Electronic Supplementary Information

Preparation of large size, few-layer black phosphorus nanosheets via phytic acid-assisted liquid exfoliation

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Experimental details

Materials

Black phosphorous was from Smart Elements (99.998%). Phytic acid, Eosin Y alcohol soluble (EY) and Trioctylphosphine oxide（TOPO）was from Aladdin Chemistry Co. Ltd. N, N-dimethylformamide (DMF, dried), ethanol (EtOH, dried), Cyclohexane were purchased from Rionlon Bohua (Tianjin) Pharmaceutical& Chemical Co. Ltd. Tetrabutylphosphonium tetrafluoroborate was from Shanghai Chengjie Chemistry Co. Ltd. Glucose was obtained from Sinopharm Chemical Reagent Co. Ltd. Na_2HPO_4 was from Tianjing Hongyan Chemical Reagent Factory.

Liquid Exfoliation of Black Phosphorus

Black phosphorus crystals were ground into granular pieces using a mortar and pestle in an argon glovebox. Then 5 mg black phosphorous powder was dissolved into 5 mL DMF in a vial, with the simultaneous addition of 20 mg phytic acid as assisted small molecule. The vial was tightly capped and wrapped with parafilm to prevent air exposure before placing into a bath sonicator customized for long sonication time, operated 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 8-hour sonication at high power without intermittence, the black phosphorus powder transformed into brown solution and was subsequently centrifuged for 5 min at 2000 rpm to precipitate the undissolved phytic acid and non-exfoliated bulk BP. To further remove dissolved phytic acid, a speed of 16,000 rpm was applied and the obtained precipitate was re-suspended in DMF. 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.

Characterization

Spectroscopic measurement

The collection of UV/VIS absorption spectra was performed on a TU-1810 Spectr ophotometer (Beijing Purkinje General Instrument, China). The steady-state fluorescence spectra were collected on a Perkin–Elmer LS 55 fluorescence spectrometer. The NIR Fluorescence was obtained on a FLS 920 fluorescence spectrometer equipped with an InGaAs NIR detector (Edinburgh Instrument, UK). 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 nm-2400 nm was employed as the excitation source and the samples were purged with nitrogen to remove oxygen in the solution before measurements.

Other characterizations

The size and morphology of samples were characterized using field-emission scanning electron microscopy (FE-SEM, Hitachi S4800) at an accelerating voltage of 5.0 kV. The samples for SEM analysis were prepared by dripping the sample onto silicon wafer. The TEM micrographs were obtained using a Tecnai G^2 F20 Field Emission Transmission Electron Microscope equipped with energy-dispersive X-ray (EDX) spectroscopy. 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. X-ray photoelectron spectroscopy (XPS) was performed on AXIS Ultra. P element content was determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Agilent 725-ES.

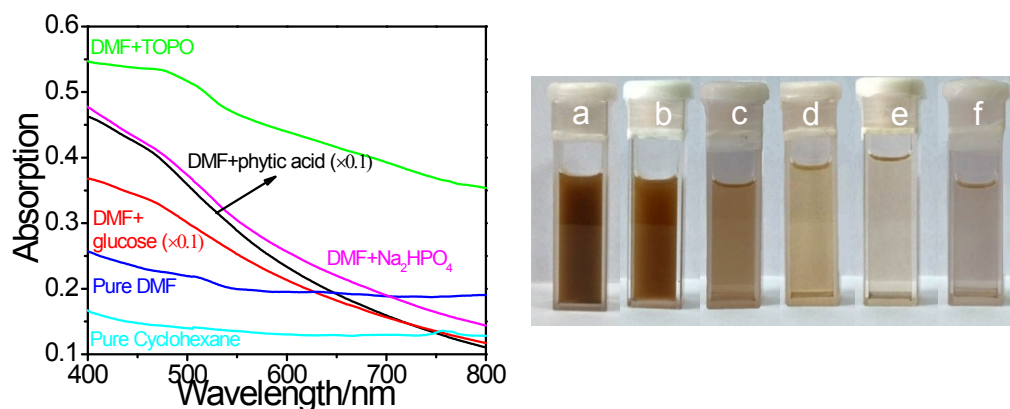**Comparison of BP solution exfoliated with different assisted molecules**

Figure S1 Left: comparison of absorption spectra of BP solution exfoliated with representative different assisted molecules. The two with phytic acid and glucose were much more concentrated and were 10 times diluted; Right: photos of BP solution exfoliated with different assisted molecules: (a) DMF+ phytic acid; (b) DMF+glucose; (c) DMF+TOPO; (d) DMF+Na_2HPO_4; (e) pure DMF ; (f) pure cyclohexane.

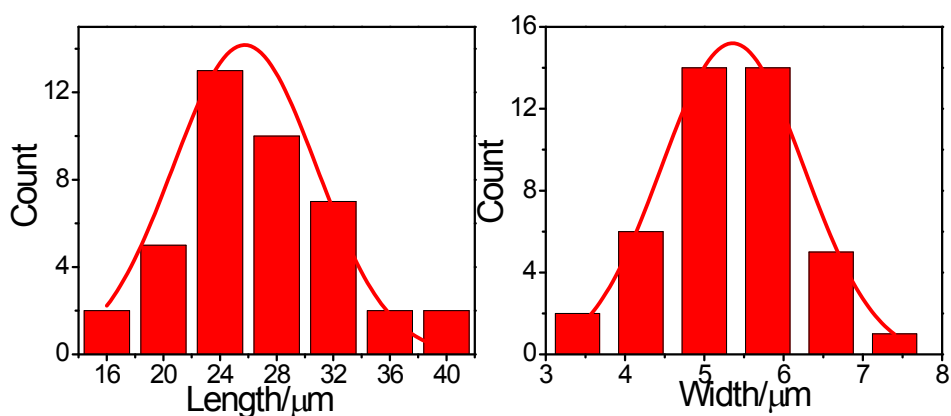**Size histograms of ~50 BP nanosheets**

Figure S2 The size histograms of ~50 nanosheets verified the homogeneity of the products, which mainly demonstrated length of ~24-28 μm and width of ~4-6 μm.
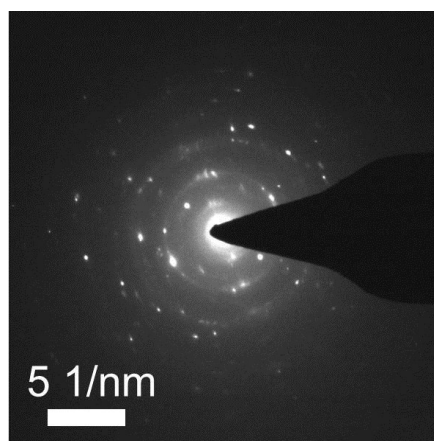
SAED patterns of BP nanosheets

Figure S3 SAED patterns of BP nanosheets. High-quality patterns of BP nanosheets were hard to acquire due to their damaged crystalline structure by the electron beam during measurement.

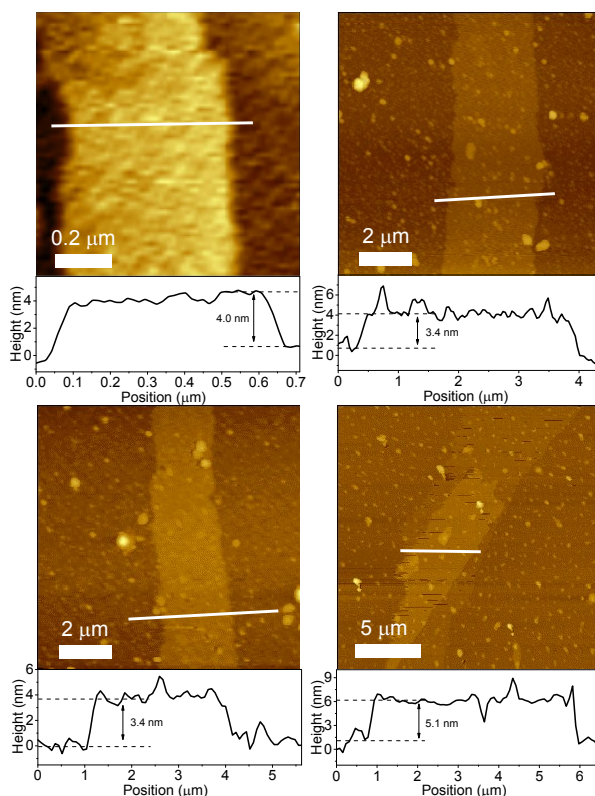**AFM images and height profiles of different size nanosheets**

Figure S4 AFM images and height profiles of different size nanosheets, with typical height of ~3-4 nm.

The molecular extinction coefficient determination of BP nanosheets
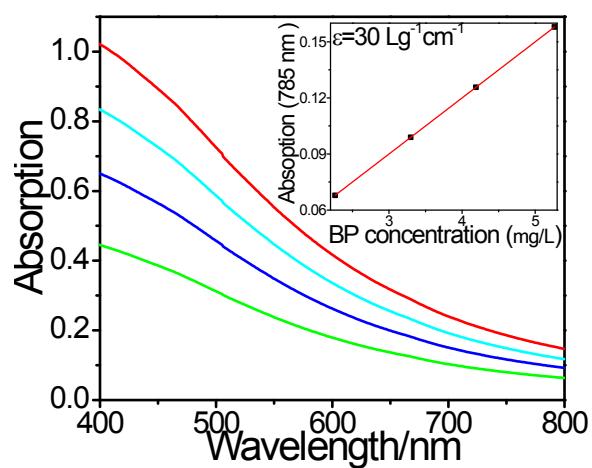

Figure S5 The molecular extinction coefficient determination of BP nanosheets. Even though at 785 nm, the value was still as large as 30 L g^{-1}cm^{-1}.
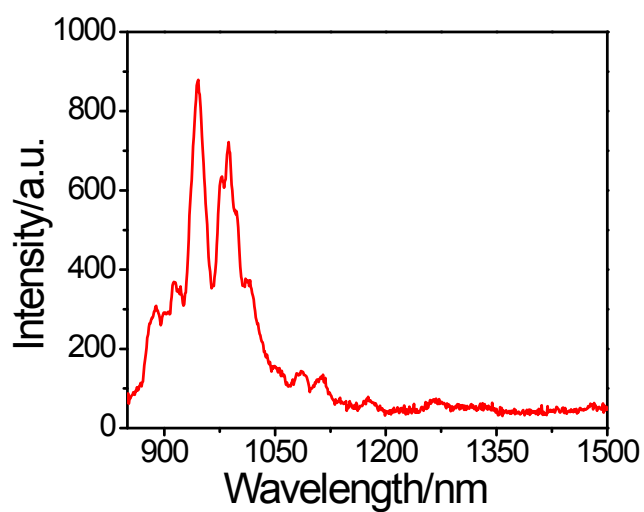
NIR fluorescence of BP nanosheets

Figure S6 NIR fluorescence of BP sheets at the excitation of 510 nm with an 850-nm cut-off filter.

Fitting methods for laser photolysis experiments

Transient decay measurements at a single wavelength detected by PMT detectors were used to extract lifetime components of relevant samples. Each probe wavelength can be fitted by a sum of up to four exponentials with a least-squares-fitting program. The exponential growth or decay process can be expressed in mathematical terms as the following equation (1):

$$I(t) = c_0 + c_1 e^{-\frac{t}{\tau_1}} + c_2 e^{-\frac{t}{\tau_2}} + c_3 e^{-\frac{t}{\tau_3}} + c_4 e^{-\frac{t}{\tau_4}}$$

eq. (1)

where $I(t)$ is the decay model reflecting the response of the sample to an infinitely short excitation, and c_0 is the background, c_1, c_2, c_3, c_4 the pre-exponential factors reflecting the weight of corresponding characteristic lifetime components of τ_1, τ_2, τ_3 and τ_4, respectively. Positive pre-exponential factors indicate decay processes whereas negative values are characteristic for growth processes.

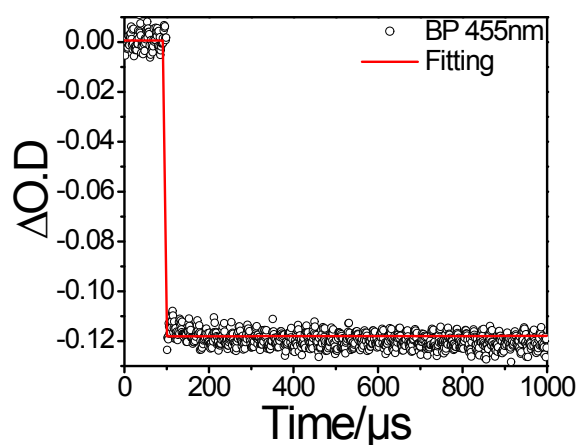**Data fitting for ground state bleaching of BP nanosheets**

Figure S7 Ground state bleaching of BP nanosheets probed at 455 nm. The fitted result indicated a very long ground state recovery time on the millisecond scale. The excitation wavelength is 450 nm.

Table S1 Tabulated fitting results of the transient absorption for the mixed EY (40.00 μM) and BP (37.60 μM) at 460 nm (EY$^{+\bullet}$) and 560 nm (^{3}EY*). The percentage numbers in parentheses indicate the corresponding weight ratio of extracted lifetime components and those rise times are specified.

Probe wavelength	τ_1	τ_2	τ_3
460 nm (EY$^{+\bullet}$)	21 μs (rise, 28%)	212 μs (51%)	Long, > ms (21%)
560 nm (^{3}EY*)	22 μs (77%)		Long, > ms (23%)

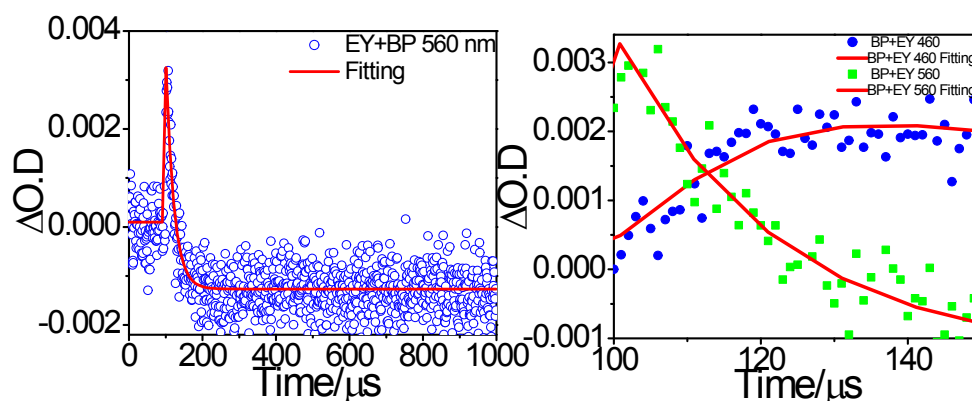**Decay curve at 560 nm for the mixed EY and BP**

Figure S8 Left: decay curve at 560 nm (^{3}EY*) for the mixed EY (40.00 μM) and BP (37.60 μM); Right: The rise at 460 nm (EY$^{+\bullet}$) occurred concomitantly with the decay at 560 nm (^{3}EY*) at early time, strong evidence verifying the oxidative quenching of the excited triplet state of EY.

The Stern-Volmer equation

The Stern-Volmer plots were then employed with the following equation (2): [1-3]

$$\frac{\tau_0}{\tau} = 1 + k\tau_0[Q]$$

eq. (2)

Where τ_0 is the lifetime of $^3EY^*$ at 560 nm, τ the corresponding reduced lifetime with increased BP concentration of $[Q]$, and k the electron transfer rate constant from EY to BP. Through linear fitting, a slope of 7.73×10^4 M^{-1} was deduced and the electron transfer rate constant k was estimated to be $\sim 3.24 \times 10^8$ M^{-1} s^{-1}.

1.   Yang, X.-J.; Chen, B.; Zheng, L.-Q.; Wu, L.-Z.; Tung, C.-H., Highly efficient and selective photocatalytic hydrogenation of functionalized nitrobenzenes. *Green Chem.* **2014,** *16* (3), 1082.
2.   Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*. 2nd ed.; Kluwer Academic, Plenum Publishers: New York, **1999**.
3.   Gao, L.-F.; Wen, T.; Xu, J.-Y.; Zhai, X.-P.; Zhao, M.; Hu, G.-W.; Chen, P.; Wang, Q.; Zhang, H.-L., Iron-Doped Carbon Nitride-Type Polymers as Homogeneous Organocatalysts for Visible Light-Driven Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2016,** *8* (1), 617-24.