Metal-free heterojunction of black phosphorus/oxygen-enriched porous g-C_3N_4 as efficient photocatalyst for Fenton-like cascade water purification

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Supporting information

Table of Contents

S1. Experimental section

Materials:

Urea, *N*-methyl pyrrolidone (NMP), 5,5-dimethyl-l-pyrroline-*N*-oxide (DMPO), potassium chloride (KCl), methyl orange (MO), rhodamine B (RhB) and catechol were purchased from Tokyo Chemical Industry. Cerium sulfate ($Ce(SO_4)_2$), potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium hexacyanoferrate ($K_4[Fe(CN)_6]$), sodium sulphate (Na_2SO_4), dibasic sodium phosphate (Na_2HPO_4), sodium dihydrogen phosphate anhydrous (NaH_2PO_4) and Nafion solution (10 vol%) were bought from Sigma Aldrich. Sulfuric acid (H_2SO_4), nitric acid (HNO_3), isopropanol (IPA) and methanol (CH_3OH) were purchased from Sinopharm Chemical ReagentCo., Ltd (China). Bulk black phosphorus (BP, XF161, purity > 99.998%) was purchased from Nanjing XFNANO Materials Tech Co., Ltd.

Synthesis of porous g-C_3N_4 nanosheets (PCN): 20 g of urea and 20 mL of deionized water were added in an alumina crucible, the alumina crucible was ultrasonicated for 5 min to form a homogeneous dispersion before was placed in the muffle furnace. The porous g-C_3N_4 nanosheets were obtained at high temperature by the thermal polycondensation of urea along with the pore-making effect of water. The temperature was rises to 400 ^oC at a ramp rate of 10 ^oC /min and maintained for 1h, then the temperature rises to 450 ^oC at the same rate and maintained for another 1 h. The light yellow porous g-C_3N_4 nanosheets were observed after the progress, which was labeled as PCN. In addition, bulk g-C_3N_4 was obtained in the same procedure without the addition of water.

Synthesis of oxygen-enriched porous g-C_3N_4 nanosheets (OPCN): The oxygen-enriched PCN were prepared by acid treatment, 1 g PCN were dispersed in the mixture acid of H_2SO_4 (5 mL) and HNO_3 (10 mL) carefully and stirred overnight, then the products were poured into 500 mL H_2O and stand still for 30 min, remove the acid though centrifugation and wash thoroughly with deionized water and ethanol, dried at 60 ^oC for 8 h for further use. The oxidized PCN was labeled as OPCN.

Synthesis of BP nanosheets: BP nanosheets were synthesized by NMP liquid

exfoliation method. Typically, 20 mg of bulk black phosphorus were dispersed in 25 mL of NMP, then the suspension were sonicated in ice water for 12 h by using an ultrasonic homogenizer (SCIENTZ-IID) with a power of 400 W. Afterward, the obtained brown solution was centrifuged at 3000 rpm for 15 min to remove non-exfoliated bulk black phosphorus, collect the supernatant for further use.

Synthesis of BP/OPCN heterostructures: BP/OPCN heterostructures were synthesized by an electrostatic self-assembly method. In brief, 0.1 g of the OPCN was dispersed into a certain amount of BP/NMP solution (ensure the quality of BP nanosheets are 2 mg, 4 mg, 6 mg, 8 mg and 10 mg, respectively), the suspension was kept stirring overnight at room temperature under Argon atmosphere. Then the products were collected by centrifugation and washed with EtOH for three times, and dried for 6 h under vacuum at 60 ^{o}C. The products were named according to mass ratios of BP nanosheets to OPCN, namely 2% BP/OPCN, 4% BP/OPCN, 6% BP/OPCN, 8% BP/OPCN and 10% BP/OPCN, respectively.

Photocatalytic H_2O_2 production: In brief, 50 mg of samples was suspended into 50 mL of aqueous solution (volume ratio of water and isopropanol is 9:1, isopropanol is hole scavengers) in a Pyrex test tube equipped with circulating condensate, and the suspension was stirred in dark for 30 min to reach the absorption-desorption equilibrium. Then, open the 300 W Xenon lamp (PLS-SXE 300) (460 mW cm^{-2}) and start the reaction, sampling 1 mL of solution every hour and filter with a 0.45 μm Millipore filter to remove the powder sample. Then the transparent liquid were injected into $Ce(SO_4)_2$ solution to determine the H_2O_2 concentration. All these reactions were executed in the air condition unless specifically stated under Ar or O_2 atmosphere.

H_2O_2 concentration measurement: In this work, $Ce(SO_4)_2$ titration method was used to measure the H_2O_2 concentration. Initially, 200 mL of $Ce(SO_4)_2$ solution (1 mM) was prepared, 0.2 mmol $Ce(SO_4)_2$ was dispersed into 200 mL 0.5 M H_2SO_4 solution, and fully ultrasonic treatment to obtain a bright yellow transparent solution. 10 mL of 1 mM $Ce(SO_4)_2$ solution was added into the 1 mL of obtained liquid and kept for 10 min to ensure the reaction completely ($2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^+ + O_2$), then

measure the concentration of Ce^{4+} before and after the reaction by UV spectroscopy to calculate the amount of H_2O_2 produced.

H_2O_2 decomposition behavior: The H_2O_2 decomposition behaviors of the as-prepared samples were carried out to evaluate the stability of produced H_2O_2 in the photocatalytic system. In brief, 50 mg samples were added into 50 mL of H_2O_2 solution (1 mM) and dispersed evenly. Open the light source to start the decomposition reaction and sampling 1 mL of the reaction solution every 15 min to measure the remaining H_2O_2.

Photocatalytic degradation of MO: Similarly, 50 mg of photocatalysts were dispersed into 100 mL of MO solution (20 ppm, 100 mL of H_2O or 90 mL of H_2O + 10 mL of IPA) in a Pyrex test tube. The mixture solution was stirred under dark for half an hour to achieve adsorption/desorption equilibrium, then turn on the 300 W Xenon lamp to start the reaction. Sampling 3 mL of solution at a certain time, remove the solids by centrifugation and filtration, then measure the solution concentration by UV-Vis spectrophotometer. Multiple cycles tests were also executed to determine the recyclability of the samples for wastewater purification.

S2. Characterization

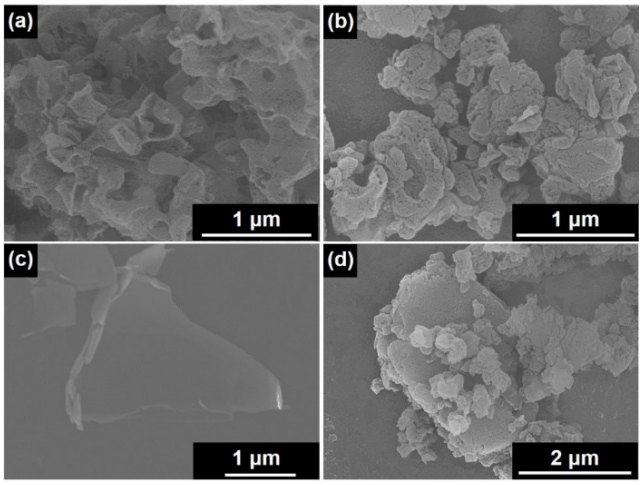

Fig. S1 SEM images of (a) PCN, (b) OPCN, (c) BP, and (d) 6% BP/OPCN heterostructure.

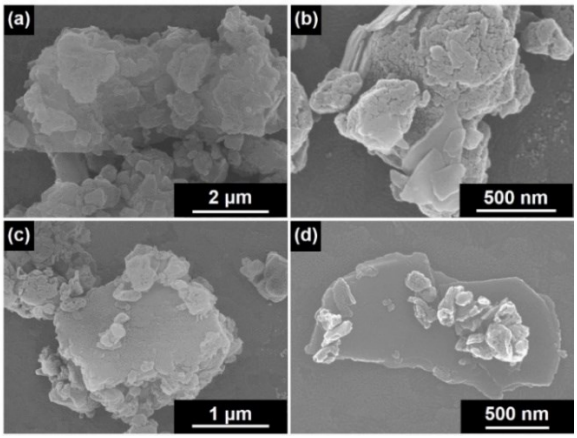

Fig. S2 SEM images of (a) 2% BP/OPCN, (b) 4% BP/OPCN, (c) 8% BP/OPCN, and (d) 10% BP/OPCN heterostructure.

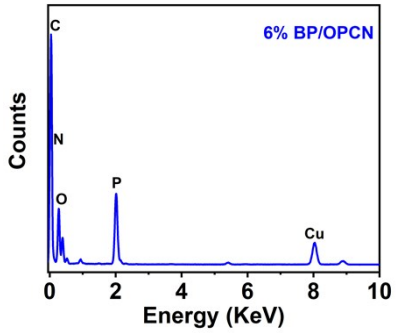

Fig. S3 TEM-EDX of 6% BP/OPCN.

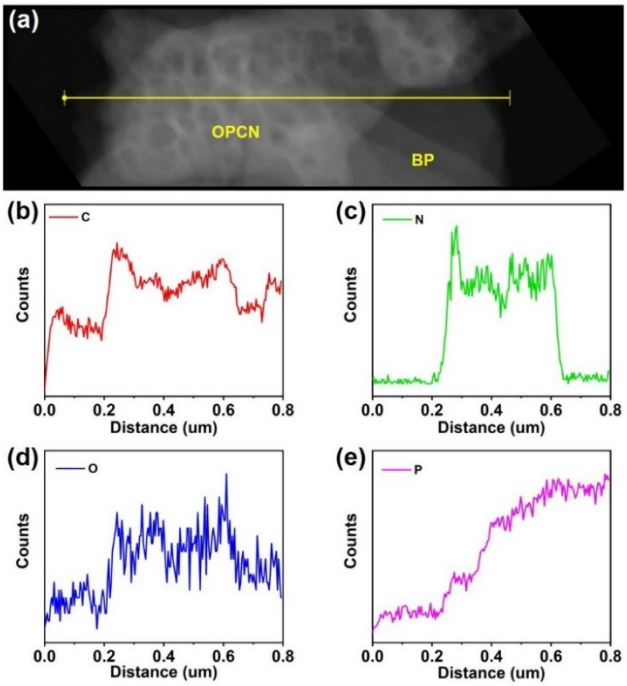

Fig. S4 (a) STEM image of 6% BP/OPCN, the corresponding linear distributions of (b) C, (c) N, (d) O and (e) P.

Table S1. Atomic % of PCN and OPCN

Element	Atomic % (PCN)	Atomic % (OPCN)
C 1s	48.99	47.19
N 1s	48.55	46.28
O 1s	2.46	6.53

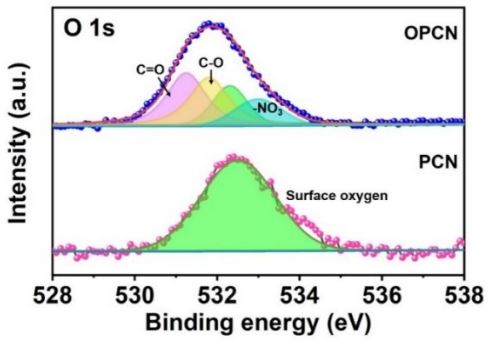

Fig. S5 High-resolution XPS spectra of O 1s.

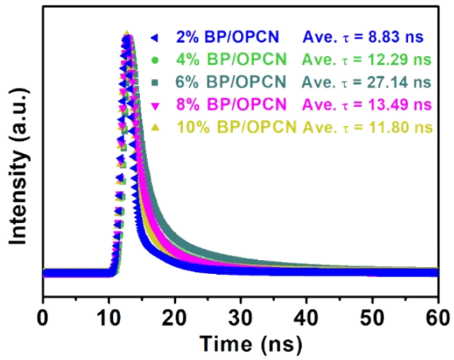

Fig. S6 TRPL spectra of BP/OPCN hybrids.

Table S2. TRPL datas of BP/OPCN hybrids

	2% BP/OPCN	**4% BP/OPCN**	**6% BP/OPCN**	**8% BP/OPCN**	**10% BP/OPCN**
τ_1 / ns	3.06	5.01	10.98	4.91	4.45
τ_2 / ns	6.12	10.01	21.96	9.82	8.89
τ_3 / ns	12.25	20.03	43.91	19.64	17.79
A_1 / %	31.64	43.17	38.90	35.47	37.51
A_2 / %	8.35	12.45	18.04	9.38	10.02
A_3 / %	60.01	44.38	43.06	55.15	52.47
Ave. τ / ns	8.83	12.29	27.14	13.49	11.8

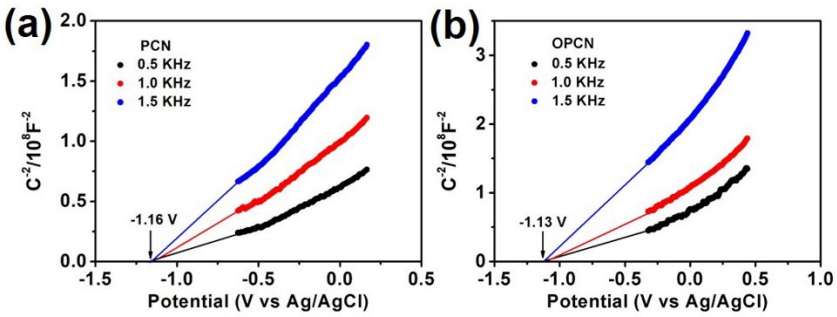

Fig. S7 Mott-Schottky plots of (a) PCN and (b) OPCN.

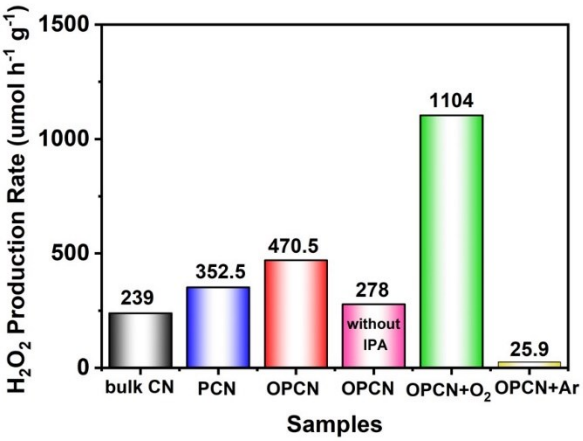

Fig. S8 Photocatalytic H_2O_2 production rate over different samples.

Table S3 Comparison of H_2O_2 generation rate of g-C_3N_4-based materials

Catalysts	**Light Source**	**Reaction Conditions**	**H_2O_2 generation Rate (μmol h^{-1} g^{-1})**	**Reference**
BP/OPCN	**300 W Xe lamp, simulated solar**	**Aqueous solution (50 mL, IPA 10 *vol.* %)**	**3463**	**This work**
g-C_3N_4/MI	300 W Xe lamp, λ > 420 nm	Aqueous solution (50 mL, TEOA 20 *vol.* %)	32	[S1]
g-C_3N_4/CNTs	300 W Xe lamp, λ ⩾ 400 nm	Aqueous solution (100 mL, HCOOH 5 *vol.* %)	326	[S2]
Ti_3C_2/g-C_3N_4	300 W Xe lamp, λ > 420 nm	Aqueous solution (50 mL, IPA 10 *vol.* %)	132	[S3]
CoP/g-C_3N_4	300 W Xe lamp, λ > 420 nm	Aqueous solution (20 mL, EtOH 10 *vol.* %)	70	[S4]
BP/CN	300 W Xe lamp, λ > 420 nm	Aqueous solution (30 mL, IPA 10 *vol.* %)	540	[S5]

PEI/g-C_3N_4	100 W Xe lamp with AM 1.5 air filter	H_2O (20 mL)	208.1	[S6]
rGO/BPQDs	300 W Xe lamp, 420 nm < λ < 780 nm	H_2O (50 mL)	60.5	[S7]
g-C_3N_4/BDI	Solar simulator, λ > 420 nm	H_2O (30 mL)	17	[S8]
g-C_3N_4/PDI/rGO	2000 W Xe lamp, λ > 420 nm	H_2O (30 mL)	24.2	[S9]
3DOM g-C_3N_4/PW	300 W Xe lamp, λ > 320 nm	H_2O (100 mL)	24	[S10]
g-C_3N_4/PWO	300 W Xe lamp, λ ⩾ 420 nm	H_2O (100 mL)	63	[S11]
g-C_3N_4/CoWO	300 W Xe lamp, λ ⩾ 420 nm	H_2O (100 mL)	97	[S12]
Phosphorus-doped porous g-C_3N_4	300 W Xe lamp, λ > 400 nm	H_2O (15 mL)	1968	[S13]

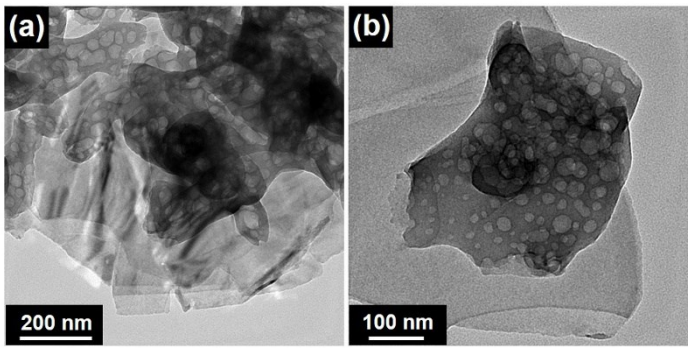

Fig. S9 TEM images of 6% BP/OPCN hybrid after the multicycles experiments.

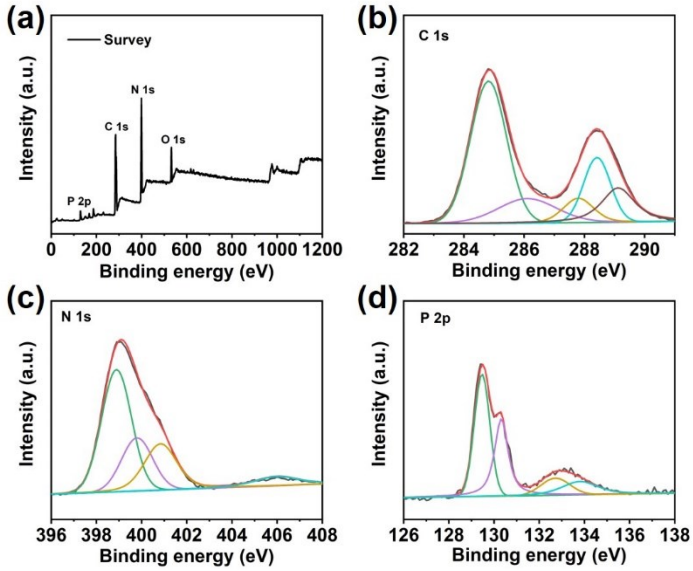

Fig. S10 XPS spectra of 6% BP/OPCN after multicycles experiments.

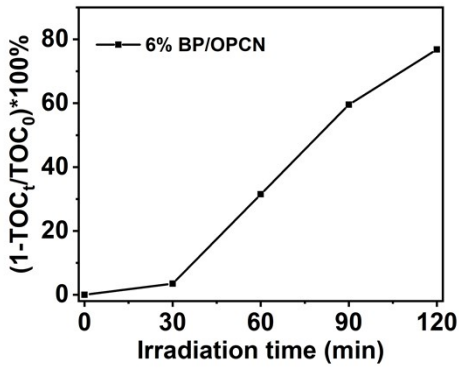

Fig. S11 The mineralization results of MO (20 ppm) degradation over 6% BP/OPCN hybrid without IPA.

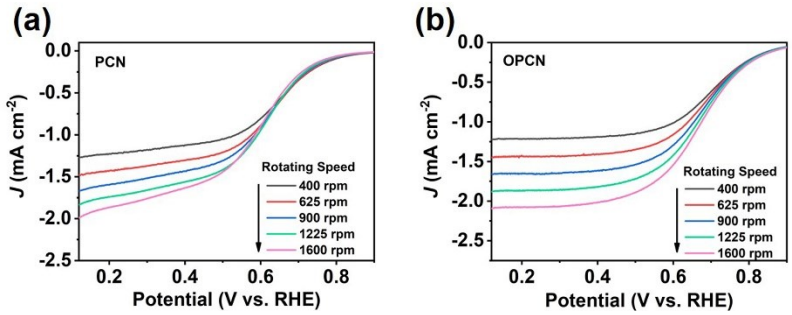

Fig. S12 LSV curves of (a) PCN and (b) OPCN.

RDE analysis of oxygen reduction reaction (ORR) was used to investigate the pathway and selectivity of O_2 reduction. The average number of electrons (n) involved

in the ORR reaction bese on the following equations (Eqs. 1-2):

$$j^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6} \quad (2)$$

j is the current density, j_k is the kinetic current density, ω is the rotating speed (rad/s), F is the Faraday constant (96485 C mol^{-1}), v is the kinetic viscosity of water (0.01 cm^2 s^{-1}), C_0 is the bulk concentration of O_2 in water (1.26×10^{-3} mol cm^{-3}), and D_0 is the diffusion coefficient of O_2 (2.7×10^{-5} cm^2 s^{-1}), respectively.

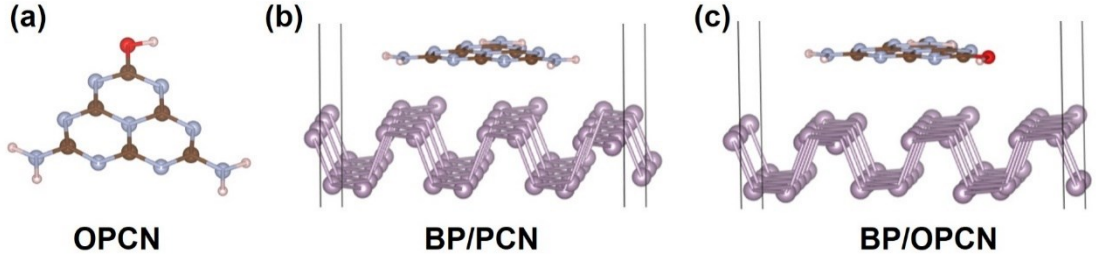

Fig. S13 The established model of (a) OPCN, (b) BP/PCN and (c) BP/OPCN.

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