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Stable high-power saturable absorber based on polymer-black-phosphorus films

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ABSTRACT

Black phosphorus (BP), a rising two-dimensional material with a layer-number-dependent direct bandgap of 0.3–1.5 eV, is very interesting for optoelectronics applications from near- to mid-infrared wavebands. In the atmosphere, few-layer BP tends to be oxidized or degenerated during interacting with lasers. Here, we fabricate few-layer BP nanosheets based on a liquid exfoliation method using N-methylpyrrolidone as the dispersion liquid. By incorporating BP nanosheets with polymers (polyvinyl alcohol or high-melting-point polyimide), two flexible filmy BP saturable absorbers are fabricated to realize passive mode locking in erbium-doped fiber lasers. The polymer-BP saturable absorber, especially the polyimide-BP saturable absorber, can prevent the oxidation or water-induced etching under high-power laser illuminations, providing a promising candidate for Q-switchers, mode lockers, and light modulators.

1. Introduction

Low-dimensional nanomaterials, due to their unique and versatile properties, have been attracting tremendous interests for numerous applications in electronics and optoelectronics [1–3]. Carbon nanotubes [4–6], silicon nanowires [7], and ZnO nanowires/nanobelts [8,9] can be regarded as one-dimensional (1D) nanomaterials, while graphene [10,11], transition metal dichalcogenide [12–16], and black-phosphorus (BP) [17] are classified as two-dimensional (2D) materials. In these 2D materials, weak Van der Waals interaction enables stacking of layers and the strong covalent bond holds atoms together in plane [18]. Such layered structures allow 2D materials to be exfoliated into mono- or few-layer nanosheets with distinct physical/chemical properties due to the dimensionality effect [19]. Owing to the zero-bandgap structure, ultrafast carrier dynamics, and high third-order nonlinearity, graphene has been used to fabricate nonlinear devices such as modulators [20] and saturable absorbers (SA) [21,22]. However, the light modulation ability is limited due to the weak absorption of monolayer graphene (2.3%). Transition metal dichalcogenides are a family of highly anisotropic layered semiconductors with the bandgap in the range of 0.8–2.1 eV, and can serve as a SA from visible to near infrared waveband [23–29] or frequency converter [30]. The absorption of transition metal dichalcogenide nanosheets is quite high (~20%) for photons with energy higher than the bandgap, while it decreases rapidly for photons at the longer wavelength [31–33].

By controlling the number of stacked atomic layers, the bandgap of BP varies from 0.3 eV (bulk) to 1.5 eV (monolayer) [34], which can bridge the gap between zero-bandgap graphene and large-bandgap transition metal dichalcogenides. Contrary to a direct and indirect bandgap of mono- and multi-layer transition metal dichalcogenides [26], BPs always display a direct bandgap in the mono-, few-, and bulk-forms [35], which is significantly beneficial to applications of high frequency optoelectronics and ultrafast photonics. Previous works demonstrated that BPs exhibit the ultrafast carrier dynamics and high third-order nonlinearity, and various types of photonic devices were fabricated, such as nonlinear SAs [34,36–38], optical modulators [39], and photodectors [40]. However, BPs, especially the few-layer BPs, are unstable and tend to be oxidized in the atmosphere [41]. Additionally, the laser induced thermal effect also accelerates the oxidation and degradation of BP. In most of the experiments, BP is placed in vacuum or inert gas to prevent the oxidation [35,42], which lost the flexibility and increases the cost of such photonic devices. As a result, it is quite urgent to develop a simple method to eliminate the instability of BPs in air for ultrafast photonic applications.

Here, the BP nanosheets are prepared with a liquid exfoliation method using N-methylpyrrolidone (NMP) as the dispersed liquid. Polyimide (PI)-BP film and polyvinyl alcohol (PVA)-BP film are formed by encapsulating the BP nanosheets into the PI or PVA solution

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respectively and then evaporating them on a heater. Soliton mode-locking operation is achieved in erbium-doped fiber lasers using the PI-BP SA or PVA-BP SA. The PI-BP film is quite stable and can afford much higher power than that of the PVA-BP film, providing a new opportunity for ultrafast optics and nonlinear optics.

2. Methods

2.1. Preparation of BP nanosheets and polymer-BP films

Several approaches, such as mechanical cleavage [43], chemical vapor deposition [44], and liquid exfoliation [17], have been adopted to prepare few- or mono-layer 2D nanosheets from bulk-state crystals. The mechanical cleavage method could prepare high-quality micrometer nanosheets, while it is unsuitable for realistic applications due to the low production efficiency. The chemical vapor deposition is capable of synthesizing large-scale mono- or few-layer 2D films, while the fabrication process relies on complex chemical reaction at very high temperature. As a comparison, liquid exfoliation method can produce mass dispersion of mono- and few-layer nanosheets under ambient conditions. Attributing to the simple fabrication method and important applications, liquid exfoliated graphene, topological insulator, transition metal dichalcogenides have been broadly used in wavelength converters, optical modulators, SAs, sensors, et al.

Multi-layer BP nanosheets are prepared by using the liquid exfoliation method, as described in Fig. 1. BP crystal is purchased from Nanjing XFNANO Materials Tech Co., Ltd. First, a piece of bulk BP crystal is put into NMP solution, and the mixture is ultrasonic treated for 4 h at power of 180 W. Second, the resulted BP solution is centrifuged at 1000 rpm for 5 min to remove large BP crystals. The 90% supernatant is collected for further applications. In the experiment, three skills are used to decrease the oxidation of the BP nanosheets. First, the small glass bottle is covered with a rubber stopper during the ultrasonication process. Second, unlike traditional liquid exfoliation methods using deionized water as the dispersed liquid, NMP is used to avoid the reaction of the BP with water or oxygen. Third, the fabrication process should be as quick as possible to reduce the exposure time of the BP.

The BP nanosheets are embedded in the polymer to protect BP from oxidation and increased the processability and compatibility of photonic devices. In the experiment, PI-BP (PVA-BP) film is formed by incorporating the PI (PVA) with BP nanosheets and then is evaporated on a heater, as shown in Fig. 1. First, the liquid PI (PVA-NMP) solution and the BP-NMP dispersion are blended at the volume ratio of 1:2 with a magnetic stirrer. Second, the prepared mixture is dropped on a substrate. Third, a thin PI-BP (PVA-BP) film is formed after evaporating the mixture under 50 °C and the ambient pressure.

2.2. Characterization of BP nanosheets and polymer-BP films

The inset of Fig. 2a shows the as-prepared BP suspension, which is homogeneous with a yellowish-brown color. This suspension is quite stable, and shows no color change or precipitation after being stored for a week under ambient condition. The BP appears to be thin-layered nanosheets, as shown in the scanning electron microscope (SEM) image (Fig. 2a). The sizes of BP nanosheets range from 500 nm to 10 μm, which mainly depends on the centrifugation rate of the fabrication process. The atomic force microscopy (AFM) image is given to measure the thickness of BP nanosheets. As illustrated in Fig. 2b, the thickness is about 4 nm, suggesting that the sample is multi-layer BP. We further characterize the nanosheets by Raman spectroscopy using a 514 nm laser. As depicted in Fig. 2c, three characteristic peaks locate at 360.3, 437.1, and 464.8 cm^{-1}, corresponding to A_g^1, B_g^2, and A_g^2 vibration modes, which agrees well with the earlier experiment [45]. As shown in Fig. 2d, the thickness of PI-BP (PVA-BP) film is measured as 40–55 μm. The BP nanosheets are encapsulated by PI (PVA), and thus oxidation reaction can be effectively prevented. Such polymer-BP films exhibiting better processability and compatibility than mechanical cleavage BPs, are quite attractive for nonlinear optical applications.

3. Results

3.1. Linear and nonlinear transmission of polymer-BP film

The visible-infrared transmission spectra of PI-BP (PVA-BP) film and pure PI (PVA) film are investigated by a spectrometer (Hitachi UV4100). As shown in Fig. 3a–b, the transmission wavelength ranges from the visible to near-infrared band, which coincides with the earlier findings [34]. We further study the nonlinear transmission of PI-BP film based on the typical balanced twin-detector measurement scheme [32]. The illumination pulse is produced by a mode-locked fiber laser (Wavelength:≈1.55 μm, pulse duration:≈1.3 ps, repetition rate:≈12.5 MHz), and the pulse intensity can be tuned by an attenuator. Then, the pulse is divided equally by a 5:5 fiber splitter. The output powers of one branch (reference beam) and the other branch (inserted with the sample) at different input powers are monitored by a dual-channel power meter. At last, the nonlinear transmission of the film is obtained by comparing the output power of two branches. As illustrated in Fig. 3c–d, the transmission (absorption) of PI-BP film increases (decreases) with the pulse intensity, which is the typical characteristic of the nonlinear saturable absorption. After fitting the results with a common model [17], the modulation depth of the PI-BP is ~0.8%, and that of the PVA-BP is ~0.3%. Actually, the modulation depth of SAs depends on the layer number and the concentration of BP. Because the liquid exfoliated BP nanosheet has a broad layer distribution, the absorption coefficient at such waveband is relatively small. By optimizing the centrifugation rate or increasing the concentration of BP

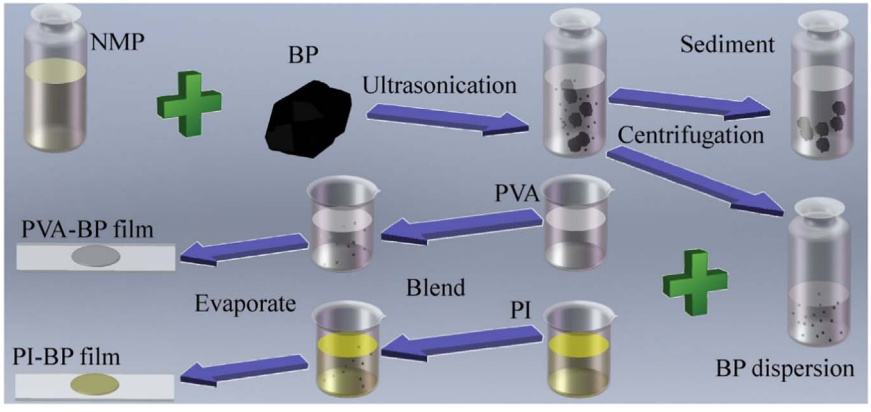

Fig. 1. Schematic diagram for preparing BP nanosheets and polymer-BP films. N-methylpyrrolidone: NMP; black-phosphorus: BP; polyvinyl alcohol: PVA; polyimide: PI.