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Pulse duration dependent nonlinear optical response in black phosphorus dispersions

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ABSTRACT

Black phosphorus (BP), is the most thermodynamically stable allotrope of phosphorus, the narrow direct band gap and the strong light-matter interaction make BP a promising nonlinear optical (NLO) nano-material. In this paper, we use the open aperture Z- scan method to measure the NLO property of BP dispersion. Saturable absorption was observed in the BP material through the excitation of Ti: sapphire laser at 800 nm. Three different excitation pulse duration (100 fs, 1 ps and 10 ps) were used in the experiments, and BP exhibited different NLO performance. The results show that nonlinear absorption coefficient and figure of merit of BP nanosheets are proportional to the pulse duration while saturable intensity is opposite to pulse duration.

1. Introduction

In the past few years, the emergency of two dimensional (2D) materials graphene has inspired the interest of scientists all over the world [1–4]. Owing to the zero-bandgap nature, graphene has a strong interaction with photons in a very wide spectral range, which has been investigated and employed in nonlinear optics [5,6]. In the wake of the discovery of graphene, many other 2D materials include transition metal dichalcogenides (TMDs), topological insulator et al. were gradually discovered and made this area much more prosperous [7–9]. Black phosphorus (BP) joined the 2D material family since 2014 and has rapidly attracted significant attentions [10]. Previous research results have confirmed that BP has tunable direct bandgap, high carrier mobility (about 1000 $cm^2/v\ s$) [11], high in-plane anisotropy, large on/off ratios($>10^5$) at the room temperature [12]. Moreover, theoretical and experimental studies have demonstrated that the bandgap of BP is strongly depends on the number of layers, ranging from ~2.0 eV for monolayer to ~0.3 eV for bulk due to the layer–layer coupling [13], which fill the present gap between the zero bandgap of graphene and wide bandgap of TMDs. Otherwise, the direct transition band structure could maintain in both few-layer and bulk state BP, which suggest the exist of the strong light-matter interaction and large nonlinear optical absorption (NLA) in BP.

The broadband NLA of BP has been demonstrated By Zhang's group, which reported multilayer BP's saturable absorption (SA) from 400 nm to 1930 nm [14]. Wang et al. also measured the broadband SA in few layers BP nanosheets and compared its superior SA performance with graphene [15]. Then, Zheng et al. investigated both the nonlinear absorption and nonlinear refraction index of BP at 800 nm band [16]. The strong optical limiting behavior was also discovered in black phosphorus, which due to the two-photon absorption at high intensity excitation [17]. Following the NLA characterization of BP, the related application in ultrafast photonics was quickly carried on. Chen et al. firstly used BP as saturable absorber for both Q-switching and mode-locking in fiber laser around 1550 nm band [18]. After that, the broadband SA in BP has been successively applied in passive mode locking or Q-switching of both fiber and solid state lasers from the visible to the mid-infrared band [19–24]. Now, BP has been proved to be a broadband optical device for ultrafast lasers. Pulse duration is an important parameter for laser, however, the NLA performance of BP under different pulse duration is still not fully studied. To promote the BP based ultrafast devices, pulse duration dependent nonlinear optical response in BP is need to carry on.

In this work, we measured the nonlinear optical absorption of BP by Z-scan measurement technique at 800 nm band. The BP dispersions always exhibit saturable absorption under the excitation of laser with

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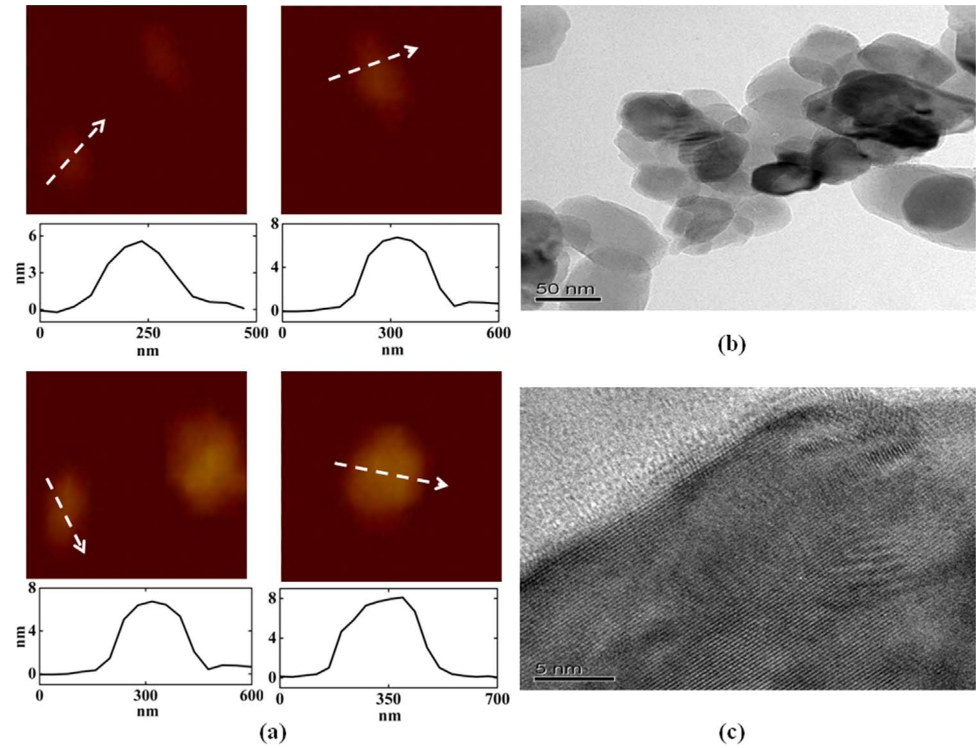

Fig. 1. (a) Typical AFM images with thickness profiles. (b) TEM and (c) High-resolution TEM image of as-prepared BP sample.

different pulse duration (100 fs, 1 ps, 10 ps) in BP dispersions. We further analysis and compared the SA parameters fitted from the experiment. The results indicate that saturable intensity is opposite to pulse duration while nonlinear optical coefficient and figure of merit are proportional to the pulse duration.

2. Preparation and characterization of BP sample

We used liquid phase exfoliation (LPE) technique to prepare BP [25,26], which is widely used in the production of the two dimensional nano-materials, such as graphene and TMDs. The BP powder was grinded from BP bulk crystal (purchased from smart elements, 99.98%). Then, the powder was dispersed in N-methyl-2-pyrrolidone (NMP) and followed by 4 h sonication. After that, the dispersion is set aside for more than 24 h and centrifugation was done in order to remove large deposits. The upper suspension of the dispersions was collected and placed in 1 mm quartz cuvette for experiments test.

Atomic force microscopy (AFM) was used to determine the size and thickness of the BP fakes, as shown in Fig. 1(a). The AFM samples were prepared by casting a few drops of the dispersions on pre-cleaned Si substrates, and followed by a high-temperature vacuum treatment, which is employed to remove the residual solvents. Through AFM images, we can observe the size of BP nanosheets is about 150–350 nm and the thickness of the samples is about 6–8 nm. Transmission electron microscopy (TEM) was performed to examine the morphology and crystallinity of the BP. From Fig. 1(b), we could see stacks of BP nanosheets with an average size of > 100 nm, which is agree with that in AFM image. The crystallinity of the BP was studied by high-resolution TEM (HR-TEM), as shown in Fig. 1(c). The clear lattice fringes on BP nanosheet indicate the sample is not oxidized and have high quality in crystallinity.

The liquid phase exfoliated BP flakes was investigated by Raman spectroscopy. As shown in Fig. 2(a), we observe three well-known characteristic peaks of BP at 367.5, 442.9, 472.2 cm^{-1}[27,28], corresponding to one out-of-plane vibration mode A_g^1 and two in-plane vibration mode $B_{2g}$and A_g^2, respectively. Raman spectra are dependent with the thickness of BP nanosheets [29,30]. The A_g^1 and A_g^2mode shift towards each other when the thickness is increased. Compared to the original bulk BP, the B_{2g} and A_g^2 vibration modes of BP nanosheets exhibit blue shifts with the decrease of layer number. It confirms the few-layer characteristic of our sample. Fig. 2(b) shows the measured linear absorption spectral range was from 400 nm to 1200 nm. By recording the light passing through the sample, it clearly shows that BP sample has a smooth absorption curve with increasing wavelength, which suggests BP samples have good absorption from visible to infrared range.

The nonlinear optical absorption of BP was measured by using Z-scan technique. The experimental setup of open aperture (OA) Z-scan is shown in Fig. 3. The sample is excited by a Ti: sapphire laser of 800 nm and1-kHz repetition rate. The beam waist of the incident light is obtained from the measurement which was fitted to be about 48.84 μm. By adjusting the position of laser pulse compressor between the two pieces of grating, the output pulse width of laser can change from 100 fs to 10 ps, and we picked 100 fs, 1 ps and 10 ps for experiments. The intensity of incident laser pulses were controlled by motorized variable attenuator in order to achieve appropriate optical power. The incident beam was divided into two different laser beams. One laser beam was focused by an objective lens perpendicularly to the solution and further monitored with photo-detector 1, while the other laser beam was monitored with photo-detector 2.

The typical Z-scan traces of BP dispersions at 800 nm are shown in Fig. 4, where normalized transmission was plotted as a function of sample position. Z-scan measurements with different pulse duration were conducted, and results of 100 fs, 1 ps and 10 ps are shown in Fig. 4(a), (b) and (c), respectively. All the curves show the saturable absorption property in the BP dispersions. Otherwise, we performed the power dependent Z-scan measurements. With the increase of the input peak intensity from 6.549 to 776.2 GW/cm^2, the peak of the open Z-scan curves correspondingly increased, which confirm the SA behavior of BP. The saturable absorption of BP can be explained by single photon absorption model, which has been explained in previous work [14].

NLA of BP obeys the following equation [31]: