Support Information

Surface P-N bonds induced local spatial charge separation and enhanced photocatalytic hydrogen production in graphitic carbon nitride

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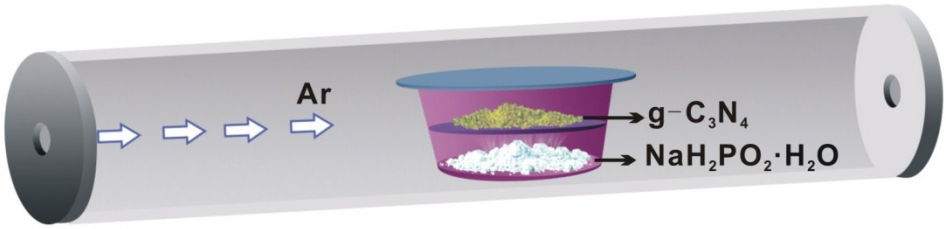


Fig. S1 The process for preparation of P-N bond modified g-C_3N_4 in the tube furnace.

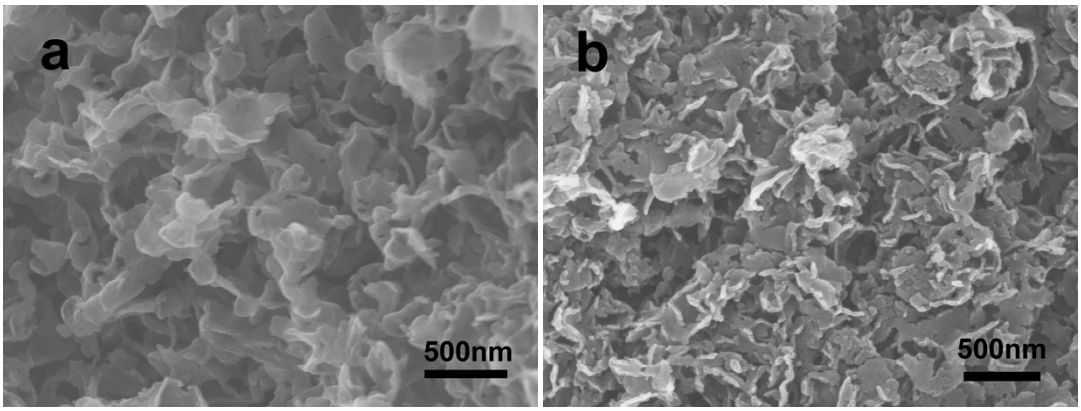


Fig. S2 SEM images of (a)CN and (b) PCN-2

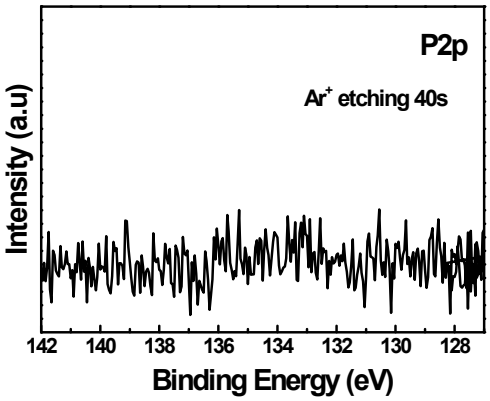
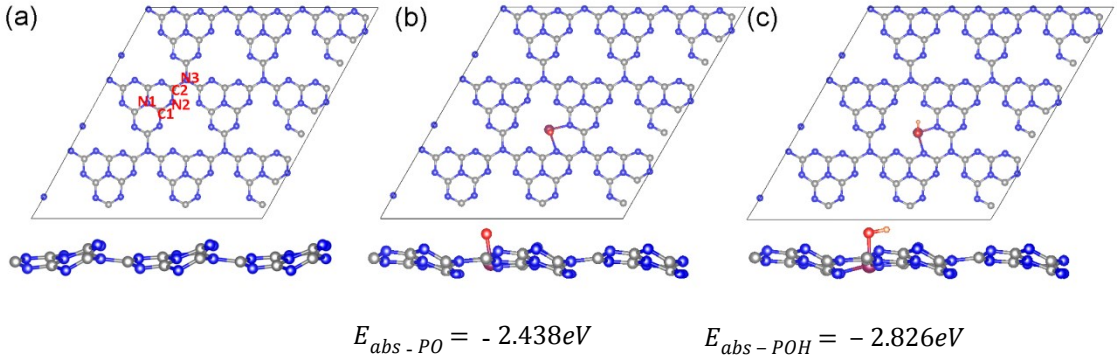


Fig. S3 P 2p spectra of PCN-2 after Ar^+ for 40s



$E_{abs\text{-}PO} = -2.438eV$ $E_{abs-POH} = -2.826eV$

Fig. S4 (a)Ball-and-stick model of monolayer from top and side views (a) g-C_3N_4, (b)P=O doped g-C_3N_4, (c)P-OH doped g-C_3N_4.

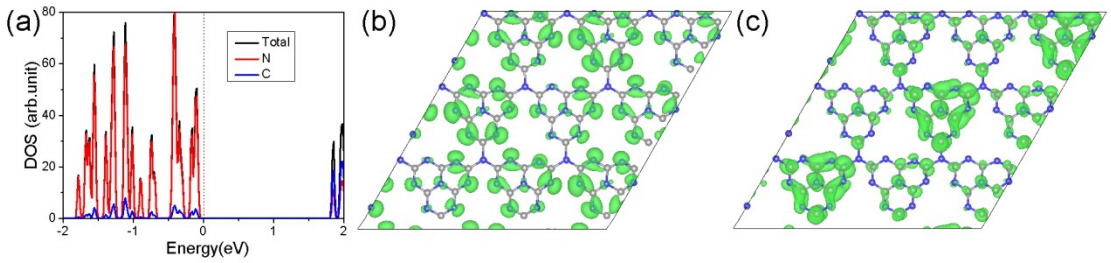


Fig. S5 (a) PDOS of monolayer g-C_3N_4, and band decomposed charge density of (b) VBM and (c) CBM of monolayer g-C_3N_4,respectively. The isovalue is 0.0007 au

Table S1 The surface N/P atomic ratio and yield of the PCN samples tested by XPS

Sample	N/P atomic ratio	Yield of post-calcination
PCN-1 (1:5-400-3h)	100:1	78%
PCN-2 (1:7.5-400-3h)	79:1	70%
PCN-3 (1:10-400-3h)	75:1	67%
PCN-4 (1:7.5-300-3h)	123:1	96%
PCN-5 (1:7.5-350-3h)	110:1	95%
PCN-6 (1:7.5-450-3h)	68:1	65%
PCN-7 (1:7.5-400-2h)	85:1	75%
PCN-8 (1:7.5-400-4h)	71:1	67%

Table S2 The performance comparison of the catalysts from the different references.

Catalyst	AQE at 420nm	Photocatalytic H_2 evolution Rate ($\mu mol \cdot h^{-1}$)	Amount of photocatalyst (mg)	Reference
Suface P-N bonds modified g-C_3N_4	8.96%	1.8mmol·h^{-1}·g^{-1}	30	This work
P -Doped C_3N_4 nanosheet	3.56%	1596μmol·h^{-1}·g^{-1}	50	1
P-doped g-C_3N_4 hexagonal microtubes	5.68%	670μmol·h^{-1}·g^{-1}	100	2
Carbon rich g-C_3N_4	4.52%	39.6 μmol·h^{-1}	10	3
P and cyano groups modified g-C_3N_4	1.3%	77.9μmol·h^{-1}·g^{-1}	100	4
Surface hydroxylation modified g-C_3N_4	9.2%	0.31 mmol·h^{-1}·g^{-1}	50	5
Carbon-doped g-C_3N_4	6.8%	125.1μmol·h^{-1}·g^{-1}	20	6
non-metal group doping g-C_3N_4	7.45%	≈1.3 mmol·h^{-1}·g^{-1}	100	7
P, Na Co-doping g-C_3N_4	-	114.2μmol·h^{-1}	50	8
Ammonia etching g-C_3N_4	-	317.6μmol·h^{-1}	50	9
P-doped g-C_3N_4 nanotubes	-	303.97μmol·h^{-1}·g^{-1}	30	10

References

1. J. R. Ran, T. Y. Ma, G. P. Gao, X. W. Du, and S. Z. Qiao. *Energy. Environ. Sci.,* 2015, 8, 3708-3717.

2. S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan and H. Fu, *Angew. Chem. Int. Ed.*, 2016, 55, 1830-1834.

3. Y. F. Li, M. Yang, Y. Xing, Z. C. Liu, Y. Yang, X. Wang, and S. Y. Song. *Small.,* 2017, 13, 1701552.

4. X. L. Liu, P. Wang, H. S. Zhai, Q. Q. Zhang, B. B. Huang, Z. Y. Wang, Y. Y. Liu, Y. Dai, X. Y.

Qin, and Z. Y. Zhang. *Appl. Catal. B-Environ.*, 2018, 232, 521-530.
5. S. X. Yu, J. Y. Li, Y. H. Zhang, M. Li, F. Dong, T. R. Zhang and H. W. Huang, *Nano. Energy*, 2018, 50, 383-392.
6. Z. Chen, T. Fan, X. Yu, Q. L. Wu, Q. Zhu, L. Zhang, J. Li, W. Fang and X.D. Yi, *J. Mater. Chem. A*, 2018,6, 15310-15319.
7. W. Xing, G. Chen,C. Li, Z. Han, Y. Hu and Q. Meng, *Nanoscale.,* 2018,10, 5239-5245
8. S. W. Cao, Q. Huang, B. C. Zhu and J. G. Yu, *J. Power. Sources.,* 2017, 351, 151-159.
9.P. J. Yang, J. H. Zhao, W. Qiao, L. Li, and Z. P. Zhu, *Nanoscale.*, 2015, 7, 18887-18890.
10. B. Liu, L. Q. Ye, R. Wang, J. F. Yang, Y. X. Zhang, R. Guan, L. H. Tian and X. B. Chen, *Acs Appl. Mater. Inter.*, 2018, 10, 4001-4009.