Supporting Information

Bandgap-tunable black phosphorus quantum dots: visiblelight-active photocatalysts

Yong-Jun Yuan,*a Shuhui Yang,a Pei Wang,a Yan Yang,a Zijian Li,a Daqin Chen,*a Zhen-Tao Yu,*b Zhi-Gang Zoub

^{a.}College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, People's Republic of China

^b·National Laboratory of Solid State Microstructures and Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory for Nano Technology, College of Engineering and Applied Science, Nanjing University, Nanjing 210093, People's Republic of China.

Materials: N-methyl-2-pyrrolidone (NMR, 99.9%, anhydrous), oleic acid (90%) and rhodamine B were purchased from Aladdin company. (Shanghai, China). Black phosphorus crystals were obtained from Xianfeng Nano Materials Tech Co. Ltd. (Nanjing, China). All the materials were used as received without any further purification.

Preparation of BPQDs: In a typical experiment for the preparation of BPQDs-1, 10 mg of BP power was added into 100 ml of NMP and oleic acid (6/4, v/v) solution in a 200 ml flask. After addition of 40 mg NaOH, the mixture was sonicated at room temperature at the power of 100 W for 30 min, and then heated at 150 °C to obtain a brown suspension solution. The resultant solution was centrifuged for 15 min at 7000 rpm. The BPQDs-2 sample was synthesized through a similar synthetic procedure in pure NMP solution.

Characterization: UV-visible absorption and photoluminescence spectra were analyzed by using Edinburgh FS5 spectrofluorometer. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HR-TEM) images of BPQDs were performed using a JEOL JEM 2010 transmission electron 200 accelerating voltage. time-resolved microscope, using а KV The photoluminescence spectra of BPQDs were recorded on an Edinburgh LifeSpec II spectrofluorometer equipped with a 375 nm picoseconds laser as the light source. The dimensional images of BPQDs were measured on an Atomic force microscopy (XE-100E, PSIA, Korea) in non-contact mode. The chemical state of BPQDs was analyzed on a VG ESCALAB MKII X-ray photoelectron spectroscopy (XPS) with an Al Kα X-ray source and a charge neutralizer. The total organic carbon (TOC) was determined by using a Bioritech (model 700) analyzer.

Photocatalytic experiment: The photocatalytic performance of all as-prepared BPQDs photocatalysts was evaluated by photodegradation of RhB aqueous solution under visible light irradiation. In a typical photocatalytic degradation of RhB experiment, 250 ml of ethanol aqueous solution contains 16 mg/L BPQDS and 20 mg/L RhB was exposed to a 300 W Xenon lamp equipped with a UV cutoff filter (λ >

420 nm). During irradiation process, 3 mL of reaction solution was taken from the reactor at time intervals of 30 minutes. The concentration of RhB was analyzed by measuring its characteristic absorption peak at 553 nm using a model 721 spectrophotometer (Shanghai Second Analytical Instrument Factory, Shanghai, China).

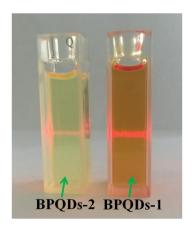


Figure S1. Typical Tyndall effect of BPQDs samples in ethanol solution.

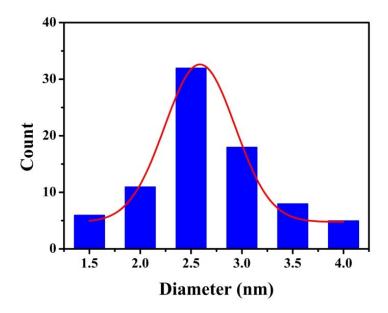


Figure S2. Statistical analysis of the size of BPQDs-1 determined by TEM.

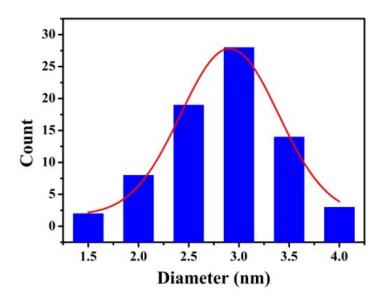


Figure S3. Statistical analysis of the size of 50 BPQDs-2 sample determined by TEM.

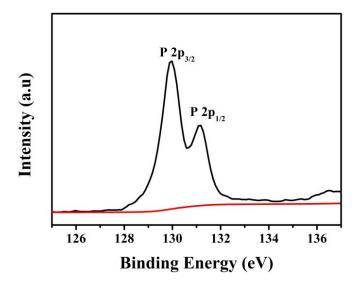


Figure S4. High-resolution XPS spectra of P 2p of BPQDs-1 sample.

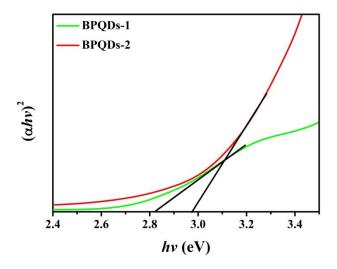


Figure S5. Plots of $(ahv)^2$ vs hv for the as-prepared BPQDs sample.

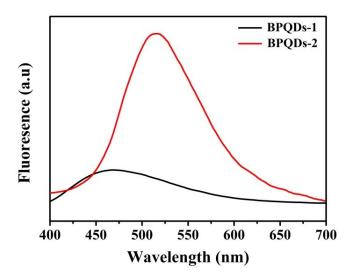


Figure S6. Fluorescence of BPQDs-1 and BPQDs-2 samples under the same measure condition.

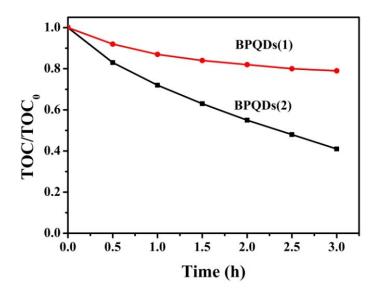


Figure S7. Kinetics of disappearance of total organic carbon (TOC) under visible light irradiation.

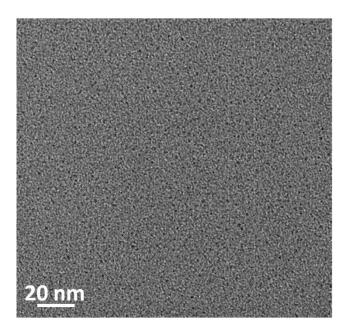


Figure S8. TEM image of BPQDs-1 after photocatalytic reaction.

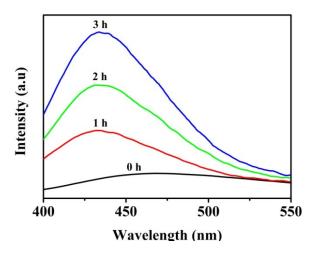


Figure S9. Time-dependent fluorescence emission spectra of TAOH formed by the reaction of TA with ·OH radicals generated by the BPQDs photocatalyst under visible-light irradiation.