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Supplementary information

A g-C₃N₄ based photoelectrochemical cell using O₂/H₂O redox couples

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SI-1 Electron-transfer number (n) calculation.

The rotating ring disk electrode (RRDE) experiment (Fig. S11) was performed with a glassy carbon disk and a platinum ring in phosphate buffer (pH = 7.2) solution (0.05 M). A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the counter electrode, respectively. The LSV scans were performed on the disk with the ring potential at 0.9 V vs. SCE to detect the H_2O_2 formed at the disk. The disk current I_{disk} results from the reaction of O_2 forming H_2O and H_2O_2 at the disk.

The electron-transfer number (n) is calculated as follows:

$$n = \frac{4I_{disk}}{I_{disk} + I_{ring}/N} \tag{1}$$

)

Here, I_{disk} is the disk current, I_{ring} is the ring current, and N is the RRDE collection efficiency, which was measured to be 0.24 by the reversible $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ system. In detail, the electrode was dipped into 0.1 mol/L KCl solution with 0.01 mol/L K₃Fe(CN)₆] and rotated with different rotation rates ($\omega = 100, 400, 900, 1600$ rpm). The disk potential was scanned from 0.4 V to -0.6 V vs. SCE at 10 mV/s, and the ring potential was set to 0.497 V vs. SCE where the reduced $[Fe(CN)_6]^{4-}$ is oxidized. The ratio of I_{ring}/I_{disk} is almost constant with ω . The calculated electron-transfer number was approximately 2.43, indicating the formation of H_2O_2 from O_2 on the disk electrode.

SI-2 Optimization of the photoelectrochemical cell

To obtain the largest maximum power density available for the photoelectrochemical cell, the $[Fe^{III}(Pc)CI]$ concentration (g[FeIII(Pc)CI])/(g[FeIII(Pc)CI]+g[g-C_3N_4]) and the total amount of the catalyst spraying (g[Fe^{III}(Pc)Cl]+g[g-C₃N₄]) on cathode, g[g-C₃N₄] on anode were optimized. The optimization experiments were performed using a one compartment cell configuration with both electrodes immersed in 0.1 M HCl and irradiated by 100 mW·cm⁻² AM 1.5G solar light at air atmosphere (Fig. S2). Note that the illumination of the cathode at air atmosphere does not affect the performance of the electrochemical cell (Fig. S18). We first compared the maximum power density of the cell for different concentration of [Fe^{III}(Pc)Cl] in a fixed amount of catalyst (Fig. S19a). The mass of the catalysts spraying on both the cathode and anode electrode was fixed to 0.5 mg \cdot cm⁻² (the electrode catalyst area was 1 cm⁻²). The maximum power density increased with the [Fe^{III}(Pc)Cl] concentration to a maximum value of 0.136 mW·cm⁻² obtained for 0.025 g_{IFeIII(Pc)CI}/g_{catalvst} and then decreased with [Fe^{III}(Pc)Cl] concentration. We speculate that the dependence of the maximum power density on the [Fe^{III}(Pc)Cl] concentration is due to the enhancement of the decomposition rate of H₂O₂ with increasing [Fe^{III}(Pc)Cl] concentration until the decomposition is sufficient to reduce all generated H₂O₂. The further increase of the [Fe^{III}(Pc)Cl] concentration decreases the g-C₃N₄ mass (the total amount of catalyst mass is kept constant) which in turn decreases the H_2O_2 generation. The amount of the cathode composite catalyst ([Fe^{III}(Pc)Cl] + $g-C_3N_4$) was optimized as well (Fig. S19b). The [Fe^{III}(Pc)Cl] concentration in the cathode electrode was set to 0.025 g_{[FeIII(Pc)CI}/g_{catalyst} and the mass of g-C₃N₄ spraying on anode electrode was fixed to $0.5 \text{ mg} \cdot \text{cm}^{-2}$. The maximum power density increased with the increase of the catalyst amount on the carbon paper to a value of $0.156 \text{ mW} \cdot \text{cm}^{-2}$ for ~1 mg $\cdot \text{cm}^{-2}$. A further increase of the catalyst amount slightly decreased the maximum power density. We further optimized the amount of anode catalyst (g-C₃N₄) spraying on the Ni mesh (Fig. S19c). Using the same cathode (1 mg \cdot cm⁻² $[Fe^{III}(Pc)CI]/C_3N_4$ composite catalyst with the $g_{[FeIII(Pc)CI]}/g_{catalyst}$ ratio of 0.025), the maximum power density increased with the increasing amount of g-C₃N₄ on the Ni mesh up to an amount of 0.5 mg·cm⁻². Larger amounts of g-C₃N₄ decreased the maximum power density. The performance of all electrodes decreases at the highest loadings may be due to the weak conductivity of the $g-C_3N_4$, which causes the decrease of the conductivity and the performance of the electrodes with the increase of the loadings.

SI-3 Solar-to-electric energy conversion efficiency.

The solar-to-electric energy conversion efficiency was evaluated by using the AM 1.5G solar simulator as the light source. The loading area of the catalyst on the photoanodes was about 1 cm².

Solar-to-electric energy conversion efficiency (%)

= [Maximum power density] × [Catalyst loading area] [Energy density of incident solar light] × [Irradiation area] $\times 100$

The maximum power density of the checked cell under 100 mW·cm⁻² AM 1.5 solar light (irradiation area 1 cm²) in 0.1 M HCl at air atmosphere was 0.156 mW·cm⁻². To subtract the power due to Ni oxidation, the solar-to-electric energy conversion efficiency was calculated by the maximum power density (0.146 mW cm⁻²) obtained from the new I-P curve with the dark curve as zero of current.

SI-4. Solar-to- H_2O_2 energy conversion efficiency. The generation rate of H_2O_2 from water by g- C_3N_4 decreases with time (Fig. S23b) with the initial generation rate of 9.58 μ mol/h. The amount of H₂O₂ generated is calculated by the corresponding calibration curve (Fig. S23a).

Solar-to- H_2O_2 energy conversion efficiency (%)

[Output power as H_2O_2]

 $\frac{1}{[Power density of incident solar light] \times [Irradiation area]} \times 100$ [Power density of incluent solar L_{g,m_1} [Enthalpy change of equation (ΔH)] × [Initial generation rate of H_2O_2] $\times 100 = 0.187\%$

[Power density of incident solar light] × [Irradiation area]

the multiplication of enthalpy change (ΔH =98.3 kJ·mol⁻¹), the power density of incident solar light (70 mW·cm⁻²) and irradiation area (2 cm⁻²).

SI-5. Additional information. The influence of gas environments of the cathode on the H_2O_2 fuel cell performance is shown in Fig. S24.

Supplementary Figures:



Fig. S1 SEM images of the electrodes: (a) and (b) SEM images of the anode (Ni mesh modified with g- C_3N_4). (c) and (d) SEM images of the cathode (carbon paper modified with [Fe^{III}(Pc)Cl]/g-C₃N₄).



Fig. S2 A digital picture of the photoelectrochemical cell. It is composed of a carbon paper modified with $[Fe^{III}(Pc)CI]/g-C_3N_4$ as the cathode (left electrode in the picture) and a nickel mesh coated with g- C_3N_4 as the anode (right electrode in picture) in 0.1 M HCl.



Fig. S3 Open-circuit potential of the photoelectrochemical cell composed of: (i) $[Fe^{III}(Pc)CI]/C_3N_4$ modified carbon paper cathode (catalyst load 0.5 mg·cm⁻², $[Fe^{III}(Pc)CI]$ concentration of 0.025 $g_{[FeIII(Pc)CI]}/g_{catalyst}$) and (ii) g-C₃N₄ modified Ni mesh anode (catalyst load 0.5 mg·cm⁻²). The test was performed using a 0.1 M HCl solution (one compartment) under AM 1.5G solar light (1 sun, 100 mW·cm⁻²) at air atmosphere. The open-circuit potential of the cell in the dark at air atmosphere is ~0.72 V. At this point, the cell has a small power density as well, due to the reduction of the H₂O₂ on the cathode produced by ORR chemically catalyzed by g-C₃N₄ and the oxidation of Ni mesh electrode.



Fig. S4 TEM images of different $g-C_3N_4$ catalysts: (a) $g-C_3N_4-0$, (b) $g-C_3N_4-1$, (c) $g-C_3N_4-2$, (d) $g-C_3N_4-4$ and (e) $g-C_3N_4-5$. These images show the typical layered morphology of $g-C_3N_4$.



Fig. S5 Nitrogen sorption isotherms and the BJH pore-size distribution curve of g-C₃N₄-3 catalyst.



Fig. S6 XRD patterns of the g-C₃N₄ catalysts. The sharp <002> diffraction peak at 27.5° and the <001> peak at 12.9° display the layered stacking with a distance of 0.326 nm and the in-planar repeating unit with a period of 0.675 nm, respectively. The data is in accord with the previous reports of C_3N_4 .^{S1,2}



Fig. S7 FT-IR spectra of the g-C₃N₄ catalysts. The intense bands at 1637.5, 1568.1, 1462.0 and 1409.9 cm⁻¹ are attributed to the stretching vibration modes of heptazine-derived repeating units. The bands at 1321.2 and 1238.2 cm⁻¹ correspond to the stretching vibration of connected units of N-(C)₃ (full condensation) or C-NH-C (partial condensation), respectively. The peak at 810.1 cm⁻¹ is the breathing mode of the tri-s-triazine units. The data is in accord with the previous reports of C_3N_4 .^{S1, 2}



Fig. S8 The UV-Vis absorption spectra of the different $g-C_3N_4$ catalysts. All exhibit an absorption edge at about 455 nm indicating that the main solar energy absorption of all the $g-C_3N_4$ catalysts is at wavelengths shorter than 455 nm.^{S2}



Fig. S9 (a) XPS C1s spectra and (b) N1s spectra of the g-C₃N₄ catalysts. The C 1s XPS spectra show a peak located at 288.0 eV which is assigned to N-C=N sp²-bonded carbon, and a weaker one at 284.3 eV assigned to graphitic carbon. The N 1s is deconvoluted into three peaks located at 400.9 eV, 399.6 eV and 398.5 eV. The peak at 400.9 eV is ascribed to quaternary N bonded to three carbon atoms in the aromatic cycles. The peak located at 399.6 eV is assigned to the tertiary N bonded to carbon atoms in the form of N-(C)₃ or H-N-(C)₂. The one at 398.5 eV is due to sp² hybridized aromatic N bonded to carbon atoms with the C=N-C form. The peak centered at 400.1 eV is attributed to π -excitations.^{S1}



Fig. S10 Free H₂O₂ in a g-C₃N₄ aqueous solution after irradiation under 70 mW \cdot cm⁻² Xenon light ($\lambda >$ 420 nm) for 12 h. The reaction systems consist of 20 mg different g-C₃N₄ catalysts dispersed in 15 mL water.



Fig. S11 RRDE measurements of oxygen reduction on $g-C_3N_4$ catalyst (disk) and H_2O_2 oxidation (ring) in a 0.05 M phosphate buffer solution (PBS, pH 7) under dark (black curve) and under xenon light (red curve). The ring electrode is set at 0.9 V (vs. SCE, saturated KCl). Rotation rate: 1600 rpm. Scan rate: 10 mV/s. The light does not affect the oxygen reduction.



Fig. S12 LSV curves of $[Fe^{III}(Pc)CI]/carbon paper electrode and Ni mesh in 0.1 M HCl containing 300 mM H₂O₂. For comparison the onset potential, the current density of the oxidation and reduction reaction was normalized by the corresponding maximum current density. The onset potential of Ni mesh electrode for H₂O₂ oxidation is 0.86 V, lower than that for H₂O₂ reduction on the <math>[Fe^{III}(Pc)CI]$ electrode (0.96 V). This proves that the H₂O₂ fuel cell which oxidizes H₂O₂ by the Ni mesh electrode and reduces H₂O₂ by the $[Fe^{III}(Pc)CI]$ electrode can produce electric power.



Fig. S13 I-V (black) and I-P (blue) curves plotted on a linear current scale of the solar-light-driven cell with the anode being irradiated under 100 mW·cm⁻² AM 1.5G solar light (circle) and in the dark (square) in 0.1 M HCl, and the fuel cell in the dark in 0.1 M HCl containing 300 mM H₂O₂ (triangle). The solar-light-driven cell is composed of [Fe^{III}(Pc)Cl]/C₃N₄ modified carbon paper cathode (catalyst load 0.5 mg·cm⁻², [Fe^{III}(Pc)Cl] concentration of 0.025 g_[FeIII(Pc)CI]/g_{catalyst}) and g-C₃N₄ modified Ni mesh anode (catalyst load 0.5 mg·cm⁻²). The fuel cell is composed of [Fe^{III}(Pc)Cl] modified carbon paper as cathode and Ni mesh as anode. The tests were operated at air atmosphere.



Fig. S14 Cell performance of the optimized photoelectrochemical cell in 0.1 M HCl containing 300 mM H_2O_2 at air atmosphere under dark. The maximum power density and the OCP is 0.08 mW·cm⁻² and 0.81 V, respectively, which are larger than those of the H_2O_2 fuel cell (0.026 mW·cm⁻² and 0.62 V, respectively) shown in Fig. 2b. This is due to the involvement of the reduction reaction of O_2 in the cathode region.



Fig. S15 Digital picture of the photoelectrochemical cell in a two-compartments with a Nafion membrane.



Fig. S16 (a) The effect of light intensities (AM 1.5G solar light) on the maximum power density of the photoelectrochemical cell. The tests were performed with the anode and the cathode being irradiated by different light intensities at N₂ atmosphere, while another electrode was in 0.1 M HCl being irradiated under AM 1.5G solar light (1 sun, 100 mW·cm⁻²) under air. (b) The effect of cell atmospheres on the maximum power density of the photoelectrochemical cell. The tests were operated with different atmospheres on the anode and the cathode under dark, while another electrode was in 0.1 M HCl being irradiated under AM 1.5G solar light (1 sun, 100 mW·cm⁻²) under air. The tests were operated with different atmospheres on the anode and the cathode under dark, while another electrode was in 0.1 M HCl being irradiated under AM 1.5G solar light (1 sun, 100 mW·cm⁻²) under air. The electrodes conditions were arranged as shown in Table S2. The error bars indicate the maximum and minimum values obtained, while the dot represents the average value.



Fig. S17 The dependence of the cell performance on the irradiation wavelength. The irradiation source was a 300W Xe lamp applying band-pass filters of $\lambda \pm 20$ nm to obtain 435, 475, 520, 600 and 650 nm (light intensity 9.30 mW·cm⁻²). The blue curve is the UV-Vis absorption spectrum of g-C₃N₄ ranging from 400-675 nm. Note that the cell power density corresponds to the UV-Vis absorption spectrum of g-C₃N₄. The error bars indicate the maximum and minimum values obtained, while the dot represents the average value.



Fig. S18 I-V (black) and I-P (blue) curves of the photoelectrochemical cell in 0.1 M HCl at air atmosphere with the cathode under dark or light, while the anode was irradiated by AM 1.5G solar light (1 sun, 100 mW \cdot cm⁻²). Note that the irradiation of the cathode does not affect the cell performance.



Fig. S19 (a) The cell performance of the photoelectrochemical cell with different concentrations of $[Fe^{III}(Pc)CI]$ ($g_{[FeIII(Pc)CI]}/g_{catalyst}$) in a fixed amount of composite catalyst spraying on the cathode. The mass of the catalysts spraying on both the cathode and anode electrode was 0.5 mg·cm⁻². (b) The cell performance of the photoelectrochemical cell with different amounts of cathode catalyst. The $[Fe^{III}(Pc)CI]$ concentration in the cathode electrode was 0.025 $g_{[FeIII(Pc)CI]}/g_{catalyst}$, and the mass of the catalyst spraying on the anode electrode was 0.5 mg·cm⁻². (c) The cell performance of the photoelectrochemical cell for different amounts of the anode catalyst. The [Fe^{III}(Pc)CI] concentration in the cathode electrode was 0.5 mg·cm⁻². (c) The cell performance of the photoelectrochemical cell for different amounts of the anode catalyst. The [Fe^{III}(Pc)CI] concentration in the cathode electrode was 0.025 $g_{[FeIII(Pc)CI]}/g_{catalyst}$, and the mass of the catalyst spraying on the cathode electrode was 0.025 $g_{[FeIII(Pc)CI]}/g_{catalyst}$, and the mass of the catalyst spraying on the cathode electrode was 0.025 $g_{[FeIII(Pc)CI]}/g_{catalyst}$, and the mass of the catalyst spraying on the cathode electrode was 0.025 $g_{[FeIII(Pc)CI]}/g_{catalyst}$, and the mass of the catalyst spraying on the cathode electrochemical cell composed of $[Fe^{III}(Pc)CI]/C_3N_4$ modified carbon paper cathode (catalyst load 1 mg·cm⁻², [Fe^{III}(Pc)CI] concentration of 0.025 $g_{[FeIII(Pc)CI]}/g_{catalyst}$) and g-C₃N₄ modified Ni mesh anode (catalyst load 0.5 mg·cm⁻²). For Fig. S19, the power densities of the cell were all obtained in a one compartment configuration applying a 0.1 M HCl solution with both electrodes under AM 1.5G solar light (1 sun, 100 mW·cm⁻²) at air atmosphere. For Fig. S19a-c the error bars indicate the maximum and minimum values obtained, while the dot represents the average value.



Fig. S20 I-V (black) and I-P (blue) curves of the photoelectrochemical cell in 0.1 M HCl solution (square) and after setting the cell dark curve as zero of current (circle).



Fig. S21 I-V (black) and I-P (blue) curves of the photoelectrochemical cell in seawater at pH 1 (circle) and after setting the cell dark curve as zero of current (square).



Fig. S22. Digital pictures of the photoelectrochemical cell modified with $g-C_3N_4$ (a) after operating at 0 V under light for 30 hours in 0.1 M HCl at air atmosphere, (b) after operating at 0 V in 0.1 M HCl solution containing 300 mM H_2O_2 under dark for 6.5 hours. (c) Digital picture of the H_2O_2 fuel cell without $g-C_3N_4$ after operating at 0 V in HCl containing 300 mM H_2O_2 under dark for 3 hours. (d) Mass loss rate of Ni mesh after different time with the cell operated at 0 V. The tests were performed with photoelectrochemical cell modified with $g-C_3N_4$ under light in 0.1 M HCl at air atmosphere (Scatter 1) or under dark in 0.1 M HCl solution containing 300 mM H_2O_2 (Scatter 2), and H_2O_2 fuel cell without $g-C_3N_4$ under dark in HCl containing 300 mM H_2O_2 (Scatter 3). Note that the Ni mesh electrode not deposited by $g-C_3N_4$ breaks due to etching after 3 hours. In contrast, the $g-C_3N_4$ /Ni electrode remains intact after 30 hours of under light and only slightly curls after working 6.5 hours under dark in a 300 mM H_2O_2 solution. The mass loss rate of the Ni mesh modified with $g-C_3N_4$ in solution containing H_2O_2 is a little smaller than that of pure Ni, while the Ni mesh deposited by $g-C_3N_4$ shows almost no loss of mass under light in 0.1 M HCl.



Fig. S23. H_2O_2 generation by light irradiation of $g-C_3N_4$: (a) the calibration curve of the absorbance of the o-tolidine indicator versus the H_2O_2 concentration and the corresponding fitting equation of the H_2O_2 concentration versus absorbance. (b) A time course of H_2O_2 production photo-catalyzed by 40 mg g- C_3N_4 in 20 mL water under 70 mW·cm⁻² xenon light for 12 h. The initial H_2O_2 generation rate calculated using the corresponding calibration curve is 9.58 µmol/h. Note that the H_2O_2 generation rate decreases with time due to the poisoning of the g- C_3N_4 catalyst by the generated H_2O_2 .



Fig. S24. The influence of gas environments of the cathode on the H_2O_2 fuel cell performance, while the anode was set at N_2 atmosphere. The H_2O_2 fuel cell was composed of a Ni mesh anode and [Fe^{III}(Pc)Cl]/carbon paper cathode in 0.1 M HCl solution containing 300 mM H_2O_2 . The almost constant power density shows that oxygen does not participate in the cathode reaction of H_2O_2 fuel cell.

Surface area of the $g-C_3N_4$ calculated from the nitrogen adsorption isotherm using the BET method.									
	g-C ₃ N ₄ -0	g-C ₃ N ₄ -1	g-C ₃ N ₄ -2	g-C ₃ N ₄ -3	g-C ₃ N ₄ -4	g-C ₃ N ₄ -5			
Surface									
area	72.52	85.24	91.33	113.71	108.32	102.78			
(cm ³ /g)									

Table S1 Surface area of the $g-C_3N_4$

Table S2 Different experimental conditions for electrodes in two separate compartments with a protonpermeable Nafion membrane in the mechanism experiments. The first two conditions are used for investigating the influence of the light intensities of the anode and the cathode on the cell performance, respectively. The last two conditions are used for investigating the influence of the gas environments of the anode and the cathode on the cell performance, respectively.

	Conditions					
Expt No.	Anode (C ₃ N ₄ /Ni)		Cathode ([Fe ^{III} (Pc)Cl]/C ₃ N ₄ /CP)			
	Light intensity	Gas environment	Light intensity	Gas environment		
1	Variation	N_2	1 sun	Air		
2	1 sun	Air	Variation	N_2		
3	0 sun	Variation	1 sun	Air		
4	1 sun	Air	0 sun	Variation		

Supplementary references

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