Electronic Supplementary Information

Small molecule-assisted fabrication of black phosphorus quantum dots with broadband nonlinear optical response

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Experimental details

Materials

The black phosphorus crystals were purchased from Smart-Elements. Phytic acid, trioctylphosphine oxide and MoS₂ were from Aladdin Chemistry Co. Ltd. Polyethylene glycol (PEG-8000) was purchased from Beijing solarbio science & Technology Co. Ltd. N-Methylpyrrolidone (NMP) was from Chengdu Kelong Chemical Reagent Factory, and was dried with CaH₂ and distilled under reduced pressure before use. Graphite and glucose were from Sinopharm Chemical Reagent Co. Ltd. β -Cyclodextrin was from Sun Chemical Technology (Shanghai) Co. Ltd. Deionized water (resistivity: 18.3 MΩ•cm) was used to prepare aqueous solution throughout the experiment.

Liquid Exfoliation of Black Phosphorus into QDs

The BP QDs were prepared by liquid exfoliation of corresponding black phosphorus crystals, which were ground into granular pieces using a mortar and pestle in an argon glovebox. Then 5 mg BP powder and 5 mg phytic acid were dispersed in 5 mL distilled NMP, and the mixture solution was subsequently sealed to insulate air, and sonicated in a bath sonicator customized for long sonication time at 50 kHz frequency. To avoid dramatic water temperature increase during sonication, an external circulating water cooling system was applied to maintain the ambient temperature of the bath sonicator. After being subjected to 10-hour sonication at high power without intermittence, the resultant brown suspension was centrifuged at 10,000 rpm for 5 min to remove the residual unexfoliated particles and undissolved phytic acid as well, and the supernatant containing BP QDs was decanted gently. Eventually, the supernatant was centrifuged at 14,000 rpm for 5 min to remove the dissolved phytic acid and the precipitate was re-suspended in solvent (NMP or H_2O) before use. The procedure was repeated for 3 times to guarantee a complete purge of phytic acid and the final product was kept in the glove box for future use.

Conjugating BP QDs with PEG

The as-prepared BP QDs precipitate dispersed in 8 mL of H₂O was mixed with 6 mg of PEG. After stirring overnight, excess PEG molecules were removed by centrifugation at 14,000 rpm and the final BP QDs@PEG products were re-suspended in H₂O.

Preparation of graphene

Preparation of graphene was based on previous literature.¹ Briefly, 5 mg graphite was dispersed in 5 mL NMP and sonicated for 20 h. The dispersion was centrifuged for 15 min at 500 rpm. After centrifugation, the supernatant was decanted by pipet and retained for use.

Preparation of 2D MoS₂

Preparation of graphene was according to previous report.² Briefly, 120 mg MoS₂ powder was poured to 120 mL 45% aqueous ethanol in a 250 mL bottle and sonicated for 20 h. The dispersion was centrifuged for 5 min at 3,000 rpm and the supernatant containing MoS_2 was decanted gently. Then the MoS_2 solution was centrifuged for 5 min at 13,000 rpm and the precipitate was dispersed in NMP for future use.

Characterization

Steady-state spectroscopic measurement

The collection of UV-Vis-NIR absorption spectra was performed on a TU-1810 Spectr ophotometer (Beijing Purkinje General Instrument, China). The Raman spectra were recorded on a Renishaw in via Raman Microscope System with the excitation wavelength of 633 nm.

Laser photolysis measurement

The laser photolysis measurement is based on the pump-probe technique, a powerful means of extracting transient excited-state dynamics of molecules.³ Briefly, a pump light excites the sample, and after a time delay, usually varying from femtosecond to microsecond time scale, a probe light interrogates the same spot. The transmitted probe light is then compared with and without the pump light to extract the transmittance change at different spectral wavelength and delay time, which reflects various molecular excited state dynamics such as excited-state absorption, ground-state bleaching and stimulated emission.

In this work, laser photolysis experiments were performed on a LP920 (Edinburgh Instrument) transient absorption spectrometer available with kinetic (PMT) and spectral (ICCD) dual detection modes. The OPO laser (Opolette HE 355 LD UVDM, Optotek Inc.) with output wavelength from 236-2400 nm was employed as the excitation source and the samples were purged with nitrogen to remove oxygen in the solution before measurements.

The detailed experimental setup is shown in Scheme S1. The sample is excited by the intense pulse of the pump source (OPO laser), and xenon lamp is employed as probe light and

passes through the sample at right angles to the path of the pump pulse. After passing through the sample the probe light is directed to a prism spectrometer. The transmitted probe light is then measured either by a PMT (for kinetic analysis at a single wavelength) or by a CCD camera (for spectral analysis at a given time). The transmission properties of the sample before, during, and after the exciting pulse are converted by the detector into electrical signals, and eventually the changes in the transmission properties are converted into changes of optical density.



Scheme S1 Laser photolysis measurement setup

Third-Order nonlinearity measurement

To measure the nonlinear optical responses of BP QDs, the Z-scan setup equipped with a Q-switched Nd:YAG laser (Continuum, Model Surelite SL-I-10) was used. The laser has two output wavelength of 532 nm and 1064 nm, with a FWHM of ~4 ns and a repetition rate of 10 Hz. The temporal and spatial profiles of the output pulses were customized with an approximate Gaussian distribution. The radius of optical spot at the focus point was about 40 μ m. For a detailed description of the setup and data fitting method, please refer to our previous publication.⁴⁻⁶

Other characterizations

The TEM micrographs were obtained using a Tecnai G^2 F30 Field Emission Transmission Electron Microscope at an operating voltage of 300 kV. Samples were dispersed onto holey carbon grids with the evaporation of excess solvent. The height and amplitude features of the products were characterized on an Atomic Force Microscope of Agilent 5500. P element content was determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Agilent 725-ES. Absorption spectra of BP QDs prepared with/without phytic acid



Figure S1 Comparison of absorption spectra of BP QDs prepared with (a) and without (b) phytic acid, and pure phytic acid control (c) in NMP solution.



Comparison of BP solution exfoliated with different assisted molecules

Figure S2 Comparison of photos of BP solution exfoliated with representative different assisted molecules, and corresponding absorption spectra with the solution diluted to 1/4 of their original concentration. The results indicated phytic acid as assisted molecules obtained the best exfoliation effects.

Characterizations of graphene and MoS₂



Figure S3 The TEM images of graphene (a, b) and MoS_2 (c); the High-Resolution TEM image of MoS_2 (d), which exhibited lattice spacings of 0.225 nm corresponding to the (103) plane.



Figure S4 Raman spectra of MoS_2 (a) and graphene (b).

	Samples	λ_{laser} (nm)	E _{laser} (μJ)	Т	β (m/W)	$I_{\rm S}$ (W/m ²)
1	BP QDs	532	3.5	0.81	-1.5×10 ⁻¹⁰	4.0×10^{11}
2	BP QDs	1064	36	0.83	-1.7×10 ⁻¹¹	2.5×10^{12}
3	MoS_2	532	3.5	0.79	-7.0×10 ⁻¹¹	7.1×10^{11}
4	MoS_2	1064	36	0.78	-8.0×10 ⁻¹²	2.7×10^{12}
5	Graphene	532	3.5	0.79	1.2×10 ⁻¹⁰	2.0×10^{14}
6	Graphene	1064	36	0.78	-1.6×10 ⁻¹¹	3.2×10^{12}
7	BP QDs@PEG	532	3.7	0.79	-1.5×10 ⁻¹⁰	4.0×10^{11}
8	BP QDs@PEG	1064	35	0.82	-2.2×10 ⁻¹¹	2.4×10^{12}

Table S1 Summary of the fitted nonlinear optical parameters for the samples.

Open aperture Z-scan data for 2D MoS_2



Figure S5 Open aperture Z-scan data (symbols) and fitted curves (solid curves) for 2D MoS_2 with linear transmittance of ~0.78 in NMP at the excitation of 1064 nm, 36 µJ (a) and corresponding plots of transmittance versus input fluence (b).

Z-scan data for BP QDs conjugated with PEG polymers



Figure S6 Open aperture Z-scan data (symbols) and fitted curves (solid curves) for BP QDs conjugated with PEG polymers with linear transmittance of ~0.81 in NMP at the excitation of 532 nm, 3.7 μ J (a) and 1064 nm, 35 μ J (c), and corresponding plots of transmittance versus input fluence, (b) and (d), respectively.

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