ≈60                 | –                         | Er:Fiber   | 1564.6 ± 0.3    | 690 ± 43  | 0.406 ± 0.010 | ≥384 | [197] |
| LPE               | Al\(_2\)O\(_3\) Passivation | ≈60 | – | Er:Fiber | 1564.6 ± 0.01 | 690 ± 24 | 0.406 ± 0.072 | ≥385 | [197] |
| LPE               | Microfiber           | 2                   | 1.69 MW                   | Er:Fiber   | 1561.7          | 882 fs    | 0.325 | ≥2  | [163] |
| Inkjet printing   | Fiber facet          | –                   | 7.5 MW cm\(^{-2}\)        | Er:Fiber   | 1562            | 605 fs    | –     | ≥714| [142] |

Nonlinear optical characteristics and applications in laser cavities using BP for mode-locked lasers. ME, mechanical exfoliation; EE, electrochemical exfoliation; LPE, liquid phase exfoliation; \(\alpha_1\), modulation depth; \(\lambda\), operating wavelength; \(t\), pulse duration; TBP, time-bandwidth product. \(\alpha_1\) indicates that layers in flakes were not given (using the thickness provided in literature for the calculation) so has been estimated instead by adopting the theoretical value of 0.6 nm for single-layer phosphorus.
this spectral region. Some progress of the nonlinear saturation property of BP at \( \approx 2 \mu m \) with small bandgap BP nanosheets have been reported recently. BP exhibits layer-dependent bandgaps, and the number of layers increases following the bandgap energy equation given by \( E_g = (1.7/n^{0.73} + 0.3) \). For example, for the 100-layer BP nanoplates, the thickness of the material is 60 nm and the bandgap energy can be modulated to 0.36 eV, which can cover the spectral region within 3.4 \( \mu m \). Sotor et al. have reported a mechanical exfoliated high-quality BP with a material thickness of 300 nm, corresponding to a bandgap up to 0.32 eV (corresponding to the wavelength region up to 3 \( \mu m \)) and then transferred onto a fiber connector tip for all-fiber integration. The as-prepared BP-SA device has shown to exhibit strong optical absorption at 2 \( \mu m \) (\( T \approx 40\% \)), as shown in Figure 10. The power-dependent nonlinear absorption indicates a modulation depth (\( \alpha_{NS} \)) of 52.2% and a nonsaturable loss (\( \Delta T \)) of 4.1%.

### 3.2. Ultrafast Fiber Lasers Using 2D BP-Based SA Devices

The inclusion of an SA device into a cavity can initiate the formation of pulse operation utilizing Q-switching technique, where the high energy output pulses typically have a repetition rate at kHz and the pulse durations of ns to \( \mu s \). This is suitable for applications where high power sources are required. In addition to Q-switching operation, mode-locking operation where pulses are initiated and stabilized by the action of SAs.
attracts great attention because such technique produces much shorter pulses (typically hundreds of fs to ps) with higher peak power at MHz repetition rate. It is notably required for applications where high peak power pulses at MHz repetition rate are needed.

In general, Q-switching and mode-locking status can exist in a same fiber-based cavity design with different threshold. The operation status transition can be achieved by a precise control of the gain and loss of the cavity through the adjustment of input pump power. However, in addition to the control of gain and loss, mode-locking operation is also significantly influenced by the balance between the nonlinearity and dispersion of the cavity, as well as the gain filter effect of the active fiber. This implies that the transition between the operating status may not always be feasible by purely adjust the pump power.

Tables 2 and 3 summarize the nonlinear optical saturable absorption properties and their applications in laser cavities using BP in the literature to date, including the nonlinear properties of few-layer BP device to mode-lock laser cavities and great progresses for demonstrated BP-based SA devices for Q-switched lasers. Chen et al. first demonstrated the nonlinear optical properties of BP-based SA device and its application of pulse-emission performance in Er-doped fiber laser cavities. The operating wavelength of BP-based ultrafast lasers has expanded since then, covering from 1 µm to 3 µm. [76,144,155–162] This manifests its applicability as a versatile 2D broadband SA candidate. For instance, a microfiber-based BPQD SA has

Figure 12. Mode-locking performance of the Er-doped fiber laser using a microfiber-based PQD-SA device: a) measured optical spectrum and b) autocorrelation of the output pulses. Reproduced under the terms of a Creative Commons Attribution 4.0 International License. Copyright 2017, Springer Nature.

Figure 13. a) Measured optical spectra of the mode-locking performance at 20 min interval. b) The drift of the central wavelengths and the 3 dB spectral widths. Reproduced under the terms of a Creative Commons Attribution 4.0 International License. Copyright 2017, Springer Nature.

Figure 14. Mode-locking performance of the fiber laser by a passivation layer encapsulated BP SA: a) optical spectrum, b) autocorrelation trace.
been reported to exhibit strong nonlinear response at 1.56 µm spectral region, indicating the potential for ultrashort-pulse generation.[163,164] Figure 11 shows the performance of a BPQD SA based Er-doped fiber laser. The performances of the output pulses are shown in Figures 12 and 13. While no evident variation of both central wavelength (with standard deviation

![Figure 15](https://www.advancedsciencenews.com)

**Figure 15.** a) Output laser spectrum over 21 d. b) Central wavelengths and spectral widths over 500 h.

![Figure 16](https://www.advancedsciencenews.com)

**Figure 16.** Output spectra at five representative wavelengths, continuously tuning from 1535 to 1565 nm.
of 0.05 nm) and spectral bandwidth (with standard deviation of 0.03 nm) can be observed, suggesting that the mode-locking operation possesses a reasonable operating performance, the stability of the BP-based device remains a critical problem for practical applications because they might easily encounter oxidation if being exposed in air without particular external protections.

While BP has shown excellent nonlinear optical properties for a variety of optoelectronic applications, the instability under ambient conditions hinders its practical applications. A number of feasible approaches have been proposed to improve the stability of BP in air, including the encapsulation of BP with a passivation layer against oxidation, e.g., parylene-C,[142] Al₂O₃,[165–167] and SiO₂,[168] utilization of functionalization process by chemical modification via aryl diazonium,[169] titanium sulfonate ligand,[170] and metal ions,[171] and chemical doping to modify the physical and chemical properties of BP.[172–175] In our review, we will focus on an approach utilizing inkjet printing technique for practical applications of BP-based devices. Through this single step, pin-hole free encapsulation process, the produced BP-based photonic devices exhibit ambient stability against degradation. To produce suitable

![Figure 17. Five autocorrelation traces belonging to different wavelengths.](image)

![Figure 18. a) Schematic of the mode-locked laser based on BP SA. b) Optical spectrum (red line) with water absorption (blue line), and the inset of the spectrum. c) Measured autocorrelation of the output. d) Radio frequency (RF) spectrum with a 70 dB signal-to-noise ratio. Reproduced with permission.[87] Copyright 2015, The Optical Society.](image)
inkjet BP ink for fabricating high quality photonic devices, an approach was developed to balance the complex and competing fluidic effects, resulting in the improvement of the quality of the BP ink.[142] To fabricate the BP-based photonic devices, few-layer BP flakes are first exfoliated using ultrasound assisted liquid phase exfoliation.[142] BP is then uniformly deposited onto an ultrathin (i.e., 1.5 μm) polymeric substrate and then packaged with 100 nm thick pin-hole free passivation layer.

The inkjet-printed BP-SA, exhibiting high optical homogeneity and environmental stability, was then integrated into an Er-doped fiber laser by sandwiching ≈1 mm × 1 mm piece between the two fiber connectors with index matching gel. Figures 14 and 15 show a typical dataset of the output characteristics of long-term environmentally stable (over 30 d against the intense light of 32.7 MW cm<sup>−2</sup>) mode-locked lasers. A wideband tunable, ultrafast fiber laser can also be achieved utilizing this inkjet-printed BP-SA. Researchers employ a wavelength tunable filter that can supply a continuous tunability from 1535 to 1565 nm with a bandwidth of 12.8 nm to select the output wavelength,[178] producing wavelength tunable picosecond pulses, with five representative spectra at the wavelength of 1535, 1543, 1549.8, 1557.1, and 1562.1 nm presented in Figures 16 and 17. Such wideband tunability of the BP-SA, along with the benefits of inkjet printing technique, suggests excellent promises of this novel direct bandgap material for future ultrafast photonic technologies.

As discussed in Section 3.1, the large regulatable bandgap of BP makes it a promising candidate for mid-infrared pulse generation. A number of demonstrations have been achieved at 2 and 3 μm.[177] Table 4 summarizes the mode-locked ultrafast lasers operating in the mid-infrared region. The first demonstration of using BP as a SA material in the mid-infrared region was reported in 2015, with an enhanced environmental stability.[46,99,155,178,179] Figure 18 shows the remarkable performances from a Tm<sup>3+</sup>-doped ultrafast fiber laser. The signal-to-background contrast of 70 dB in the fundamental radio frequency spectrum is higher than those from graphene based fiber lasers at 2 μm,[49,180,181] indicating the promising future of BP for applications in the mid-infrared region.

In addition to the pulse generation at 2 μm, rapid growing interests have triggered research into exploring the ultrashort-pulse generation in longer wavelength region, since this region is particularly important due to the characteristic absorption interests have triggered research into exploring the ultrashort-pulse generation in longer wavelength region, since this region is particularly important due to the characteristic absorption lines of several gas interest. However, mode-locked lasers operating above 2 μm remain challenging because the cavity design, optical elements and saturable absorption are more demanding than 1 μm and 2 μm. The bandgap of the multilayer BP can be tuned to ≈0.3 eV by optimizing the numbers of layers of the material, indicating the potential of BP-based SAs operating at 3 μm.

To access BP-SA based mode-locked lasers operating beyond 2 μm, an Er-doped ZBLAN fiber laser mode-locked by a BP-based SA device has been demonstrated (Figures 19 and 20). The employed BP nanosheets have a thickness of ≈143 nm (indicating a bandgap of 3.8 eV) and are transferred onto the gold-coated mirror. The nonlinear saturable absorption measurement is shown in Figure 19, indicating strong absorption at this wavelength with a modulation depth of 19% and the corresponding saturation influence of 9 mJ cm<sup>−2</sup>. Mode-locked pulses with high signal-to-background contrast (>60 dB) can be achieved by incorporating the BP SA device. The shortest achievable pulse duration was 42 ps with a TBP of 4.5, highlighting the promise of BP with thickness-dependent variable bandgap characteristics for mid-infrared photonic devices.

### 4. Conclusion and Outlook

Many investigations toward 2D nanomaterials have demonstrated a variety of complementary material properties for unprecedented future photonic applications. For ultrashort-pulsed applications, the nonlinear saturable absorption properties of a range of 2D nanomaterials are of particular interest.
for the fabrication of versatile SA devices in an inexpensive and effective way, enabled by their outstanding photonic and optoelectronic properties.

Few-layer BP has drawn considerable attention as its engineered properties by taking advantage of the layer-number dependent direct bandgap. Consequently, the reported BP SAs enable few-layer BP-based photonic devices which can be employed in mode-locked and Q-switched fiber laser sources to generate short pulse operating with pulse duration of fs–µs (Tables 2 and 3) at kHz–MHz repetition rate in the wavelength region from near-infrared to mid-infrared. Few-layer BP from a series of processing technologies have been showed on various platforms with respect to device integration strategies, including embedded in transparent polymer films and light-induced optical deposition on optical devices.

The growing interest of exploring the broad and increasing catalogue of available 2D nanomaterials encourages the researchers to search for new physics and technology breakthroughs. While a variety of 2D nanomaterials have been demonstrated to behave as ultrafast wideband optical switches for mode-locking and Q-switching fiber-based light switches for the near infrared to the mid-infrared region (i.e., from ≈1 to 3 µm) (Table 5), we hope to further investigate how to engineer the properties through different fabrication procedures because the reliability of these 2D nanomaterial based ultrafast optical switches are required to be proven to the same degree as incumbent saturable absorber technology such as SESAM. A number of issues are pressing research problems to be addressed, including the relatively high nonsaturable loss (typically above 5% for the fiber-based devices) of the current 2D nanomaterial saturable absorbers limit the fiber-based light sources efficiency that could be obtained.

The van der Waals heterostructures, stacked by different single-layers, may appear to be the next frontier in the future research as they combine layers from a number of different 2D nanomaterials to create a new material system with remarkable optical properties for desirable applications. The development of quantum mechanics and materials science has provided theoretical tools to analyze size-dependent behavior on the nanoscale of such materials. Researchers have considered how to improve the manufacturing techniques to scale fabrication to be well-suited for integration with a variety of photonic devices. 2D nanomaterials will have a revolutionary technological impact in photonics to match the current research interest. However, the commercial applications of these wideband and flexible intensity-dependent materials beyond laboratory demonstrations rely on the robustness, long-term stability and the mass manufacturable devices possibility. The most challenging issue will be in translating these controlled laboratory research to environmental stable and mass manufacturable photonic devices. The true technological success of transferring the laboratory demonstrations to commercially applications will leverage benefits in ultrashort-pulse fiber-based light sources in future technology.

Table 5. Key parameters of 2D-material-based mode-locked fiber lasers at 2 µm.

| Saturable absorber | Output power [mW] | Central wavelength [nm] | Pulse duration [fs] | Signal-to-noise ratio [dB] | Ref. |
|--------------------|-------------------|-------------------------|-------------------|--------------------------|-----|
| Graphene           | 1.41              | 1953.3                  | 2100              | 50                       | [180]|
| Graphene           | 1.35              | 1884                    | 1200              | 70                       | [181]|
| Graphene           | 2                 | 1940                    | 3600              | 50                       | [49] |
| MoS₂               | –                 | 1905                    | 843 000           | >55                      | [206]|
| WS₂                | 0.6               | 1941                    | 1300              | ≈72                      | [207]|
| MoSe₂              | 4.3               | 1912                    | 920               | 65                       | [208]|
| Topological insulator | –              | 1935                    | 795               | 76                       | [209]|
| BP                 | 1.5               | 1910                    | 739               | >70                      | [87] |
| BP                 | 2.5               | 1880–1940               | 1580              | –                        | [144]|
| BP                 | 11                | 2094                    | 1300              | >55                      | [178]|

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Conflict of Interest

The authors declare no conflict of interest.
Keywords
2D nanomaterials, black phosphorus, fiber lasers,mode-locked lasers, saturable absorber

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