Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Surface-state-induced upward band bending in P doped g-C_3N_4 for the formation of isotype heterojunction between bulk g-C_3N_4 and P doped g-C_3N_4: Photocatalytic hydrogen production

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Fig. S1. Zeta potentials of CN, PCN and 11 CPCN catalysts

Fig. S2. SEM EDS of CN, PCN and 11 CPCN catalysts

Fig. S3. TEM images for Pt fringes on 11 CPCN heterojunction catalysts after the reaction

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Fig. S11. Optimization of catalysts amount with different weight % of Pt

Table S1. Hydrogen production rate of bulk P-doped g-C_3N_4

Table S2. Comparison of H_2 production rate with previously reported isotype heterojunction catalysts based on g-C_3N_4

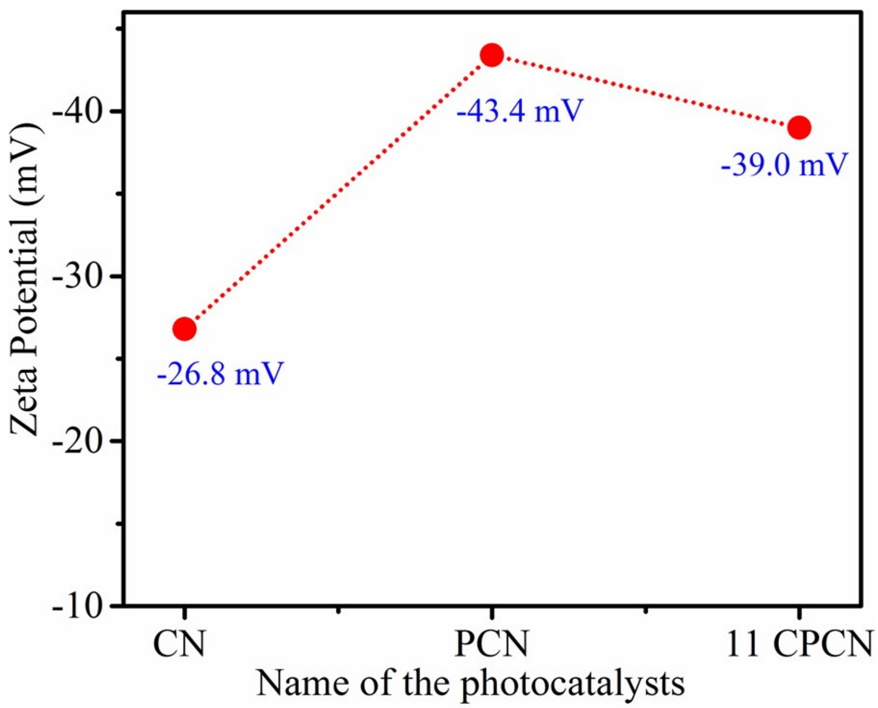


Fig. S1. Zeta potentials of CN, PCN and 11 CPCN catalysts

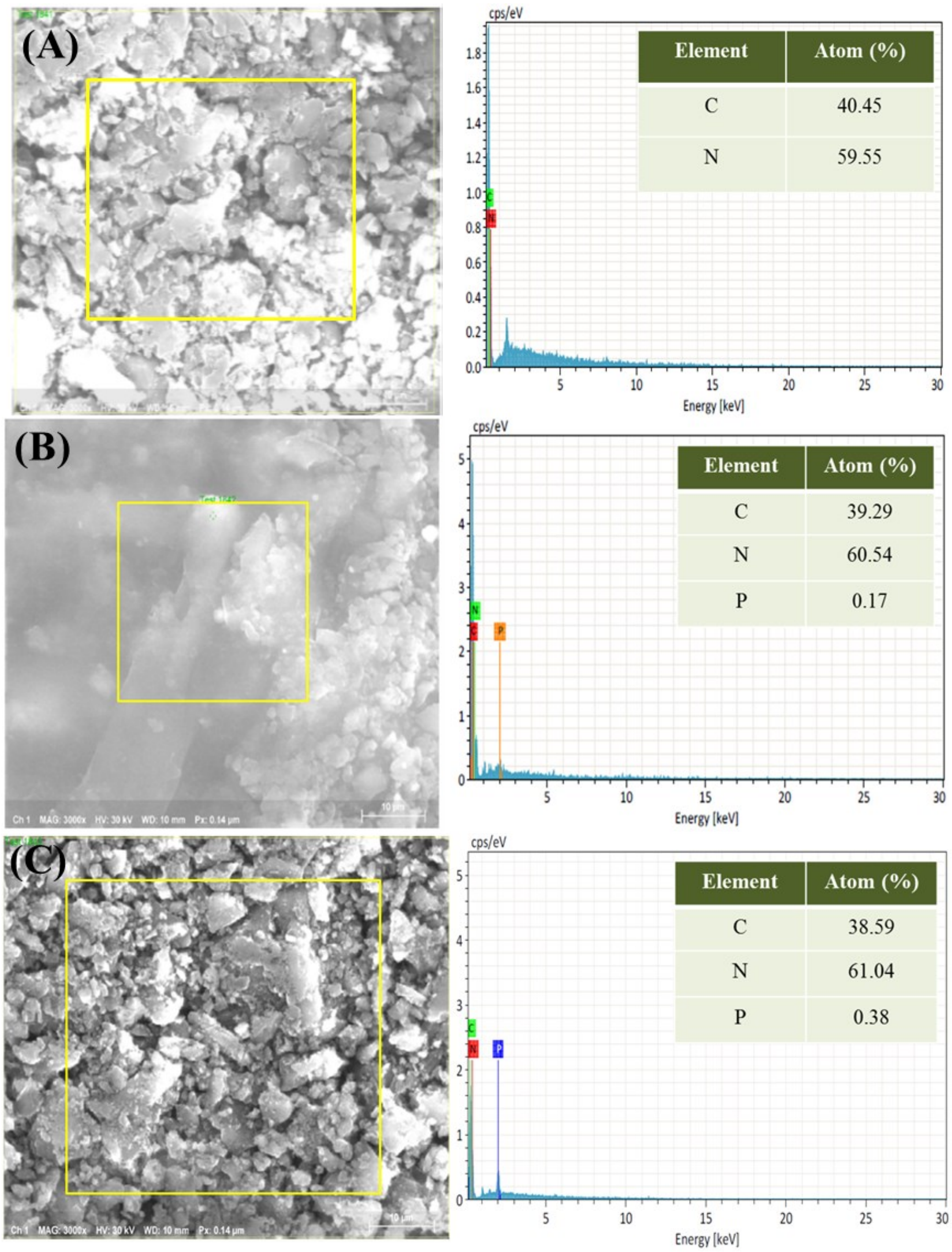


Fig. S2. SEM EDS of (A) CN (B) PCN and (C) 11 CPCN catalysts

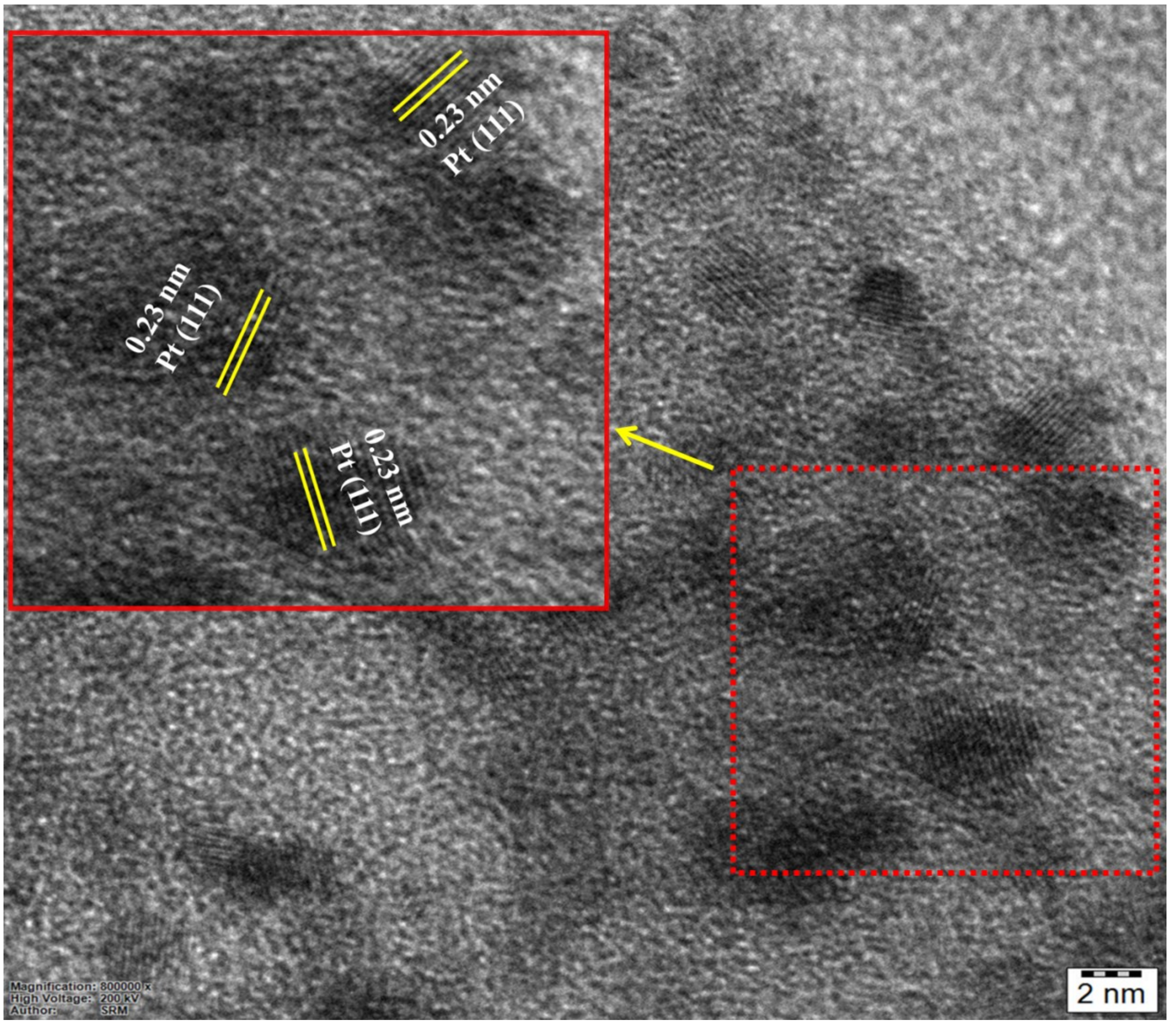
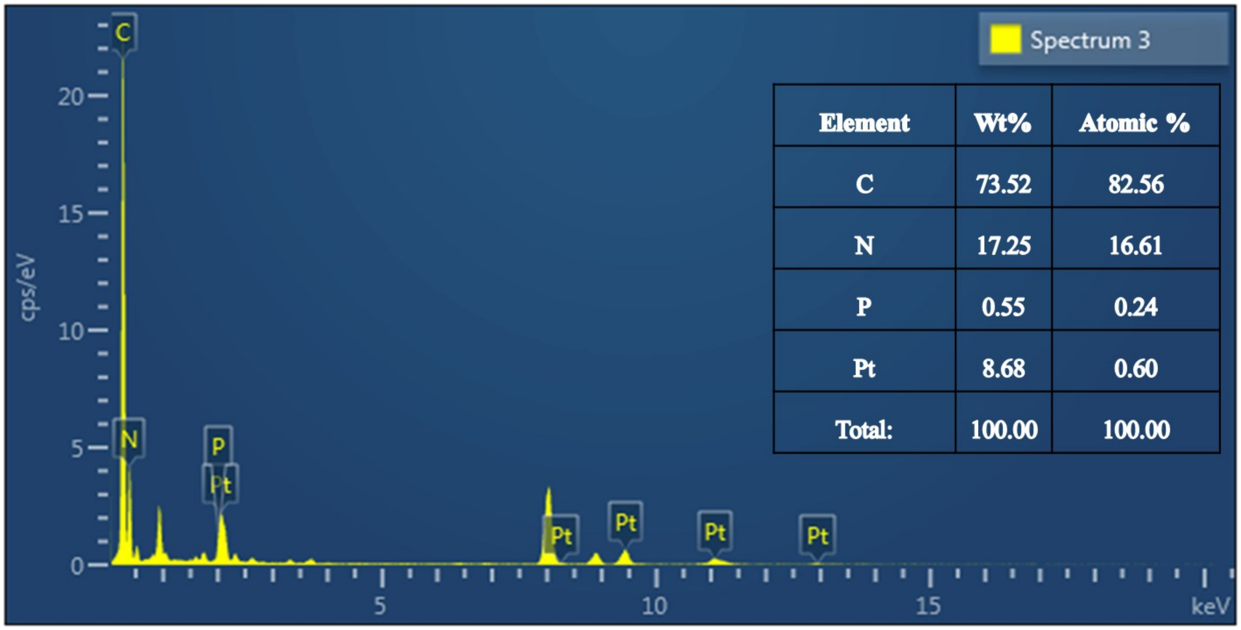


Fig. S3. TEM images for Pt fringes of the used 11 CPCN heterojunction catalysts



Element	Wt%	Atomic %
C	73.52	82.56
N	17.25	16.61
P	0.55	0.24
Pt	8.68	0.60
Total:	100.00	100.00

Fig. S4. TEM-EDX of 11 CPCN heterojunction catalysts after the reaction

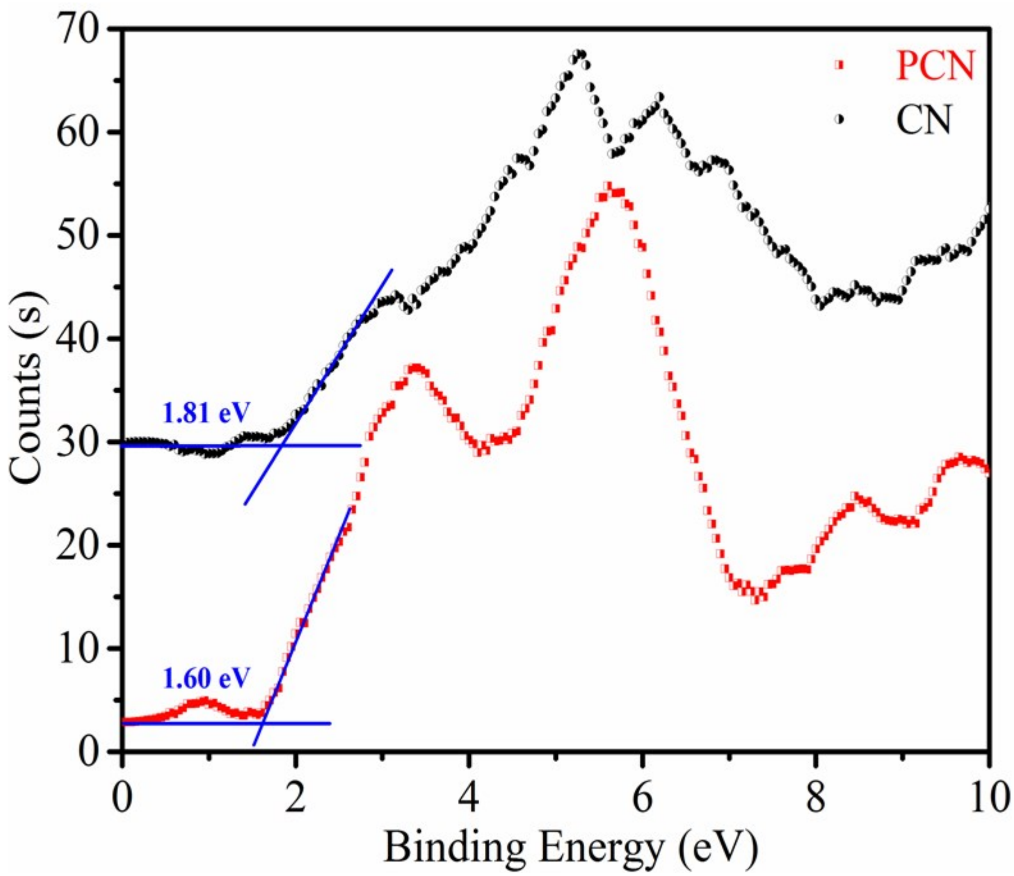


Fig. S5. XPS Valence band spectra of CN and PCN

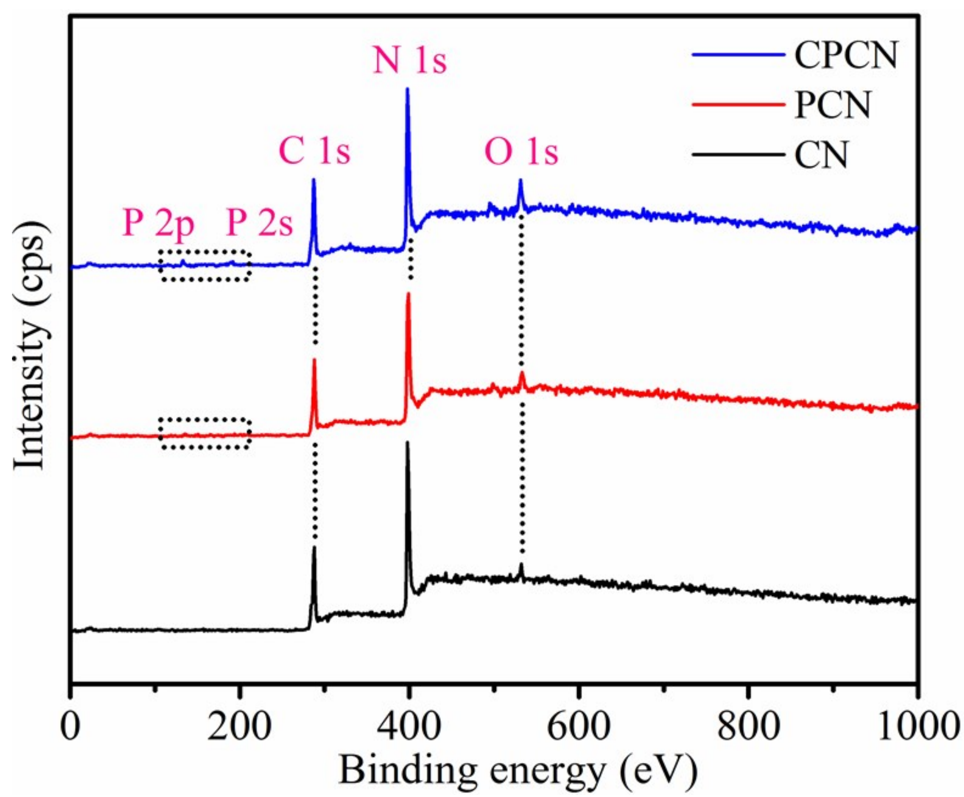


Fig. S6. XPS survey scan spectra of CN, PCN and 11 CPCN

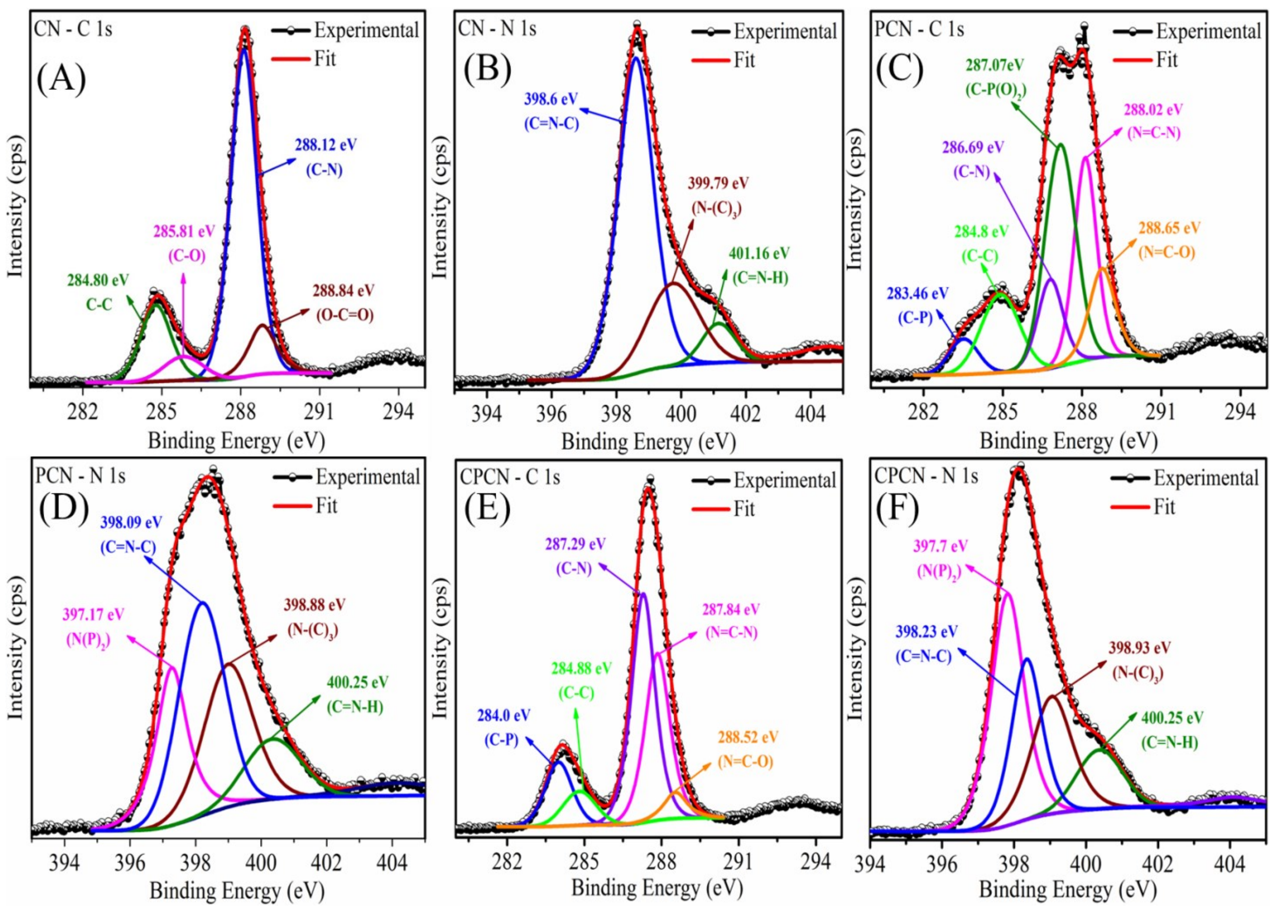


Fig. S7. XPS of C 1s and N 1s spectra (A & B) CN (C & D) PCN (E & F) 11 CPCN catalysts

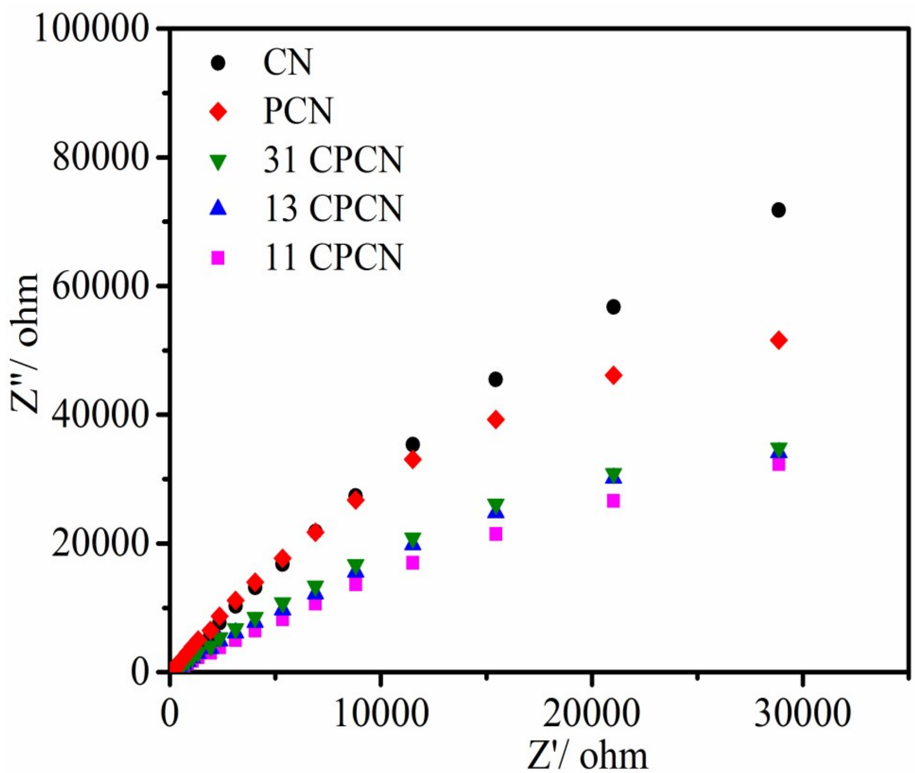


Fig. S8. Electrochemical (EIS) impedance spectroscopy

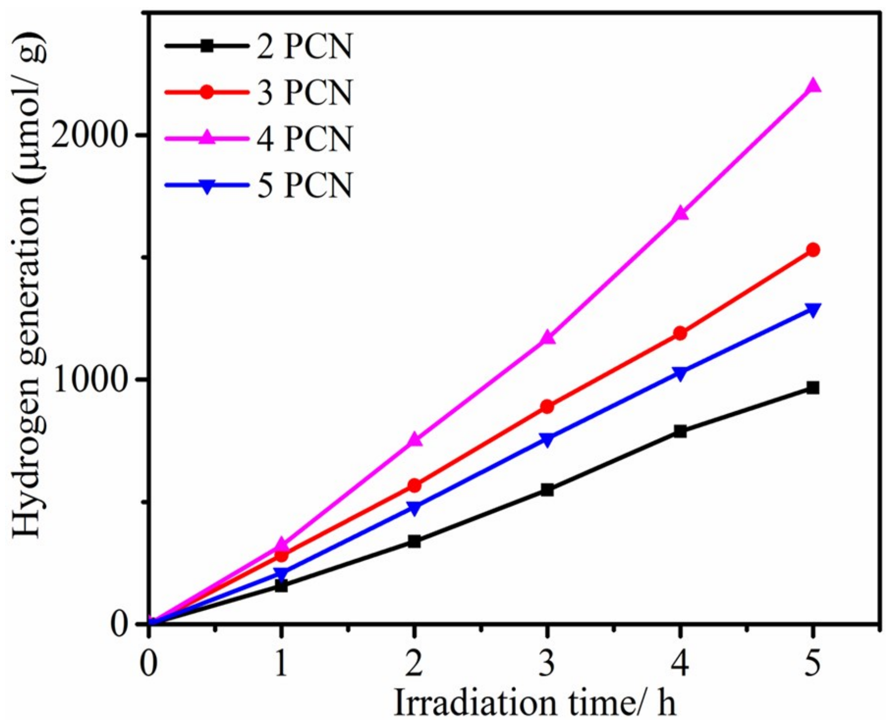


Fig. S9. Photocatalytic activity of optimization of phosphorous on CN

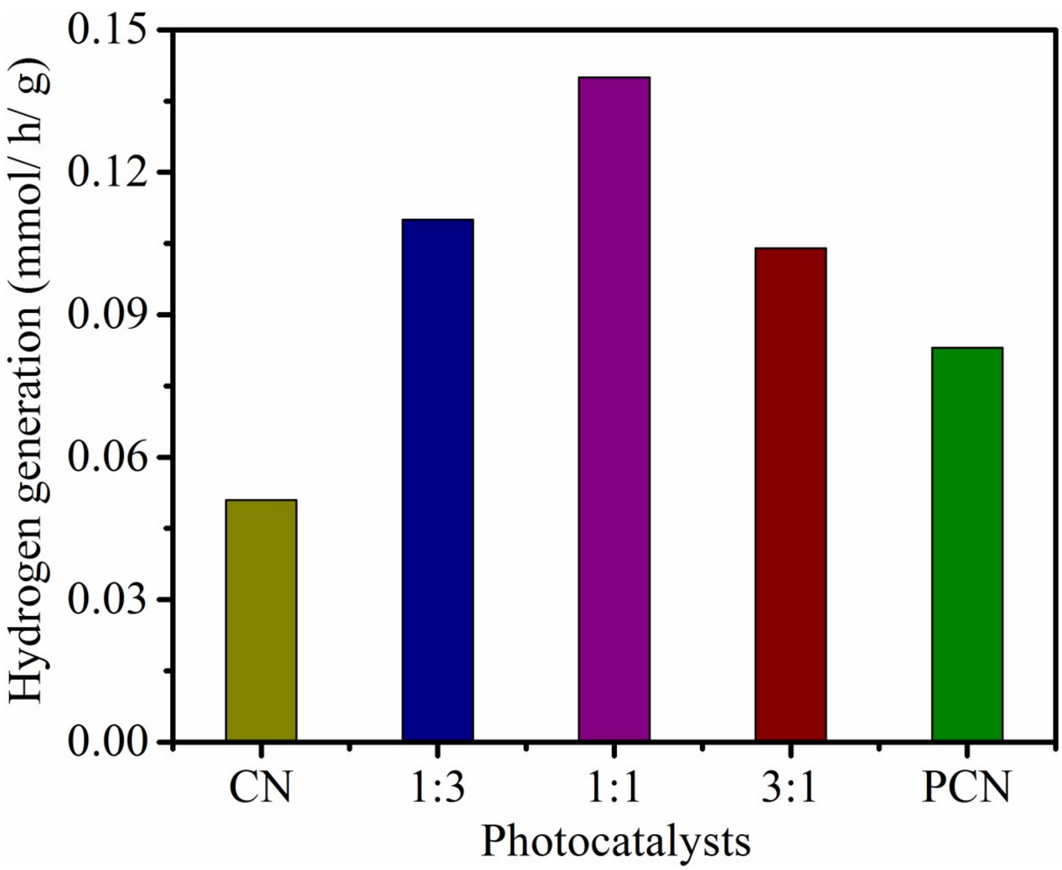


Fig. S10. Photocatalytic activity of the catalysts without Pt

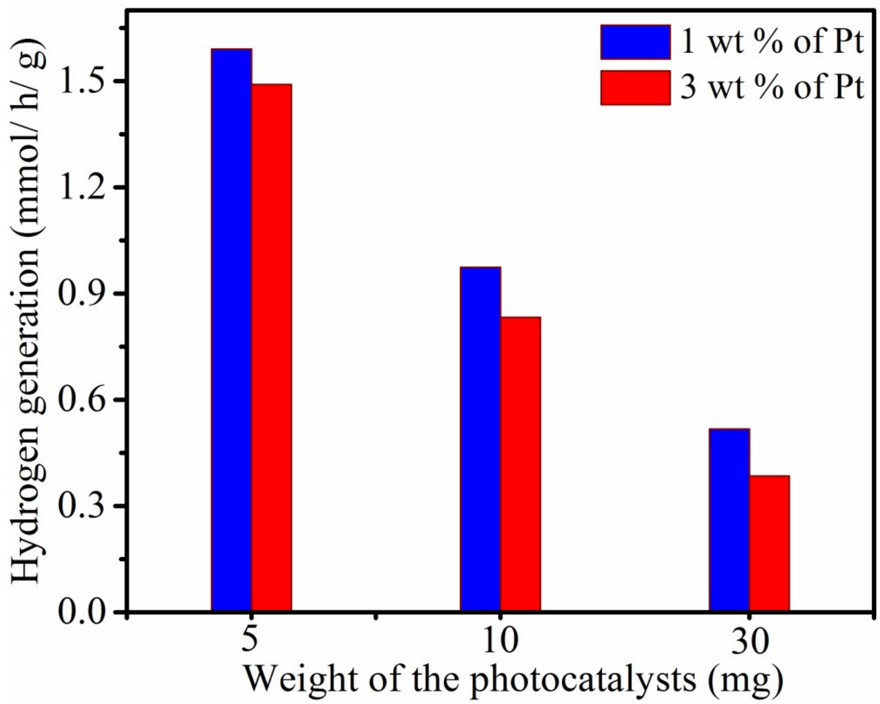


Fig. S11. Optimization of catalysts amount with different weight % of Pt

Table S1. Hydrogen production rate of bulk P-doped g-C_3N_4

S. No.	Source	Catalysts	Synthesis condition	Catalysts amount (mg)	Sacrificial agent	Wt % of Pt	Light source	H_2 production (mmol/h/g)	Ref.
1.	Melamine & Phosphoric acid	Flower like P-g-C_3N_4	550°C, 4 h, N_2 flow, 2.3°C/ min	50	10 Vol % TEOA	3	300 W Xe lamp with 400 nm UV Cut-off	0.256	S1
2.	Melamine & Phosphoric acid	Tubular P-g-C_3N_4	Hydrothermal followed by 500°C, 4 h	100	20 mL methanol	1	300 W Xe lamp with 400 nm UV Cut-off	0.067	39
3.	Melamine & Sodium pyrophosphate	Carbon defected tubular P-g-C_3N_4	Autoclave at 180°C, 10 h and 500°C, 4 h, 2.5°C/ min	100	20 mL methanol	1	300 W Xe lamp with 400 nm UV Cut-off	0.057	34
4.	Guanidinium hydrochloride & hexachlorocyclotriphosphazene	P doped g-C_3N_4	500°C, 4h, 2°C/ min	100	10 Vol % TEOA	3	300 W Xe lamp with 400 nm UV Cut-off	0.050	S2
5.	Melamine & 2-amino ethyl phosphonic acid	Bulk P-g-C_3N_4	500°C, 3 h, N_2 flow and 550°C, 5 h	50	20 Vol % TEOA	1	300 W Xe lamp for 40 min then 400 nm UV Cut-off	0.510	S3
6.	Melamine & $(NH_4)_2HPO_4$	Bulk P-g-C_3N_4	520°C, 2 h, 5°C/ min	50	20 Vol % TEOA	1	300 W Xe lamp for 40 min then 400 nm UV Cut-off	0.153	S3
7.	Dicyandiamide & $(NH_4)_2HPO_4$	P doped g-C_3N_4	520°C, 2 h, 5°C/ min	1000	10 Vol % methanol	1	250 W Na lamp with UV cut-off portion	0.052	S4
8.	Melamine & (hydroxyethylidene)diphosphonic	Mesoporous P-g-C_3N_4	500°C, 3 h, N_2 flow	50	10 Vol % TEOA	3	300 W Xe lamp with 400 nm UV Cut-off	0.104	S5

	acid								
9.	Melamine & Sodium tripyrophos phate	P-doped g-C_3N_4	550°C, 2 h, 5°C/ min	50	25 vol % methanol	1	350 W Xe arc lamp	0.191	S6
10.	Melamine & Sodium dihydrogen phosphate	Bulk P-doped g-C_3N_4	520°C, 4 h, 5°C/ min	5	20 Vol % MeOH	1	250 W Xe arc lamp for 1 h then 400 nm UV Cut-off	0.603	This work

Table S2. Comparison of Hydrogen production rate with previously reported isotype heterojunction catalysts based on g-C_3N_4

S. No.	Photocatalysts	Light Source	Experimental conditions	H_2 evolution rate (mmol/ h/ g)	Ref.
1.	g-C_3N_4/g-C_3N_4	300 W Xe lamp (λ > 420 nm)	50 mg catalyst, 15 vol % TEOA, 1 wt% of Pt	0.029	38
2.	1D/2D g-C_3N_4	150 W metal halide lamp with UV cut-off filter (λ > 420 nm)	100 mg catalysts, 10 vol % TEOA, 0.5 wt % of Pt	0.241	S7
3.	g-CNNS/ g-CNNF (NS-nanosheet/ NF-nanofibre)	300 W Xe lamp (λ > 420 nm)	50 mg catalysts, 10 vol % TEOA, 1 wt% of Pt	1.375	S8
4.	Meso-g-C_3N_4/ g-C_3N4	300 W Xe lamp with AM 1.5 G filter	50 mg catalysts, 20 mL MeOH	0.115	25
5.	g-C_3N_4/ B-doped g-C_3N_4 quantum dot	300 W Xe lamp (λ > 420 nm)	50 mg catalysts, 10 vol % TEOA, 1.5 wt % of Pt	0.070	S9
6.	g-C_3N_4/ S-g-C_3N_4	Visible light	--	0.190	S10

7.	g-C_3N_4/ P-g-C_3N_4	250 W Xe lamp for 1h prior to visible light (UV cut-off filter λ > 420 nm)	5 mg catalysts, 20 mL MeOH, 1 wt% of Pt	1.590	This work

References

(1) H. Yanga, Y. Zhou, Y. Wang, S. Hu, B. Wang, Q. Liao, H. Li, J. Bao, G. Ge, S. Jia, *J. Mater. Chem. A*, **2018**, 6, 16485-16494.

(2) Y. Zhou, L. Zhang, J. Liu, X. Fan, B. Wang, M. Wang, W. Ren, J. Wang, M. Li, J. Shi, *J. Mater. Chem. A*, **2015**, 3, 3862-3867.

(3) J. Ran, T. Y. Ma, G. Gao, X.-W. Duc, S. Z. Qiao, *Energy Environ. Sci.*, **2015**, 8, 3708-3717.

(4) S. Hu, L. Ma, J. You, F. Li, Z. Fan, G. Lu, D. Liu, J. Gui, *Appl. Surf. Sci*, **2014**, 311, 164-171.

(5) Y.-P. Zhu, T. -Z. Ren, Z. -Y. Yuan, *ACS Appl. Mater. Interfaces*, **2015**, 7, 16850-16856.

(6) S. Cao, Q. Huang, B. Zhu, J. Yu, *J. Power Sources*, **2017**, 351, 151-159.

(7) S. Mahzoon, S. M. Nowee, M. Haghighi, *Renew. Energy*, **2018**, 127, 433-443.

(8) H. Li, H. Tian, X. Wang, M. Pi, S. Wei, H. Zhu, D. Zhang, S. Chen, *ACS Appl. Energy Mater.*, **2019**, 2, 4692-4699.

(9) Y. Wang, Y. Li, J. Zhao, J. Wang, Z. Li, *Int. J. Hydrog. Energy*, **2019**, 44, 618-628.

(10) J. Zhang, M. Zhang, R. -Q. Sun, X. Wang, *Angew. Chem*. **2012**, 124, 10292 - 10296.