Supporting Information

Microwave-Assisted Heating Synthesis: A General and Rapid Strategy for Large-Scale Production of High Crystalline g-C₃N₄ with Enhanced Photocatalytic H₂ Production

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Experimental Section

Synthesis of graphitic carbon nitride

In a typical process for preparing $g-C_3N_4$ samples through MW-assisted heating synthesis, 6 g urea ($\geq 97.0\%$, Sigma-Aldrich) was grounded for 30 min in a mortar and then transferred to an

alumina crucible (25 mL) covered with another crucible (50 mL) and sealed with aluminum silicate. The crucible was then put into a big alumina crucible (200 mL), buried with the CuO powder (\geq 98.0%, Sigma-Aldrich), and irradiated by microwave for desired time in a domestic microwave oven (NN-C784MF, Panasonic) at various MW power. For comparison purpose, urea was also heated at 550 °C for 6 h in Ar atmosphere, and this product was designated as CN550.

For examining the generality of this MW-assisted heating synthesis, the other nitrogen-rich compounds of melamine (3 g), cyanamide (3 g), and thoiurea (3 g) were also used as precursors to prepare the $g-C_3N_4$ samples under the same condition for 15 min reaction at a maximum power of 1000 W, and the obtained products were labeled as MM, MC, and MT, respectively.

Characterizations

X-ray powder diffraction (XRD) data were collected on a Shimadzu XRD-6000 X-ray diffractometer using Cu K α 1 radiation at a scan rate of 1°/min. The acceleration voltage and the applied current were 40 kV and 40 mA, respectively. Morphology of the obtained samples was observed by field emission scanning electron microscopy (SEM: JEOL JSM-7600F) and transmission electron microscopy (TEM: JEOL JEM-2100F). UV–vis diffuse reflectance spectra (DRS) were recorded over the spectral range 320-800 nm on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). BaSO₄ was used as a reflectance standard. Fourier transform infrared spectra (FTIR) of the samples were recorded between 400 and 4000 cm⁻¹ on an IRAffinity-1 FTIR spectrometer. The solid state ¹³C NMR experiments were carious out on a Bruker Advance 500 M spectrometer. Time-resolved PL spectra was obtained over a HORIB FluoroMax-4P spectrometer with an excitation wavelength of 325 nm at room temperature. The surface area of the obtained samples was determined by the BET method from N₂ adsorption

isotherms at 77 K (ASAP-2020, Micromeritics). The photoluminescence (PL) spectra were obtained on a Shimazu RF-5310PC fluorometer at an excitation wavelength of 320 nm.

Photocatalytic measurements

Photocatalytic H₂ production reactions were carried out in a 50-mL closed quartz flask reactor, which was sealed with Suba Seal rubber septa (Sigma-Aldrich). Typically, 10 mg of the prepared g-C₃N₄ catalysts was suspended in 10 mL aqueous solution of triethanolamine (TEOA, 15 vol. %). Pt (0.5 wt %) as co-catalyst for H₂ production was *in-situ* photo-deposited upon g-C₃N₄ surface through injecting small amount of H₂PtCl₆ solution (61 uL, 0.16 wt. %) into the reactor. The reactor was purged with argon to drive away the residual air. The photocatalytic hydrogen evolution was initiated by irradiating the suspension with a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter ($\lambda > 420$ nm). The gas product were analyzed periodically through a gas chromatograph (GC-7890A, Agilent) with a TCD detector.

The Methyl Orange (MO) degradation in aqueous solution were further evaluated. In a typical photocatalytic experiment, 10 mg of the g-C₃N₄ catalyst was dispersed in MO aqueous solution (100 mL, 4 mg•L⁻¹). The photocatalytic reaction was initiated by irradiating the suspension with a 300-W xenon lamp (MAX-302, Asahi Spectra, USA). An ultraviolet cut-off filter was installed to provide the visible light ($\lambda > 420$ nm). Prior to irradiation, the suspension was magnetically stirred in dark for 30 min to establish the adsorption/desorption equilibrium over catalyst. During the photodegradation reaction, samples were withdrawn at regular intervals and centrifuged to separate photocatalysts for analysis. The MO concentration was monitored by measuring the absorption intensity at its maximum absorbance wavelength of λ = 462nm using a UV-visible spectrophotometer (UV-1800, Shimadzu) in a 1cm path length spectrometric quartz cell.

Photoelectrochemical measurements

 $g-C_3N_4$ electrode was prepared through spin coating $g-C_3N_4$ powder upon ITO glass (1.0 cm x 1.0 cm). ITO glass was rinsed using ultrapure water and acetone several times. $g-C_3N_4$ powder suspension was first prepared by dispersing $g-C_3N_4$ powder (10 mg) in ethonal (20 mL) with the assistance of sonication, then dropped on the surface of the ITO through spin coating at 2000 rpm. Finally, the obtained $g-C_3N_4$ film was heated to 300 °C for 10 min in air to obtained the $g-C_3N_4$ electrode.

Photoelectrochemical measurements were carried out in a three-electrode configuration in an aqueous Na_2SO_4 electrolyte (0.5 M) by an electrochemical analyzer (CHI-633C, Shanghai Chenhua, China). g-C₃N₄ electrode was used as working electrode, SCE as the reference electrode, and Pt as the counter electrode. Photocurrent density under visible light irradiation were obtained by using a 500 W xenon lamp fitted with a 420 nm cut-off filter.

Measurement of •OH radicals generated from oxidation by photogenerated holes

The \cdot OH radical reactions were performed as following: 10 mg of each sample ($MCN_{1000-18}$ and CN550) was suspended in 10 mL solution containing 10 mM of NaOH and 5 mM of terephthalic acid (TA). Prior to irradiation by visible light, the suspension was stirred in dark for 10 min. After 10 min visible light irradiation, the solution was centrifuged. Then the upper clear solution was measured for the fluorescence of the TAOH by a spectrofluorometer (Shimazu RF-5310PC) at an excitation wavelength of 320 nm.

Quantum efficiency measurement

The apparent quantum efficiency (QE) was measured at 420 nm by using a band pass filter (half width: 10 nm) under the identical reaction condition for H_2 production. The number of incident

photons from the Xenon lamp is measured with a power meter (1831-R, Newport). The QE value can be calculated by using the following equation.

 $QE = \frac{2 \times \text{ the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\%$ (1)



Fig. S1. SEM image of CN550 sample.



Fig. S2. Photocatalytic H_2 production rate over g-C₃N₄ samples (denoeted as CNx, x refers the heating time (h)) fabricated at 550 °C for various time in Ar atmosphere and g-C₃N₄ sample fabricated at 550 °C for 1 h in air (CN1A) through urea polymerization.



Fig. S3. UV-visible absorption spectra of MCN₁₀₀₀₋₁₈ and CN550 sample.



Fig. S4. TEM image of Pt-loaded MCN₁₀₀₀₋₁₈ sample. The ultrafine Pt particles was photoloaded upon the $g-C_3N_4$ surface.



Fig. S5. Photodegradation activity of CN550 and $MCN_{1000-18}$ sample for MO dye. The inset shows the MO absorption spectra as a function of reaction time.



Fig. S6. Transient fluorescene decay profile of CN550 and $MCN_{1000-18}$ in water.

Table S1 Fitted lifetimes of the fluorescence decay profiles

| Sample | A ₁ (%) | τ_1 | A ₂ (%) | τ_2 | A ₃ (%) | τ ₃ | τ |
|------------------------|--------------------|----------|--------------------|----------|--------------------|----------------|------|
| CN550 | 24 | 3.43 | 72 | 0.6 | 4 | 17.4 | 1.94 |
| MCN ₁₀₀₀₋₁₈ | 32 | 4.1 | 64 | 0.93 | 4 | 19.6 | 2.76 |



Fig. S7 FT-IR spectra of products at 1000 MW power for various reaction time.



Fig. S8. The urea polymerization process in microwave-assisted heating.



Fig. S9. SEM images of products at 1000 MW power for various reaction time, (a) 9 min, (b) 12 min, (c) 15 min, and (d) 18 min.



Fig. S10. N_2 adsorption-desorption isotherms of products at 1000 MW power for various reaction time.



Fig. S11. Optical absorption spectra of products at 1000 MW power for various reaction time.



Fig. S12. XRD patterns of products at 250 MW power for (a) 15 min, and (b) 60 min.



Fig. S13. XRD patterns of products at 660 MW power for (a) 15 and (b) 18 min.



Fig. S14. (a) XRD patterns and (b) FT-IR spectra of products obtained from MW irradiated melamine (MM), cyanamide (MC), and thiourea (MT) for 15 min.



Fig. S15. Photocatalytic H₂ production activities of MC, MM, and MT sample.



Fig. S16. Photocatalytic H₂ production rate of MCN₁₀₀₀₋₁₅, MC, MT, and MM.