Supporting Information

Engineering black phosphorus to porous g-C_3N_4-metal-organic framework membrane: a platform for highly boosting photocatalytic performance

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Experimental

Materials: Urea and succinic anhydride were purchased from Sigma Aldrich. $Cu(NO_3)_2\cdot 3H_2O$, 1,3,5-Benzenetricarboxylic acid (H_3btc), 5,5-dimethyl-l-pyrroline-*N*-oxide (DMPO) and *N*-methyl pyrrolidone (NMP) were purchased from Tokyo Chemical Industry. *N, N*-Dimethylformamide (DMF), Triethanolamine (ETOA) and ethanol were purchased from Sinopharm Chemical ReagentCo., Ltd (China). Bulk black phosphorus (BP, XF161, purity>99.998%) and conductive carbon nanotube film (CNF) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. All the chemicals were analytical reagent and used without further purification.

Materials preparation*:* For Porous g-C_3N_4, porous g-C_3N_4 was synthesized by the thermal polycondensation of urea and the water act as the foaming agent. In detail, 5 g urea was dissolved into 20 mL deionized water, the clear solution was transferred into an alumina crucible which was placed in a muffle furnace. The mixture was heated at 400 ^oC for 1 h at a ramp rate of 10 ^oC /min, and then the temperature rises to 450 ^oC at the same rate and maintained for another 1 h. After the muffle furnace cooled to the room temperature, the light yellow porous g-C_3N_4 was observed, and labeled as PCN.

For PCN-HK, firstly, the amino (-NH_2) groups on the surface of porous g-C_3N_4 were modified by carboxyl. 0.5 g succinic anhydride and 50 mg PCN were dissolved in 25 mL DMF, the mixture were ultrasonicated for 10 min, and then was stirred for 12 h. The suspension was washed for three times with ethanol, and dried at 60 ^oC for 8 h for further use. The decoration of PCN by MOF was executed through a step-by-step assembly strategy. Typically, 20 mg of carboxylated PCN was dispersed in 25 mL of $Cu(NO_3)_2\cdot 3H_2O$ ethanol solution (10 mM) and was stirred for 15 min at room temperature, the suspension was washed with EtOH for three times. Then the products were dispersed in 25 mL of 1, 3, 5-Benzenetricarboxylic acid ethanol solution (5 mM) and were stirred for further 30 min evenly, then to be washed with EtOH. This process was repeated for several times, finally, the PCN modified by HKUST-1 was obtained and labeled as PCN-HK.

For ultrathin black phosphorus (BP) nanoflakes, the ultrathin BP nanoflakes were prepared by using a basic NMP solvent exfoliation. In detail, 20 mg bulk BP was dispersed into 20 mL of NMP solution, and the mixture was sonicated for 6 h by employing an ultrasonic homogenizer (SCIENTZ-IID) under ice cooling at 80 W output power, the ultrasound probe was operated for 2 s and stopped for 2 s. The obtained brown yellow suspension was centrifuged at 3000 rpm for 10 min to remove the unexfoliated particles and the collect the supernatant for further use.

For BP/PCN-HK and BP/PCN heterojunctions, BP/PCN-HK hybrids were synthesized as the following process: 50 mg of PCN-HK were dispersed in 20 mL of NMP and was ultrasonicated to form a homogeneous dispersion, then a certain amount of BP NMP solution was added, the suspension was protected by Argon and then was stirred overnight, the products were collected by centrifugation, and washed with EtOH for three times. The weight ratios of BP to PCN-HK were 2, 4, 6, 8 and 10 wt%, then the samples were labelled as 2% BP/PCN-HK, 4% BP/PCN-HK, 6% BP/PCN-HK, 8% BP/PCN-HK and 10% BP/PCN-HK, respectively. In addition, BP/PCN heterojunctions were prepared as the same condition except that PCN-HK was replaced by PCN, and marked as 2% BP/PCN, 4% BP/PCN, 6% BP/PCN, 8% BP/PCN, and 10% BP/PCN, respectively.

For BP/PCN-HK membrane, the above BP/PCN-HK ethanol solution was centrifuged at 5000 rpm for 5 min, and the supernate was used to fabricate the photocatalyst membrane. Then the dispersion was filtrated under vacuum through the conductive carbon nanotube film (CNF) support, and the photocatalyst membrane was dried in vacuum at room temperature. The BP/PCN-HK membrane was labelled as BP/PCN-HKM.

Computational details and model: All first-principles calculations were realized in the software Vienna ab-inito simulation package (VASP) in which the exchange-correction functional adopted the Perdew-Burke-Ernzerhof formula under generalized gradient approximation. The projected augemented wave (PAW) method with a cut-off energy of 500 eV was condsiered during self-consistent calcilations. The structural optimizations stopped until the interation of energy and forces satisfied 10^{-4} eV and -0.05 eV/Å. According to the experimental band gap for BP (0.89 eV) and g-C_3N_4 (2.7 eV), bilayer BP and monolayer g-C_3N_4 was constructed as a planar heterojunction structure. The charge density difference $\Delta\rho$ after forming heterojunction was calculated by $\Delta\rho = \rho_{heterojunction} - \rho_{g-C_3N_4} - \rho_{BP}$

in which $\rho_{heterojunction}$, $\rho_{g-C_3N_4}$ and ρ_{BP} are the intrinsic electron density of heterojunction, bare g-C_3N_4 and BP.

***Characterization and photoelectrochemical measurements**:* Scanning electron microscopy (SEM) (Hitachi S-4800), X-ray energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) (Hitachi H600 with 200 kV acceleration voltage), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed to characterize the morphology and composition of the samples. X-ray diffraction (XRD) measurements were collected on a X'Pert-Pro MPD. X-ray photoelectron spectroscopy (XPS) was measured on a ESCALAB 250Xi spectrometer. Thermo gravimetric analysis (TGA, TG209 F1 Libra) was used to record the percentage of MOF. UV-vis spectrophotometer (CARY50), Fourier transform infrared (FT-IR) spectrometer (Nicolet 4700), Raman spectra (Renishaw Invia, UK, excitation wavelength = 532 nm) and Photoluminescence (PL) spectra (FLS920, excitation wavelength = 360 nm) were carried out to analysis the optical properties of the photocatalysts. Moreover, the electrochemical properties were conducted using CHI 660B electrochemical system (Shanghai, China) as the electrochemical workstation. Samples for electron spin-resonance spectroscopy (ESR) was recorded on JES-X320 spectrometer, 50 mM 5,5-dimethyl-l-pyrroline-*N*-oxide (DMPO) solution was used as paramagnetic species spin-trap agent, aqueous dispersion for •OH trapping and methanol dispersion for $\bullet O_2^-$ trapping. Finally, The photocatalytic degradation of NO were detected by Thermo Environmental Instruments, Inc, 42i-TL.

***Electrochemical evaluation**:* A CHI 660B electrochemical workstation (Shanghai, China) was conducted to research the electrochemical properties of the prepared photocatalysts. This experiment was executed in a conventional three-electrode cell, Pt plate was used as the counter electrode and calomel electrode was used as the reference electrode, the samples were made as the working electrode, Na_2SO_4 (0.1 M) was used as the electrode solution. The photoelectrode was fabricated by loading 8 mg of sample on the surface of indium-tin oxide (ITO) glass (1 cm × 3 cm) evenly and a 300W Xenon lamp was used as the light source.

***Photocatalytic performance evaluation**:* For Photocatalytic NO removal, **t**he photocatalytic performance of the prepared photocatalysts were evaluated by photocatalytic NO (600 ppb level) removal experiments. The photocatalytic NO (600 ppb level) removal experiments were performed to evaluate the photocatalytic activity of the as-prepared samples in a cylindrical continuous flow reactor at ambient temperature under visible light irradiation. The cylindrical continuous flow reactor was made of stainless steel and covered with quartz glass with a volume of 2.26 L ($\pi R^2 H = \pi \times 6^2\ cm^2 \times 20\ cm$). In a typical measurement, 150 mg of photocatalysts were placed on the surface of square plank, which was placed in the center of glass reactor. The concentration of NO was modulation to 600 ppb via NO gas (10 ppm, N_2 balance) and air stream, the flow rate of the mixed gas was controlled at 1.2 L min^{-1}. The desired humidity level of the air flow was controlled at 50% by passing the air stream through a humidification chamber. After adsorption-desorption equilibrium (about 30 min) was achieved, two 300 W commercial Xenon lamp was turned on which was placed outside the reactor above the reactor vertically. A NO_x analyzer (Thermo Environmental Instruments, Inc., 42i-TL) was employed to measure the concentration of NO continuously, and the removal efficiency η (%) of NO was calculated as: η (%) = ($1 - C/C_0$) × 100%, where C and C_0 were the concentrations of NO in the outlet stream and the feeding stream, respectively.

For photocatalytic H_2 evolution, the photocatalytic HER was executed in the online photocatalytic H_2 production system (LbSolar-3AG, PerfectLight Beijing). Generally, 20 mg of photocatalysts were poured into 100 mL aqueous solution (volume ratio of water and TEOA which is the hole sacrificial is 9:1). A 3wt% (respect to Pt) $H_2PtCl_6 \cdot 6H_2O$ solution was added, the homogeneous solution was obtained by sonication for half an hour, and then the solution was degassed thoroughly. A 300 W Xenon lamp with an optical filter (λ>400 nm) was turned on and the hydrogen produced was detected by gas chromatography (GC D7900P, TCD detector, N_2 cattier, 5 Å molecular sieve column, Shanghai Fechcomp).

Trapping experiments of visible-light induced active species*:* KI, $K_2Cr_2O_7$, *t*-BuOH (TBA) and *p*-benzoquinone (PBQ) were utilized as scavengers of photoinduced holes (h^+), electrons (e^-), hydroxyl radical ($\cdot OH$) and superoxide radical ($\cdot O_2^-$), respectively. 150 mg of photocatalysts containing different trapping agents (3 mmol) were dispersed in ethanol (20 mL) and ultrasonicated for 2 h and then were covered on the CNF and drying at 80 °C until the ethanol was removed. Then, the photocatalysts membranes were used for NO removal.

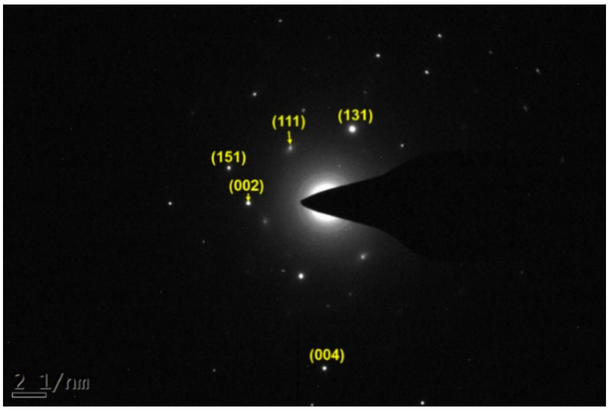


Fig. S1 TEM-SAED pattern of BP.

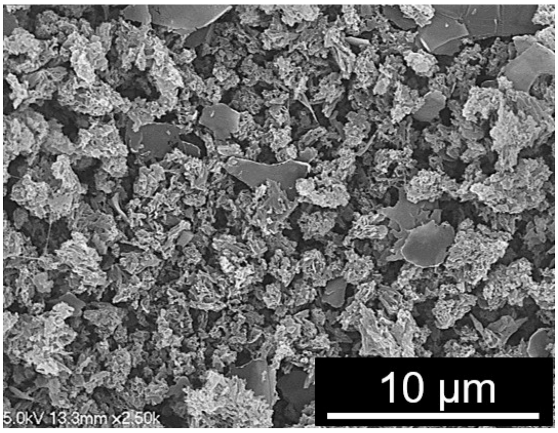


Fig. S2 SEM images of 6% BP/PCN-HKM.

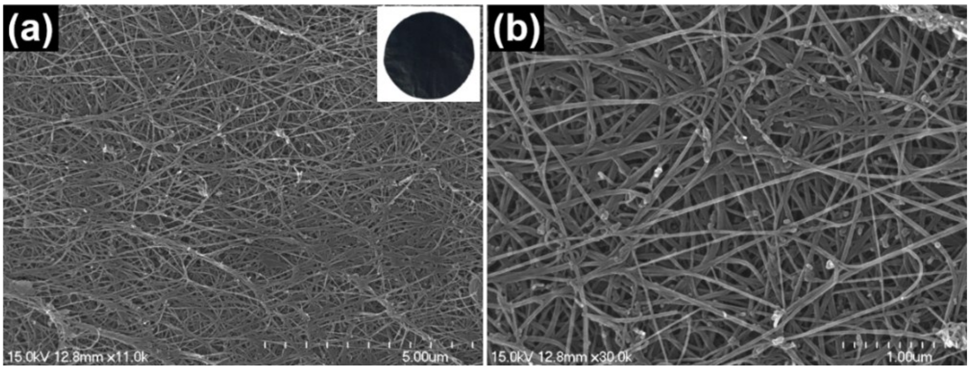


Fig. S3 SEM images of conductive carbon nanotube film (CNF) and its photograph (inset in (a)).

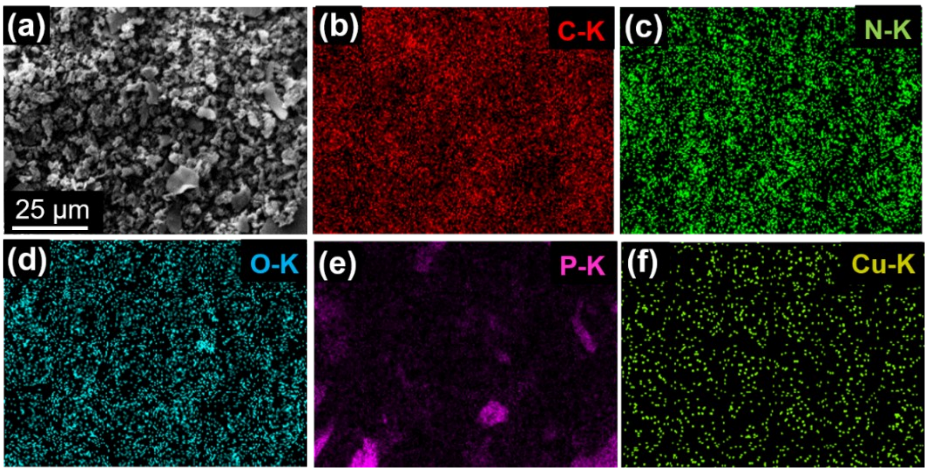
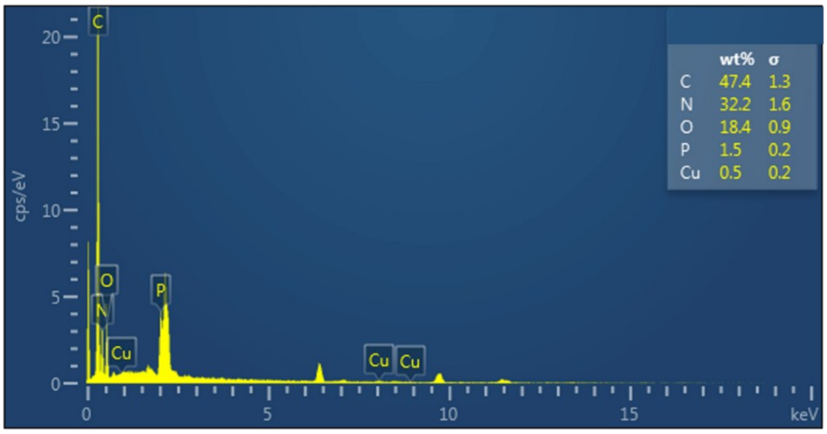


Fig. S4 SEM image of 6% BP/PCN-HKM (a) and EDS mapping images of C (b), N (c), O (d), P (e) and Cu (f).



	wt%	σ
C	47.4	1.3
N	32.2	1.6
O	18.4	0.9
P	1.5	0.2
Cu	0.5	0.2

Fig. S5 SEM-EDS of 6% BP/PCN-HKM.

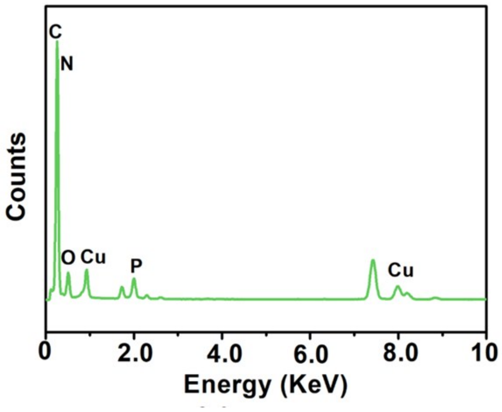


Fig. S6 TEM-EDX of 6% BP/PCN-HK.

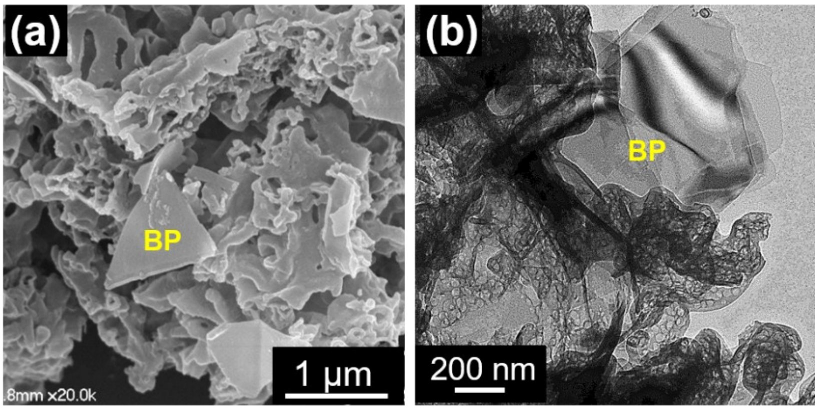


Fig. S7 SEM (a) and TEM (b) images of 6% BP/PCN.

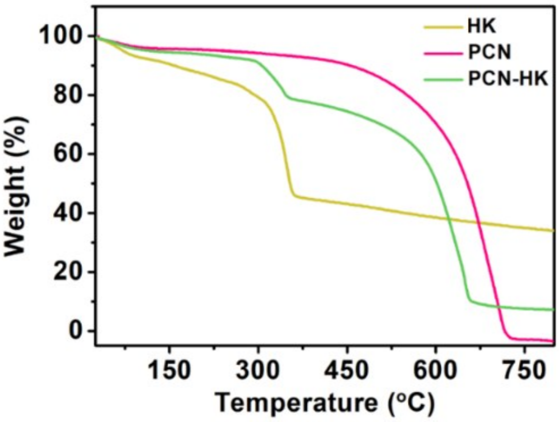


Fig. S8 TGA curves of HK, PCN and PCN-HK.

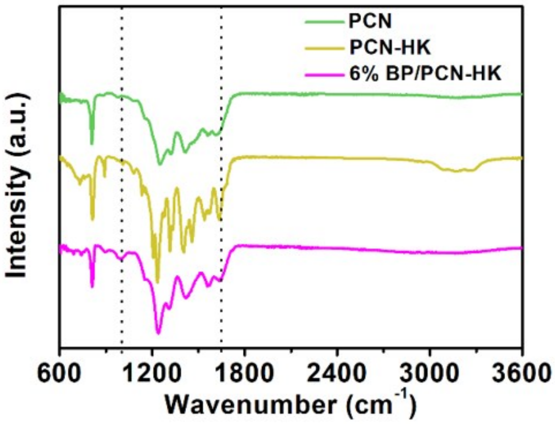


Fig. S9 FTIR spectra of PCN, PCN-HK and 6% BP/PCN-HK.

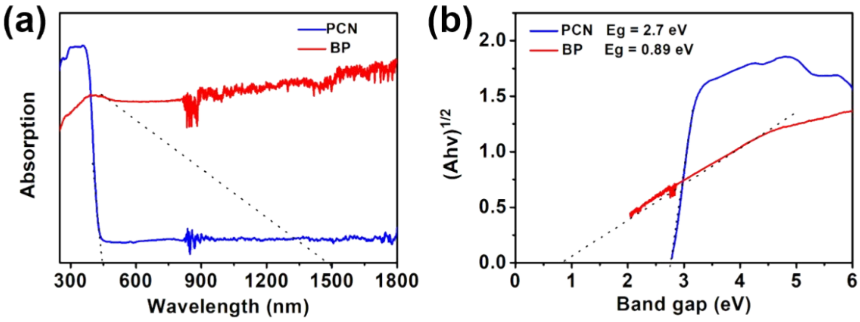


Fig. S10 (a) UV-vis DRS spectra of PCN and BP, (b) estimated band gap.

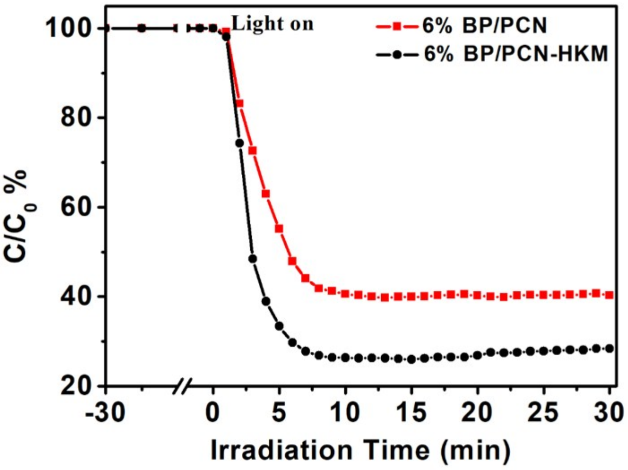


Fig. S11 NO removal of 6% BP/PCN and 6% BP/PCN-HKM.

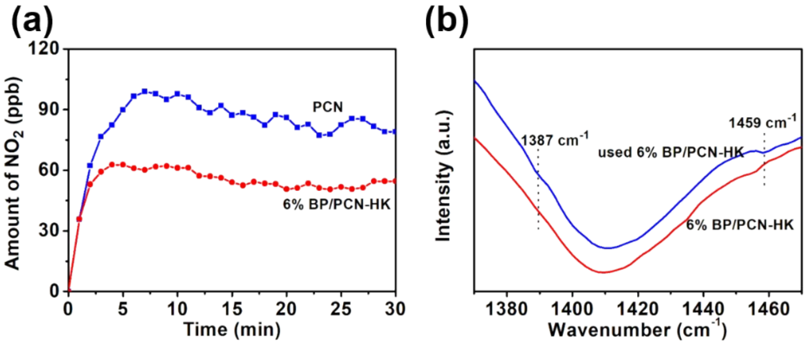


Fig. S12 (a) Monitoring of NO_2 intermediates during irradiation and (b) FTIR spectra of 6 % BP/PCN-HK before and after irradiation.

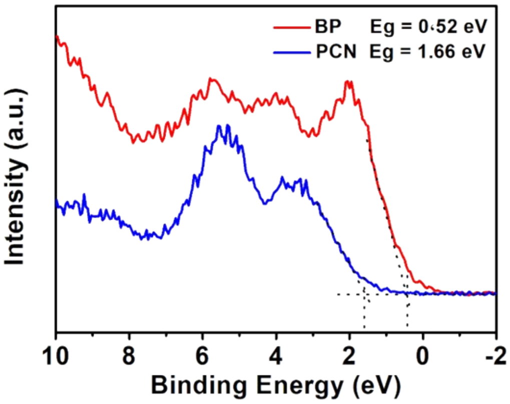


Fig. S13 VB XPS of BP and PCN.

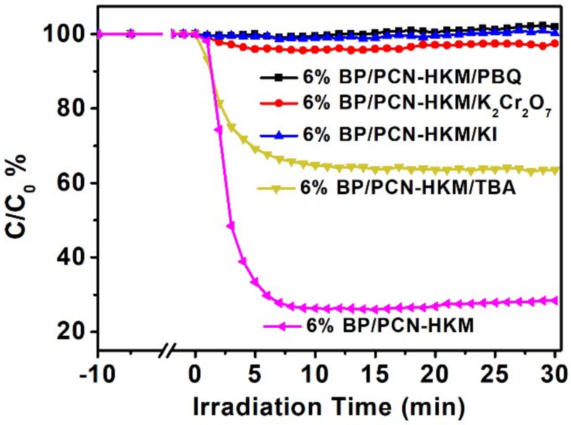


Fig. S14 Capture experiments were carried out in 6% BP/PCN-HKM system