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Supporting Information

Phosphorus-doped porous carbon nitride for efficient sole production of hydrogen peroxide via photocatalytic water splitting with a two-channel pathway

Jingjing Cao,§ Hui Wang,§ Yajie Zhao, Yan Liu, Hui Huang, Mingwang Shao*, Yang Liu* and Zhenhui Kang**

Institute of Functional Nano and Soft Materials Laboratory (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, PR China

*Correspondence to: hhuang0618@suda.edu.cn, yangl@suda.edu.cn, zhkang@suda.edu.cn

§ These authors contributed equally to this work.

1. Quantum efficiency (QE) calculation.

In the following, the QE determination was described at $\lambda_0 = 420$ nm for CPN. The 10 mg catalyst was added to 15 mL water, and the catalyst solution was irradiated for 8 h. The average intensity of irradiation was determined to be 31.27 mW/cm^2 and the irradiation area was 9.07 cm^2. The number of incident photons (N) is 1.73×10^{22} as calculated by equation (1). The amount of H_2O_2 molecules generated in 8 h was 225 μmol. The quantum efficiency is calculated from the following equation (2).

$$N = \frac{E\lambda}{hc} = \frac{31.27 \times 10^{-3} \times 9.07 \times 3600 \times 8 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.73 \times 10^{22} \quad \textbf{(1)}$$

$$QE = \frac{2 \times the\ number\ of\ evolved\ H_2O_2}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 225 \times 10^{-6}}{1.73 \times 10^{22}} \times 100\% = 1.57\% \quad \textbf{(2)}$$

2. SCC conversion efficiency calculation from solar simulator measurement.

For the determination of SCC efficiency, a solar simulator (420 nm ≤ λ ≤ 700 nm) was used with 10 mg catalyst and 15 mL ultra-pure water under at atmospheric pressure. The amount of H_2O_2 molecules generated in 8 h was 157 μmol. The free energy for H_2O_2 formation is 117 kJ mol $^{-1}$. After 8 h illumination, the average intensity of light source was determined to be 16.47 mW/cm^2 and the irradiation area was calculated as 9.07 cm^2. Therefore, the total input energy is 0.149 W. Finally, the SCC is determined to 0.43%. At the same time, a AM 1.5G solar simulator (100 mW/cm^2) was also used to determine the SCC efficiency, with 10 mg catalyst and 15 mL ultra-pure water under at atmospheric pressure. The amount of H_2O_2 molecules generated in 2 h was 75 μmol. Finally, the SCC is determined to 0.14%.

$$\textbf{SCC efficiency (\%)} = \frac{[\,\Delta G\ for\ H_2O_2\ generation\ (J\ mol^{-1})\ ] \times [\,H_2O_2\ formed\ (mol)}{[total\ input\ energy\ (w)]\ \times [reaction\ time\ (s)]} \times 100$$

$$= \frac{117\ \times 1000\ \times 157\ \times 10^{-6}}{0.149\ \times 8\ \times 60\ \times 60} \times 100\% = 0.43\%$$

$$\textbf{SCC efficiency (\%)} = \frac{[\,\Delta G\ for\ H_2O_2\ generation\ (J\ mol^{-1})\ ] \times [\,H_2O_2\ formed\ (mol)}{[total\ input\ energy\ (w)]\ \times [reaction\ time\ (s)]} \times 100$$

$$= \frac{117\ \times 1000\ \times 75\ \times 10^{-6}}{0.907\ \times 2\ \times 60\ \times 60} \times 100\% = 0.14\%$$

3. Electron transfer number calculation.

The test data are stored in a CHI920C electrochemical workstation (CH Instruments, Shanghai, China). The electron transfer number (n) can be calculated according to the following formula. $n = 4I_d / (I_d + I_r/N)$. Where I_d and I_r represent the disk and ring current respectively, and N is the rotating disk-ring electrode (RRDE) collection efficiency. The averaged collection efficiency N is 0.43. To determine the electron transfer number (n), photocatalysts modified RRDE electrodes measurements were performed in N_2-saturated ultrapure water at a rotating speed of 1600 rpm and a scan rate of 10 mV·s^{-1}. The disk potential was set at open-circuit voltage, while the ring potential was set at 0.9

V vs. SCE to detect H_2O_2 generation.

3. Supplementary figures.

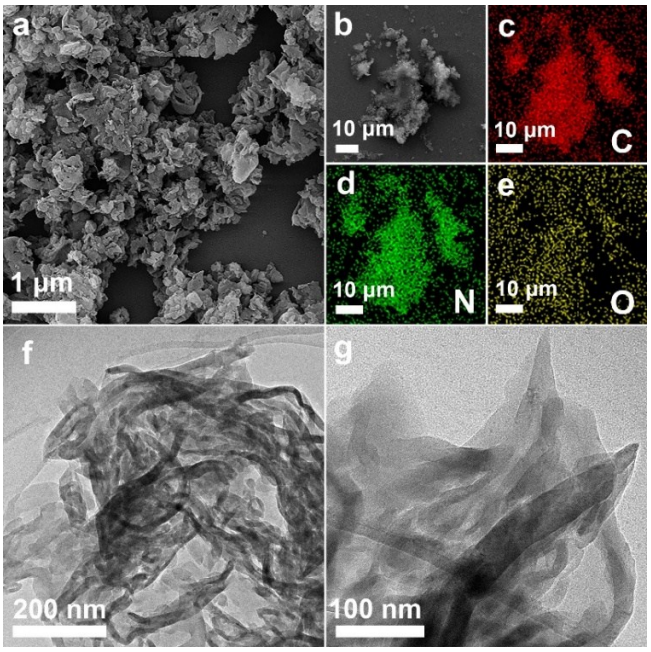


Figure S1. (a) and (b) SEM images of C_3N_4. (c-e) The corresponding EDS elemental mappings of constituent elements of C_3N_4. (f) and (g) TEM images of C_3N_4.

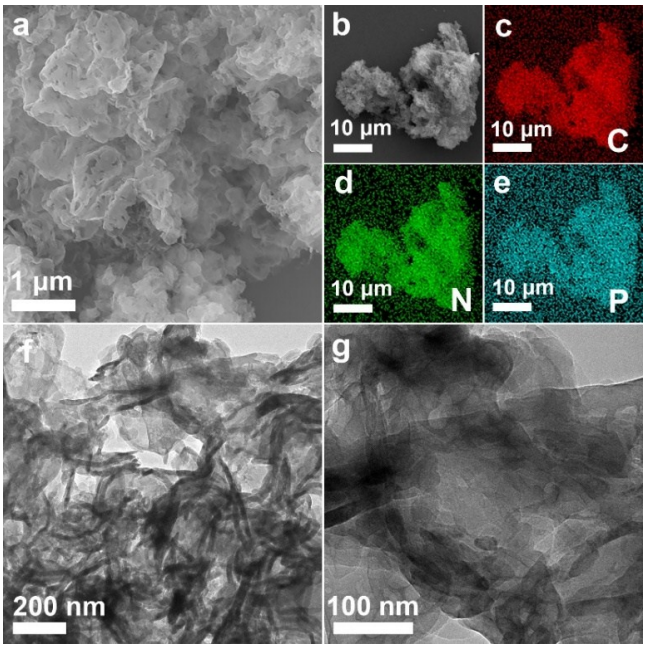


Figure S2. (a) and (b) SEM images of CP. (c-e) The corresponding EDS elemental mappings of constituent elements of CP. (f) and (g) TEM images of CP.

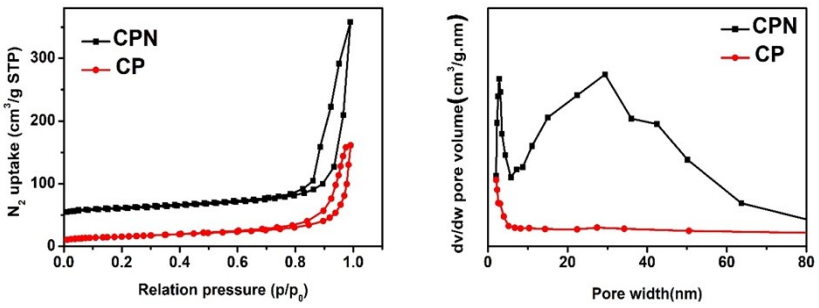


Figure S3. (a) The Nitrogen adsorption–desorption isotherms of CP (red line) and CPN (black line). (b) The pore size distribution curves of CP (red line) and CPN (black line).

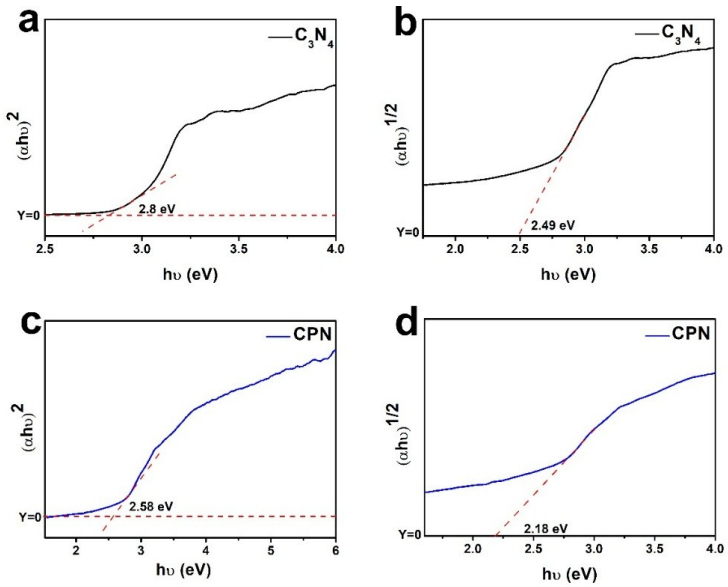


Figure S4. Determination of band gap of C_3N_4 composition based on Kubelka–Munk function (a) when r=2 and (b) when r=1/2. Determination of band gap of CPN composition based on Kubelka–Munk function (c) when r=2 and (d) when r=1/2. (Fig. S4a and S4c show good linear fit when using r = 2, (no good linear fit is obtained from r = 1/2) and consistent with previous work, proving C_3N_4 and CPN are direct band gap materials).

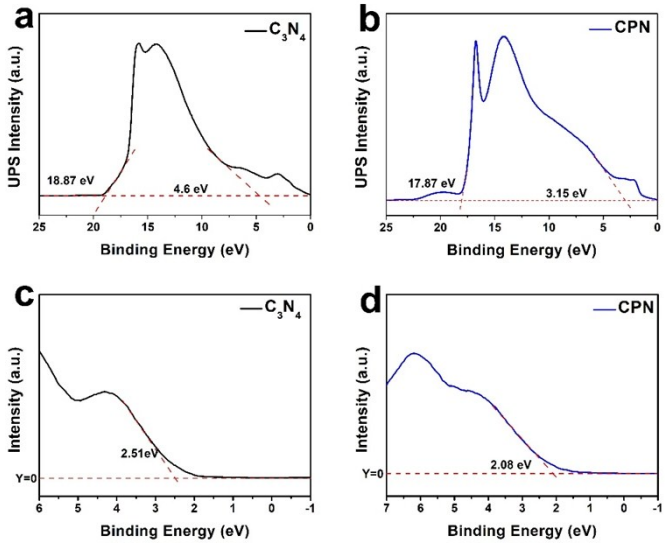


Figure S5. The UPS spectra of (a) C_3N_4 and (b) CPN. VBXPS spectra of (c) C_3N_4 and (d) CPN.

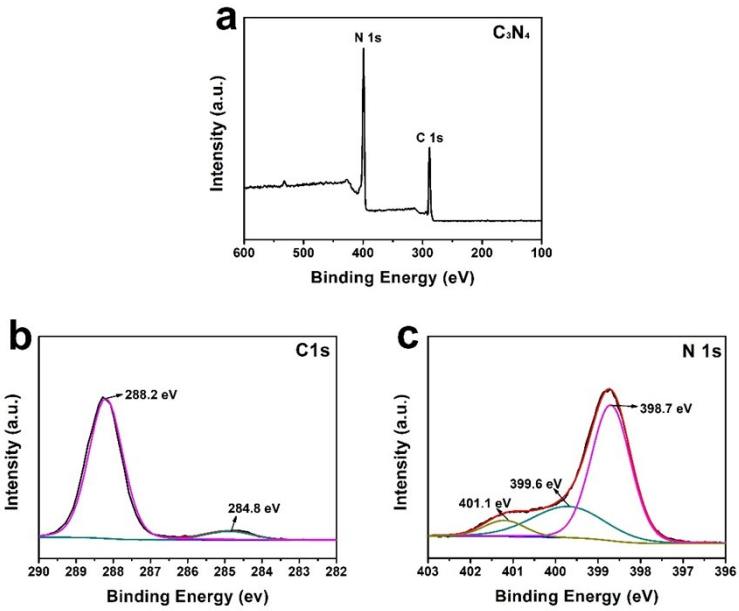


Figure S6. (a) XPS survey spectra and high-resolution XPS spectra of C_3N_4 for (b) C 1s and (c) N 1s.

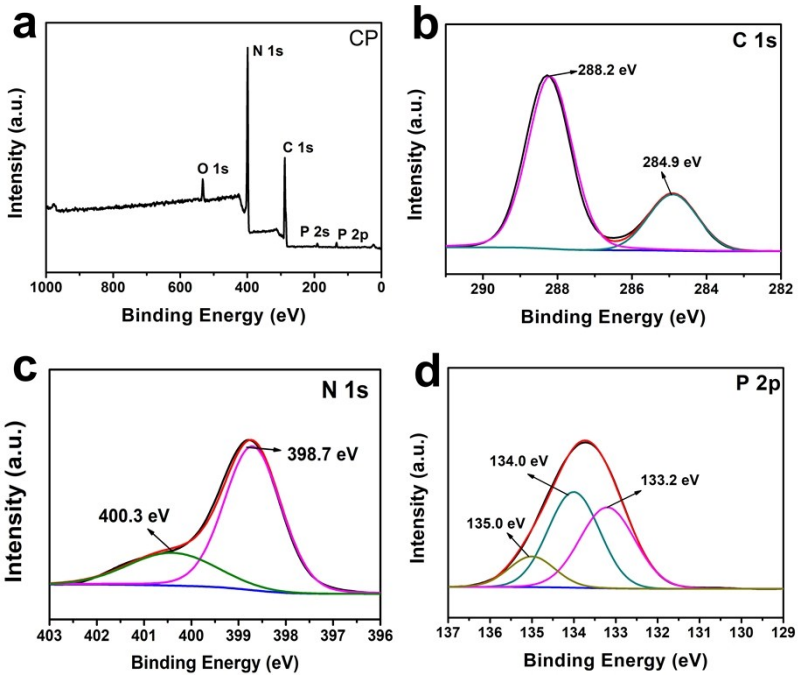


Figure S7. (a) XPS survey spectra and high-resolution XPS spectra of CP for (b) C 1s, (c) N 1s and (d) P 2p.

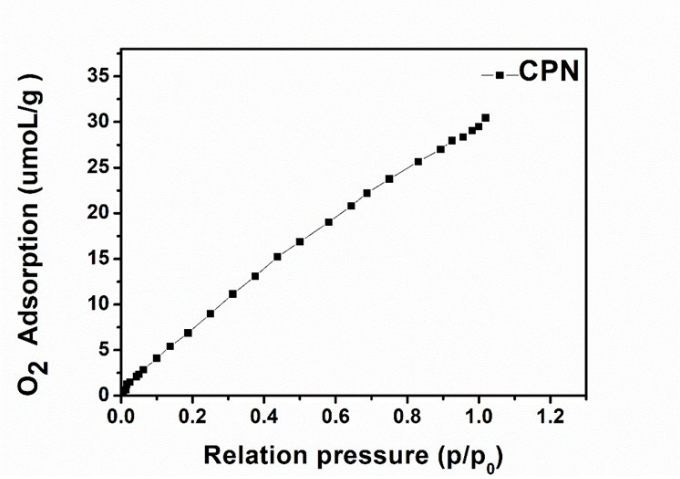


Figure S8. O_2 adsorption isotherm of CPN at 298 K.

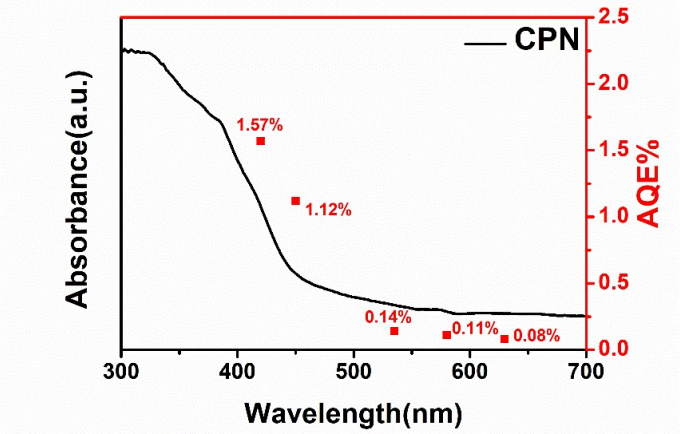


Figure S9. The quantum efficiency of CPN at different wavelengths.

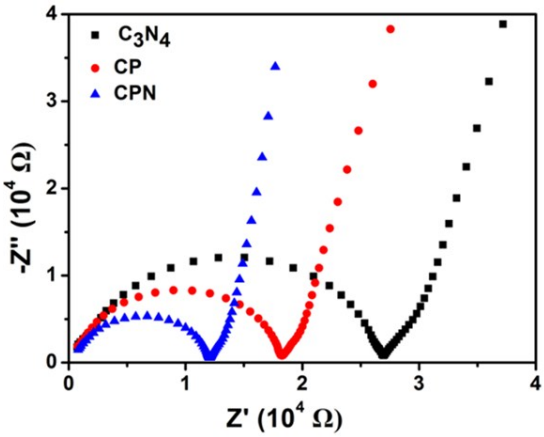


Figure S10. EIS Nyquist plots spectra of C_3N_4 (black line), CP (red line) and CPN (blue line).

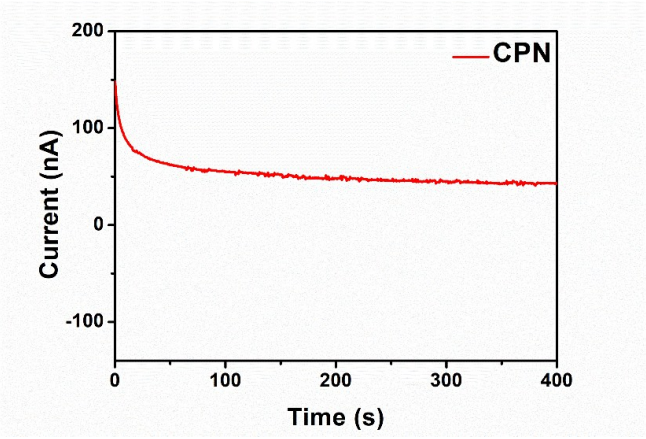


Figure S11. The i-t curve of CPN. (The photocurrent was measured at open circuit potential in 0.1 M Na_2SO_4 solution with light irradiation of $\lambda > 420$ nm (scan rate: 50 mV s^{-1})).

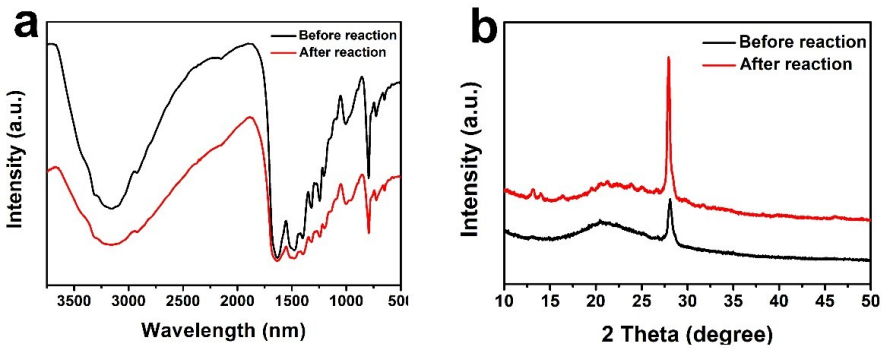
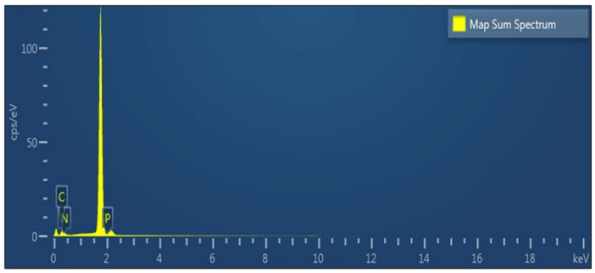


Figure S12. Comparison of FTIR spectra and XRD patterns before (black line) and after (red line) six cycles of CPN.

4. Supplementary tables.

Table S1. Atomic percentage of different elements according to EDS elemental mappings.



Map Sum Spectrum	
Element	**Atomic %**
C	35.56
N	60.04
P	4.4
Total	100

Table S2. Atomic percentage of different elements according to XPS.

Element	Atomic %
C	35.09
N	53.35
O	5.84
P	5.72
Total	100

Table S3. The analysis of the percentages of different bonds according to XPS.

Sample	P=N (%)	P-N (%)	P=O (%)
CP	0.44	0.43	0.13
CPN	0.26	0.70	0.04