Research article

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The pump fluence and wavelength-dependent ultrafast carrier dynamics and optical nonlinear absorption in black phosphorus nanosheets

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Abstract: Pump fluence and probe wavelength-dependent ultrafast carrier dynamics and optical nonlinear absorption in black phosphorus nanosheets are investigated by transient absorption spectroscopy and open-aperture Z scan techniques. The decay time becomes longer with larger wavelengths under pump wavelengths of both 400 nm and 800 nm excitation. For 800 nm excitation, pump fluence-dependent lifetime shows complex behaviors, which might be due to the competition between the linear absorption and two photon absorption. For 400 nm excitation, an additional decaying channel is observed at a larger pump fluence, which is explained by an effective subband structure. In open-aperture Z scan measurements, strong saturation absorption is observed in the visible region over a broad band from 450 nm to 700 nm. The saturation intensity shows an increasing trend with increase in the wavelength. Also, the saturation intensities under different pulse widths and solvents are discussed in detail. Our results show that black phosphorus nanosheets have great potential in future ultrathin optoelectronic devices.

Keywords: black phosphorus; carrier dynamics; excited-state absorption; optical nonlinear absorption; saturation absorption.

1 Introduction

Following the discovery of graphene, other two-dimensional (2D) materials have attracted great attention due to their unique optical properties and high specific surface areas [1], which are important for sensors [2], transistors [3], catalysis [4], photodetectors [5], and energy storage applications [6]. Although most attention has been given to the 2D transition metal dichalcogenides (TMD) [7], black phosphorus (BP) has emerged as a promising layered semiconductor material for optical and optoelectronic applications since 2014 [8]. BP, as one of the many allotropes of phosphorus, is a crystalline lattice of phosphorus atoms which can be exfoliated into 2D layers due to the strong in-plane covalent bonds and the weak out-of-plane van der Waals forces [9]. According to different layers and morphology, BP can be classified as bulk BP, few-layer BP, or monolayer BP [10]. Usually, a BP nanosheet is a layered structure and resembles graphite [11]. They are typically graphene-like 2D inorganic nanosheets with versatile properties, which mostly originate from the anisotropic compressibility of BP, due to the asymmetrical crystal structures [12]. Unlike other 2D materials, BP preserves the direct bandgap from the monolayer (~2.0 eV) to bulk (~0.3 eV), making it a perfect complement to the gapless graphene and TMD (usually with a larger bandgap) [13, 14]. Because its bandgap covers the visible to mid-infrared spectral range, BP is a good candidate for future broadband optoelectronic devices. The electron relaxation time is a fundamental parameter for BP nanostructures and significantly affects the performance of optoelectronic devices, such as photodetectors, solar cells, and

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pulsed lasers. Many nonlinear optical and spectroscopic techniques have been extensively applied to study the time-resolved and nonlinear optical properties of BP [15, 16]. Among these, femtosecond transient absorption (TA) spectroscopy is a powerful technique to investigate electronic and vibrational dynamics [17]. The ultrafast carrier dynamics of BP nanosheets (thickness larger than 20 nm) have recently been extensively studied [18, 19]. For monolayer large-area BP nanosheets, strong anisotropic properties were observed [20–23] under weak pump laser fluence. By contrast, BP nanosheets with smaller sizes were usually dispersed in organic solvent or on film, which is used as an ensemble for the investigation of ultrafast photonics. The carrier dynamics in BP nanosheets dispersed in organic solvents have been reported extensively [24–26], especially in the near-infrared spectral region. Moreover, broadband nonlinear absorption in the near-infrared spectral region was observed for single/few-layer BP nanostructures such as nanosheets and nanoparticles, which can be used as saturable absorbers for Q-switched mode-locking lasers [27, 28]. Recently, BP nanosheets have exhibited an exotic, pump-wavelength and pump-fluence dependence in photocatalytic aqueous solution [29, 30]. However, there are only few reports about the carrier dynamics and nonlinear absorption of BP nanosheets in aqueous solution at the visible range. Although some publications show that BP nanosheets immersed in water would be stable for more than 2 weeks [31], there are very few systematic studies [24]. For many applications related to the biology [32], the water is used as solvent, rather than the organic solution [33].

In this work, ultrafast carrier dynamics and nonlinear absorption of BP nanosheets in aqueous solution across the visible spectral region were investigated. Pump fluence-dependent TA was measured with the excitation wavelength at both 400 nm and 800 nm. Excitation under different pump wavelengths can help to understand the effective band structure of the BP nanosheets. To study the decaying channels at different energy levels, for each pump excitation wavelength, TA was also measured with multiple probe wavelengths. In order to gain deeper insight for the absorption process, an open-aperture Z scan was performed with the excitation wavelength from 450 nm to 700 nm. The nonlinear absorption of BP nanosheets under different laser excitations is discussed in detail. To our knowledge, it is the first time that the nonlinear absorption of BP nanosheets has been measured in the visible region by nanosecond Z scan measurement.

2 Experimental methods

2.1 Preparation of BP nanosheets

BP nanosheets are prepared by liquid exfoliation from a bulk sample [31, 34]. Some 50 mg of the bulk BP (MuKenano, China) is dispersed in 100 ml of distilled water that is bubbled with argon to eliminate the dissolved oxygen molecules to avoid oxidation. The mixed solution is then sonicated in ice water for 8 h. Here, the ice water is used to keep the system at a relatively low temperature. Later, the resultant brown suspension is centrifuged at 1500 rpm for 10 min to remove the residual unexfoliated particles and the supernatant is collected for further use. The concentration of the BP nanosheets aqueous solution is determined by the evaporation weighting method. After measuring the concentration, the solution is diluted to a concentration of 0.2 mg/ml. In order to prevent oxidation and thermal degradation, the BP nanosheets aqueous solution is sealed in a fridge at 4°C. Based on the liquid exfoliation method, a series of dispersions of BP nanosheets immersed in water are prepared. The BP nanosheets can be stable in water for more than 2 weeks without obvious degradation in the dark, and their nanosheet morphology is preserved [31].

2.2 Optical experimental setup

2.2.1 TA spectroscopy

The laser beam (1 kHz) is originally generated by a femtosecond Ti:sapphire regenerative amplifier (Astrella, Coherent) that generates ~35 fs pulses at 800 nm. A BBO crystal is then used to double the photon energy to 400 nm, after which a band-pass filter is used to block the residual laser beam at 800 nm. A pump beam at 400 nm or 800 nm is used in all the TA measurements in this study. Laser pulses at 800 nm are focused onto a sapphire window to produce white-light continuum (WLC) extending from 420 nm to 750 nm, which is divided into a probe beam and a reference beam. The intensity of the 800 nm laser pulse is adjusted by an iris and a neutral density filter to make the WLC probe beam stable. The probe beam is focused onto a quartz cuvette (optical path of 2 mm) containing a BP aqueous solution with a spot size of 1 mm in diameter, and the pump beam spot size is ~2 mm. Pump and probe beams are spatially overlapped at the sample position by the measurement of a standard sample. A 500 Hz mechanical chopper is used to modulate the probe

beam. Two highly sensitive spectrometers (Avantes-950F, Avantes, Appeldoorn, the Netherlands) are used to collect the probe and reference beams intensity. The relative delay between the pump and probe pulse is controlled by a stepper motor-driven optical delay line (TSA-200, Zolix, Beijing, China). The group-velocity dispersion of the WLC is calibrated by optical Kerr signal from the SiO_2 substrate. All measurements were performed at room temperature.

2.2.2 Open-aperture Z scan

The open-aperture Z scan measurements were carried out by a Q-switched Nd:YAG nanosecond laser (Surelite II, Continuum, Santa Clara, CA, USA) and optical parametric oscillator (APE OPO, Continuum) operating at wavelengths from 410 nm to 700 nm [35]. The laser beam is focused on a quartz cuvette (2 mm) filled with a BP nanosheets aqueous solution. The incidence and transmittance signals are monitored as the sample moves along the motorized stage (TSA200, Zolix). The open-aperture Z scan signals are collected by a power meter (J-10MB-LE, Coherent, Santa Clara, CA, USA) and then recorded by an energy meter (EPM2000, Coherent).

3 Results and discussions

3.1 Characterization of BP nanosheets

The absorbance spectrum is measured at room temperature using a UV-vis spectrometer (TU-1901, Persee, Auburn, CA, USA), as shown in Figure 1A. Strong absorption can be observed from the visible to near-infrared regime. As shown in the inset of Figure 1A, the schematic diagram of the crystal structure shows the relative position of two adjacent sheets and the interlayer spacing is 0.53 nm [36]. The BP nanosheets aqueous solution is very stable in the dark and there was no obvious change in the absorbance spectrum, even after 2 weeks. Due to unavoidable aggregation and overlapping, the size and thickness of the BP nanosheets are estimated by atomic force microscopy and transmission electron microscopy (TEM). A typical TEM image revealed the ultrathin and overlapped features of BP nanosheets as shown in Figure 1B, of which the size is about 100 nm or 200 nm in the field of vision. From the TEM image shown in Figure S2, the size varies from 100 nm to 1000 nm, which agrees with previously reported results

Figure 1: Absorbance spectrum and structural characterizations of black phosphorus (BP) nanosheets.

(A) Absorbance spectrum of black phosphorus (BP) nanosheets. The upper inset is the schematic lattice structure of multilayer BP and the inset at the bottom is the picture for the aqueous solution of BP nanosheets. (B) Transmission electron microscopy (TEM) images of the BP nanosheets. (C) High-resolution TEM image. The insets are schematic illustration of the atomic arrangements and the corresponding selective area electron diffraction (SAED) pattern. (D) Atomic force microscopy image of BP nanosheets.

[31]. In Figure 1C, the high-resolution TEM image shows the high quality of the freestanding BP nanosheets. The zoom-in image shows the (040) plane of BP nanosheets and the measured lattice distance is 2.6 Å. A selective area electron diffraction pattern of (040), (022) and (220) planes can be observed clearly after being processed by the standard JCPDS (73-1358), as shown in Figure 1C. Atomic force microscopy indicates that the average thickness of BP nanosheets is 3–6 nm as shown in Figure 1D. Considering the aggregation and overlapping during the deposition and the drying processes, the average layer number is about four to eight layers.

3.2 Ultrafast carrier dynamics of BP nanosheets

To study the ultrafast carrier dynamics of BP nanosheets, we performed broadband TA spectroscopy. In general, after the pump pulses, electrons are excited to the conduction band in a few tens of femtoseconds through the Franck-Condon transition, leaving holes in the valence band [13]. Then, the hot electrons on the conduction band

will cool down by electron-electron and electron-phonon scatterings, which bring the electrons to the conduction band minimum. Finally, the electrons on the conduction band will relax back to the valence band through different decaying channels. Because of the redistribution of electrons in this whole process, the refractive index changes, which is captured by the probe pulses. Here, to study the carrier dynamics under different pump conditions, the broadband TA under both 400 nm and 800 nm pump was investigated under comparable conditions. For 400 nm, the carrier dynamics under a relatively high intensity suggests an additional decay channel, which can be explained by an effective subband structure.

We first used 400 nm as the pump wavelength with a relatively low intensity, the photon energy of which is much higher than the largest possible bandgap of BP nanosheets (~2 eV). Figure 2A shows the contour of broadband TA signals with probe wavelengths ranging from 470 nm to 720 nm and the pump fluence was fixed at 6.4×10^3 mW/cm². Figure 2B shows the corresponding spectra of the change of optical density at different time delays. A positive absorption change suggests the excited-state absorption (ESA) occurs in the whole spectral region,

Figure 2: Wavelength and fluence dependent (low fluence region) ultrafast carrier dynamics of BP nanosheets with pump wavelength at 400 nm. (A) Two-dimensional (2D) mapping of transient absorption (TA) spectra for black phosphorus (BP) nanosheets pumped at 400 nm with a fluence of 6.4×10^3 mW/cm². (B) Spectra of change of optical density at different delay times. (C) Carrier dynamics (at 400 nm pump) at different probe wavelengths with pump fluence fixed at 6.4×10^3 mW/cm². (D) Carrier dynamics (at 400 nm pump) at different pump fluences from 5.1×10^3 mW/cm² to 1.1×10^4 mW/cm² with a probe wavelength fixed at 520 nm.

which agrees with previous results in BP nanosheets [37] and quantum dots [26, 38]. Here, the ultrafast carrier dynamics are investigated under four different probe wavelengths (500 nm, 540 nm, 580 nm, 620 nm) as shown in Figure 2C. For a certain pump fluence (6.4×10^3 mW/cm²), the decay time becomes longer with longer probe wavelengths. At a longer wavelength, electrons on the lower energy states would more likely be probed, which depopulates slower than higher lying states. A similar phenomenon was observed in graphite [39]. Figure 2D shows the pump fluence-dependent carrier dynamics at 520 nm (probe wavelength) and the data can be well fitted with a single exponential function [40]. With the pump fluence increasing, the fitted lifetime decreases from 148.9 ps to 76.2 ps, which is usually attributed to the carrier density dependence of electron phonon coupling [25].

TA with a 520 nm probe and 400 nm pump at a relatively high pump fluence (3.8×10^4 mW/cm²) is shown in Figure 3A. The data cannot be fitted by the single exponential function, implying two different relaxation channels. We denote the faster process with decay time τ_1 and the slower process with decay time τ_2 . As shown in Figure 3B,

at a longer probe wavelength, both τ_1 and τ_2 increase, which shows the same trend as the τ fitted with a single exponential function at low fluence (left panel of Figure 3C). In the right panel of Figure 3C, for relatively low fluence, τ shows a decreasing trend with increase in the fluence. However, for higher fluence, τ_2 shows an increasing trend. At the same time, τ_2 becomes significantly larger than τ_1 . Usually, in 2D materials, the faster decaying process is related to the electron-electron scattering and the slower decaying process is associated with electron-phonon scattering for a single conduction band approximation [26]. However, due to the abnormal fluence-dependent carrier lifetime in relatively high fluence, the approximation might not be valid. For 2D materials, due to the quantum confinement, there exist other subbands above the lowest conduction band. Wang et al. [29] successfully explained the wavelength-dependent optical switching effect in BP nanosheets by an effective subband model. Here, based on the observance of the difference in low fluence and high fluence, we modify the subband structure proposed by Wang et al. [29] and construct it as shown in Figure 3D. When the pump fluence is low, only the lowest subband

Figure 3: Comparison of the carrier dynamics between low pump fluence region and high pump fluence region for pump wavelength at 400 nm. (A) Transient absorption (TA) (red dot) signals measured with pump wavelength at 400 nm (3.8×10^4 mW/cm²) and probe wavelength at 520 nm, fitted with the double-exponential function (black line). The blue line and green line represent the faster decaying process and the slower decaying process, respectively. (B) Carrier dynamics at different probe wavelengths (500 nm, 540 nm, 580 nm, 620 nm) with 400 nm pump at a fluence of 3.8×10^4 mW/cm². (C) Left panel: probe wavelength-dependent lifetime (pump at 400 nm) at low fluence (6.4×10^3 mW/cm², red circle) and high fluence (3.8×10^4 mW/cm², blue square for τ_2). Right panel: pump fluence-dependent carrier lifetimes in the low fluence (red square) and high fluence (blue square) regions. (D) Schematic illustration of the subband structure of black phosphorus (BP) nanosheets and the carrier dynamics (with 400 nm laser as pump) at the weak pump fluence (left) and the strong pump fluence (right) condition, respectively.

(CB₁) will be filled. With the pump fluence increases, CB₁ will be filled with more and more electrons until saturation. Above the saturation fluence, the extra electrons will start to fill the next subband (CB₂) at a higher energy level. Electrons on CB₂ need to go through an extra step before recombining with holes, which is, decaying into CB₁ first, which effectively elongates the lifetime of electrons on the CB₁. This process is similar to the intervalley scattering in III-V semiconductors [41, 42]. However, since BP is a direct bandgap material, there do not exist other lower lying indirect bands. This scattering process should not be considered. With this picture in mind, the behavior of τ_1 can be easily understood. At a low pump fluence, since the pump has not reached the second effective subband, no faster relaxation process exists. At a high pump fluence (larger than 2.4×10^4 mW/cm²), the faster relaxation channel appears. Measured at 3.8×10^4 mW/cm², for a longer probe wavelength, τ_1 becomes longer as shown in Figure 3B. At 520 nm, with the pump fluence increasing from 2.4 mW/cm² to 6.3 mW/cm², τ_1 decreases from 17.4 ps to 12.1 ps. Before the pump fluence reaches high enough to trigger the third subband, the decaying process associated with the second subband should behave like the normal

single band (because there is no electron scattering from the higher band). So, both the wavelength and fluence-dependent lifetime behave similarly to the one at low fluence (τ).

As a comparison, the ultrafast dynamics under an 800 nm pump were investigated. From the absorbance spectrum (Figure 1A), the absorbance at 800 nm (~1.55 eV) is much smaller than that of 400 nm. For BP nanosheets prepared via the liquid-phase exfoliation method, the quasiband gap (which can be taken as an average bandgap) could be much larger than that of mechanically exfoliated samples, which might originate from strain-induced band structure change [29]. From the absorbance spectrum, the quasiband gap of our BP nanosheets is derived to be about 1.9 eV, which is larger than 1.55 eV (as shown in Figure S1). So, it is difficult to excite electrons in the valence band through single photon absorption, which explains why the absorption at 800 nm is much weaker than that at 400 nm.

To study the TA at comparable conditions, the pump fluence for 800 nm excitation is adjusted by a neutral density filter to make sure the peak values of TA signals before normalization are similar to those under weak 400 nm excitation, which can be seen in Figures 2B and 4B.

Figure 4: Wavelength and fluence dependent ultrafast carrier dynamics of BP nanosheets with pump wavelength at 800 nm. (A) Two-dimensional (2D) mapping of transient absorption (TA) spectrum for black phosphorus (BP) nanosheets pumped at 800 nm with the pump fluence at 8.4×10^4 mW/cm². (B) Spectra of change of optical density at different delay times. (C) Carrier dynamics (at 800 nm pump) at different probe wavelengths with pump fluence fixed at 8.4×10^4 mW/cm². (D) Carrier dynamics at different pump (at 800 nm) fluences from 4.2×10^4 mW/cm² to 2.9×10^5 mW/cm² with probe wavelength fixed at 520 nm.

In Figure 4C, similar to the 400 nm pump, the fitted decay time increases at longer wavelengths. From the pump fluence-dependent carrier dynamics, as shown in Figure 4D, there are two distinct features under 800 nm and 400 nm excitation. Firstly, at all fluences, the lifetimes under 800 nm excitation are much shorter than that with 400 nm excitation. Secondly, the lifetime under 800 nm excitation firstly increases with fluence and then decreases, while that under 400 nm excitation decreases monotonically. Although the quasi-bandgap derived from the absorbance spectrum is about 1.9 eV, the BP nanosheets are still a broadband absorption material due to the distribution of thickness. In thicker nanosheets, the actual bandgap could be well below 1.55 eV and linear absorption could occur. From another perspective, at a relatively low fluence when no two photon absorption (TPA) happens, the laser (800 nm) cannot “see” all the samples in the solution. So, the effective subband structures in Figure 3D cannot directly be applied here. With the pump wavelength at 800 nm, TPA of BP nanosheets was observed under a pump fluence of about 10^4 mW/cm² [43]. This pump fluence is about the same order of magnitude used in our experiment, indicating that both linear absorption and TPA exist in our case. The effective lifetime ($\tau_{\text{effective}}$) measured here has two components: τ_{TPA} and τ_{linear} . The ultrafast decaying process induced by TPA at the 800 nm pump is expected to be similar to that of the 400 nm pump, since the photon energy of 400 nm equals the total photon energy of two photons at 800 nm. However, for linear absorption, only those nanosheets with bandgaps smaller than 1.55 eV can be excited. From monolayer to bulk in BP, with increasing thickness, the interlayer interaction becomes stronger, resulting in stronger scattering [44]. So, the lifetime associated with linear absorption (τ_{linear}) in thicker BP nanosheets would be shorter than the TPA lifetime (τ_{TPA}) in thinner nanosheets. The value of $\tau_{\text{effective}}$ is expected to be between τ_{TPA} and τ_{linear} , which explains why the measured lifetime under 800 nm pump is much shorter than that under 400 nm excitation. Under different fluences, the ratio of electrons participating in linear absorption and TPA will change and the effective decay time could change accordingly. With this picture in mind, the following hypothesis is proposed. At a relatively low fluence, only thick samples can be excited through one photon absorption, which gives short lifetimes. With increasing fluence, TPA gets stronger so that electrons can be excited in thinner samples, which have longer lifetimes. Then, under even higher fluence, for the single photon absorption, the saturation effect could occur in thick samples, which introduces stronger scattering and significantly decreases the lifetime again. Here, we need to point

out that the saturation effect is determined by the band structure, but the critical fluence at which TPA happens is determined by the nonlinear coefficient of material. For different concentrations or thickness distributions, TPA might happen after the saturation effect for single photon absorption. At even larger fluence, the lifetime should increase again and approach the one at 400 nm pump asymptotically. That is because with larger fluence, more and more electrons would be preferably excited by the TPA process, which is similar to the single photon absorption at 400 nm. Limited by the equipment, we did not observe this phenomenon within our pump fluence range. Further research is needed to investigate the fluence-dependent lifetime at even larger fluences. Here, we need to point out that the carrier lifetime measured at 520 nm is actually larger than the one at 540 nm with the same fluence at 8.4×10^4 mW/cm², which is shown in Figure S5. However, since the difference of the lifetime measured at these two wavelengths is only about 1 ps, the abnormal relatively large fitted lifetime at 520 nm might be due to the relatively large experimental error (temperature, humidity, laser stability), so the true lifetime at 520 nm could still possibly be smaller than the one at 540 nm. By contrast, as discussed above, at 520 nm with the pump fluence at 8.4×10^4 mW/cm², the lifetime increases compared with that at a low fluence, because of the TPA. So, another possible reason is that since the lifetime at one wavelength first increases and then decreases with increase in the fluence, for 520 nm, the effective lifetime might be just around the peak position with the fluence at 8.4×10^4 mW/cm². To prove this, further experimental investigation is necessary to scan the region from 500 nm to 540 nm with a much smaller spectrum width. Also, the wavelength-dependent lifetime needs to be measured under different fluences. The detailed discussion for this issue can be found in the Supplementary Material.

3.3 The nonlinear absorption of BP nanosheets

To understand the nonlinear process in BP nanosheets at high fluence, broadband open-aperture Z scan measurements with a nanosecond laser were performed. To our best knowledge, this is the first time that the nonlinear absorption is mapped in the whole visible region. In order to eliminate the possibility of nonlinearity induced by heat accumulation from multiple laser pulses, we used a laser with a low repetition rate (10 Hz). To validate our nanosecond open-aperture Z scan experiment, the nonlinear absorption coefficients of carbon disulfide were

firstly measured (Figure S3 in Supplementary Information), which is consistent with the reported results [45].

Figure 5A shows the results for different wavelengths at 0.22 GW/cm². For all the wavelengths investigated here, strong saturation absorption (SA) is observed when the sample is across the laser focus ($z=0$). Figure 5B shows the fluence-dependent Z scan measurement at 520 nm from 0.01 GW/cm² to 0.64 GW/cm². From 0.01 GW/cm² to 0.36 GW/cm², the peak becomes higher and broader, which indicates a stronger saturation effect. However, at the highest incident fluence (0.64 GW/cm²), a dip appears around the focus, meaning an increase of absorption. This phenomenon is usually called reverse saturable absorption (RSA), which is due to an additional channel associated with the absorption process. There are several possible reasons. Usually, the RSA can be related to TPA. However, even at the highest fluence (0.64 GW/cm²), it is still quite small compared to $\sim 10\text{--}10^2$ GW/cm² [46, 47]. Another possible mechanism is ESA, which can actually happen at relatively low intensity [48]. After the hot electrons fall down to the conduction band minimum, they can absorb another photon and be excited again to an even higher energy level. With laser power increase, the electrons on the conduction band minimum will build up. The more electrons on the conduction band minimum, the stronger the ESA would be. And eventually, it could become even stronger than the saturation effect from single photon absorption. Combining the effect from SA and the RSA, the total absorption coefficient can be written as [49]:

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_s} + \beta I \quad (1)$$

where α_0 is the linear absorption coefficient, I_s is the saturation intensity, and β is the nonlinear absorption coefficient. In order to eliminate the nonlinear effect from the solvents, the Z scan measurement was done for the solvents at the same conditions without BP nanosheets.

We fitted all the data from the Z scan measurements with the following equation [50]:

$$T(z) = \sum_{m=0}^{\infty} \frac{\left(\frac{\alpha I_0 L_{\text{eff}}}{1 + z^2/z_0^2} \right)^m}{(1+m)^{3/2}} \quad (2)$$

where $T(z)$ is the normalized transmittance, I_0 is peak intensity at focus, z is the position of the sample with respect to the focal position, z_0 is the Rayleigh range, $L_{\text{eff}} = (1 - e^{-\alpha_0 L})/\alpha_0$ is the effective length, and L is the thickness of the sample. As shown in Figure 5C, I_s becomes larger at longer wavelengths. Although the wavelength-dependent saturation intensities were reported by many groups, the results are not consistent for different pulse widths and the underlying mechanism is still not understood well. Lu et al. [14] performed the Z scan measurement by both femtosecond and picosecond lasers [14]. In their experiments, the saturation intensity was found to be larger for smaller wavelengths for both femtosecond and picosecond excitation [14]. Zhang et al. [51] measured the saturation intensity of BP nanosheets with a picosecond laser (40 ps spectral linewidth, 10 Hz repetition rate) at three different wavelengths (1064 nm, 532 nm, 355 nm) and the measured saturation intensity also shows a decreasing trend with increasing wavelength. Huang et al. [52] conducted the nanosecond Z scan measurement (6 ns spectral linewidth, 10 Hz repetition rate) at 532 nm and 1064 nm and found that the saturation intensity is larger for 1064 nm, which agrees with our results. Based on the reported results and our results, the following hypothesis is proposed. For a femtosecond laser, the pulse duration is extremely short so that the saturation effect should be limited within a small energy range associated with the excitation. For larger photon energy (shorter wavelength), there are usually more optical transition channels available so that it would be harder to be saturated. For a picosecond laser, the pulse width from literature is around 20–30 ps, which is comparable to the lifetime. After the electrons are

Figure 5: Nanosecond open-aperture Z scan measurement for BP nanosheets.

(A) Nanosecond open-aperture Z scan measurement under different wavelengths in the visible region. (B) Fluence-dependent open-aperture Z scan measurement at 520 nm. The fluence changes from 0.01 GW/cm² to 0.64 GW/cm². The black solid lines are the fitting curves.

(C) Wavelength-dependent saturation intensity at 0.22 GW/cm².

Table 1: Saturation intensity of black phosphorus (BP) nanosheets under different pulse widths and solvents.

Pulse width (fs)	Wavelength (nm)	Solvent	T (%)	I_s (GW/cm ²)	Pulse width	Wavelength (nm)	Solvent	T (%)	I_s (GW/cm ²)
100	400	IPA	70.5	455.3 ± 55 [14]	20 ps	355	IPA	30.3	1.3×10^{-3} [51]
100	800	IPA	85.6	334.6 ± 55 [14]	30 ps	532	IPA	31.0	7.6×10^{-3} [51]
100	800	NMP	68	123 [25]	40 ps	1064	IPA	36.0	3.1×10^{-2} [51]
~100	800	CHP	86.2	459 [27]	6 ns	532	NMP	79.7	4.85×10^{-2} [52]
100	1330	CHP	80.3	382 ± 60 [27]	6 ns	1064	NMP	81.9	1.37×10^{-1} [52]
100	800	NMP	–	535.3 [4]	6 ns	532	CHP	20	10–126 [53]
340	515	CHP	–	~50 [54]	6 ns	480	Water	36.4	7.2×10^{-2}
340	1030	CHP	–	~500 [54]	6 ns	530	Water	33.0	7.1×10^{-2}
340	1030	CHP	~80	300 [55]	6 ns	680	Water	69.4	2.8×10^{-1}

CHP, N-cyclohexyl-2-pyrrolidone; IPA, isopropanol; NMP, N-methyl-2-pyrrolidone.

excited by the laser, they will fall down to the conduction band minimum and build up. For a relatively small photon energy, it will be affected more and have a smaller saturation intensity. For the nanosecond laser, the behavior of the wavelength dependent saturation intensity is just the opposite of femtosecond and picosecond lasers. Since the pulse duration is much longer than the lifetime, the whole system (BP nanosheets) should be in the steady-state condition. If we apply the parabolic approximation to the conduction band, it is easy to see that around the band minimum, there are more states. So, around the conduction band minimum, the total number of electrons decaying back after one lifetime period should be much more than those at a relatively high energy state, which effectively makes up more available states and increases the saturation intensity.

The saturation intensities under different pulse widths and solvents are summarized in Table 1. For femtosecond laser excitation, I_s is much larger than that for picosecond and nanosecond lasers [56]. One possible reason might be the much shorter pulse width of the femtosecond laser. For the picosecond and nanosecond lasers, since the duration of one pulse is quite long, the electrons excited by the pulse front could screen the excitation from the later part of the laser pulse so that the saturation intensity could be much lower. Also, for different qualities of nanosheets and dispersion concentration, it is reasonable that the absorption might be different. From another perspective, by controlling the concentration, the saturation intensity can be easily controlled in the broadband visible region, which can be used in Q-switched mode-locking lasers and optical modulators [27].

4 Conclusion

Pump fluence and wavelength-dependent ultrafast carrier dynamics and optical nonlinear absorption in BP

nanosheets are measured by TA spectroscopy and the open-aperture Z scan technique. For 400 nm, an additional decaying channel is observed at a large pump fluence, which is explained by an effective subband structure. For 800 nm, the abnormal fluence-dependent lifetime is observed and might originate from the competition between the linear absorption and TPA. For both 400 nm and 800 nm as pump, the decay time becomes longer with larger wavelengths. For the first time, the nonlinear absorption of BP nanosheets is mapped in the visible region by the nanosecond Z scan measurement, in which strong SA is observed over a broad band from 450 nm to 700 nm. The saturation intensity shows an increasing trend with increasing wavelength. Under different pulse widths and solvents, the measured saturation intensities are discussed in detail. Our results demonstrate that BP nanosheets provide a great platform to study optical nonlinearity and have great potential in ultrathin optoelectronic devices.

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References

- [1] Coleman JN, Lotya M, O'Neill A, et al. Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* 2011;331:568–71.
- [2] Mayorga-Martinez CC, Sofer Z, Pumera M. Layered black phosphorus as a selective vapor sensor. *Angew Chem Int Ed Engl* 2015;54:14317–20.

- [3] Li L, Yu Y, Ye GJ, et al. Black phosphorus field-effect transistors. *Nat Nanotechnol* 2014;9:372–7.
- [4] Xu Y, Wang Z, Guo Z, et al. Solvothermal synthesis and ultrafast photonics of black phosphorus quantum dots. *Adv Opt Mater* 2016;4:1223–9.
- [5] Engel M, Steiner M, Avouris P. Black phosphorus photodetector for multispectral, high-resolution imaging. *Nano Lett* 2014;14:6414–7.
- [6] Jiang J, Shao G, Zhang Z, et al. Ultrapstability and color-tunability of CsPb(Br/I)₃ nanocrystals in P-Si-Zn glass for white LEDs. *Chem Commun* 2018;54:12302–5.
- [7] Wang QH, Kalantar-Zadeh K, Kis A, Coleman JN, Strano MS. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat Nanotechnol* 2012;7:699–712.
- [8] Koenig SP, Doganov RA, Schmidt H, Castro Neto A, Oezylmaz B. Electric field effect in ultrathin black phosphorus. *Appl Phys Lett* 2014;104:103106–9.
- [9] Zhang H. Ultrathin two-dimensional nanomaterials. *ACS Nano* 2015;9:9451–69.
- [10] Gusmao R, Sofer Z, Pumera M. Black phosphorus rediscovered: from bulk material to monolayers. *Angew Chem Int Ed Engl* 2017;56:8052–72.
- [11] Liu H, Neal AT, Zhu Z, et al. Phosphorene: an unexplored 2D semiconductor with a high hole mobility. *ACS Nano* 2014;8:4033–41.
- [12] Liu H, Du Y, Deng Y, Peide DY. Semiconducting black phosphorus: synthesis, transport properties and electronic applications. *Chem Soc Rev* 2015;44:2732–43.
- [13] Xie Z, Zhang F, Liang Z, et al. Revealing of the ultrafast third-order nonlinear optical response and enabled photonic application in two-dimensional tin sulfide. *Photonics Res* 2019;7:494–502.
- [14] Lu SB, Miao LL, Guo ZN, et al. Broadband nonlinear optical response in multi-layer black phosphorus: an emerging infrared and mid-infrared optical material. *Opt Express* 2015;23:11183–94.
- [15] Wu Z, Ni Z. Spectroscopic investigation of defects in two-dimensional materials. *Nanophotonics* 2017;6:1219–37.
- [16] Zhao H, Zhang W, Liu Z, et al. Insights into the intracellular behaviors of black-phosphorus-based nanocomposites via surface-enhanced Raman spectroscopy. *Nanophotonics* 2018;7:1651–62.
- [17] You JW, Bongu SR, Bao Q, Panoiu NC. Nonlinear optical properties and applications of 2D materials: theoretical and experimental aspects. *Nanophotonics* 2019;8:63–97.
- [18] Surrente A, Mitoglu A, Galkowski K, et al. Onset of exciton-exciton annihilation in single-layer black phosphorus. *Phys Rev B* 2016;94:075425–30.
- [19] Huber MA, Mooshammer F, Plankl M, et al. Femtosecond photo-switching of interface polaritons in black phosphorus heterostructures. *Nat Nanotechnol* 2017;12:207–11.
- [20] Zereszki P, Wei Y, Ceballos F, et al. Photocarrier dynamics in monolayer phosphorene and bulk black phosphorus. *Nanoscale* 2018;10:11307–13.
- [21] He J, He D, Wang Y, et al. Exceptional and anisotropic transport properties of photocarriers in black phosphorus. *ACS Nano* 2015;9:6436–42.
- [22] Ge S, Li C, Zhang Z, et al. Dynamical evolution of anisotropic response in black phosphorus under ultrafast photoexcitation. *Nano Lett* 2015;15:4650–6.
- [23] Meng S, Shi H, Jiang H, Sun X, Gao B. Anisotropic charge carrier and coherent acoustic phonon dynamics of black phosphorus studied by transient absorption microscopy. *J Phys Chem C* 2019;123:20051–8.
- [24] Guo Z, Zhang H, Lu S, et al. From black phosphorus to phosphorene: basic solvent exfoliation, evolution of Raman scattering, and applications to ultrafast photonics. *Adv Funct Mater* 2015;25:6996–7002.
- [25] Xu Y, Jiang X-F, Ge Y, et al. Size-dependent nonlinear optical properties of black phosphorus nanosheets and their applications in ultrafast photonics. *J Mater Chem C* 2017;5:3007–13.
- [26] Jiang X-F, Zeng Z, Li S, et al. Tunable broadband nonlinear optical properties of black phosphorus quantum dots for femtosecond laser pulses. *Materials* 2017;10:210–20.
- [27] Wang K, Szydłowska BM, Wang G, et al. Ultrafast nonlinear excitation dynamics of black phosphorus nanosheets from visible to mid-infrared. *ACS Nano* 2016;10:6923–32.
- [28] Luo Z-C, Liu M, Guo Z-N, et al. Microfiber-based few-layer black phosphorus saturable absorber for ultra-fast fiber laser. *Opt Express* 2015;23:20030–9.
- [29] Wang H, Jiang S, Shao W, et al. Optically switchable photocatalysis in ultrathin black phosphorus nanosheets. *J Am Chem Soc* 2018;140:3474–80.
- [30] Elbanna O, Zhu M, Fujitsuka M, Majima T. Black phosphorus sensitized TiO₂ mesocrystal photocatalyst for hydrogen evolution with visible and near-infrared light irradiation. *ACS Catal* 2019;9:3618–26.
- [31] Wang H, Yang X, Shao W, et al. Ultrathin black phosphorus nanosheets for efficient singlet oxygen generation. *J Am Chem Soc* 2015;137:11376–82.
- [32] Chen W, Ouyang J, Liu H, et al. Black phosphorus nanosheet-based drug delivery system for synergistic photodynamic/photothermal/chemotherapy of cancer. *Adv Mater* 2017;29:1603864–70.
- [33] Qiu M, Wang D, Liang W, et al. Novel concept of the smart NIR-light-controlled drug release of black phosphorus nanostructure for cancer therapy. *Proc Natl Acad Sci USA* 2018;115:501–6.
- [34] Hao C, Wen F, Xiang J, et al. Liquid-exfoliated black phosphorus nanosheet thin films for flexible resistive random access memory applications. *Adv Funct Mater* 2016;26:2016–24.
- [35] Shao Y, Chen C, Han J, Kong D, Wu W, Gao Y. Wavelength-dependent nonlinear absorption and ultrafast dynamics process of WS₂. *OSA Contin* 2019;2:2755–63.
- [36] Xia F, Wang H, Jia Y. Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics. *Nat Commun* 2014;5:4458–63.
- [37] Suess RJ, Jadidi MM, Murphy TE, Mittendorff M. Carrier dynamics and transient photobleaching in thin layers of black phosphorus. *Appl Phys Lett* 2015;107:081103–6.
- [38] Chen L, Zhang C, Li L, et al. Ultrafast carrier dynamics and efficient triplet generation in black phosphorus quantum dots. *J Phys Chem C* 2017;121:12972–8.
- [39] Breusing M, Ropers C, Elsaesser T. Ultrafast carrier dynamics in graphite. *Phys Rev Lett* 2009;102:086809–12.
- [40] Zhang Y, Zhang F, Xu Y, et al. Self-healable black phosphorus photodetectors. *Adv Funct Mater* 2019;29:1906610–9.
- [41] Gupta S, Whitaker JF, Mourou GA. Ultrafast carrier dynamics in III-V semiconductors grown by molecular-beam epitaxy at very low substrate temperatures. *IEEE J Quantum Electron* 1992;28:2464–72.

- [42] Becker P, Fragnito H, Brito Cruz C, et al. Femtosecond intervalley scattering in GaAs. *Appl Phys Lett* 1988;53: 2089–90.
- [43] Chen R, Tang Y, Zheng X, Jiang T. Giant nonlinear absorption and excited carrier dynamics of black phosphorus few-layer nanosheets in broadband spectra. *Appl Opt* 2016;55:10307–12.
- [44] Vy T, Soklaski R, Liang Y, Yang L. Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus. *Phys Rev B* 2014;89:235319–24.
- [45] Liu Z-B, Liu Y-L, Zhang B, et al. Nonlinear absorption and optical limiting properties of carbon disulfide in a short-wavelength region. *J Opt Soc Am B* 2007;24:1101–4.
- [46] Zheng X, Chen R, Shi G, Zhang J, Xu Z, Jiang T. Characterization of nonlinear properties of black phosphorus nanoplatelets with femtosecond pulsed Z-scan measurements. *Opt Lett* 2015;40:3480–3.
- [47] Wang Y, Huang G, Mu H, et al. Ultrafast recovery time and broadband saturable absorption properties of black phosphorus suspension. *Appl Phys Lett* 2015;107: 091905–9.
- [48] Meng X, Zhou Y, Chen K, et al. Anisotropic saturable and excited-state absorption in bulk ReS_2 . *Adv Opt Mater* 2018;6:201800137–44.
- [49] Wu W, Chai Z, Gao Y, et al. Carrier dynamics and optical nonlinearity of alloyed CdSeTe quantum dots in glass matrix. *Opt Mater Express* 2017;7:1547–56.
- [50] Gao Y, Zhang X, Li Y, et al. Saturable absorption and reverse saturable absorption in platinum nanoparticles. *Opt Commun* 2005;251:429–33.
- [51] Zhang F, Wu Z, Wang Z, Wang D, Wang S, Xu X. Strong optical limiting behavior discovered in black phosphorus. *RSC Adv* 2016;6:20027–33.
- [52] Huang J, Dong N, Zhang S, Sun Z, Zhang W, Wang J. Nonlinear absorption induced transparency and optical limiting of black phosphorus nanosheets. *ACS Photonics* 2017;4:3063–70.
- [53] Szydłowska BM, Tywoniuk B, Blau WJ. Size-dependent nonlinear optical response of black phosphorus liquid phase exfoliated nanosheets in nanosecond regime. *ACS Photonics* 2018;5:3608–12.
- [54] Zhang S, Li Y, Zhang X, et al. Slow and fast absorption saturation of black phosphorus: experiment and modelling. *Nanoscale* 2016;8:17374–82.
- [55] Hanlon D, Backes C, Doherty E, et al. Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics. *Nat Commun* 2015;6:8563–73.
- [56] Valligatla S, Haldar KK, Patra A, Desai NR. Nonlinear optical switching and optical limiting in colloidal CdSe quantum dots investigated by nanosecond Z-scan measurement. *Opt Laser Technol* 2016;84:87–93.

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