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Black phosphorus quantum dots for femtosecond laser photonics

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ABSTRACT

As a rising two-dimensional (2D) nanomaterial, layered black phosphorus (BP) nanosheets have shown promising applications in electronics and photonics. Besides the 2D layered structure, recently black phosphorus quantum dots (BPQDs) exhibiting unique optoelectronic properties had been successfully fabricated. However, the nonlinear optical properties of BPQDs at the telecommunication band have not been investigated. Herein, we synthesized the BPQDs by using a liquid exfoliation method that combined probe sonication and bath sonication. It was found that the evident saturable absorption ability of BPQDs at 1.55 μm waveband could be clearly observed. As for the applications of ultrafast photonics, we fabricated the BPQDs saturable absorber (BPQDs-SA) and applied it to an ultrafast laser. By virtue of the excellent nonlinear optical properties of BPQDs, the fiber laser delivers the stable pulse train with duration as short as 291 fs, whose performance could, to the best of our knowledge, compete with nowadays' commercial optical saturable absorber devices. In addition, due to the highly nonlinear optical effect generated by the fabricated BPQDs-SA, the multi-soliton nonlinear dynamics in the fiber laser were also investigated. The obtained results suggest that the BPQDs could be an attractive nonlinear optical material for applications in the field of nonlinear optics.

1. Introduction

The discovery of two-dimensional (2D) materials opens up new opportunities for applications in the various fields such as electronics and photonics [1–5]. By virtue of the unique features such as wideband absorption, ultrafast carrier dynamics and 2D planar advantage, interests in investigating electronic and photonic applications of 2D materials are strongly stimulated. Graphene [6], as a typical 2D material, have been successfully prepared and discovered to possess various applications, ranging from ultrafast saturable absorbers (SAs) [7–12], to photo-detectors [13], sensors [14], and optical limiter [15]. However, the zero-bandgap property of graphene would degenerate its light modulation ability that limits its potential applications in the related fields. Inspired by the successful story of graphene, more and more attentions have been directed to the exploration of new members of 2D material family [16]. The atomic layered transition-metal dichalcogenides (TMDs) was demonstrated to be another 2D material with excellent properties [17–24]. For example, it was found that monolayer MoS_2, a representative 2D TMDs, possesses higher resonant absorption than graphene at the specific waveband [25]. Thus, few-layered MoS_2 could be regarded as a preferred nonlinear optical material for some specific wavebands. Nevertheless, the enhanced nonlinear optical absorption of the monolayer MoS_2 mainly locates in the visible waveband range due to a relatively large band gap (~1.9 eV).

From the view point of practical applications, the 2D materials with the bandgap at the optical communication band (~0.8 eV) are more popular due to the increasing interests in fabricating high-performance optical communication photonic devices. Note that the bandgaps of the conventional 2D materials such as graphene and TMDs fall outside the optical communication band. Therefore, it is encouraged to explore other high quality 2D materials that could satisfy the requirement of high-quality applications for the field of optical communication. Fortunately, black phosphorus (BP) has recently been rediscovered as an anisotropic 2D material with layer dependent direct bandgap from 0.3 eV (bulk) to 1.5 eV (monolayer) [26–29]. Unlike TMDs which only become the direct type of semiconductor at its monolayer format, the

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energy band-gap of BPs was always direct for different thickness. The unique bandgap structure makes the layered BP materials bridge the space between zero-bandgap graphene and large-gap TMDs, which will find important applications for optoelectronics and electronics, and particularly for the optical communication devices [30–34].

Apart from the 2D layered structure, ultrasmall quantum dot (QD), which is another type of nanomaterials, shows some interesting optoelectronic properties due to the quantum confinement and edge effects [35,36]. Indeed, the 2D materials such as graphene and MoS_2 QDs have been demonstrated to be as the attractive mediums for various applications such as in biomedicine, photovoltaics, and optoelectronics devices [37–39]. Regarding the BPs, very recently the BPQDs have been successfully prepared by using the facile top-down approach [40] or liquid exfoliation method [41]. As for the applications of BPQDs, to date the prepared BPQDs have been used to fabricate memory device or employed as photothermal agents [40,41]. On the other hand, as we know the nonlinear optical response of optical materials is vital to the applications of ultrafast photonics. Recently, the nonlinear optical response of the BPQDs at 800 nm waveband was observed [42]. However, so far few nonlinear optical response of BPQDs at telecommunication band was investigated as well as its application in ultrafast photonics [42,43]. Considering the unique characteristics of newly developed BPQDs, it would be interesting to investigate the nonlinear optical response of BPQDs and to see whether it is suitable for applications of ultrafast photonics for telecommunication band.

Bearing this in mind, herein we firstly prepared the ultrasmall BPQDs by using a liquid exfoliation method that combined probe sonication and bath sonication. By using Z-scan technique, it was found that the nonlinear saturable absorption could be observed at optical communication waveband, indicating that the as-prepared BPQDs could be used as an ultrafast mode locker. As a proof-of-concept experiment, the BPQDs were deposited onto the microfiber to perform as a saturable absorber (SA) for ultrafast fiber laser via evanescent field interaction. With the fabricated BPQDs-SA, the fiber laser delivers stable 291 fs mode-locked pulse-train. The achieved results suggest that the BPQDs could be an alternative high-quality nonlinear optical material for ultrafast photonics.

2. Sample preparation and characterization of the BPQDs SA

The procedure of BPQDs synthesis is similar to those previously reported [40,41]. Briefly, 0.5 mg of BP powder purchased from Smart Elements was added into 1 mL of N-methyl-2-pyrrolidone (NMP) in a mortar and the mixture was ground for 20 min. The mixture was then transferred into a 15 mL glass vial and another 3 mL of NMP was added in it. After the glass vial was carefully sealed, the vial was put in an ice-bath sonicator and was sonicated at the power of 200 W for 3 h. The resultant dispersion was centrifuged at speed of 7000 rpm for 20 min. Then the supernatant containing BPQDs was used for the following experiment. The image of the prepared BPQDs solution was presented in the inset of Fig. 1(a). Raman scattering spectroscopy of the BPQDs in Fig. 1(a) shows that there are three unique Raman peaks located at 362, 438, and 466 cm^{-1} which are corresponding to the A^1g, B_{2g}, and A^2_g vibrational modes of the phosphorus atoms in BP [44]. All the three peaks having a little blue shift from the bulk BP Raman shows that the thickness of BPQDs is very thin. Transmission electron microscopy (TEM) is performed to examine the morphology of the BPQDs. As can be seen from Fig. 1(b), the size of BPQDs is around 4 nm.

By employing the Z-scan technique, the nonlinear optical response of the as-prepared BPQDs was measured in our experiment. Different from the experimental setup in our previous report [45], the pump source here is replaced by a femtosecond laser (center wavelength: 1550 nm; pulse duration: 120 fs; and repetition rate: 1 kHz). Note that in order to avoid optical damage and multiple-photon effect, we carefully adjusted the average power of the femtosecond pulse to 110 μW by using the optical attenuators. Fig. 2(a) displays the normalized Z-scan peak curve of BPQDs and the corresponding fitting curve, which are typical saturable absorption curves with a sharp peak located at the beam focus point. The results demonstrated that the prepared BPQDs possess evident saturable absorption effect at 1550 nm waveband. Based on the relation between laser beam spot size and relative separation, the nonlinear saturable absorption curve could be derived, as shown in Fig. 2(b). As can be seen here, the saturation intensity is 1.5 MW/cm^2 and the modulation depth is 9.0%. Therefore, the measured results indicate that the as-prepared BPQDs can be performed as a SA for ultrashort pulse generation in lasers.

Since the BPQDs possess the saturable absorption effect at 1550 nm, in order to be applied to ultrafast erbium-doped fiber (EDF) laser, we fabricated a SA based on few-layer BPQDs by depositing the BPQDs onto the microfiber using the optical deposition technique. Compared with the other SA fabrication methods, the optical deposition method owns several advantages due to its unique geometry, such as higher optical damage threshold of few-layer BPQDs and stronger light-matter interaction. The detailed process of the fabrication of microfiber-based BPQDs-SA is similar to that in our previous reports [46]. In this experiment, the diameter of the fabricated microfiber is 12 μm and the concentration of the BPQDs/NMP solution 0.05 mg/mL. After completing the SA fabrication, Fig. 3 presents the microscope image of the prepared microfiber-based BPQDs-SA, where we can see that the BPQDs were well deposited around microfiber. Here, the deposition length of few-layer BPQDs is about ~387 μm, and the insertion loss of BPQDs-microfiber SA is 3.7 dB. Note that thanks to the unique geometric structure of microfiber-based BPQDs SA, the disadvantage of BPQDs, lack of stability in the air, could be eased in some degree [32]. From the viewpoint of practical applications, the structure of microfiber-based BPQDs SA could be optimized by wrapping something on the outside of BPQDs to avoid it is exposed to air.

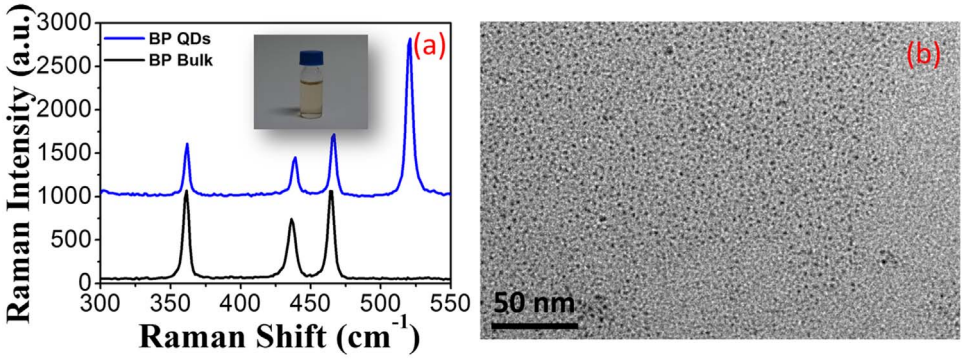

Fig. 1. Characterizations of the BPQDs. (a) Raman scattering spectroscopy of the BPQDs. Inset: Image of the BPQDs solution; (b) TEM image of the BPQDs.