# Electronic Supplementary Information

## A black/red phosphorus heterostructure for efficient

## visible-light-driven photocatalysis

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### **Experimental section:**

**Synthesis.** Purification of red phosphorus: In a typical experiment, 2 g of commercial red phosphorus (AR, >99 %) was added into 15 mL H<sub>2</sub>O, and hydrothermally treated at 200 °C for 12 h in 25 mL autoclave to clear the oxide layers. After being milled for 0.5 h using agate mortar (size: ~5-15  $\mu$ m), the red phosphorus could be subjected to photocatalytic application or as the precursor for the BP-RP heterostructure.

Fabrication of BP-RP heterostructures: the BP-RP heterostructures were prepared by means of mechanical ball milling at ambient temperature and pressure. The purified red phosphorus powder and agate balls (diameter: 3/8 and 3/16 in.) were put into a agate vial having a capacity of 50 cm<sup>3</sup> with a ball to powder ratio of 20:1 (red phosphorus 1.6 g), and the ball milling process was conducted under an Ar atmosphere for 45 min, 2 h and 12 h with the rotation speed of 450 rounds/ min.

The black phosphorus was used as received and confirmed by XRD pattern (Fig. 1b).

Commercial CdS (A. R. size <100 nm) was directly used here without further purification.

**Characterization.** SEM was measured on a FEI Quanta 400 microscope. The TEM was measured by a Philips Tecnai F20 instrument and a CM-120 microscope (Philips, 120 kV). TEM images were processed by Digital Micrograph (Gatan, USA). The powder XRD patterns were recorded on a Rigaku SmartLab X-ray diffractometer using Cu K $\alpha$  irradiation ( $\lambda = 1.5406$ Å). The accelerating voltage and applied current were 40 kV and 40 mA. UV–vis diffuse reflectance spectra were achieved using a

UV–vis spectrophotometer (Cary 100 scan spectrophotometers, Varian). FT-IR spectra were recorded on a Perkin Elmer Frontier spectrometer on samples embedded in KBr pellets. X-Ray photoelectron spectroscopy (XPS) was performed using a Sengyang SKL-12 spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer and twin anode Mg K $\alpha$  radiation (1253.6 eV) or Al K $\alpha$  radiation (1496.3 eV) X-ray sources.

**Photoconductivity, photocatalytic experiments and OH radicals test.** Photoelectric properties measurements were carried out on an electrochemical workstation (CHI 660C, Shanghai Chen Hua Instrument Company, China). A conventional three-electrode system was used for photoelectric properties test: the work electrode was connected with the as-prepared wafers directly, a Ag/AgCl electrode as the reference electrode and a platinum wire electrode as the counter electrode. The electrolyte solution was 0.1 M NaSO<sub>4</sub> in water. The photocurrent response to on–off cycles was recorded under the illumination of a fiber optics equipped with a tungsten lamp (Cole-Parmer illuminator, 41720 series). The light intensity was about 200 mW/cm<sup>2</sup>.

Photocatalytic evaluation of all the powder samples (red phosphorus, black phosphorus, BP-RP heterostructures and CdS) under visible light (VL) irradiation was performed using a 300 W xenon lamp with a UV cutoff filter ( $\lambda < 420$  nm) as light source. The VL intensity was measured by a light meter (LI-COR, USA) and the light intensity for the experiments was fixed at 193 mW/cm<sup>2</sup>. In a typical test, 50 mg catalyst was placed in 50 mL 10 ppm RhB solution. Before irradiation, this solution

was magnetically stirred in dark for 60 min to ensure the establishment of an adsorption/desorption equilibrium between the photocatalyst and organic pollutants. At different time intervals, 1.5 mL of the sample was collected and test using UV-vis spectrometer. The concentration of RhB was measured according to the absorbance at 550 nm.

The dark control experiments (labeled "in dark") were performed using the same devices and procedure. However, during the experiment, the light source kept closed.

The dynamic experiments during the initial 30 minutes were performed using the same devices and procedure. However, the data was recorded every 10 minutes.

A stock terephthalic acid solution with final concentrations of  $4 \times 10^{-4}$  M terephthalic acid and  $2 \times 10^{-3}$  M NaOH was prepared. 20 mg of BP-RP heterostructure powder was placed in 20 mL of the stock solution. The solution was irradiated by a 300 W halogen lamp (with a 400 nm filter). At every 10 min, 1.5 mL of the suspensions were collected and centrifuged. The resulted supernatants were subjected to PL measurements. Fluorescence spectra of generated 2-hydroxyterephthalic acid were measured on a Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 320 nm.

#### DFT calculations for Black phosphorus.

VASP[1] computational package was used for all the calculations in this article. We applied projector-augmented-wave method with HSE06 functional.[2] Electronic convergence limit was set to be  $1 \times 10^{-5}$  eV. Optimization of atomic coordinates was considered to be converged if Hellmann–Feynman force was smaller than  $1 \times 10^{-2}$ 

 $eVÅ^{-1}$ . The Black phosphorus slab (111) consists of 5-layers of P atoms. The 2 layers at the bottom were fixed during optimization. The vacuum region is about 10 Å in height. We applied Monkhorst–Pack scheme  $6 \times 6 \times 1$  for k-point selection and resulted in 29 irreducible k-points.



Fig. S1 A EDX spectrum of BP-RP Heterostructure.



**Fig. S2** (a) A low-resolution TEM image of the BP-RP heterostructure, HRTEM images of (b) crystalline black phosphorus, (c) amorphous red phosphorus and (d) their interface in the BP-RP heterostructure. (HRTEM image also see **Fig. 1c**)



Fig. S3 TGA curves of the BP-RP heterostructure and pure red phosphorus.

As both red phosphorus and the BP-RP heterostructure are composed of  $P^0$  atoms, they could not be differentiated by common spectroscopic methods. Herein, TGA was used to roughly estimate the weight percent of black phosphorus in the heterostructure. The pure red phosphorus would not oxidize until 370 °C (*weight loss value* denoted as  $m_{370}$  in Fig. 1, blue curve), while the oxidation of the heterostructure starts at 300 °C (denoted as  $m_{300}$  in Fig. 1, blue curve). All the phosphorus (black and red) is estimated to be oxidized at the top point (denoted as  $m_{top}$ ).

. Therefore, the composition of black phosphorus is estimated as follow:

Composition (black phosphorus) =  $(m_{370}-m_{300})/(m_{top}-m_{300})$ 

The results from TGA measurements show approximately 50 wt% of black phosphorus in the heterostructure obtained after milling for 2 h.

Black phosphorus in other heterostructures is also estimated using this method (c.a. 30 % by milling 45 min and c.a. 70 % by milling 12 h).



Fig. S4 FT-IR spectra of black phosphorus, red phosphorus and BP-RP heterostructure.



Fig. S5 P 2p spectrum of BP-RP Heterostructure.



**Fig. S6** Photocurrent response of the BP-RP heterostructure with a bias potential of -0.2 V (*vs*.Ag/AgCl), under irradiation of visible light.



Fig. S7 Optical image of RhB degradation over the BP-RP heterostructure under visible light irradiation.



**Fig. S8** VLD photocatalytic degradation of RhB over CdS, red phosphorus and BP-RP heterostructure within initial 30 min (data recorded every 10 min), and their kinetics curves accordingly.



**Fig. S9** (a) The optical images and (b) XRD patterns of heterostructures obtained after milling for 45 min (30 % black phosphorus) and 12 h (70 % black phosphorus); (c) and (d) their corresponding TGA curves.



Fig. S10 VLD photocatalytic degradation of RhB over heterostructures with different

contents of black phosphorus.



**Fig. S11** The figure shows the DFT band structure for black phosphorus slab with (111) surface exposed.

Our calculated band gap value of black phosphorus  $E_g=0.32$  ev, which was consistent with the ones reported in the range of 0.31-0.36 eV. [3-5]

#### Reference

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