

## Supplementary Information

### **Hantzsch Ester as Hole Relay Significantly Enhanced Photocatalytic Hydrogen Production**

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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. Hantzsch ester (Diethyl 1,4-Dihydro-2,6-dimethyl-3,5-pyridine dicarboxylate, denoted as DHPE) was purchased from Shanghai Dibai Technology 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. And diethyl pyridine-3,5-dicarboxylate was obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical grade and used directly, without further purification. And double distilled water was get through a SZ-93A auto-double distillation apparatus (Ya Rong Corp., Shanghai, China), the double distilled water was used in all experiments.

### *Preparation of photocatalysts.*

At first, put urea (5.0 g) in an alumina crucible, which has the cover. Then, the alumina crucible was calcined in muffle furnace. The alumina crucible on the condition that calcined at 823 K for 4 h, under an air atmosphere, with a heating rate of  $5 \text{ K} \cdot \text{min}^{-1}$ . At last, after the sample cooling to room temperature naturally, the resulting yellow powders were collected for further use.

### *Characterizations*

Fourier transformed infrared (FT-IR): FT-IR spectra were recorded on a Nicolet Magana-IR 750 spectrometer in a range from 400 to  $4000 \text{ cm}^{-1}$ .

**X-ray diffraction (XRD).** XRD profiles of the g- $\text{C}_3\text{N}_4$ , DHPE and  $\text{C}_3\text{N}_4/\text{DHPE}$  with different proportion of DHPE 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  $10^\circ$  to  $60^\circ$ .

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

**Ultraviolet-visible spectroscopy (UV-vis).** The diffuse reflectance UV-vis

absorption spectra of the photocatalysts were recorded by a Shimadzu spectrophotometer (Model 2501 PC). And the UV-vis absorption spectra of aqueous solutions were obtained using a Shimadzu UV-2510 spectrophotometer. The scanning wavelength range was from 200 nm to 800 nm.

**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 performed on an electrochemical analyzer (Chenhua Instrument Company, Shanghai, China) in a standard three-electrode configuration with a Pt wire as the counter electrode, Ag<sup>+</sup>/AgCl (in saturated KCl) reference electrode, and indium-tin oxide (ITO) glass as the working electrode. Na<sub>2</sub>SO<sub>4</sub> (0.5M) aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 2 mg of the g-C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub>/4% DHPE sample was mixed with 1 mL of distilled water, respectively. Then, 2 cm × 0.5 cm ITO glass electrode was covered with this slurry and dried at 120 °C for 30 min. Irradiation proceeded by a Xe arc lamp through a UV cutoff filter ( $\lambda \geq 420$  nm), it is the same with the photocatalytic hydrogen production. The amperometric photocurrents were measured for each switch on/off event with a bias voltage of 0.5V and -0.5V. The electrochemical impedance spectroscopies (EIS) were recorded under visible light and a bias of -1 V.

#### ***Photocatalytic hydrogen production.***

Photocatalytic H<sub>2</sub> evolution from water splitting was carried out in an outer pyrex top-irradiation reaction vessel (500 mL) connected to a glass closed gas circulation

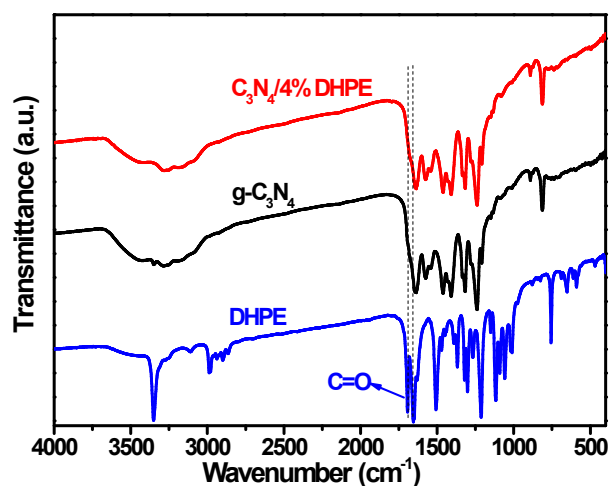
system. In a typical experiment, 50 mg of g-C<sub>3</sub>N<sub>4</sub> powder and different amounts of DHPE were dispersed in an aqueous solution (100 mL) containing 10% triethanolamine as sacrificial electron donor. And 1% Pt, as a co-catalyst to boost H<sub>2</sub> generation was loaded onto the surface of the catalyst by in situ photodeposition method using H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. 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<sub>2</sub> as carrier gas). After the reaction, the mixture of DHPE and g-C<sub>3</sub>N<sub>4</sub> was separated from the reaction solution for further characterization. The catalysts are denoted as C<sub>3</sub>N<sub>4</sub>/x DHPE, where x (x = 2, 4, 6 %) refers to the weight content of DHPE in C<sub>3</sub>N<sub>4</sub>/DHPE samples.

The apparent quantum yields (AQY) was calculated at different monochromatic light irradiation by using C<sub>3</sub>N<sub>4</sub>/4% DHPE 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:

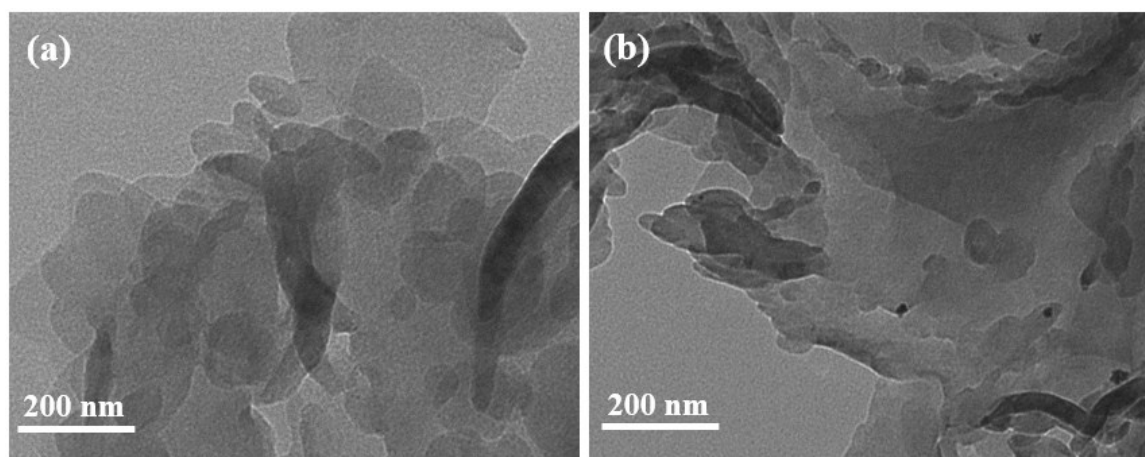
$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{\text{Number of evolved H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\% \end{aligned}$$

In the FT-IR spectrum of DHPE, the band at  $1690\text{ cm}^{-1}$  is assigned to the stretching mode of C=O,<sup>1</sup> when the C=O group is involved in hydrogen bonds, the resonance will take place and then influence its stretching wavenumbers.<sup>2</sup> The vibration of C=O shifts to a low wavenumber of  $1670\text{ cm}^{-1}$ , as observed in the spectrum of  $\text{C}_3\text{N}_4/\text{DHPE}$  composite, this result indicates that the hydrogen bonding has been formed between g- $\text{C}_3\text{N}_4$  and DHPE.<sup>2</sup>

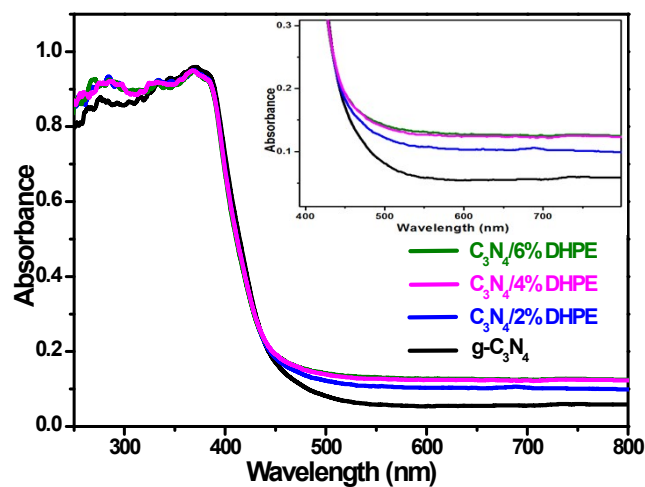
The literatures report that the  $\pi$ - $\pi$  interaction is easily formed between graphitic  $\text{C}_3\text{N}_4$  and organic small molecules with  $\pi$ -conjugated structure.<sup>3,4</sup> Therefore, strong  $\pi$ - $\pi$  interaction can occur between graphitic g- $\text{C}_3\text{N}_4$  and  $\text{sp}^2$  C=C DHPE molecules, which can facilitate the charge transfer between them.



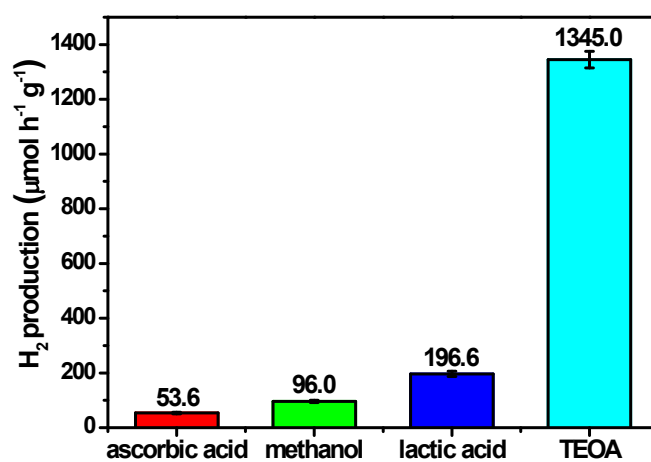
**Fig. S1** The FTIR spectra of DHPE, g- $\text{C}_3\text{N}_4$  and  $\text{C}_3\text{N}_4/4\%\text{ DHPE}$  composite.



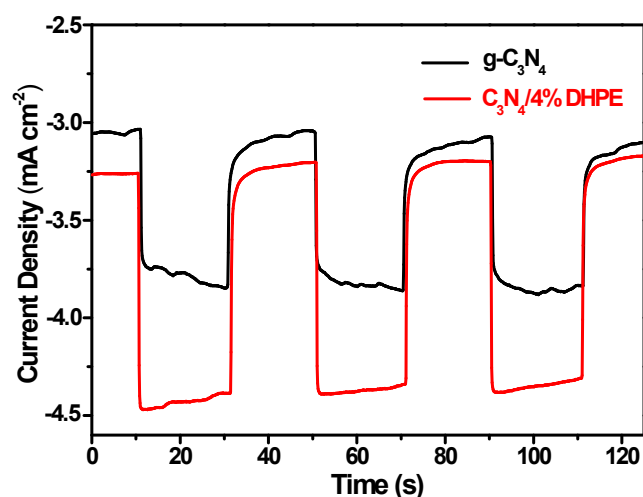
**Fig. S2** TEM images of (a) pure g-C<sub>3</sub>N<sub>4</sub> and (b) C<sub>3</sub>N<sub>4</sub>/4% DHPE.



**Fig. S3** The diffuse reflectance spectra of g-C<sub>3</sub>N<sub>4</sub>, DHPE and C<sub>3</sub>N<sub>4</sub>/DHPE composites.



**Fig. S4** Comparison of photocatalytic hydrogen evolution rates on C<sub>3</sub>N<sub>4</sub>/4% DHPE 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 cut-off filter; temperature, 10 °C.



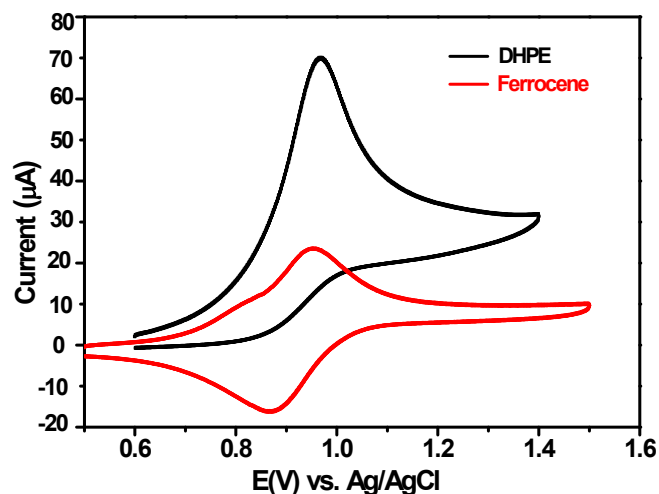
**Fig. S5** Transient photocurrent responses for g-C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>4</sub>/4% DHPE under visible light irradiation ( $\lambda \geq 420$  nm, [Na<sub>2</sub>SO<sub>4</sub>] = 0.5 M, bias voltage of -0.5V).

The HOMO energy levels of DHPE were evaluated through cyclic voltammetry (CV) experiments.<sup>5</sup> The HOMO energy level can be calculated from the value of reduction potential according to the following formula:

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

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

where  $E_{\text{Fc}}$  is the onset reduction potential vs. Ag<sup>+</sup>/AgCl electrode.



**Fig. S6 (A)** Condition: Cyclic voltammogram of the Ferrocene (Fc) and DHPE collected in 0.1 M of Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile, scanned at 100 mV/s, Ag<sup>+</sup>/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 DHPE 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 <sub>2</sub> evolution ( $\mu\text{mol h}^{-1} \text{g}^{-1}$ )	Refs
Ni <sub>2</sub> P/g-C <sub>3</sub> N <sub>4</sub>	1% Ni <sub>2</sub> P	300 W Xe lamp with a cut off filter ( $\lambda > 420 \text{ nm}$ )	362.4	36
PPy-g-C <sub>3</sub> N <sub>4</sub>	3% Pt	300 W Xe lamp with a cut off filter ( $\lambda > 400 \text{ nm}$ )	154.0	37
CdS QDs/g-C <sub>3</sub> N <sub>4</sub>	1% Pt	300 W Xe lamp with a cut off filter ( $\lambda > 400 \text{ nm}$ )	172.7	38
C <sub>3</sub> N <sub>4</sub> /DHPE	1% Pt	300 W Xe lamp with a cut off filter ( $\lambda \geq 420 \text{ nm}$ )	1345.0	Our work

## REFERENCES

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