## **Supporting Information**

# n/n junctioned g-C<sub>3</sub>N<sub>4</sub> for enhanced photocatalytic $H_2$ generation

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**Experimental & Figure S1-S2** 

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#### Experimental

## **Materials Preparation**

All chemicals used were analytical grade and were used without further treatment. The g-C<sub>3</sub>N<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> nanojunctionwas prepared by a facile thermal treatment method. Typically, 2 g of urea and 4 g of thiourea were dissolved with 30 mL of deionized water and stirred to get a clear solution. The solution was then dried at 80°C overnight to get the molecular composite precursors. The precursors were heated at 550°C for 2 h in air with a heating rate of 2°C/min in a muffle furnace, followed by naturally cooling to room temperature. The resultant yellow sample was collected and ground into powders for use without further treatment. The as-prepared g-C<sub>3</sub>N<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> nanojunction was labeled as M-CN. For comparison, 6 g of urea and thiourea were treated separately under the same thermal conditions. The as-prepared samples of pure g-C<sub>3</sub>N<sub>4</sub> were labeled as U-CN and T-CN, respectively.

## Characterization

Structural and chemical properties were studied with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The XRD patterns were obtained using a RigakuMiniflexX-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$ = 1.5418 Å). The specific surface area and pore size distribution curves of the samples were acquired at 77 K on Model ASAP 2020 Micromeritics. Brunauer-Emmett-Teller method and Barrett-Joyner-Halenda model were adopted to calculate the surface area and pore size distribution of the samples, respectively. XPS data were collected using a Kratos Axis 165 X-ray photoelectron spectrometer.Spectra were acquired using a photo beam of 1486.6 eV, selected from an Al/Mg dual-anode X-ray source. The morphologies of the samples were evaluated by transmission electron microscopy (TEM). The TEM study was

performed on a JEOL JEM-2010 TEM. The electron accelerating voltage was 200 kV. Fourier transform infrared (FT-IR) spectrawere recorded on a Thermo-Nicolet iS 10 FT-IR spectrometer with an attenuated total reflectance unit. The reflectance spectra were collected with an Agilent Cary 60 UV-Vis spectrometer with a fiber optical reflectance unit. MgO power was used as the reference material. The Raman spectra were collected on an EZRaman-N bench top Raman spectrometer. The Raman spectrometer was equipped with a diode laser and the excitation wavelength was 785 nm. The spectrum range was from 100 to 3000 cm<sup>-1</sup>.

## **Electrochemical measurements**

Electrochemical measurements were carried out in a three-electrode system at room temperature. A Ti electrode coated with the sample, a Pt wire and an Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively. 1.0 M KOH aqueous solution was used as the electrolyte. For the fabrication of the working electrode, 50 mg of the sample was mixed with an amount of Nafion solution homogeneously. The obtained sample deposited onto the as-washed Ti foil with a controlled area of 1 cm<sup>2</sup>, and then dried in air. The Mott-Schottky measurement was performed using on a Biologipotentiostat/EIS electrochemical workstation in the frequency of 10<sup>5</sup> Hz. The reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). The calibration was performed in a high purity hydrogen saturated 1 M KOH electrolyte with Pt wire as the working electrode.

#### Photocatalytic activity tests

To evaluate the photocatalytic activity, the photocatalytic hydrogen evolution reaction was carried out in a 270 mL photochemical reactor. A 150 W Xenon lamp was used as the simulated

sunlight source. 20 mg sample was suspended in 100 mL aqueous solution containing 50 vol% methanol. The 1.5 wt% Pt was photodeposited by addition of  $H_2PtCl_6$  at the beginning. The suspension was de-aerated by purging with argon for 30 min before light irradiation. The amount of  $H_2$  evolved was determined using gas chromatography (TCD, thermal conductivity detector, Argon carrier gas). The hydrogen evolution rate was measured at 2 h intervals during the test.



**Fig. S1.** N<sub>2</sub> isothermal adsorption and desorption and the Barrett-Joyner-Halenda (BJH) pore size distribution curves of the U-CN, T-CN and M-CN.



Fig. S2. Stability of photocatalytic performance of M-CN