Supplementary information

Ultrathin graphitic carbon nitride nanosheets with remarkable photocatalytic hydrogen production under visible LED irradiation

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Experimental

Synthesis of bulk g-C₃N₄ from urea (step 1)

The graphitic carbon nitride was prepared using the same method that we had previously reported¹. Typically, 20g urea (AR, Sinopharm Chemical Reagent Co., Ltd) was put in a crucible with a cover under ambient pressure in air, heated to 550 °C for 3 hours with a ramp rate of 2.3 °C/min to complete the reaction. A yellow-colored product was obtained.

Synthesis of g-C₃N₄ nanosheets (step 2)

 $g-C_3N_4$ nanosheets was synthesized by thermal treatment of bulk $g-C_3N_4$ (0.5g) in a crucible exposed to ambient pressure. The bulk $g-C_3N_4$ was put in a Muffle Furnace (Isotemp Programmable Muffle Furnace 650 Series, Fisher Scientific) and heated to 520 °C for 2 h with a ramp rate of 5 °C/min to complete the reaction. A white-colored product was obtained. The weight of the powders was 0.1 g.

Pt loaded g-C₃N₄ nanosheets

Platinum as a typical hydrogen evolution catalyst is utilized as the co-catalyst. Pt nanoparticles loaded $g-C_3N_4$ nanosheets was obtained by a photo-deposition approach using H₂PtCl₆ as platinum source. Firstly, 0.3 mL H₂PtCl₆·6H₂O (10 mg mL⁻¹, AR, Sinopharm Chemical Reagent Co.,Ltd) was mixed with 100 mL $g-C_3N_4$ aqueous dispersion (1 mg mL⁻¹) to obtain a 3 wt% Pt content. Prior to irradiation under a 300 W Xe lamp (PLS-SXE 300, Beijing trusttech) for 2 hours, oxygen in the reactor was removed by N₂ bubbling for 30 min. The Pt loaded $g-C_3N_4$ nanosheets was subsequently obtained by filtering and drying at 60 °C. The size of Pt nanoparticles is about 2nm (Fig. S8).

Hydrogen evolution reaction

The photocatalytic activity of $g-C_3N_4$ nanosheets for hydrogen production was evaluated using triethanolamine (TEOA) as sacrificial electron donor. 50mg photocatalyst powders were dispersed in 100ml aqueous solution containing 10 vol% TEOA. The 460 nm high-power LED was used as

the light source (the power intensity was measured to be 70 mW cm⁻²), and a 300W Xe lamp (UV cut-off filter, $\lambda > 400$ nm) was also introduced as control. The evolved gases were analyzed by gas chromatography (Beijing aulight, GC-7900) equipped with a thermal conductive detector (TCD), using nitrogen as the carrier gas.

Photoelectrochemical measurements

The photoelectrochemical measurements were performed using an electrochemical workstation (CHI 760D Shanghai Chenhua Instrument, China) in a conventional three-electrode configuration. Ag/AgCl (saturating KCl) and Pt wire were selected as reference electrode and counter electrode, respectively. To prepare the working electrodes, 5 mg g-C₃N₄ samples (bulk or nanosheets) were dispersed in a solution containing 0.95 ml deionized water (18.2 M Ω) and 25 µL 10 wt% Nafion aqueous solution. The mixture was ultrasonicated for 15 min to obtain a homogeneous catalyst ink. 15 µL photocatalyst dispersion was then dropped onto a mirror polished glassy carbon electrode and dried in air at 60 °C. A custom-designed high-power visible LED (λ =460 nm±20 nm, Fig. S1) was utilized as the light source.

Characterization

The morphology and microstructure of $g-C_3N_4$ was investigated by transmission electron microscopy (TEM) and high resolution TEM using a FEI Tecnai G2 F20 S-Twin microscope at 200 KV. The thickness of the nanosheets was evaluated by atomic force microscopy (AFM) using a Bruker Dimension Icon microscope. The chemical states of elements were measured on a VG ESCALAB 210 X-ray photoelectron spectrometer (XPS). Nitrogen adsorption-desorption isotherms were performed at 77 K using a Micromeritics ASAP 2020 equipment. Powder X-ray diffraction (XRD) measurements were collected on a Bruker D8 Advance diffractometer with Cu K_a radiation (λ =1.5406 Å). The UV-Vis absorption spectra were obtained on a Shimadzu UV-2550 UV-vis spectrophotometer equipped with a diffuse-reflectance sphere. The photoluminescence spectra were recorded using a LabRam HR 800 spectrometer. Fourier transformed infrared (FTIR) spectra were recorded using a Nicolet 6700 FTIR spectrometer by KBr pellets.

Additional Figures and Results



Fig. S1 Image of SINANO-LED light A custom-designed LED light (λ =460 nm±20 nm) from the lab of SINANO.



Fig. S2 Typical SEM images of bulk g-C₃N₄ (a), g-C₃N₄-nanosheets (b).

The scanning electron microscopy (SEM) can provide more morphology details about the layer structures. The bulk $g-C_3N_4$ obtained without the secondary calcination reveal a compact coral-like structure (Fig. S2a), while the $g-C_3N_4$ -nanosheets presents a loose and silk-like lamellar (Fig. S2b).



Fig S3 AFM image of g-C₃N₄ nanosheets (a), thickness analyses (b).



Fig. S4 Typical TEM images of bulk g-C₃N₄ (a), g-C₃N₄ nanosheets (b) under lower magnification.



Fig. S5 FT-IR spectra of g-C₃N₄ and g-C₃N₄-nanosheets, measured as KBr pellets.

The strong IR absorption bands in Fig. S5 revealed a typical molecular structure of bulk $g-C_3N_4$ and $g-C_3N_4$ nanosheets. We can obviously see that the $g-C_3N_4$ nanosheets is similar to the bulk $g-C_3N_4$. The spectra present several major bands in the 1200-1650 cm⁻¹. As our group reported that the intense bands at 1637.94, 1575.69, 1461.04 and 1408.05 cm⁻¹ were assigned to typical stretching vibration modes of heptazine-derived repeating units ². The bands at 1317.02 and 1238.99 cm⁻¹ corresponded to stretching vibration of connected units of C-N(-C)-C (full condensation) or C-NH-C (partial condensation), which was also supported by the stretching vibration modes of the broad weak band around 3281.11 cm⁻¹ for hydrogen-bonding interactions. The characteristic mode of triazine units at 813.74 cm⁻¹ was presented.



Fig. S6 Barret-Joyner-Halenda (BJH) pore size distribution curves for bulk g-C₃N₄ and g-C₃N₄nanosheets.



Fig. S7 XPS survey spectra of g-C₃N₄-nanosheets (a-c) and bulk g-C₃N₄ (d-f)

Figure S7 shows two C 1s peaks centering at 288.4 eV and 285.0 eV, corresponding to sp²-bonded carbon (N-C=N) and graphitic carbon respectively. The N 1s spectrum can be fitted into four binding energies. Two main signals at 398.9 eV and 400.6 eV are related to pyridinic N and pyrrole N, respectively. A weak peak at 401.5 eV corresponds to N bonded three carbon atoms in the aromatic cycles. The 404.4 eV peak is attributed to the π -excitations.



Fig. S8 XPS elemental analysis of bulk g-C₃N₄ and g-C₃N₄-nanosheets (a), relative content of different types of N1s (b).



Fig. S9 Plots of $(\alpha hv)^{1/2}$ vs. photon energy of bulk g-C₃N₄ and g-C₃N₄-nanosheets.



Fig. S10 Process of preparation g-C₃N₄-nanosheets in tube furnace.



Fig. S11 TEM images of Pt nanoparticles loaded on the g-C₃N₄-nanosheets.



Fig. S12 Transient photocurrent responses of g-C₃N₄ and g-C₃N₄-nanosheets in 6M NaOH aqueous solution under visible LED light irradiation at 1V vs Ag/AgCl

Quantum efficiency calculations

Quantum efficiency (QE) test and calculation was carried out according to the equations reported by Liu *et al* ³. The power intensity of the LED light source was determined to be 70 mW cm⁻² by a spectroradiometer (Beijing Aulight, GEL-NP2000), and the irradiation area was 46.16 cm². In equation 1, the number of incident photons (N) is calculated to be 1.34×10^{23} . Considering the amount of H₂ production under LED irradiation of 5 hours was 12.8 mmol, the quantum efficiency can be calculated from equation 2.

$$N = \frac{E\lambda}{hc} = \frac{70 \times 10^{-3} \times 46.16 \times 3600 \times 5 \times 460 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 1.34 \times 10^{23}$$
Equation 1
$$QE = \frac{2 \times the number of \ evolved \ H_2 \ molecules}{the \ number \ of \ incident \ photons} \times 100\% = 11.5\%$$
Equation 2

References

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