Supporting Information

The doping of phosphorus atoms into graphitic carbon nitride with highly enhanced photocatalytic hydrogen evolution

Xiao-Xiang Fang,[a] Liu-Bo Ma,[a] Kuang Liang,[a] Sheng-Jie Zhao,[a] Yi-Fan Jiang,[a] Cong Ling,[a] Tan Zhao,[a] Tuck-Yun Cheang,[*b] and An-Wu Xu[*a]

[a]*Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemistry Physics, University of Science and Technology of China, Hefei 230026, China. E-mail: anwuxu@ustc.edu.cn*

[b]*Department of Breast and Thyroid Surgery, The First Affiliated Hospital of Sun Yat-Sen University, Guangzhou 510080, China.*

Table S1. *Physicochemical properties of g-C_3N_4 and phosphorus doped g-C_3N_4 synthesized from different precursors.*

Precursors of g-C_3N_4	Sources of P atoms	SA1[a] (m^2 g^{-1})	SA2[b] (m^2 g^{-1})	HER[c] (μmol h^{-1} g^{-1})	Ref
Dicyandiamide	$(NH_4)_2HPO_4$	11	17	N/A[d]	S1
Dicyandiamide	$BmimPF_6$[e]	21	31	N/A	S2
Dicyandiamide	$(NH_4)_2HPO_4$	11	11	N/A	S3
Melamine	H_3PO_4	9	28	570.00	S4
Melamine	4-DPPBA[f]	15	24	757.80	counterpart
Urea	4-DPPBA	90	135	2610.80	this work

[a] the BET surface area of pure g-C_3N_4; [b] the BET surface area of P doped g-C_3N_4; [c] H_2 evolution rate of P doped g-C_3N_4; [d] not available; [e] 1-butyl-3-methylimidazolium hexafluorophosphate; [f] 4-(diphenylphosphino)benzoic acid.

Table S2. *Nonmetal-doped g-C_3N_4 and their properties (Ratios of PL intensity and photocurrent were estimated from reported data). NA: not available.*

Doping Element	Precursor	Ratio of PL intensity (optimal/pure)	Ratio of photocurrent (optimal/pure)	H_2 Evolution Rate (μmol h^{-1} g^{-1})	Reference
P	4-DPPBA (P) Urea (g-C_3N_4)	0.17	3.00	2611	Our work
B	Ph_4BNa (B) Urea (g-C_3N_4)	0.67	1.20	440	S5
B	$BmimBF_4$ (B) DCDA (g-C_3N_4)	0.42	1.89	110	S6
N	N_2H_4•H_2O (N) Melamine (g-C_3N_4)	0.81	2.36	554	S7
O	H_2O_2 (O) Melamine (g-C_3N_4)	0.07	4.00	1200	S8
O	H_2O_2 (O) DCDA (g-C_3N_4)	0.16	NA	375	S9
F	NH_4F (F)	NA	NA	130	S10

	DCDA (g-C_3N_4)				
S	Thiourea (S)	0.53	2.78	122	S11
	CN_2H_2 (g-C_3N_4)				
S	Thiourea (S/ g-C_3N_4)	0.33	NA	1375	S12
Br	NH_4Br (Br)	0.67	2.5	960	S13
	Urea (g-C_3N_4)				
I	NH_4I (I)	0.14	3.00	760	S14
	DCDA (g-C_3N_4)				
I	Iodine (I)	0.05	2.44	890	S15
	Melamine (g-C_3N_4)				

We have compared the ratios of PL intensity and photocurrent (optimal/pure) and H_2 evolution rate of our sample with other nonmetal doped g-C_3N_4 samples, as shown in Table S2, our PCN-5 sample reveals an obvious decrease of peak intensity compared with pristine g-C_3N_4, suggesting the restriction of electron-hole recombination. Besides, a higher and rapid photocurrent is generated after P doping, indicating more charge carriers are produced and their mobility is enhanced. So, we suggest the charge separation and transfer are enhanced by phosphorus doping, leading to the highest H_2 evolution rate as compared to other nonmetal doped g-C_3N_4 in Table S2.

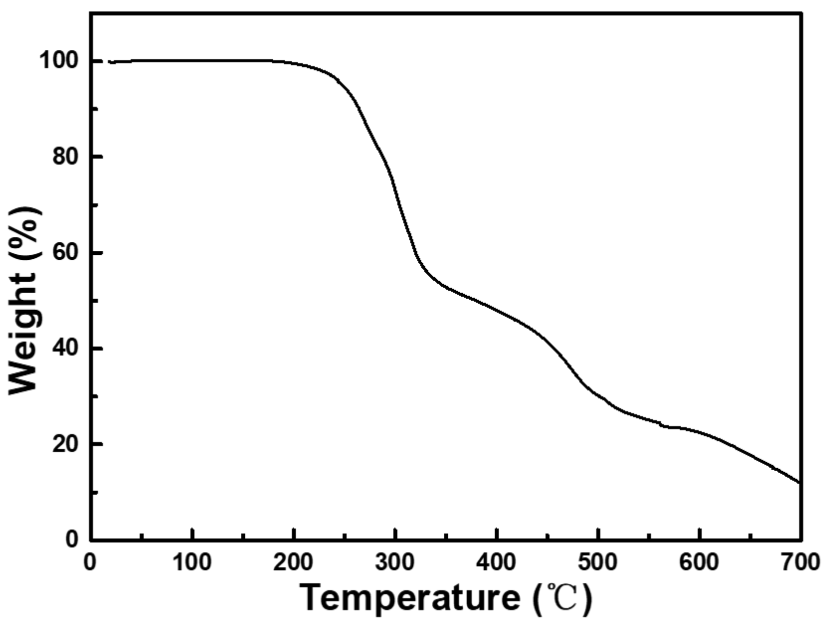

Fig. S1 *TG curve of 4-DPPBA molecules.*

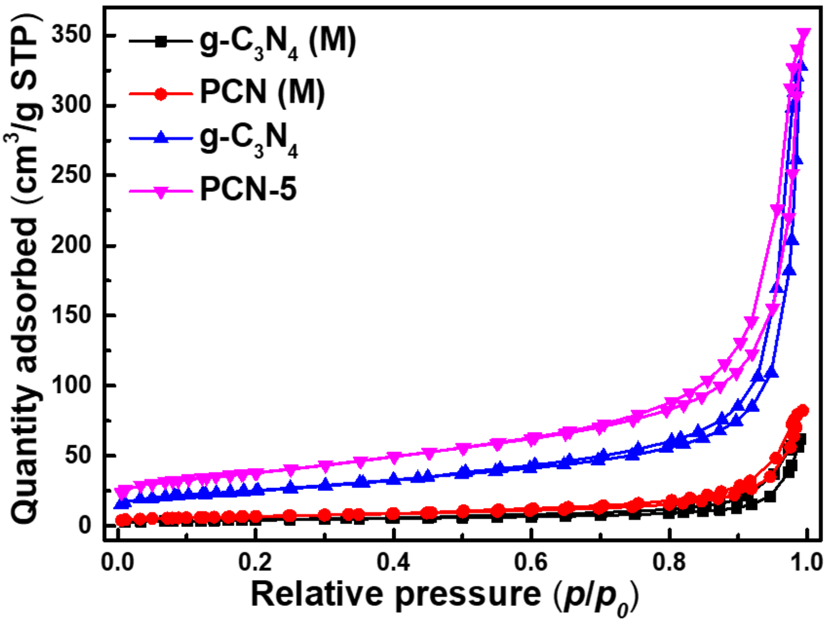

Fig. S2 *Nitrogen adsorption-desorption isotherms of g-C_3N_4 (M), PCN (M), g-C_3N_4 and PCN-5.*

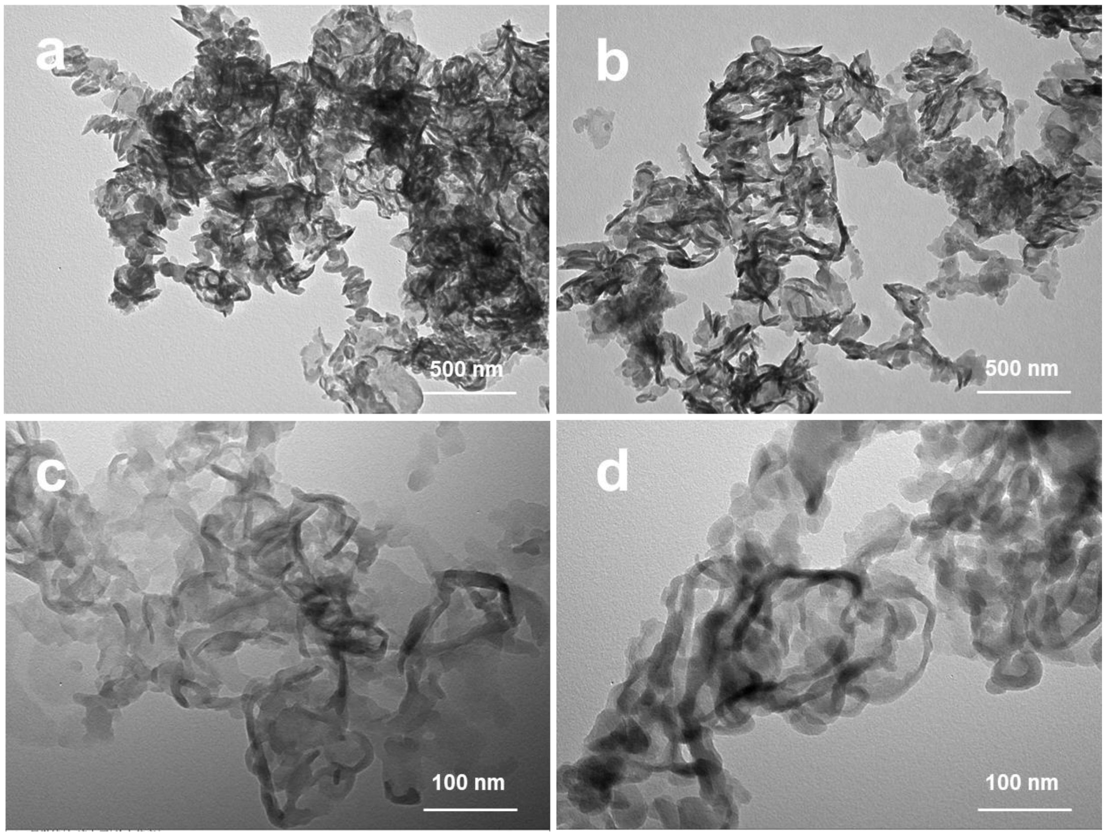

Fig. S3 *TEM images of (a, c) g-C_3N_4 and (b, d) PCN-5.*

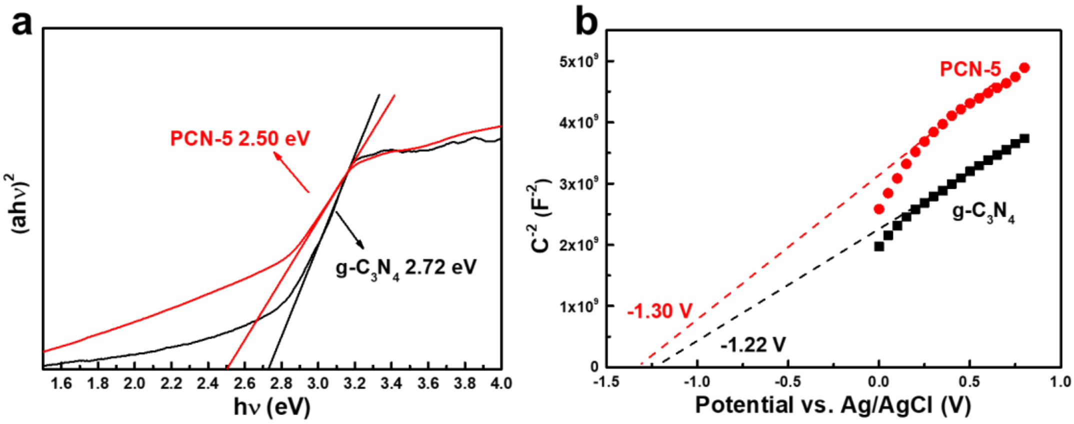

Fig. S4 *(a) Band gaps and (b) Mott-Schottky plots of g-C_3N_4 and PCN-5 conducted at 1 Hz.*

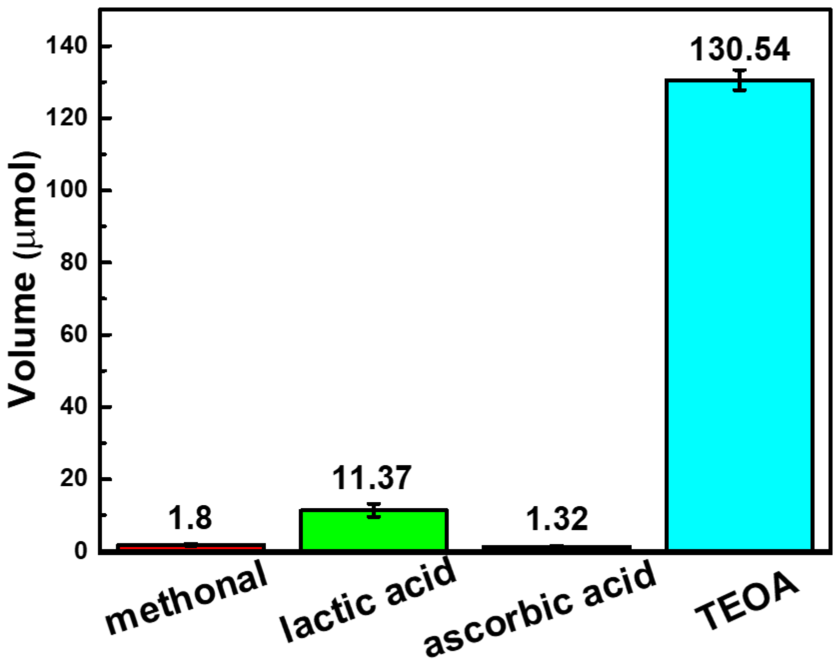

Fig. S5 *Comparison of photocatalytic HER on PCN-5 photocatalyst in the presence of different sacrificial agents under visible light ($\lambda \geq 420$ nm). Reaction conditions: catalyst, 50 mg; 100 mL of solution containing sacrificial agents; light source, xenon lamp (300 W) with a cutoff filter; temperature, 10 °C.*

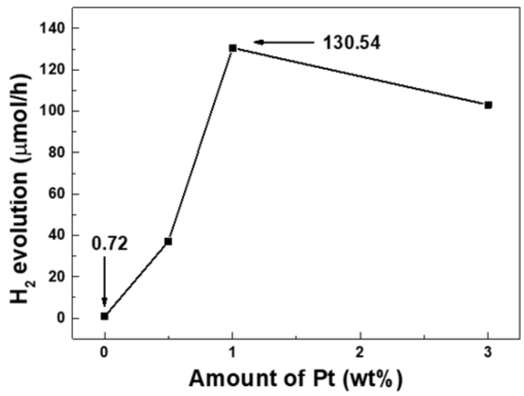

Fig. S6 *Effect of Pt loading amount on photocatalytic hydrogen evolution of PCN-5 under visible light irradiation (λ ≥ 420 nm).*

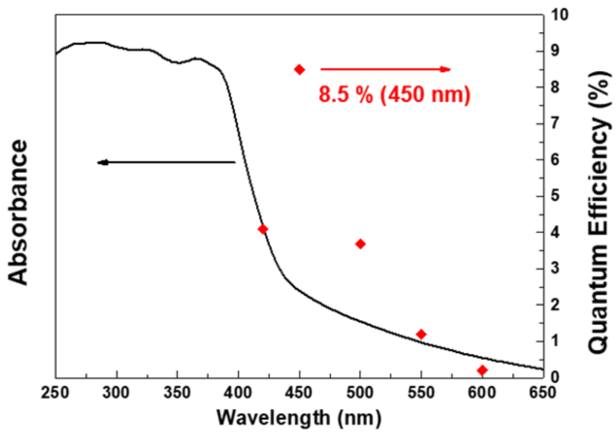

Fig. S7 *Wavelength-dependent apparent quantum yield for the photocatalytic hydrogen evolution reaction over PCN-5.*

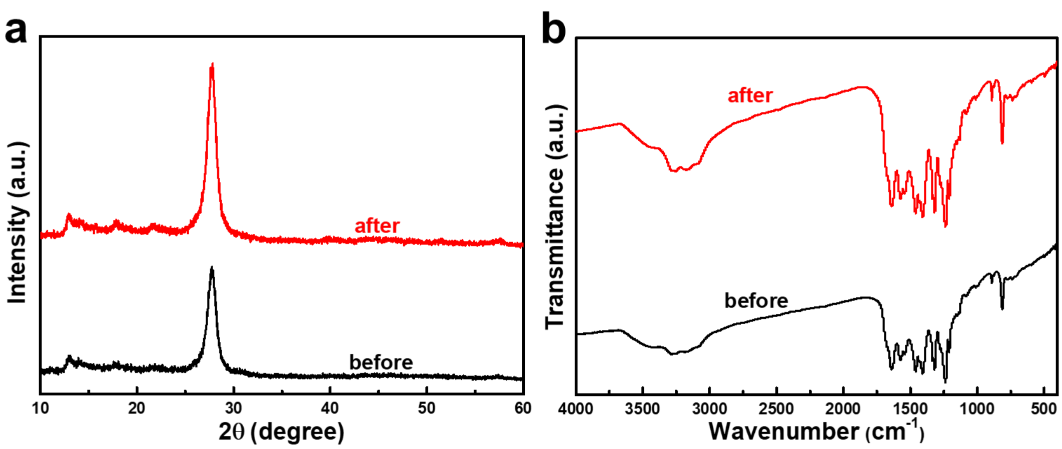

Fig. S8 *(a) XRD patterns and (b) FTIR spectra of PCN-5 before and after photocatalytic reaction.*

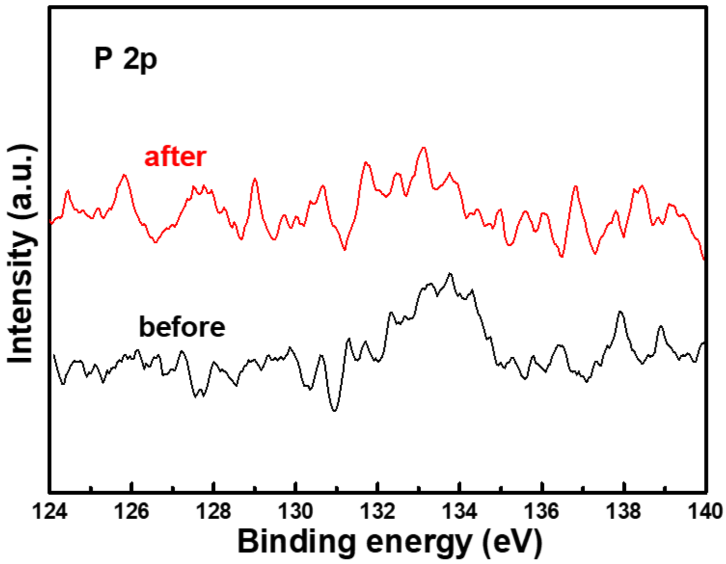

Fig. S9 *High-resolution XPS spectra of P 2p for obtained PCN-5 before and after photocatalytic experiment.*

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