Supporting Information

Title: Strong optical limiting behavior discovered in black phosphorus

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**S1. Preparation processes of BPns.**

The detailed preparing processes of BPns were shown in Figure S1. The purchased original BP was powder. We carried out a further grind using agate mortar in order to increase the component of 2D BPns. The grinded powder was dissolved in isopropyl alcohol (IPA). The dispersion liquid was ultra-sonicated for three hours to effectively exfoliate the stratified structure of BPns. Then the dispersion liquid was settled for 36 hours to precipitate the large BP grains. After centrifugation for 30 minutes with a speed of 1500 rpm, the dispersion liquid became apparently stratified. The top one fourth of the dispersion liquid was used as the experiment sample, which was collected and stored in a quartz colorimetric utensil with 2 mm thickness.

![Figure S1. Preparation processes of BPns.](image-url)
S2: Linear absorption.

Figure S2 (a) shows the prepared three samples with different concentrations. Their transmission spectra are shown in Figure S2 (b). The smooth curve indicates that transmittance is almost a constant in the range of 350 to 1100 nm. The transmittances of 1# to 3# sample are around to be 32%, 47% and 70%. Using the equation $T_{\text{abs}}=\exp(-\alpha_0 L)$, where $T_{\text{abs}}=T/T_0$ and $L=2$ mm, the linear absorption coefficients $\alpha_0$ (1# $\rightarrow$ 3#) are calculated to be 5.65, 3.78 and 1.78 cm$^{-1}$, respectively.

Figure S2. As-prepared 1#, 2# and 3# BPns samples and their linear transmission spectra.
S3: NLO experimental setup.

The experimental setup of open-aperture Z-scan technique was shown in Figure S3. The laser resource was a dye mode-locked Nd:YAG laser (PY61C-10, Continuum Inc, America) operating at 1064 nm, 40 ps pulses, with 10 Hz repetition rate. A piece of KTP crystal was used to generate the frequency doubling laser (532 nm) with a pulse width of 30 ps. Furthermore, the third harmonic laser of 355 nm with 20 ps pulse width was generated with a BBO crystal, by the sum-frequency of 1064 and 532 nm. Mirror $M_1$ is high transparent at 532 nm ($T>80\%$) and high reflective at 1064 nm ($R>99.5\%$), to serve as the filter of the fundamental laser. Mirror $M_2$ is high transparent at 355 nm ($T>60\%$) and high reflective at 1064, 532 nm ($R>99.5\%$), to serve as the filter of the fundamental and frequency doubling lasers. The focal length of the convex lens is 30 cm at 1064 nm.

Figure S3. Open-aperture Z-scan experimental setup with 1064, 532 and 355 nm excitations.
S4: Z-scan result of graphene.

The graphene was manufactured using chemical exfoliation method. The sample concentration is around to be 0.50 mg/mL, which is the same as our 1# sample of BPns. The Figure S4 displays the Z-scan result of graphene with 1064 nm excitation when the intensity at the focus (z = 0) is 69 MW·cm$^{-2}$. The fitted saturable intensity $I_s$ and 2PA coefficient $\beta$ were 2.5 MW·cm$^{-2}$ and 5.4 cm·GW$^{-1}$, respectively. The cross section of 2PA ($\sigma_{2PA} = \hbar \omega \beta N_0^4$, where $\hbar \omega$ is the excitation photon energy and $N_0 \approx 2.5 \times 10^{19}$ cm$^{-3}$ is the sample density) is calculated to be $0.40 \times 10^{-48}$ cm$^4$ s photon$^{-1}$. The imaginary part of the third-order NLO susceptibility, $\text{Im}\chi^{(3)}$, is related to the 2PA coefficient $\beta$. Their relationship can be expressed by the Equation S1, where $c$ is the vacuum light speed, $n_0$ is the linear refractive index and $\omega$ is the angular frequency of the excitation light. The FOM value can be calculated from $|\text{Im}\chi^{(3)}/\alpha_0|$, where $\alpha_0$ is the linear absorption coefficient of graphene at 1064 nm. Based on the experimental result, the $\text{Im}\chi^{(3)}$ and FOM values of graphene are determined to be $9.8 \times 10^{16}$ m$^3$·(sW)$^{-1}$ and $3.3 \times 10^{14}$ m$^4$·(sW)$^{-1}$, respectively.

$$\text{Im}\chi^{(3)} = \frac{c^2 n_0^2}{240 \pi^2 \omega} \beta (m / W)$$  \hspace{1cm} (S1)
Figure S4. Z-scan result of graphene with 1064 nm excitation when the peak intensity is 69 MW/cm² (the points are the experimental data and the solid line is the fitted curve).