

## Supporting Information

### **Mechanistic Insights into N-hydroxyphthalimide Modified Graphitic Carbon Nitride Boosted Photocatalytic Hydrogen Production**

Liu-Bo Ma,<sup>a</sup> Kuang Liang,<sup>a</sup> Gang Wang,<sup>a</sup> Xiao-Xiang Fang,<sup>a</sup> Cong Ling,<sup>a</sup> Tan Zhao,<sup>a</sup>  
Miza Kombo,<sup>a</sup> Tuck-Yun Cheang,<sup>\*b</sup> and An-Wu Xu<sup>\*a</sup>

<sup>a</sup>*Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical  
Sciences at the Microscale, The First Affiliated Hospital, University of Science and  
Technology of China, Hefei, 230026, China.*

<sup>b</sup>*Department of Breast and Thyroid Surgery, The First Affiliated Hospital of Sun Yat-  
Sen University, Guangzhou 510080, China.*

*\*To whom correspondence should be addressed.*

*E-mail: 13631322559@163.com*

*Email: [anwuxu@ustc.edu.cn](mailto:anwuxu@ustc.edu.cn)*

## EXPERIMENTAL SECTION

### *Chemicals*

Urea ( $\geq 99\%$ ) was purchased from Sinopharm Chemical Reagent Co., Ltd. N-hydroxyphthalimide (NHPI) was purchased from Shanghai Taitan Technology Co., Ltd. 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. And all chemicals were used as received without further purification. Besides, double distilled water used in all experiments was purified through a SZ-93A auto-double distillation apparatus (Ya Rong Corp., Shanghai, China).

### *Preparation of photocatalysts*

Firstly, urea (10.0 g) was added to an alumina crucible with the cover. Then, under an air atmosphere, the alumina crucible was calcined at 823 K for 4 h in a muffle furnace with a heating rate of  $5 \text{ K} \cdot \text{min}^{-1}$ . After the samples cooling to room temperature naturally, the resulting yellow powder was collected for further use.

### *Characterizations*

Fourier transformed infrared (FT-IR) spectra were recorded on a Nicolet Magana-IR 750 spectrometer in a range from 400 to  $4000 \text{ cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) patterns were acquired with a Thermo ESCALAB 250 system. X-ray diffraction (XRD) patterns of the powders were obtained by using a Rigaku diffractometer (MXPAHF, Japan) with Cu  $K\alpha$  irradiation ( $\lambda = 1.541 \text{ \AA}$ ), with the operating voltage 40 kV and current 200 mA. And the scanning angle was from  $10^\circ$  to  $60^\circ$ . The TEM observation was done using a JEOL JEM12010 high resolution transmission electron microscope operated at 200 kV. The diffuse reflectance UV-vis absorption spectra of the photocatalysts were recorded by a Shimadzu spectrophotometer (Model 2501 PC). The UV-vis absorption spectra of aqueous solutions were carried out using a Shimadzu UV-2510 spectrophotometer. And the scanning wavelength range was from 300 nm to 700 nm. The steady-state photoluminescence (PL) measurement was conducted on a fluorescence spectrophotometer (JY Fluorolog-3-Tau) with the excitation wavelength at 325 nm.

The time-resolved photoluminescence (TRPL) measurement was 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. N<sub>2</sub> adsorption-desorption isotherms were measured at 77 K by an adsorption instrument (Micromeritics ASAP 2010 system) and the Brunauer-Emmett-Tellers specific surface area (SBET) was calculated using a multi-point BET method. Cyclic voltammetry (CV) test was conducted using an electrochemical workstation (CHI 760E, Chenhua Instrument Company, Shanghai, China). Electron paramagnetic resonance (EPR) measurement was carried out on a Bruker model A300 spectrometer.

Photoelectrochemical test was done based on a standard three-electrode system by CHI 760E electrochemical workstation (chenhua Instrument Company, Shanghai, China), composed of Ag/AgCl as the reference electrode, indium-tin oxide (ITO) glass as the working electrode and Pt wire as the counter electrode and. Na<sub>2</sub>SO<sub>4</sub> (0.5 M) was used as the electrolyte solution. The g-C<sub>3</sub>N<sub>4</sub> and CN/2 wt% NHPI electrodes were prepared by depositing suspensions made of g-C<sub>3</sub>N<sub>4</sub> or CN/2 wt% NHPI and water (the concentration of g-C<sub>3</sub>N<sub>4</sub> and CN/2 wt% NHPI was 2 mg/mL) onto ITO glass, respectively. The amperometric photocurrents were measured for each switch on/off event with a bias voltage of 0.5V and -0.5V. The electrochemical impedance spectroscopies (EIS) were recorded under visible light and a bias of -1V.

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

Photocatalytic H<sub>2</sub> evolution from water was carried out in an outer top-irradiation gas-closed Pyrex glass system (500 mL). Typically, 50 mg of g-C<sub>3</sub>N<sub>4</sub> powder and 2 mg of NHPI were dispersed in an aqueous solution (100 mL) containing 10 ml triethanolamine (TEOA) as sacrificial holes donor. Then, 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 of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. Before the photocatalytic reaction, the solution was evacuated for 30 min to remove air completely prior to irradiation with a 300 W xenon lamp (Perfect Light, PLS-SXE300C, Beijing), which is equipped with a cut-off filter ( $\lambda \geq 420$  nm) to remove ultraviolet light. Besides, the temperature of the reaction

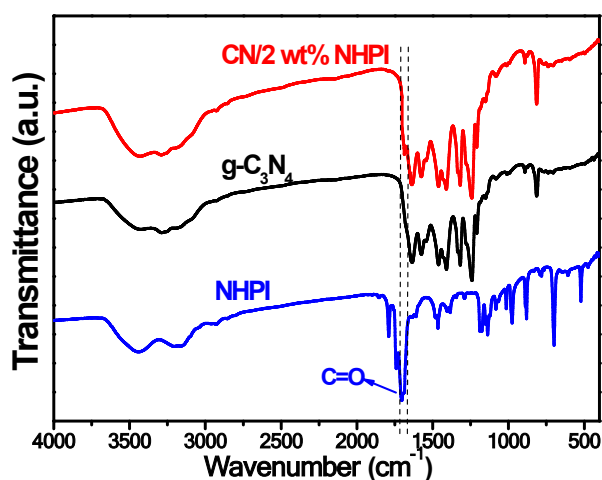
solution was maintained at 10 °C by a flow of cooling ethylene glycol. The amount of hydrogen evolution from photocatalytic splitting water was measured by an on-line gas chromatography (GC1120, Shanghai Sunny Hengping Limited, HTCD) and N<sub>2</sub> was used as the carrier gas. After the reaction, the mixture of NHPI and g-C<sub>3</sub>N<sub>4</sub> were separated from the reaction solution for further characterization, the catalysts are denoted as CN/x NHPI, where x (x = 1, 2, 4 wt%) refers to the weight content of NHPI in CN/NHPI sample.

The apparent quantum yield (AQY) was calculated at different monochromatic light irradiation by using CN/2 wt% NHPI 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:

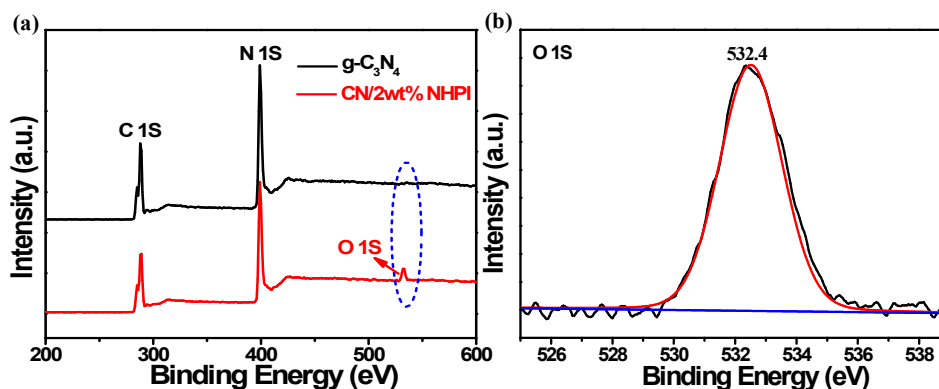
$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{\text{Number of evolved H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\% \end{aligned}$$

The FT-IR spectra were recorded on a Nicolet Magana-IR 750 spectrometer in the

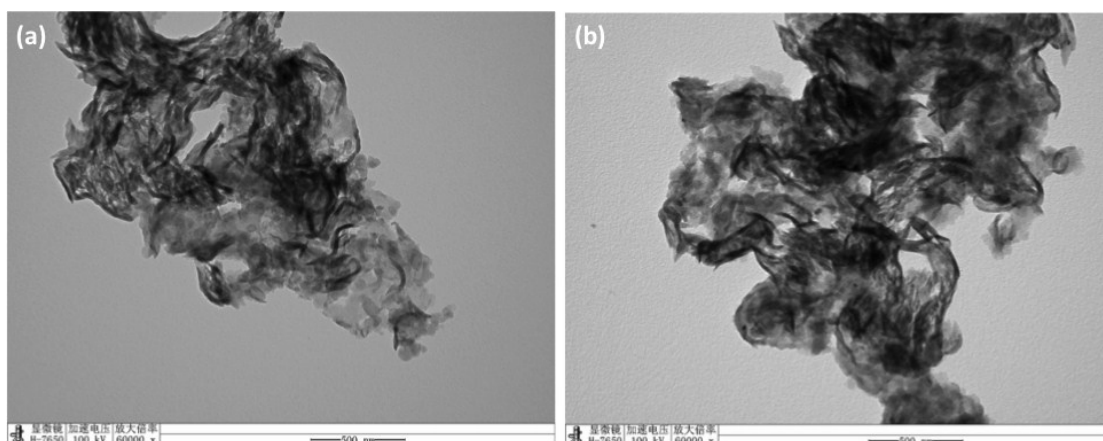
range of 4000-400  $\text{cm}^{-1}$ . In the FT-IR spectrum of NHPI, the band at 1690  $\text{cm}^{-1}$  is assigned to the stretching mode of C=O,<sup>1</sup> when the C=O group is involved in hydrogen bonds, the resonance will take place and then influence its stretching wavenumbers.<sup>2</sup> The vibration of C=O shifts to a low wavenumber of 1670  $\text{cm}^{-1}$ , as observed in the spectrum of CN/NHPI composite, this result indicates that the hydrogen bonding has been formed between g- $\text{C}_3\text{N}_4$  and NHPI.<sup>2</sup>



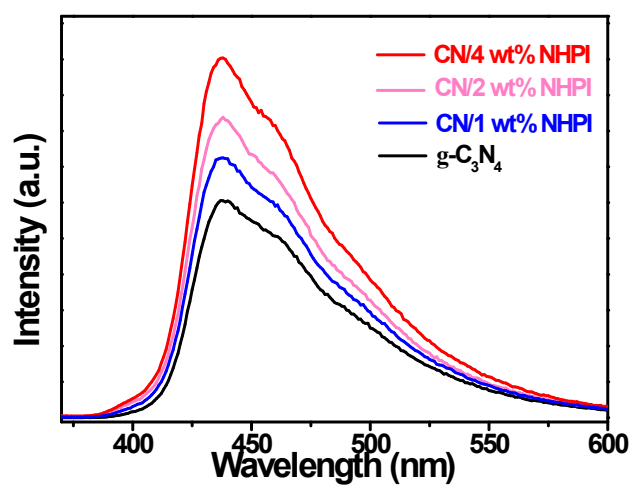
**Fig. S1** The FT-IR spectra of NHPI, g- $\text{C}_3\text{N}_4$  and CN/2 wt% NHPI composite.



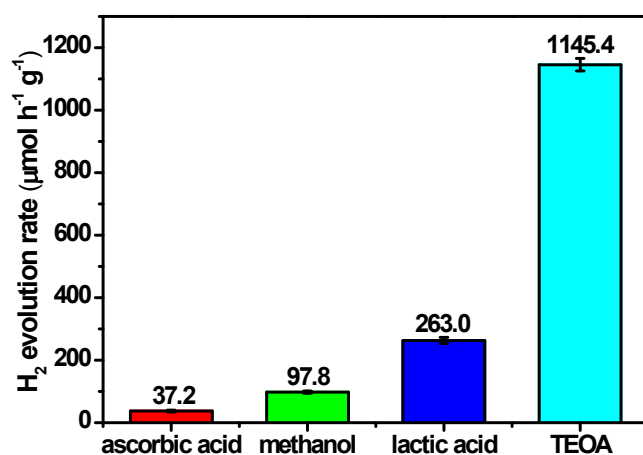
**Fig. S2** (a) XPS survey spectra of g- $\text{C}_3\text{N}_4$  and CN/2 wt% NHPI composite; (b) High-resolution XPS spectra of O 1s for CN/2 wt% NHPI composite.



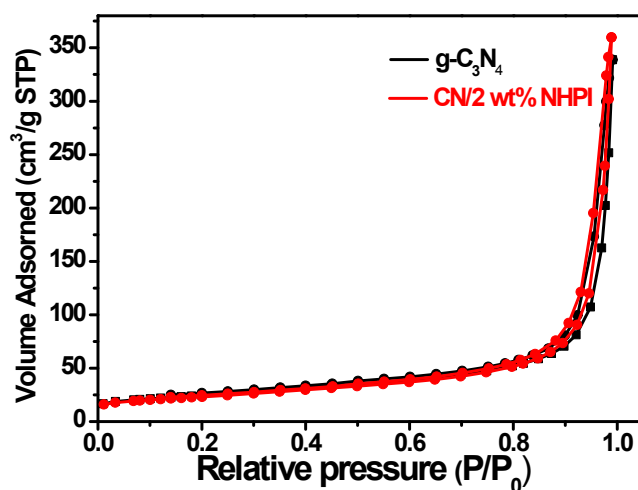
**Fig. S3** TEM images of (a) pure  $g\text{-C}_3\text{N}_4$  and (b) CN/2 wt% NHPI.



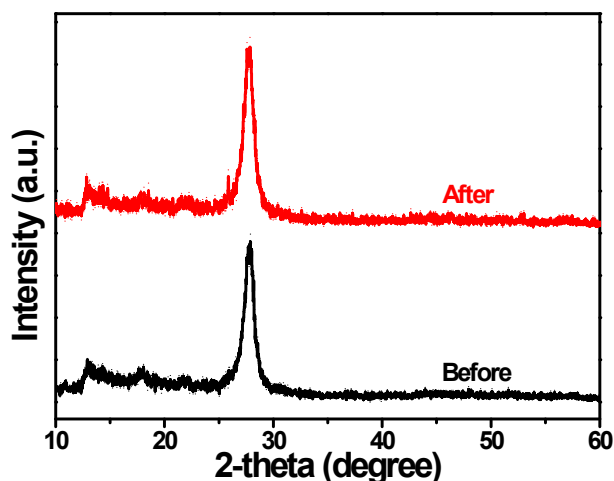
**Fig. S4** Steady-state photoluminescence spectra of  $g\text{-C}_3\text{N}_4$  and CN/NHPI photocatalysts with different weight contents of NHPI.



**Fig. S5** Comparison of photocatalytic hydrogen evolution rate on CN/2wt% NHPI 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 reagent; light source, xenon lamp (300 W) with a cut-off filter; temperature, 10 °C.



**Fig. S6** Nitrogen adsorption-desorption isotherms of g-C<sub>3</sub>N<sub>4</sub> and CN/2 wt% NHPI composite.



**Fig. S7** XRD spectra of CN/2 wt% NHPI composite before and after recycle photocatalytic experiment.

The HOMO energy level of NHPI was evaluated through cyclic voltammetry (CV) experiment.<sup>1</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.  $\text{Ag}^+/\text{AgCl}$  electrode.

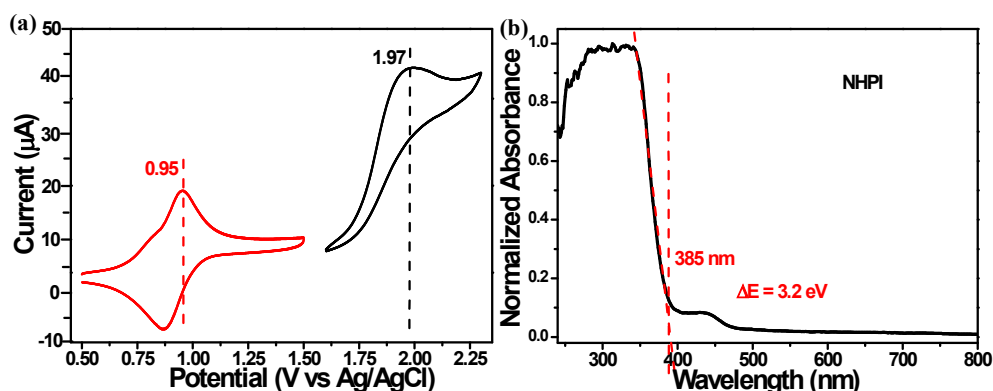
The HOMO/LUMO energy gap ( $\Delta E$ ) can be evaluated from UV-vis absorption spectrum of NHPI, and thus the HOMO energy level can be determined:

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

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

where the  $\lambda_{\text{max}}$  is maximum absorption wavelength of the chromophore.





**Fig. S8** (a) Condition: Cyclic voltammogram of the Ferrocene (Fc) and NHPI collected in 0.1 M of  $\text{Bu}_4\text{NPF}_6$  in acetonitrile, scanned at 100 mV/s,  $\text{Ag}^+/\text{AgCl}$  as the reference electrode, freshly polished 3.0 mm diameter glassy carbon button electrode served as the working electrode, Pt wire as the counter electrode. The concentration of NHPI in solution was approximately 1 mM. (b) UV-vis diffuse reflectance spectrum of NHPI.

**Table S1.** Comparison our study of other results in literature toward photocatalytic  $\text{H}_2$  production.

Photocatalyst	Cocatalyst	Light source	$\text{H}_2$ evolution ( $\mu\text{mol h}^{-1} \text{g}^{-1}$ )	Refs
$\text{MoS}_2/\text{g-C}_3\text{N}_4$	1% Pt	300 W Xe lamp with a cut off filter ( $\lambda > 420 \text{ nm}$ )	231	38
$\text{PPy-g-C}_3\text{N}_4$	3% Pt	300 W Xe lamp with a cut off filter ( $\lambda > 400 \text{ nm}$ )	154	39
$\text{g-PAN/g-C}_3\text{N}_4$	1.5% Pt	300 W Xe lamp with a cut off filter ( $\lambda > 400 \text{ nm}$ )	370	40
CN/NHPI	1% Pt	300 W Xe lamp with a cut off filter ( $\lambda \geq 420 \text{ nm}$ )	1145.4	Our work

## REFERENCES

- 1 J. Lee, M. Byranvand, G. Kang, S. Y. Son, S. Song, G. W. Kim and T. Park, *J. Am. Chem. Soc.* 2017, **139**, 12175-12181.
- 2 F. Tamaddon, Z. Razmi, and A. A. Jafari, *Tetrahedron let.*, 2010, **51**, 1187–1189.
- 3 Z. H. Sun, W. M. Sun, C. T. Chen, G. H. Zhang, X. Q. Wang and D. Xu, *Spectrochimica Acta Part A*, 2011, **83**, 39–45.