

Supporting Information

Graphitic Carbon Nitride/CoTPP Type-II Heterostructures with Significantly Enhanced Photocatalytic Hydrogen Evolution

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EXPERIMENTAL SECTION

Materials

Urea ($\geq 99\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd. Triethanolamine (TEOA, $\geq 78\%$), methanol ($\geq 99\%$), lactic acid ($\geq 85\%$) and ascorbic acid ($\geq 99\%$) were also obtained from Sinopharm Chemical Reagent Co., Ltd. Cobalt (II)meso-Tetraphenylporphine (CoTPP) was purchased from Frontier scientific company Ltd. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 37\%$ Pt basis) was bought from Aldrich. All the chemicals were of analytical grade, thus they were used as received from the manufactures without any purification. Besides, the double distilled water which was used in all experiments was get through a SZ-93A auto-double distillation apparatus (Ya Rong Corp., Shanghai, China).

Preparation of photocatalysts.

Firstly, 10.0 g of urea was added into covered alumina crucible and calcined at 550 °C for 4 h in a muffle furnace in air atmosphere, at the heating rate of 5 °C min^{-1} . After 4 h, the sample was left to cool naturally to room temperature, which leads to the formation of yellow powder (g- C_3N_4), and was collected for further analysis.

Characterizations.

X-ray diffraction (XRD). XRD profiles of the g- C_3N_4 , CoTPP and $\text{C}_3\text{N}_4/\text{CoTPP}$ with different proportion of CoTPP were obtained by using X-ray diffraction (MXPAHF, Japan) with Cu $\text{K}\alpha$ irradiation ($\lambda = 1.541 \text{ \AA}$) at 40 kV and 200 mA. The scanning angle was from 10° to 70°.

X-ray photoelectron spectroscopy (XPS). XPS spectra of g- C_3N_4 , CoTPP and $\text{C}_3\text{N}_4/\text{CoTPP}$ were performed by using ESCALAB 250 high-performance electron spectrometer, which was set to monochromated Al $\text{K}\alpha$ radiation as the excitation source.

Transmission electron microscopy (TEM). The TEM observations were done using a JEOL JEM12010 high resolution transmission electron microscope operated at 200 kV.

Ultraviolet visible (UV-vis). The diffuse reflectance UV-vis absorption spectra of the photocatalysts were recorded by a Shimadzu spectrophotometer (Model 2501 PC).

The steady-state Photoluminescence (PL). The steady-state photoluminescence (PL) measurements were conducted on a fluorescence spectrophotometer (JY Fluorolog-3-Tau) with the excitation wavelength at 325 nm.

The time-resolved photoluminescence (TRPL). TRPL measurements were measured on a LaserStrobe Time-Resolved Spectrofluorometer (Photon Technology International (Canada) Inc.) with a USHIO xenon lamp source, a GL-302 high-resolution dye laser (lifetimes 100 ps to 50 ms, excited by a Nitrogen laser) and a 914 photomultiplier detection system.

Cyclic voltammetry (CV). CV tests were conducted using an electrochemical workstation (CHI 760E, Chenhua Instrument Company, Shanghai, China).

Photoelectrochemical measurements. Photoelectrochemical tests were done at CHI 760E electrochemical workstation (chenhua Instrument Company, Shanghai, China) based on a standard three-electrode system, composed of Ag/AgCl as the reference electrode, Pt wire as the counter electrode and indium-tin oxide (ITO) glass as the working electrode. Na₂SO₄ (0.5 M) was used as the electrolyte solution. The g-C₃N₄ and C₃N₄/CoTPP electrodes were prepared by depositing suspensions made of g-C₃N₄ or C₃N₄/CoTPP and water (the concentration of g-C₃N₄ and C₃N₄/CoTPP was 2 mg/mL) onto ITO glass, respectively. The amperometric photocurrents were measured for each switch on/off event with a bias voltage of 0.5 V under the visible light irradiation. The electrochemical impedance spectroscopies (EIS) were recorded

under visible light and a bias of -1 V.

Photocatalytic hydrogen production.

Photocatalytic H_2 evolution from water splitting was carried out in an outer pyrex top-irradiation reaction vessel (500 mL) connected to a glass closed gas circulation system. In a typical experiment, 50 mg of g- C_3N_4 powder and different amounts of CoTPP were dispersed in an aqueous solution (100 mL) containing 10% triethanolamine as sacrificial electron donor. And 1 wt% Pt, as a co-catalyst to boost H_2 generation was loaded onto the surface of the catalyst by in situ photodeposition method using $H_2PtCl_6 \cdot 6H_2O$. And every experiment was repeated for three times. In order to make sure anaerobic conditions in the reaction system, the solution was evacuated 1 h to remove air completely before irradiation by a 300 W xenon lamp (Perfect Light, PLS-SXE300C, Beijing). The xenon lamp is equipped with a cut-off filter ($\lambda \geq 420$ nm) to remove ultraviolet light. Besides, the Pyrex reactor with a double layer was continuously stirred. A flow of cooling ethylene glycol was used during the photocatalytic reaction to maintain the temperature of the reaction solution at 10 °C. The amount of hydrogen evolution from photocatalytic splitting water was measured using an on-line gas chromatography (GC1120, Shanghai Sunny Hengping Limited, HTCD, N_2 as carrier gas). After the reaction, the mixture of CoTPP and g- C_3N_4 was separated from the reaction solution for further characterization. The catalysts are denoted as C_3N_4/x CoTPP, where x (x = 3, 4, 5 wt%) refers to the weight content of CoTPP in $C_3N_4/CoTPP$ samples.

The apparent quantum yields (AQY) was calculated at different monochromatic light irradiation by using $C_3N_4/4$ wt% CoTPP photocatalyst (irradiated by a 300 W Xe lamp using the bandpass filter of $\lambda \pm 5$ nm for 420, 450, 500, 550, 600 nm, according to the equation given below:

$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{\text{Number of evolved H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\% \end{aligned}$$

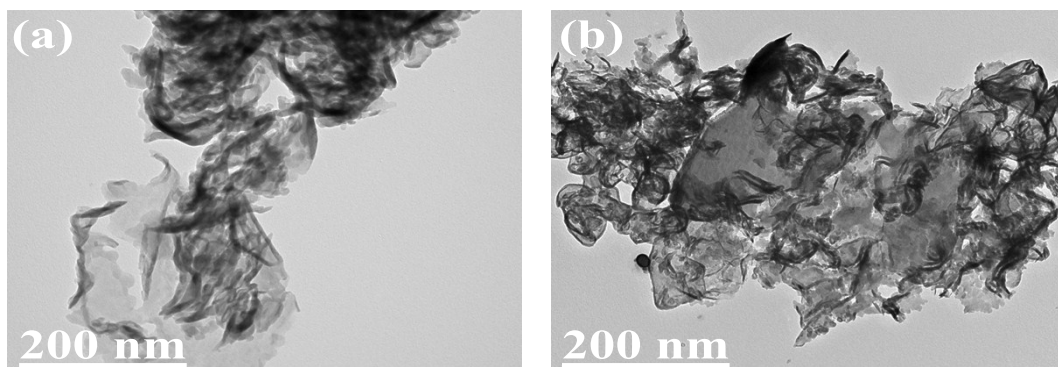


Fig. S1 TEM images of (a) pure g-C₃N₄ and (b) C₃N₄/4 wt% CoTPP photocatalyst.

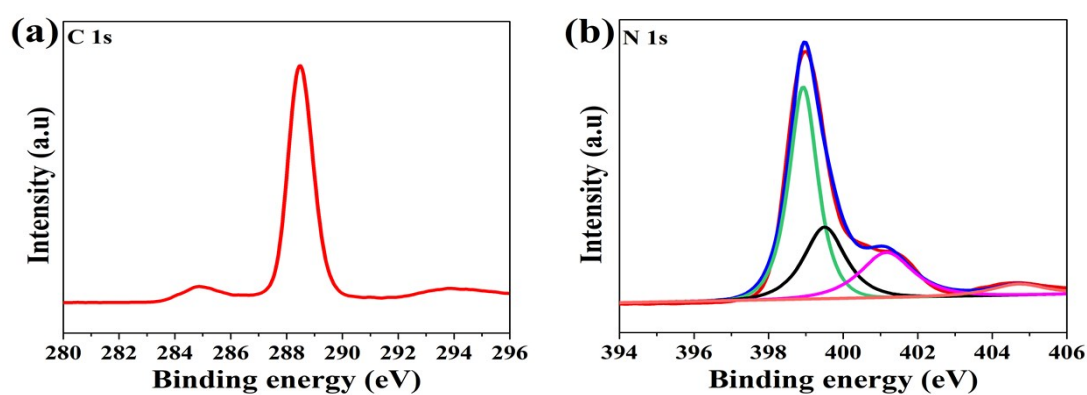


Fig. S2 XPS spectra of (a) C 1s region and (b) N 1s region for C₃N₄/4 wt% CoTPP photocatalyst.

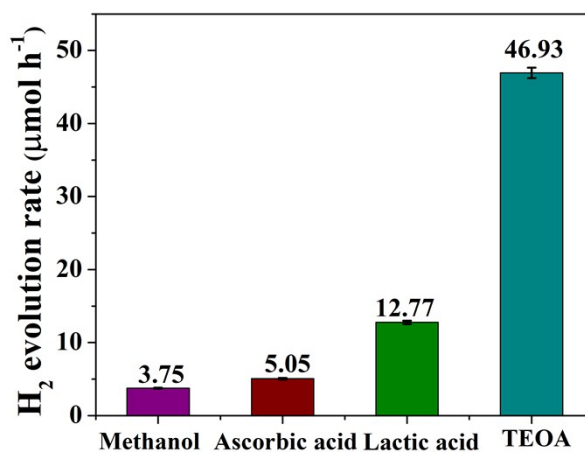


Fig. S3 Comparison of photocatalytic hydrogen evolution rates on C₃N₄/4 wt% CoTPP composite photocatalyst in the presence of different sacrificial reagents under visible light ($\lambda \geq 420$ nm). Reaction conditions: catalyst, 50 mg;

100 mL of solution containing sacrificial reagents; light source, xenon lamp (300 W) with a cutoff filter; temperature, 10 °C.

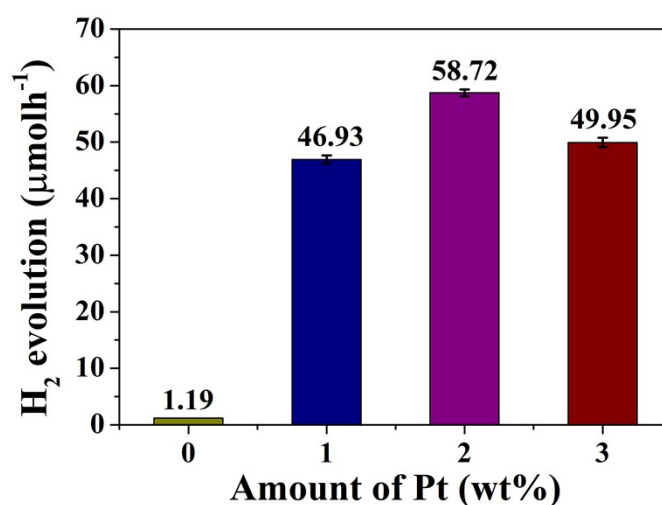


Fig. S4 Effect of the Pt loading amounts on photocatalytic hydrogen evolution of C₃N₄/4 wt% CoTPP under visible light irradiation ($\lambda \geq 420$ nm).

As shown in Fig. S4, it can be seen that C₃N₄/4 wt% CoTPP heterostructure photocatalyst exhibits low photocatalytic activity without Pt cocatalyst, but significantly improves after loading Pt and reaches a maximum value of 2 wt% Pt loading. However, there is not too much difference in hydrogen production when loading 2 wt% Pt or 1 wt% Pt, this leads us to choose 1 wt% Pt loading amount. In addition, we minimize the use of Pt because it is a rare and too expensive noble metal.

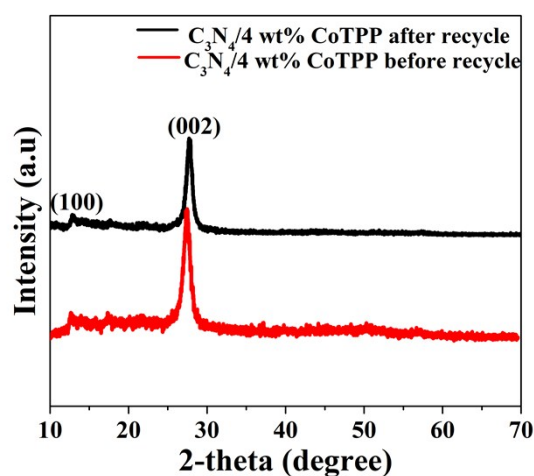


Fig. S5 XRD patterns of C₃N₄/4 wt% CoTPP composite photocatalysts before and

after 20 h hydrogen evolution reaction.

The HOMO and LUMO energy levels of CoTPP were evaluated through cyclic voltammetry (CV) experiment.¹⁻³ The HOMO energy level can be calculated from the value of oxidation potential according to the following formula:

$$E_{\text{OX}} = E_{\text{Ag}^+/\text{AgCl}} - E_{\text{Fc}}$$

$$E(\text{HOMO}) = -(E_{\text{onset, ox}} + 4.8_{(\text{Fc})}) \text{ eV}$$

Where $E_{\text{onset, ox}}$ is the onset oxidation potential vs. Ag/AgCl electrode.

Furthermore, the HOMO/LUMO energy gap (ΔE) can be evaluated from the data of UV-vis absorption spectra, and thus the LUMO energy level can be determined:

$$\Delta E(\text{HOMO/LUMO}) = (1240/\lambda_{\text{max}}) \text{ eV}$$

Where λ_{max} is the maximum absorption wavelength of the chromophore.

$$E(\text{HOMO}) = E(\text{LUMO}) - \Delta E(\text{HOMO/LUMO})$$

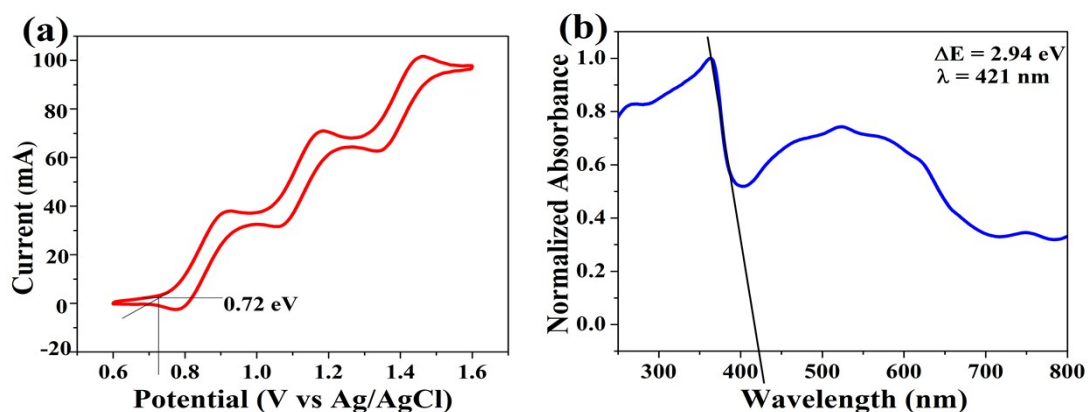


Fig. S6 (a) Cyclic voltammogram of CoTPP collected in 0.1 M Bu₄NPF₆ in CH₂Cl₂ solution. Condition: the concentration of CoTPP in solution, 1 mM; medium: 0.1 M Bu₄NPF₆; reference electrode, Ag/AgCl; working electrode, glassy carbon; auxiliary electrode, Pt; degasses with nitrogen for 15 min before measurement; 298 K; scan rate, 100 mV/s. (b) Calculation of band gap between HOMO and LUMO of CoTPP.

Table. S1 Comparison of our study with other results in the literature towards photocatalytic H₂ production.

Photocatalyst	Cocatalyst	Light source	H ₂ evolution ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Refs
g-PAN/g-C ₃ N ₄	1.5 wt% Pt	300 W Xe lamp with a cutoff filter ($\lambda > 400 \text{ nm}$)	370	30
g-C ₃ N ₄ /PEDOT	1 wt% Pt	High energy Xe lamp with a cut off filter ($\lambda > 400 \text{ nm}$)	327	42
MoS ₂ /gC ₃ N ₄	1 wt% Pt	300 W Xe lamp with a cutoff filter ($\lambda > 400 \text{ nm}$)	231	43
C ₃ N ₄ /CoTPP	1 wt% Pt	300 W Xe lamp with a cutoff filter ($\lambda \geq 420 \text{ nm}$)	938.6	Our work

Table. S2 Comparison of quantum yield of our study with various reported C₃N₄-based type-II heterostructural photocatalysts.

Photocatalysts	Co-catalyst (wt %)	Sacrificial Reagents	AQY (%)	Refs
g-C ₃ N ₄ /P3HT	1	Na ₂ S-Na ₂ SO ₃	2.9 ($\lambda = 420 \text{ nm}$)	44
(FeTPP) ₂ O/g-C ₃ N ₄	-	TEOA	0.0415 ($\lambda = 420 \text{ nm}$)	45
g-C ₃ N ₄ /CoFe ₂ O ₄	1	TEOA	3.35 ($\lambda = 420 \text{ nm}$)	46
g-C ₃ N ₄ /NiFe ₂ O ₄	1	TEOA	2.46 ($\lambda = 420 \text{ nm}$)	46
C ₃ N ₄ /CoTPP	1	TEOA	4.2 ($\lambda = 420 \text{ nm}$)	Our work

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