Electronic Supplementary Information

Sulfur-Doped g-C₃N₄ Photocatalyst for Significantly Steered Visible Light Photocatalytic H₂ Evolution from Water Splitting

Xiao-Jie Lu, ‡^a Li Xu, ‡^b Ikram Ullah,^a Hong-Bao Li, ^{*b} and An-Wu Xu^{*a}

^aDivision of Nanomaterials and Chemistry, Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.

^bInstitutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Ministry of Education, Anhui Graphene Engineering Laboratory, Anhui University, Hefei, Anhui 230601, P. R. China.

[‡]These authors contributed equally to this work.

*Corresponding Authors: Hong-Bao Li; <u>lihb@ahu.edu.cn</u> An-Wu Xu; <u>anwuxu@ustc.edu.cn</u>

Experimental Section

1. Materials

The primary reagents used in this study, including urea ($\geq 99\%$), ethanol (EtOH, $\geq 99.8\%$) and triethanolamine (TEOA, $\geq 99\%$), were purchased from Sinopharm Chemical Reagent Co., Ltd. 4-Mercaptobenzoic acid (4-MBA, $\geq 99\%$) and chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, \geq 37.5% Pt basis) was bought from Aladdin Co., Ltd. All of the above chemicals were used as purchased without further purification. Moreover, the deionized water used in all experiments with a resistivity of 18.2 M Ω at 25 °C, was purified through Direct-Q 3 UV water purification system (Millipore Corp., France).

2. Preparation of Photocatalysts

Pristine g-C₃N₄ was prepared by a previously reported one-step thermal polymerization method. In a typical synthesis procedure, 10 g of urea was calcined at 550 °C for 2 h with a heating rate of 5 °C min⁻¹ in a muffle furnace to obtain the yellow powder. S-doped g-C₃N₄ (denoted by S-CN) was prepared similarly but using uniformly mixed urea and 4-MBA as the precursor. The preparation method is shown as follows: 10 g of urea and different amounts (3, 5, 7, 9 mg) of 4-MBA acid were dissolved in a mixed solvent (20 mL ethanol and 5 mL deionized water). Subsequently, the mixed solution was heated at 80 °C in a water bath to remove solvent while continuous stirring. After that, the obtained white powder further dried at 60 °C under vacuum conditions overnight to get the solid precursors. The solid composite precursors were moved into a semiclosed alumina crucible with a cover and then heated to 550 °C at a heating rate of 5 °C min⁻¹ in a muffle furnace and maintained for 2 h. After the thermal treatment, the crucible was naturally cooled to room temperature in the muffle furnace to obtain light-brown samples (denoted as S-CN-X, where X represent the amount of 4-MBA). As a comparison, 10 g of melamine and 7 mg of 4-MBA were homogeneously mixed and calcined at 550 °C for 2 h in air as a counterpart which was denoted as S-CN-7 (M). The sample of $g-C_3N_4$ (M) was prepared in the same way without adding 4-MBA.

3. Characterization

Scanning electron microscopy (SEM) images were obtained on GeminiSEM 450. The transmission electron microscopy (TEM) images were attained using a H-7650 HITACHI transmission electron microscope. The high-resolution transmission electron microscopy (HRTEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, energy dispersive spectroscopy (EDS) and elemental mapping results were obtained using a FEI Talos F200X field emission high resolution transmission electron microscope at 200 kV accelerating voltage. Thermogravimetric analysis (TGA) was performed by NETZSCH TG 209 F1 Libra TGA analyzer at a heating rate of 10 °C min⁻¹ in the air atmosphere with α -Al₂O₃ as the reference. The nitrogen physisorption was measured with a Micromeritics ASAP 2460 apparatus. The X-ray diffraction (XRD) patterns were recorded on a TTR-III Theta ThetaRotating anode X-ray diffactometer operated at 40 kV and 200 mA using Cu $K\alpha$ ($\lambda = 1.54178$ Å) monochromatized irradiation in all cases. The X-ray photoelectron spectroscopy (XPS) and valence band X-ray photoelectron spectra (VBXPS) were collected on a Thermo ESCALAB 250Xi X-ray photoelectron spectrometer equipped with a monochromatic Xray source of Al Ka of 1486.6 eV at 150 W, and 30 eV pass energy. The C 1s peak at 284.6 eV was used as an internal standard to compensate for the sample charging. XPS spectra were fitted with the XPSPEAK41 software in the subsequent step. The Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet 8700 Fourier Transform Infrared spectrometer on samples

embedded in KBr pellets. The UV–Vis diffuse reflectance spectra (DRS) of obtained photocatalysts were measured on a Shimadzu 3700 DUV UV-Vis spectrophotometer at room temperature, using BaSO₄ as the reflectance standard reference. The UV-Vis DRS spectra were then converted to Tauc plots in order to estimate the optical band gap [i.e., the curve of converted $(\alpha hv)^2$ versus hv from the UV-Vis spectrum, in which α , h, and v are the absorption coefficient, Planck constant, and light frequency]. The electron paramagnetic resonance (EPR) measurements were carried out with a JEOL JES-FA200 ESR spectrometer (300 K, 9.066 GHz, X-band). The steady-state photoluminescence (PL) spectra were measured at room temperature with a fluorescence spectrophotometer (JY Fluorolog-3-Tau) under an incident light of 370 nm. The time-resolved photoluminescence (TRPL) decay curves were recorded on a LaserStrobe time-resolved spectrofluorometer (Photon Technology International (Canada) Inc.) with a GL-302 high-resolution dye laser (lifetimes 100 ps to 50 ms, excited by a nitrogen laser), a 914 photomultiplier detection system and a USHIO xenon lamp source.

4. Photocatalytic Experiments

As illustrated in Figure S22, the photocatalytic water-splitting (H₂ evolution) experiments with the use of triethanolamine (TEOA) as sacrificial agent were carried out in a Pyrex top-irradiation reaction vessel associated with a glass closed gas circulation system. Typically, 50 mg of photocatalyst powder was dispersed in an aqueous solution (100 mL) containing 10 vol% TEOA in the reaction cell. Then, 1 wt% Pt was loaded onto the surface of the catalyst by in-situ photodeposition of H₂PtCl₆·6H₂O aqueous solution as cocatalyst, resulting in a near neutral condition in the reaction system. The system was evacuated for 30 min to degassed completely and ensure anaerobic conditions in the reaction system, followed by the visible light irradiation with a 300W Xe lamp (Perfect Light, CEL-HXF300-T3, Beijing China Education Au-light Technology Co., Ltd.) equipping with an optical UV cut-off filter to control the wavelength of incident light ($\lambda \ge 420$ nm). Moreover, a cooling water circulation machine was attached to maintain the constant temperature of the suspension during the entire photocatalytic reaction at 10 °C and Pyrex reactor with a double layer was continuously stirred. The evolved H₂ gases was sampled every 1 h through an on-line automated flow-injection apparatus, and then analyzed by using an on-line gas chromatography (GC1120, Shanghai Sunny Hengping Limited) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column, using Argon as the carrier gas. After the reaction, the photocatalysts were separated from the reaction solution for further use and characterization. For a stability test, the system was evacuated every 4 h and repeated 5 times (i.e., a 20 h recycling experiment with intermittent evacuation every 4 h).

The apparent quantum yield (AQY) of H₂ evolution was determined by using the S-CN-7 photocatalyst with a procedure similar to that of the H₂ evolution test, except that the irradiation was supplied by monochromatic light of the 300 W Xe lamp equipped with different bandpass filters of $\lambda \pm 5$ nm for 420, 450, 500, 550, and 600 nm. Generally, for a single-component photocatalytic system, the AQE value was calculated by the equation given below:

$$AQY (\%) = \frac{Number of reacted electrons}{Number of incident electrons} \times 100\%$$
$$= \frac{Number of evolved H_2 molecules \times 2}{Number of incident photons} \times 100\%$$

5. Photoelectrochemical Measurements

The photoelectrochemical tests of the photocatalysts were measured at room temperature using a CHI 760E (Shanghai Chenhua Limited, China) electrochemical workstation based on a standard three-electrode system, that is made up of a saturated Ag/AgCl (in saturated KCl solution) as the reference electrode, a platinum wire as the counter electrode, a fluorine-doped tin oxide (FTO) glass deposited with the photocatalysts as the working electrode and Na₂SO₄ (0.5 M, 100 mL) as the electrolyte solution. To make a working electrode, 2 mg of catalysts were dispersed into 1 mL ethanol containing 10 μ L Nafion (5 wt%, D520, DuPont Inc., USA) by ultrasonication. The resulting dispersion was then transferred onto a piece of FTO glass (an effective area of about 1.0 cm²) using a spin-coating method and dried at 60 °C for 2 h in an oven to form the final electrode.

The transient photocurrent responses were tested for each switch on/off (300 W Xe lamp) event with a bias voltage of 0.5 V. The electrochemical impedance spectroscopy (EIS) curves were measured under visible light and a bias of -0.2 V to evaluate the charge-transfer ability of the catalysts, and its frequency ranging from 10 MHz to 100 KHz.

6. DFT Calculations

Density functional theory (DFT) calculations were carried out using the Vienna ab initio Simulation Package (VASP) code.^{1,2} The interaction and exchange correlation energy between electrons and ions were characterized by the projector augmented wave (PAW)³ method and Perdew-Burke-Eznerhof (PBE)⁴ exchange-correlation functional. The cutoff energy of 450 eV for the plane-wave basis set was adopted. The spin-polarized calculations were employed for all systems. The convergence criterion for the residual force was set to 0.02 eV/A and 10^{-4} eV during the structure relaxation. A vacuum layer of 15 Å was built to model the catalyst surface, which is enough to avoid the interaction between two periodic units. The Brillouin zone was sampled with the Monkhorst-Pack mesh with a $2 \times 2 \times 1$ k-point grid. The unit cells of pure g-C₃N₄ and S-CN-7 used in the calculations are shown in Figure S23.



Figure S1. (a) XPS survey spectra, (b) high-resolution XPS spectra for O 1s of complex (Urea +

4-MBA), 4-MBA, and Urea.



Figure S2. XRD patterns of complex (Urea + 4-MBA), 4-MBA, and Urea (inset is the XRD partial magnification of the complex and Urea).



Figure S3. TGA curve of 4-MBA molecules at atmosphere with a ramping rate of 10 °C min⁻¹.



Figure S4. TGA curves of g-C₃N₄ and S-CN-7 samples at atmosphere with a ramping rate of 10 °C min⁻¹.



Figure S5. The SEM images of (a) g- C_3N_4 , (b) S-CN-7, and (c) g- C_3N_4 (M).



Figure S6. The TEM images of (a-b) $g-C_3N_4$ and (c-d) S-CN-7.



Figure S7. N₂ adsorption-desorption isotherms of g-C₃N₄ (M), S-CN-7 (M), g-C₃N₄, and S-CN-7.



Figure S8. The corresponding pore size distribution calculated by the BJH method for $g-C_3N_4$ (M), S-CN-7 (M), $g-C_3N_4$, and S-CN-7.



Figure S9. The XRD patterns of as-prepared g-C₃N₄, S-CN-3, S-CN-5, S-CN-7, and S-CN-9.



Figure S10. FT-IR spectra of as-prepared g-C₃N₄, S-CN-3, S-CN-5, S-CN-7, and S-CN-9.



Figure S11. XPS survey spectra of S-CN-7 photocatalyst (inset is the partial magnification of the S signal of S-CN-7).



Figure S12. High-resolution XPS spectra for O 1s of g-C₃N₄ and S-CN-7.



Figure S13. UV-Vis DRS spectra of as-prepared $g-C_3N_4$, S-CN-3, S-CN-5, S-CN-7, and S-CN-9 (inset is the optical photogragh).



Figure S14. EPR spectra of as-prepared g-C₃N₄ and S-CN-7.



Figure S15. PL emission spectra of as-prepared g-C₃N₄, S-CN-3, S-CN-5, S-CN-7, and S-CN-9.



Figure S16. Comparison of photocatalytic hydrogen evolution rates on S-CN-7 photocatalyst in the presence of different sacrificial reagents under visible light irradiation. Reaction conditions: 50 mg of photocatalysts, 100 mL of solution containing sacrificial reagents (10 vol%), xenon lamp (300 W) with a cutoff filter ($\lambda \ge 420$ nm), temperature at 10 °C.



Figure S17. Photocatalytic H₂ evolution rates over different samples during control experiments: (a) g-C₃N₄ without the Pt co-catalyst, (b) g-C₃N₄ with 1 wt% Pt, (c) S-CN-7 without the Pt co-catalyst, and (d) S-CN-7 with 1% Pt co-catalyst. Reaction conditions: 50 mg of photocatalysts; 100 mL of solution containing sacrificial reagents, H₂O/TEOA = 9 : 1 (vol/vol); light source, xenon lamp (300 W) with a cutoff filter ($\lambda \ge 420$ nm); temperature at 10 °C.



Figure S18. Effect of Pt loading amount on photocatalytic hydrogen evolution of S-CN-7 under visible light irradiation ($\lambda \ge 420$ nm).



Figure S19. The XRD patterns of S-CN-7 photocatalyst before and after cycle test.



Figure S20. FT-IR spectra of S-CN-7 photocatalyst before and after cycle test.



Figure S21. High-resolution XPS spectra of S 2p for obtained S-CN-7 before and after cycle test.



Figure S22. Photocatalysis equipment picture of our water splitting system.



Figure S23. (a) Supercell of pure $g-C_3N_4$. (b) Supercell of S-CN-7.

Precursors of g-C ₃ N ₄	Sources of S atoms	BET ₁ ^[a] (m ² g ⁻¹)	BET ₂ ^[b] (m ² g ⁻¹)	HER ^[c] (µmol h ⁻¹ g ⁻¹)	Ref.
Melamine Cyanuric acid rGO	DMSO	92	189	NA ^[d]	5
Melamine	$(NH_4)_2S_2O_8$	10	37	880	6
Urea	2-Thiobarbituric acid	105	136	952	7
Melamine	Sublimed sulfur	6	74	982	8
Melamine	4-MBA ^[e]	11	16	315	counterpart
Urea	4-MBA	62	82	2662	this work

Table S1. Physicochemical properties of $g-C_3N_4$ and S-doped $g-C_3N_4$ synthesized from different precursors.

[a] the BET surface area of pure $g-C_3N_4$; [b] the BET surface area of S doped $g-C_3N_4$; [c] H_2 evolution rate of S doped $g-C_3N_4$; [d] not available; [e] 4-Mercaptobenzoic acid.

Samples	C (%)	N (%)	O (%)	S (%)	N/C
g-C ₃ N ₄	41.81	55.85	2.35	-	1.34
S-CN-7	44.28	53.52	2.07	0.13	1.21

Table S2. XPS determined atomic ratio of $g-C_3N_4$ and S-CN-7.

Table S3. Kinetic analysis of emission decay for $g-C_3N_4$ and S-CN-7.

Samples	τ ₁ (ns)	Rel (%)	$ au_2$ (ns)	Rel (%)	τ 3 (ns)	Rel (%)	τ (ns)	X ²
g-C ₃ N ₄	3.52	50.00	13.74	29.93	0.96	20.06	2.68	1.09
S-CN-7	1.89	50.00	6.63	27.29	0.50	22.71	1.32	1.17

Precursor (Doping Element)	Light Source	Conditions	$\begin{array}{c} HER_1{}^{[a]}\\ (\mu mol \ h^{-1}\\ g^{-1}) \end{array}$	HER ₂ ^[b] (μmol h ⁻¹ g ⁻¹)	Ref
4-MBA (S) Urea (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 420 \text{ nm}) \end{array}$	10 vol% triethanolamine, 1 wt% Pt	337	2662	This work
$(NH_4)_2S_2O_8$ (S) Melamine (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 400 \text{ nm}) \end{array}$	10 vol % methanol, 2 wt% Pt	139	880	6
2-Thiobarbituric acid (S) Urea (g-C ₃ N ₄)	500W xenon lamp $(\lambda \ge 420 \text{ nm})$	17 vol% triethanolamine, 1 wt% Pt	169	952	7
Sublimed sulfur (S) Melamine (g-C ₃ N ₄)	$300W \text{ xenon} \\ \text{lamp} \\ (\lambda \ge 420 \text{ nm})$	10 vol% triethanolamine, 1 wt% Pt	125	982	8
Thiourea (S) Isopropanol (O) Urea (g-C ₃ N ₄)	$300W \text{ xenon} \\ \text{lamp} \\ (\lambda \ge 420 \text{ nm})$	10 vol% triethanolamine, 3 wt% Pt	537	3645	9
Thiourea/thiocyanuric acid (S) HCCP (P) Melamine (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 420 \text{ nm}) \end{array}$	20 vol% triethanolamine, 3 wt% Pt	263	1969	10
[Emim]BF ₄ (B) Urea (g-C ₃ N ₄)	350W xenon lamp $(\lambda \ge 365 \text{ nm})$	12.5 vol% triethanolamine, 1 wt% Pt	309	901	11
N ₂ H ₄ •H ₂ O (N) Melamine (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 400 \text{ nm}) \end{array}$	10 vol% triethanolamine, 3 wt% Pt	98	554	12
(NH ₄) ₂ S ₂ O ₈ (O) Urea (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 420 \text{ nm}) \end{array}$	20 vol% triethanolamine, 1 wt% Pt	560	4110	13
H ₂ O ₂ (O) (NH ₄) ₂ HPO ₄ (P) Thiourea (S) Melamine (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 420 \text{ nm}) \end{array}$	20 vol% triethanolamine, 3 wt% Pt	465	2479	14
$NH_4F(F)$ Urea (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 420 \text{ nm}) \end{array}$	10 vol% triethanolamine, 3 wt% Pt	432	745	15

Table S4. Recently published nonmetal-doped $g-C_3N_4$ and their properties.

Na ₄ P ₂ O ₇ (P) Melamine (g-C ₃ N ₄)	$300 \text{W xenon} \\ \text{lamp} \\ (\lambda \ge 420 \text{ nm})$	20 vol % methanol, 1 wt% Pt	60	570	16
H ₃ PO ₃ (P) Melamine (g-C ₃ N ₄)	$300W \text{ xenon} \\ \text{lamp} \\ (\lambda \ge 420 \text{ nm})$	20 vol % methanol, 1 wt% Pt	90	670	17
HCl (Cl) Cyanuric acid/ melamine / barbituric acid (g-C ₃ N ₄)	A white LED array	10 vol% triethanolamine, 3 wt% Pt	10	380	18
NH ₄ Br (Br) Urea (g-C ₃ N ₄)	$\begin{array}{c} 300 \text{W xenon} \\ \text{lamp} \\ (\lambda \geq 420 \text{ nm}) \end{array}$	10 vol% triethanolamine, 3 wt% Pt	400	960	19
NH ₄ Br (Br) melamine (g-C ₃ N ₄)	$300W \text{ xenon} \\ \text{lamp} \\ (\lambda \ge 420 \text{ nm})$	10 vol% lactic acid, 1 wt% Pt	225	1354	20
Iodine (I) melamine (g-C ₃ N ₄)	$300W \text{ xenon} \\ \text{lamp} \\ (\lambda \ge 420 \text{ nm})$	10 vol% triethanolamine, 3 wt% Pt	98	890	21

[a] H_2 evolution rate of pure g-C₃N₄; [b] H_2 evolution rate of nonmetal-doped g-C₃N₄.

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