

Supporting information

Biomolecular L-tryptophan as a hole mediator anchored on g-C₃N₄ exhibits remarkably enhanced photocatalytic H₂ evolution

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Experimental section

Materials

Urea ($\geq 99\%$) and Levorotatory-tryptophan (L-trp) was purchased from Aldrich. Triethanolamine (TEOA, $\geq 78\%$), lactic acid ($\geq 85\%$), methanol ($\geq 99\%$), and ascorbic acid ($\geq 99\%$) were purchased from Sinopharm Chemical Reagent Co., 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 chemical reagents were used without further purification. In addition, the double distilled water used in all experiments was purified employing a SZ-93A auto double distillation apparatus (Ya Rong Corp., Shanghai, China).

Preparation of photocatalysts

In a typical synthesis procedure, urea (6.0 g) was put into an alumina crucible with the cover placed in a muffle furnace, then calcined at $550\text{ }^\circ\text{C}$ for 4 h in air condition with the heating rate of $5\text{ }^\circ\text{C min}^{-1}$. After the samples cooling to room temperature naturally, the resulting yellow powders were gathered for further use. Typically, g- C_3N_4 /L-trp (named as CN/L-trp) was obtained directly by homogeneously mixing g- C_3N_4 and L-trp in aqueous solution. The detail is that 50 mg of g- C_3N_4 powder and different amounts of L-trp were dispersed through ultrasonication in an aqueous solution (100 mL). 1 wt% Pt was deposited on the surface of the mixed catalyst through photodeposition method using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as the precursor. Finally, the g- C_3N_4 /L-trp loaded with Pt catalyst was obtained. The photocatalysts are named as CN/x L-trp, where x (x = 4, 8, 10, 12 wt%) represent the real weight amount of L-trp in CN/x L-trp sample.

Photocatalytic hydrogen production

Photocatalytic H_2 evolution from water splitting was performed in a Pyrex top-irradiation reaction vessel (500 mL) associated with a glass closed gas circulation system. Typically, the as-prepared sample was dispersed in an aqueous solution (100 mL) containing 10 ml triethanolamine (TEOA) as sacrificial electrons donor. Before the photocatalytic reaction, to assure vacuum environment, the solution was evacuated for 1 h to remove air completely prior to irradiation with a 300 W xenon lamp (Perfect

Light, PLS-SXE300C, Beijing) equipping with a cut-off filter to control the wavelength of incident light ($\lambda \geq 420$ nm). Moreover, a flow of cooling ethylene glycol was used during the photocatalytic reaction to keep the temperature of the reaction solution at 10 °C and Pyrex reactor with a double layer was continuously stirred. Finally, the evolved H₂ gases were analyzed by using an on-line gas chromatograph (GC1120, Shanghai Sunny Hengping Limited, HTCD, N₂ carrier). The mixture of L-trp and g-C₃N₄ was separated from the reaction solution for further use and characterization.

The apparent quantum yield (AQY) was calculated under disparate monochromatic light irradiation by using CN/10wt% L-trp photocatalyst (irradiated by a 300 W Xe lamp using a bandpass filter of $\lambda \pm 5$ nm for 420, 450, 500, 550, 600 nm), according to the equation given below:

$$AQY (\%) = \frac{\text{Number of reacted electrons}}{\text{Number of incident electrons}} \times 100\%$$

$$= \frac{\text{Number of evolved H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\%$$

Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku diffractometer (MXPAHF, Japan) with Cu K α irradiation ($\lambda = 1.541$ Å), with an operating voltage of 40 kV and a current of 200 mA. The scanning angle was from 10° to 70°. The UV-vis absorption spectra of the aqueous solutions were recorded using a Shimadzu UV-2510 spectrophotometer scanning with the wavelength range from 200 nm to 800 nm. The diffuse reflectance UV-vis absorption spectra of the photocatalysts were recorded with a Shimadzu spectrophotometer (Model 2501 PC). Transmission electron microscopy (TEM) images were obtained using a HITACHI H-7650 transmission electron microscope operated at 100 kV. The steady-state photoluminescence (PL) measurement was conducted on a fluorescence spectrophotometer (JY Fluorolog-3-Tau) with the motivation wavelength at 370 nm. Time-resolved spectrofluorometer (Photon Technology International (Canada) Inc.) equipped with a USHIO xenon lamp source, a

GL-302 high-resolution dye laser (lifetimes 100 ps to 50 ms, excited with a nitrogen laser) and a 914 photomultiplier detection system. CV tests were employed using an electrochemical workstation (CHI 760E, Chenhua Instrument Company, Shanghai, China). N₂ adsorption-desorption isotherms were performed at 77 K through an adsorption instrument (Micromeritics ASAP 2010 system) and the Brunauer-Emmett-Teller specific surface area (SBET) was calculated using a multi-point BET method. Electron paramagnetic resonance (EPR) measurement was tested by a Bruker model A300 spectrometer.

Photoelectrochemical measurements.

Photoelectrochemical tests were recorded by an electrochemical analyzer (Chenhua Instrument Company, Shanghai, China) in a standard three-electrode configuration with a Pt wire as the counter electrode, Ag⁺/AgCl (saturated with KCl) reference 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 CN/10 wt% L-trp electrodes were operated as follows: 2mg sample mixed well with 1 mL water and 20 uL Nafion solution (5 wt%) by sonication was deposited on ITO glass with a fixed area of 1 cm², respectively. The amperometric photocurrents were tested for each switch on/off event with a bias voltage of 0.5 V. The EIS curves were recorded under visible light with a bias of -1 V. The frequency range was from 0.01Hz to 10⁶ Hz in parallel to an alternating current signal amplitude of 5 mV.

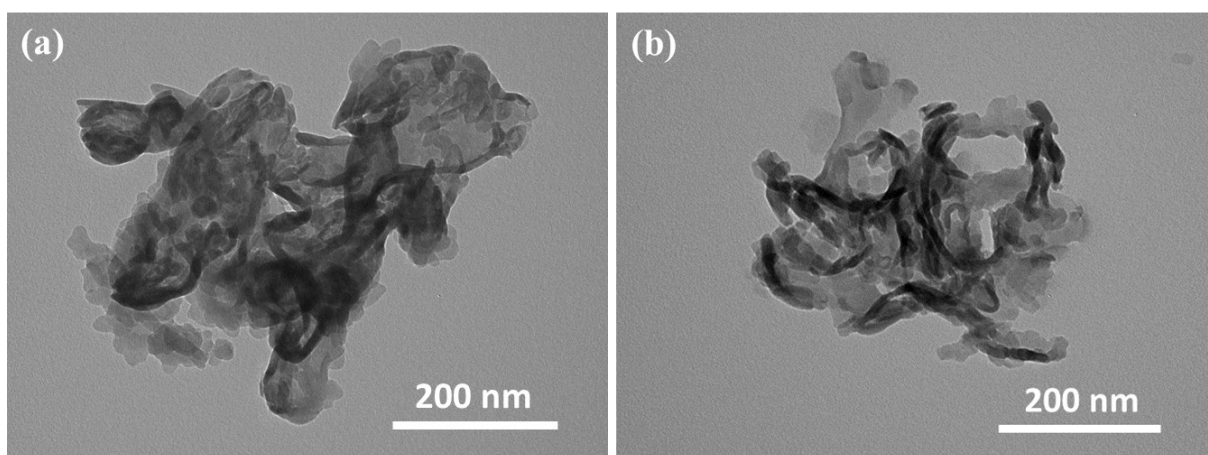


Fig. S1 TEM images of (a) pure g-C₃N₄ and (b) CN/10 wt% L-trp

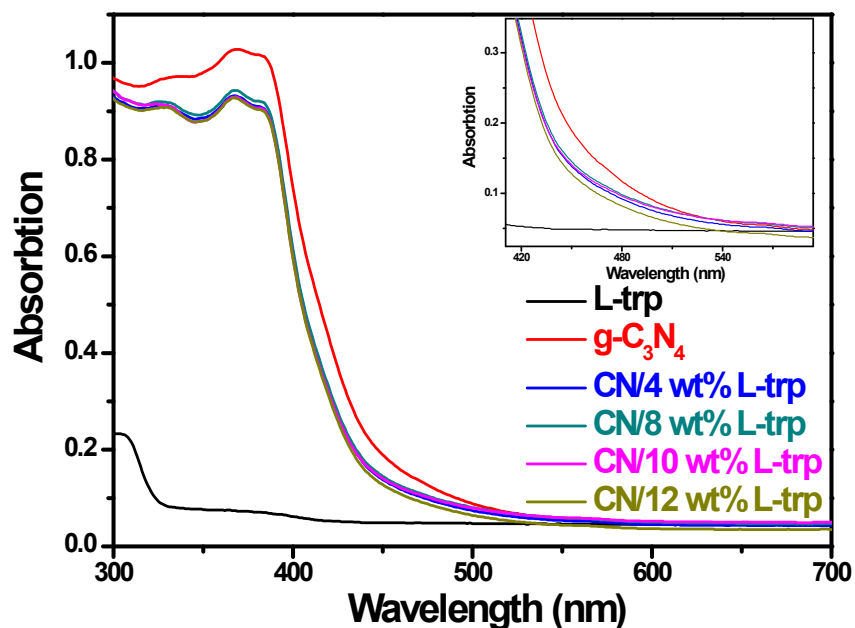


Fig. S2 The diffuse reflectance spectra of g-C₃N₄, L-trp and CN/L-trp composites.

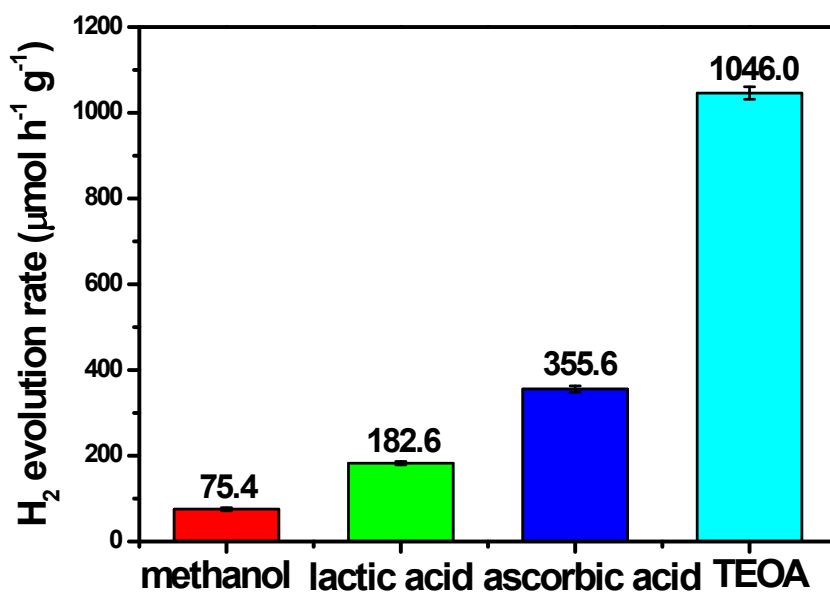


Fig. S3 Comparison of photocatalytic hydrogen evolution rate on CN/10 wt% L-trp photocatalyst in the presence of various sacrificial reagents under visible light ($\lambda \geq 420$ nm). Reaction conditions: catalyst, 50 mg; 100 mL of aqueous solution containing sacrificial reagent; light source, xenon lamp (300 W) with a cut-off filter; temperature,

10 °C.

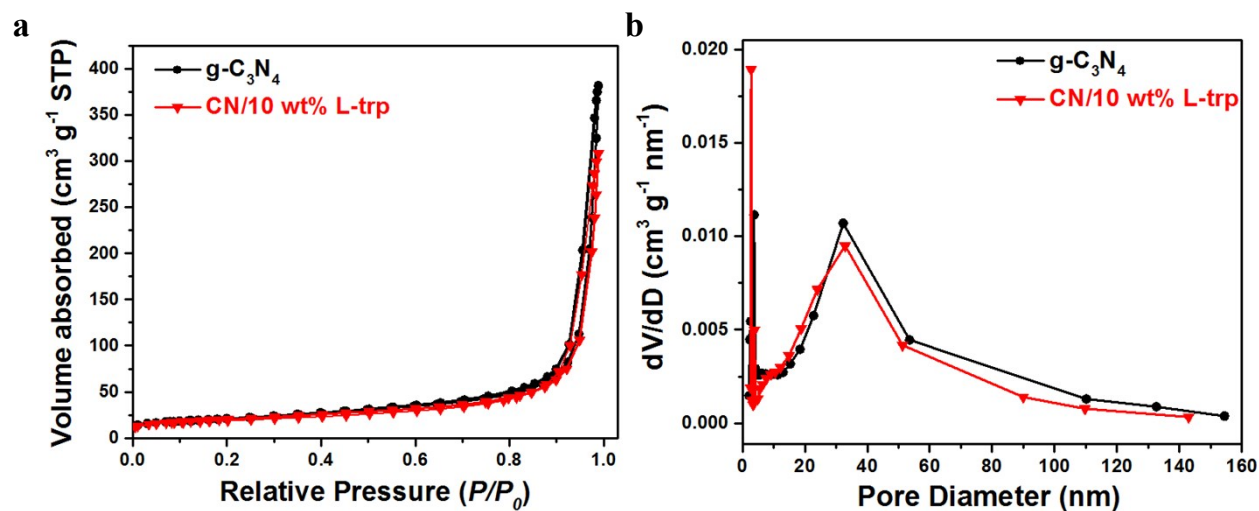


Fig. S4 (a) Nitrogen adsorption-desorption isotherms and (b) corresponding pore size distribution curves for g-C₃N₄ and CN/10 wt% L-trp composites .

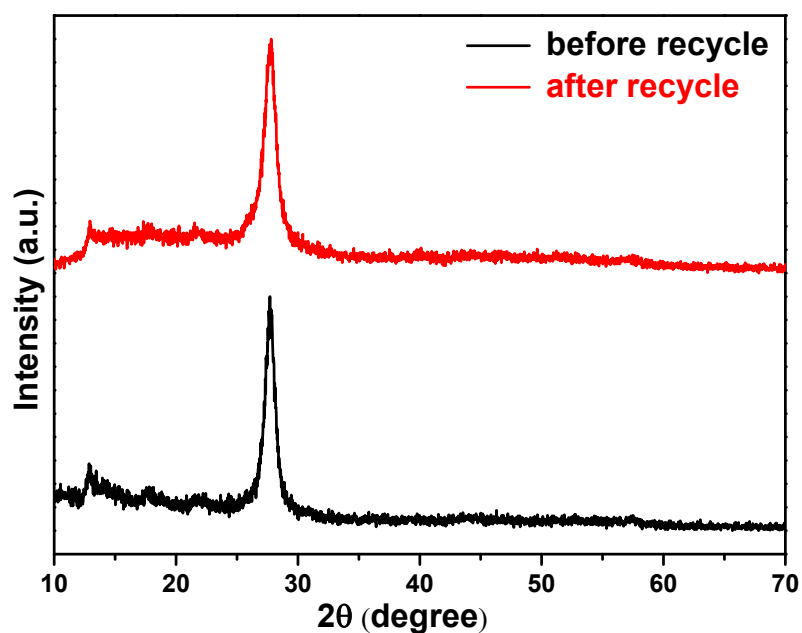


Fig. S5 XRD spectra of CN/10 wt% L-trp composite before and after recycle photocatalytic experiment.

Fourier transform infrared (FTIR) spectra were obtained using a Nicolet Magna-IR 750 spectrometer with the range from 400 to 4000 cm^{-1} over samples inserted in KBr pellets.

As shown in the Fig. S6, in the FT-IR spectrum of L-trp, the band at 1667 cm^{-1} is assigned to the stretching mode of COO^- group.^{1,2} When the $\text{C}=\text{O}$ (COO^-) group is involved in intermolecular hydrogen bonding, the resonance will take place and then influence their stretching wave-numbers.^{3,4} The vibration of carboxylate $\text{C}=\text{O}$ moves to low wave-number 1650 cm^{-1} in the spectrum of CN/10 wt% L-trp composite, indicating that the hydrogen bonding has been formed between L-trp and $\text{g-C}_3\text{N}_4$.³ Moreover, the previous studies reported that noncovalent π - π stacking interactions can easily exist between the tri-s-triazine unit of the $\text{g-C}_3\text{N}_4$ and the aromatic ring of molecule.^{5,6} Consequently, strong π - π interaction can occur between graphitic $\text{g-C}_3\text{N}_4$ and the aromatic ring of L-trp molecules.

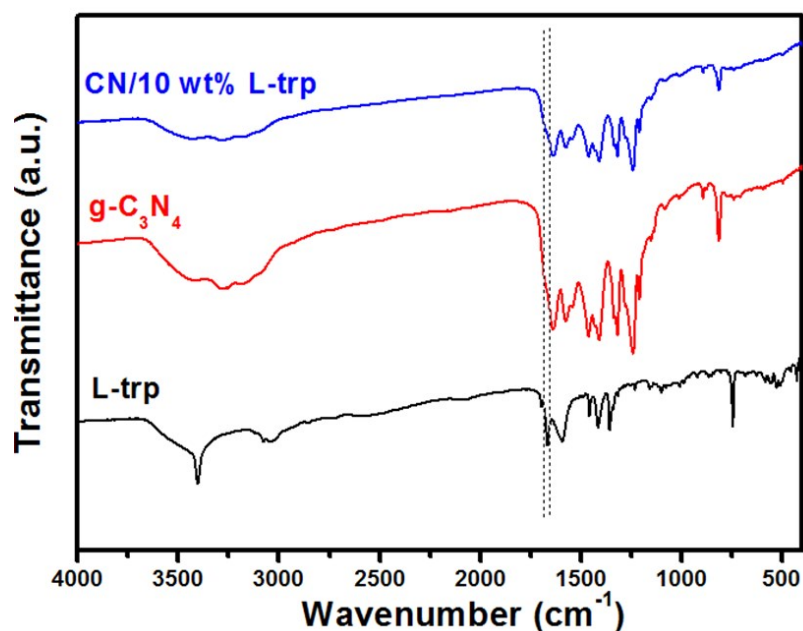


Fig. S6 The FTIR spectra of L-trp, $\text{g-C}_3\text{N}_4$ and CN/10 wt% L-trp composite.

The HOMO energy level of L-trp was evaluated through cyclic voltammetry (CV) experiment.^{7,8} The HOMO energy level can be calculated from the value of reduction potential according to the following formula:

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

$$HOMO = -(4.80_{(Fc)} + E_{OX}) \text{ eV}$$

where E_{Fc} is the onset reduction potential vs. Ag⁺/AgCl electrode.

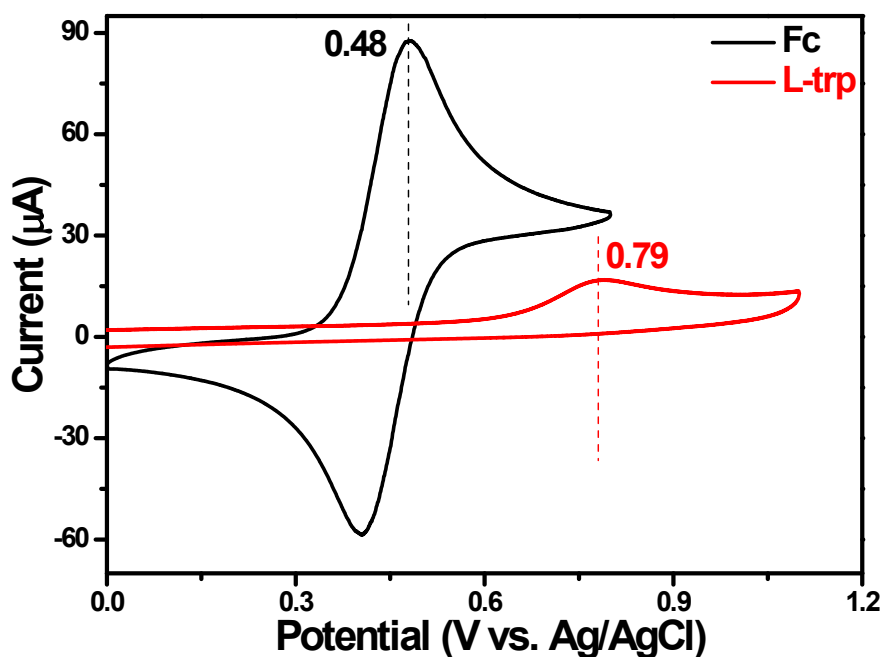


Fig. S7 Condition: Cyclic voltammogram of the Ferrocene (Fc) and L-trp collected in 0.1 M of Bu₄NPF₆ in acetonitrile, scanned at 100 mV/s, Ag/AgCl as a reference electrode, freshly polished 3.0 mm diameter glassy carbon button electrode served as the working electrode, Pt wire as a counter electrode. The concentration of L-trp in solution was approximately 1 mM.

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

Photocatalyst	Cocatalyst	Light source	H ₂ evolution ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Refs
Amorphous carbon/g-C ₃ N ₄	1.0 % Pt	350 W Xe lamp with a cut off filter ($\lambda > 420 \text{ nm}$)	212.8	36
CdS QDs/g-C ₃ N ₄	1.0 % Pt	300 W Xe lamp with a cut off filter ($\lambda > 400 \text{ nm}$)	172.7	37
P-TCN	1.0 % Pt	300 W Xe lamp with a cut off filter ($\lambda > 420 \text{ nm}$)	570.0	38
CN/L-trp	1.0 % Pt	300 W Xe lamp with a cut off filter ($\lambda \geq 420 \text{ nm}$)	1046.0	This work

References

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