Hierarchical carbon nitride tube with oxygen doping and carbon defects promotes solar-to-hydrogen conversion

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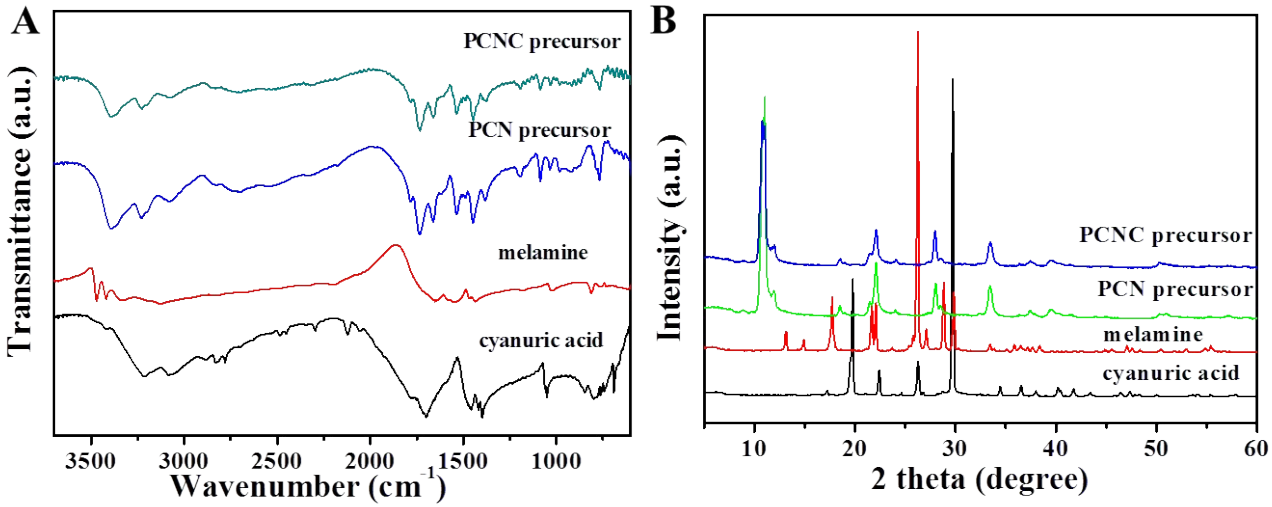

Figure S1 A) FT-IR spectra and B) XRD patterns of cyanuric acid, melamine, PCN precursor and PCNC precursor.

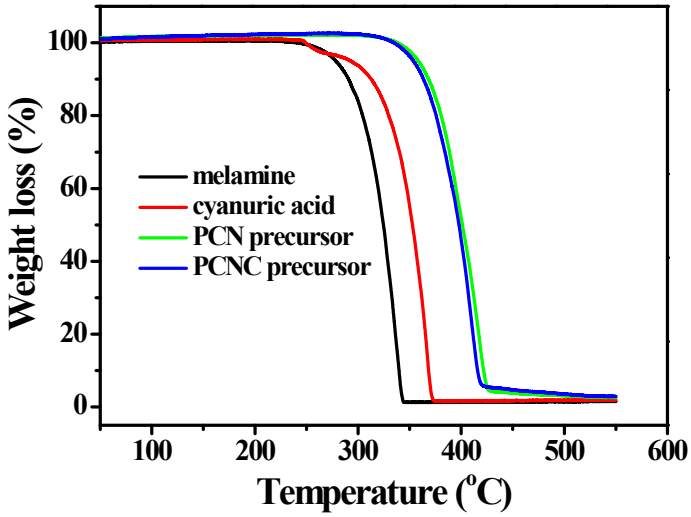

Figure S2 Thermogravimetric analysis of different precursors.

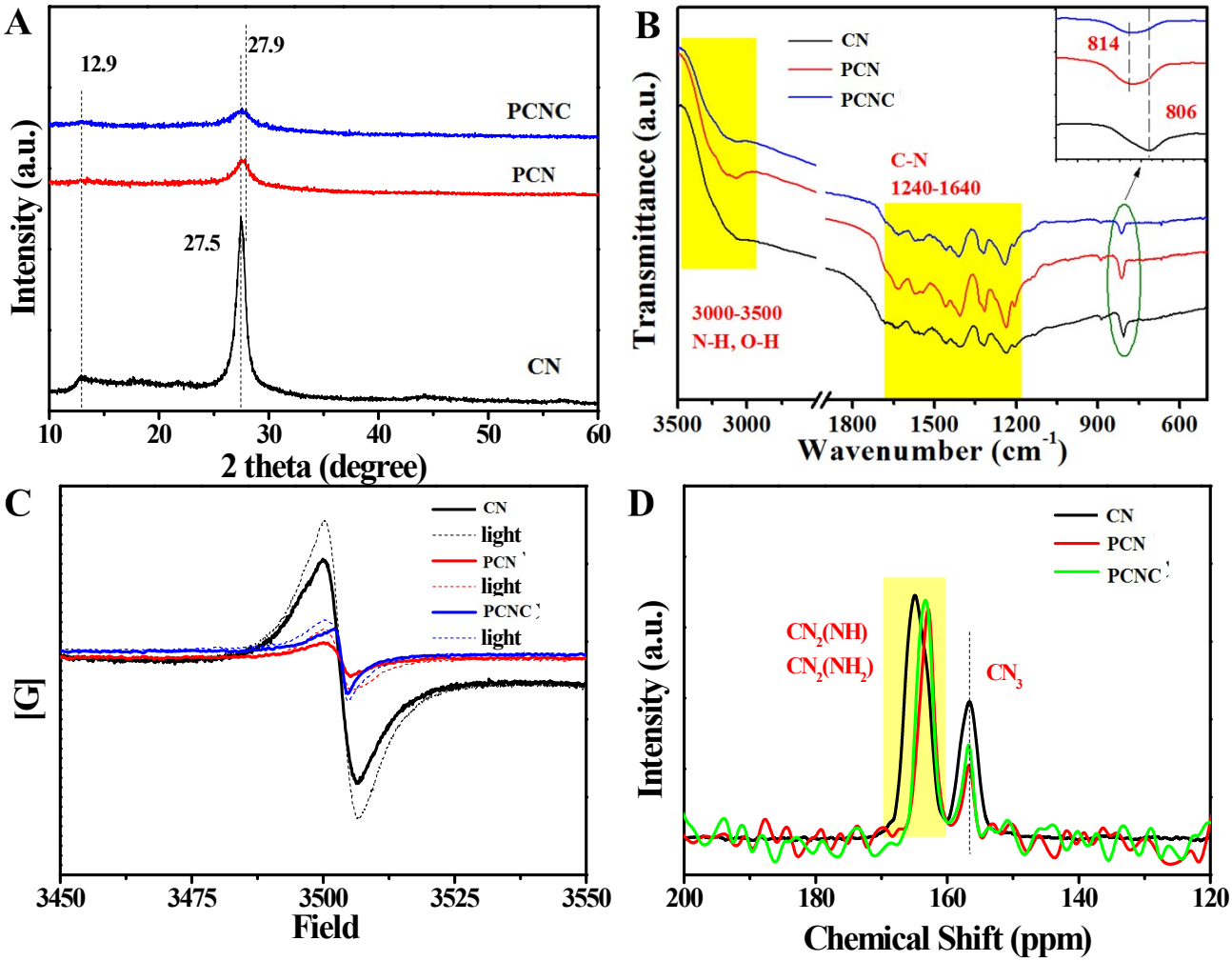

Figure S3 A) XRD patterns, B) FT-IR spectra, C) room-temperature EPR spectra, D) solid-state ^{13}C NMR spectra of CN, PCN and PCNC.

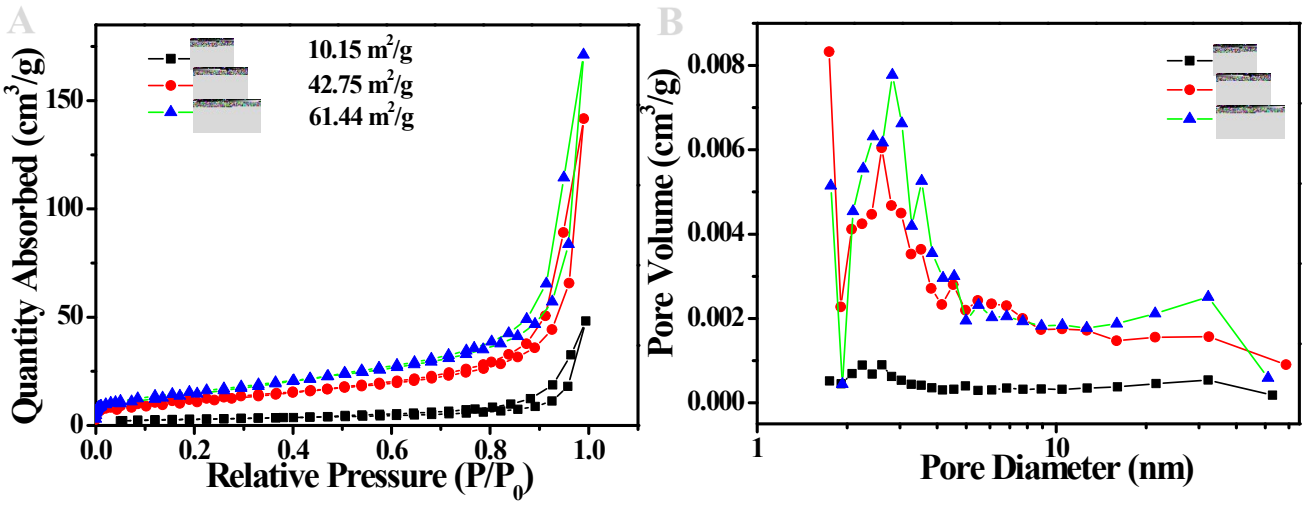

Figure S4 A) N_2 isothermal adsorption-desorption curves and B) Pore-size distribution of CN, PCN and PCNC.

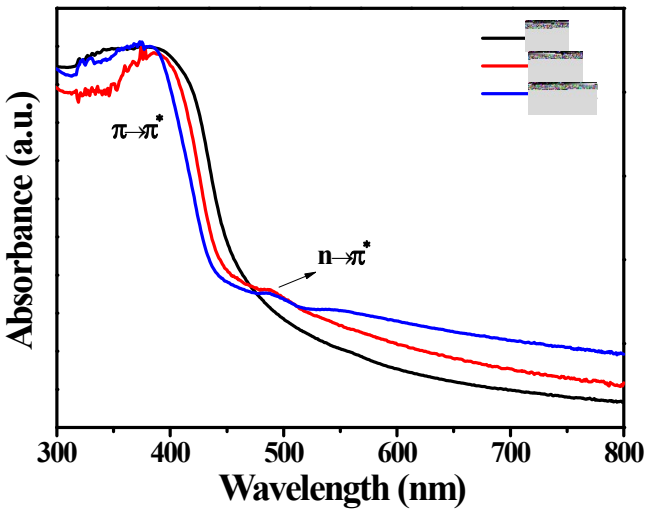

Figure S5 UV-Vis absorption spectra of CN, PCN and PCNC.

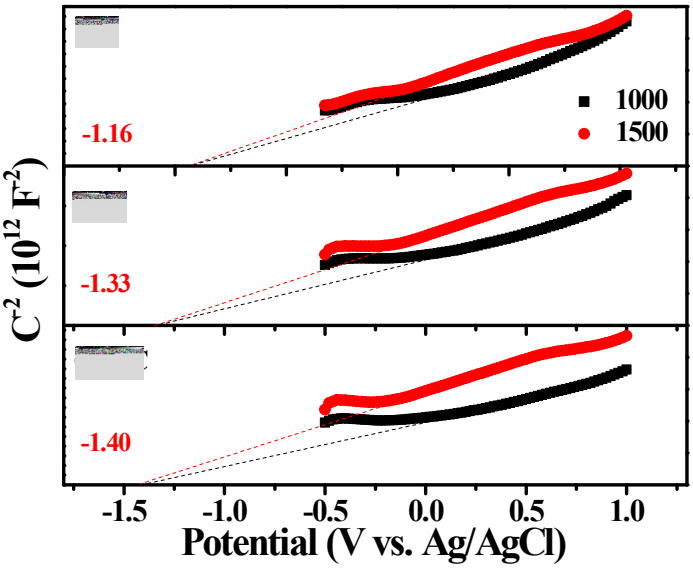

Figure S6 Electrochemical Mott-Schottky curves of CN, PCN and PCNC.

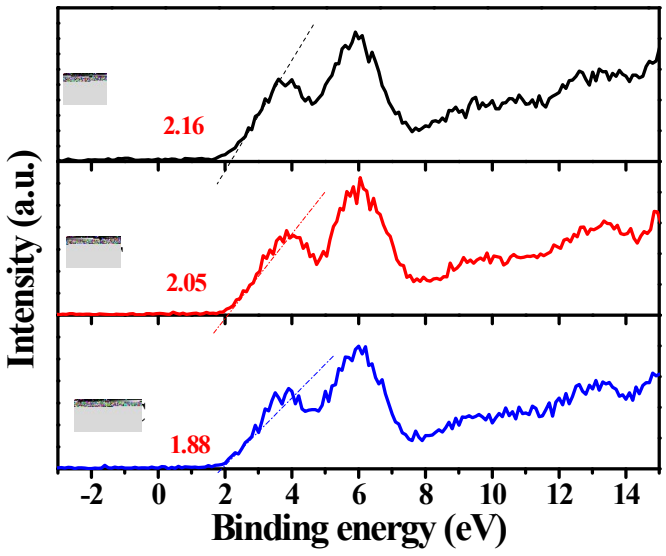

Figure S7 VB-XPS spectra of CN, PCN and PCNC.

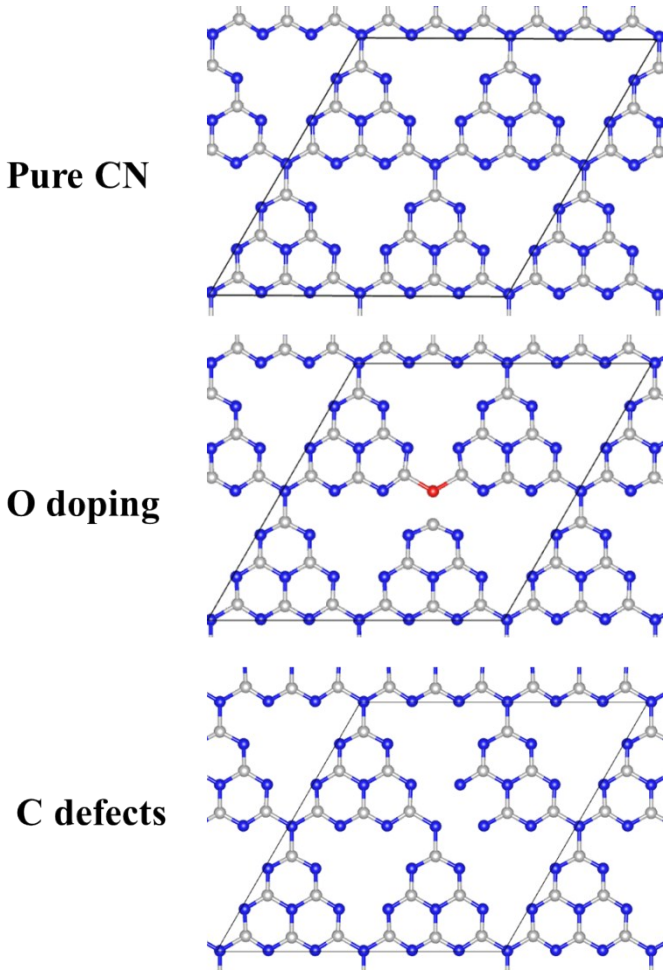

Figure S8 Three molecular models of the graphitic lattice (blue: N; grey: C; red: O)

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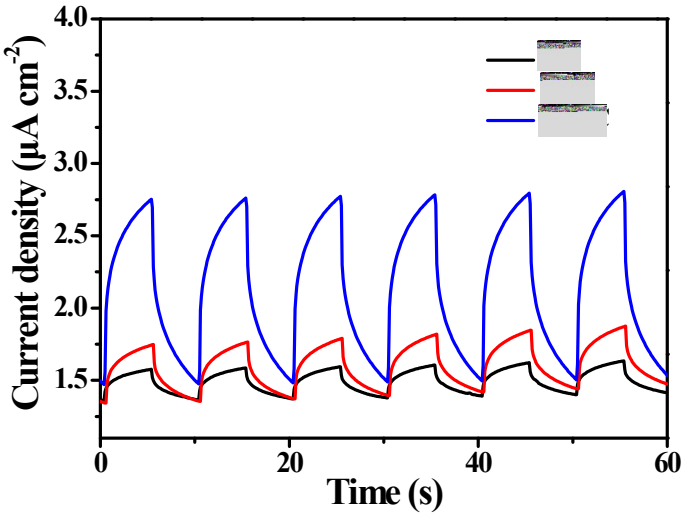

Figure S9 Photocurrent density of CN, PCN and PCNC, measured under visible light illumination.

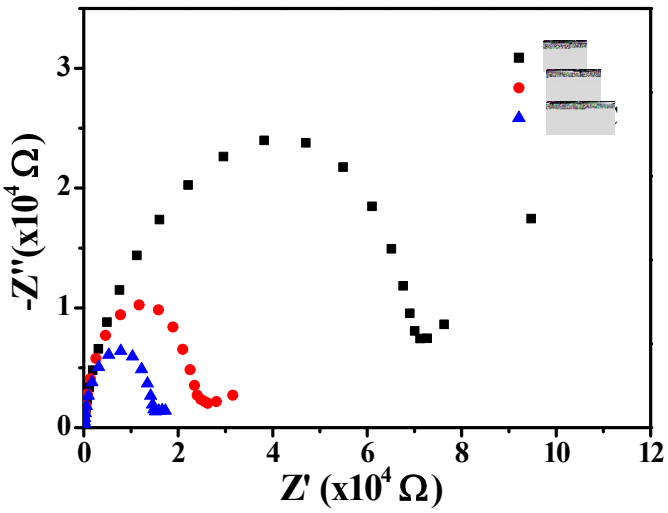

Figure S10 Electrochemical impedance spectroscopy Nyquist plots of CN, PCN and PCNC under ambient conditions

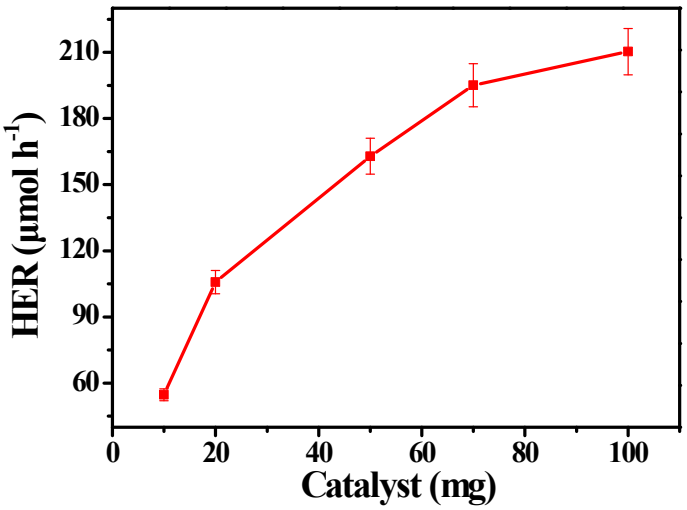

Figure S11 Hydrogen evolution rates versus different concentrations of catalyst.

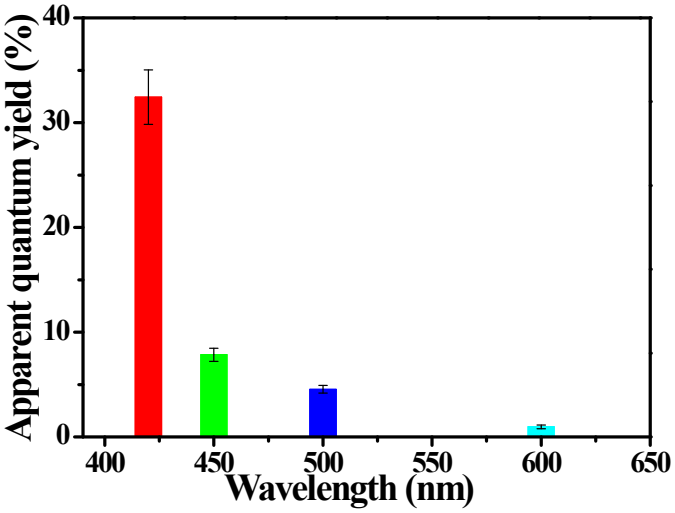

Figure S12 Wavelength dependent apparent quantum yields of PCNC.

Table S1 Statistical peak area ratios of samples.

	CN	PCN	PCNC
Surface C/N ratio	**0.67**	**0.68**	**0.65**
Peak (N-(C)$_3$) ratio	**1**	**0.79**	**0.70**
Peak (N-H) ratio	**1**	**1.37**	**1.66**

Table S2 Elemental analysis of samples.

Sample	C [%]	N [%]	H [%]	O [%]
CN	**35.23**	**62.53**	**1.629**	**0.611**
PCN	**34.35**	**60.36**	**1.735**	**3.555**
PCNC	**33.78**	**59.76**	**1.846**	**4.614**

Table S3 HER results comparison of similar type carbon nitride based photocatalysts.

Samples	Light source	Catalyst use/cocatalyst loading	Hydrogen evolution/μmol h^{-1} g^{-1}	AQY/% 420 nm	reference
PCN	300 W Xe lamp (λ > 420 nm)	20 mg/3 wt% Pt	2040.7	–	This work
PCNC	300 W Xe lamp (λ > 420 nm)	20 mg/3 wt% Pt	5289.9	32.4	This work
OCNA-6	300 W Xe lamp (λ > 420 nm)	25 mg/3 wt% Pt	662.8	20.42	S1
ONLH-600	300 W Xe lamp (λ > 420 nm)	30 mg/5 wt% Pt	340	10.3	S2
PCNT-3	300 W Xe lamp (λ > 420 nm)	50 mg/3 wt% Pt	2020	4.32	S3
P-TCN	300 W Xe lamp (λ > 420 nm)	100 mg/1wt% Pt	670	5.68	S4
CN-SP	300 W Xe lamp (λ > 420 nm)	100 mg/1 wt% Pt	570	_	S5
g-C_3N_4 nanotubes	300 W Xe lamp (λ > 400 nm)	10 mg/3 wt% Pt	11580	6.8	S6
PTYS CN-2	300 W Xe	50 mg/1 wt% Pt	740	11.8	S7

	lamp (λ > 420 nm)				
few-layer C_3N_4	300 W Xe lamp (λ > 420 nm)	20 mg/1 wt% Pt	7990	9.8	S8
CN-75	300 W Xe lamp (λ > 420 nm)	50 mg/3 wt% Pt	4158	_	S9

Reference

1. W. Jiang, Q. Ruan, J. Xie, X. Chen, Y. Zhu and J. Tang, Appl. Catal. B Environ., 2018, **236**, 428–435.
2. Y. Wang, M. K. Bayazit, S. J. A. Moniz, Q. Ruan and J. Tang, Energ. Environ. Sci., 2017, 10, 1643-1651.
3. M. Wu, J. Zhang, B.-b. He, H.-w. Wang, R. Wang and Y.-s. Gong, Appl. Catal. B: Environ., 2019, 241, 159-166.
4. S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan and H. Fu, Angew. Chem. Int. Ed. Engl., 2016, 55, 1830-1834.
5. S. Guo, Y. Tang, Y. Xie, C. Tian, Q. Feng, W. Zhou and B. Jiang, Appl. Catal. B: Environ., 2017, 218, 664-671.
6. Z. Mo, H. Xu, Z. Chen, X. She, Y. Song, J. Wu, P. Yan, L. Xu, Y. Lei, S. Yuan and H. Li, Appl. Catal. B: Environ., 2018, 225, 154-161.
7. N. Tian, K. Xiao, Y. Zhang, X. Lu, L. Ye, P. Gao, T. Ma and H. Huang, Appl. Catal. B: Environ., 2019, 253, 196-205.
8. Y. Xiao, G. Tian, W. Li, Y. Xie, B. Jiang, C. Tian, D. Zhao and H. Fu, J. Am. Chem. Soc., 2019, 141, 2508-2515.
9. S. Zhao, J. Fang, Y. Wang, Y. Zhang and Y. Zhou, ACS Sustainable Chem. Eng., 2019, , 7, 10095−10104.