Electronic Supplementary Information

Sulfur-bubble template-mediated synthesis of uniform porous g-C₃N₄ with superior photocatalytic performance

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Experimental Section

1. Materials

Sublimed sulfur was purchased from Tianjin Chemical. Melamine ($C_3H_6N_6$) and chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Sigma-Aldrich. Triethanolamine (TEOA) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. All chemicals were used as received without further treatment.

2. Preparation of photocatalysts

Pure g-C₃N₄ was prepared by directly heating melamine at 600 °C for 2 h under a gentle Ar gas flowing. The sulfur-mediated g-C₃N₄ products were prepared as follows: Firstly, 2 g melamine mixed with a certain amount of sublimed sulfur and ground in an agate mortar for about 30 min. Then, the mixture was transferred into an alumina boat and sintered under a gentle Ar flow at 600 °C for 2 h. The mass ratios of sublimed sulfur: melamine was 0.5:1, 1:1, and 1.5:1, respectively.

3. Characterization

X-ray diffraction (XRD) were measured using a Rigaku D/max-2000 diffractometer with Cu Ka radiation (λ =0.15406 nm). X-ray photoelectron spectroscopy (XPS) spectra were recorded on an HI5700ESCA instrument with an Al-Ka (1486.6 eV) monochromatic X-ray radiation. Fourier transform infrared spectra were measured utilizing IR Affinity-1 FTIR spectrometer. Elemental analysis (EA) was carried out on Vario EL cube elementar. The BET specific surface area was calculated from Nitrogen adsorption–desorption isotherms determined on an AUTOSORB-1-MP surface analyzer at 77 K. The morphologies of the photocatalysts were carried out on a FEI Quanta 200F field emission scanning electron microscopy (FESEM) and a FEI, Tecnai G2 S-Twin transmission electron microscopy (TEM). thermogravimetricdifferential scanning calorimetry analysis (TG-DSC) was conducted on a SDT Q600 TG-DSC instrument. The UV–vis diffuse reflectance spectra (DRS) were recorded on a TU-1900 spectrophotometer and were converted from reflection to absorbance through the standard Kubelka–Munk method using BaSO₄ as the reflectance standard. The photoluminescence (PL) spectra were obtained on a Perkin-Elmer, LS-55 luminescence spectrometer with an excitation wavelength of 375 nm at room temperature.

4. Photocatalytic Reactions

4.1 Photocatalytic H₂ evolution Reactions

The photocatalytic H₂ evolution reactions were performed in a gas-tight circulation system with a side window. The photocatalyst (0.1 g) powder was suspended in aqueous solution (300 mL) containing triethanolamine (10 vol %) as a sacrificial agent, loading Pt (1.5 wt %) as cocatalyst by photodeposition of H₂PtCl₆·6H₂O. The suspensions were stirred and irradiated under a 300 W Xe lamp with a cutoff filter ($\lambda > 400$ nm). Prior to irradiation, suspensions were dispersed by sonication for 5 min and N₂ was purged through the system for 25 min to remove oxygen. The amount of evolved H₂ was detected by an online gas chromatography (Agilent 7890, TCD) with Argon as the carrier gas.

4.2 Photocatalytic degradation of RhB

The photo-oxidation activity of the photocatalysts were evaluated via the

photocatalytic degradation of RhB under visible light irradiation ($\lambda > 400$ nm). In a typical experiment, the photocatalyst (0.05 g) was suspended in 10 mg L⁻¹ RhB solution (100 mL). Before irradiation, the suspensions were dispersed by sonication for 5 min and stirred for 1 h in the dark to obtain adsorption–desorption equilibrium between the RhB and the photocatalyst. The suspensions were then stirred and irradiated under a 300 W Xe lamp with a cutoff filter ($\lambda > 400$ nm). During the irradiation process, about 4 mL of suspension was taken from the reaction cell every 10 min and centrifuged to remove the photocatalyst. The absorbance of the RhB solutions in degradation was detected on TU–1900 UV–vis spectrophotometer.



Fig. S1 XPS survey spectra and S 2p XPS spectra of pure $g-C_3N_4$ and sulfur-mediated $g-C_3N_4$

(1:1), which reveals that no sulfur species can be detected in the sulfur-mediated $g-C_3N_4$.



Fig. S2 FT-IR spectra of pure $g-C_3N_4$ and sulfur-mediated $g-C_3N_4$ (1:1), confirming the formation of $g-C_3N_4$ phase in sulfur-mediated $g-C_3N_4$.



Fig. S3 SEM images of (a) pure $g-C_3N_4$ and (b) sulfur-mediated $g-C_3N_4$ (1:1). The uniform pores can be found in the sulfur-mediated $g-C_3N_4$ (1:1).



Fig. S4 TEM images of sulfur-mediated $g-C_3N_4$ with the sublimed sulfur content of (a) of 0.5:1 and (b) of 1.5:1, which suggests that the sulfur-mediated $g-C_3N_4$ with different sublimed sulfur contents also display uniform porous structures.



Fig. S5 TEM images of porous $g-C_3N_4$ obtained from (a) sublimed sulfur with urea (0.5:1), and (b) sublimed sulfur with thiourea (0.5:1). It is found that uniform porous sulfur-mediated $g-C_3N_4$ can be also obtained by replacing melamine with urea or thiourea.



Fig. S6 TG-DSC thermograms for heating the mixture of sublimed sulfur and melamine (1:1).

In the DSC curve, the endothermic peaks at 120 and 434.6 °C is ascribed to the melting and vaporization of sulfur respectively [1]; while the strongest endothermic peak around 360 °C corresponds to the sublimation and thermal condensation of melamine [2]. That is, sublimed sulfur was first melt at around 120 °C acting as a molten flux to facilitate reactant molecules diffusion and contact; upon about 360 °C, the thermal condensation of melamine occurs; when heating at around 434.6 °C, sublimed sulfur volatilizes to sulfur bubbles acting as soft templates; the polymeric porous g-C₃N₄ sheets were finally obtained with the sulfur bubbles off; which clearly presents the formation process of porous sulfur-mediated g-C₃N₄ in the course of heating.

Reference:

[1] X. M. He, L. Wang, W. H. Pu, J. G. Ren, W. Wu, C.Y. Jiang and C. R. Wan. J. Therm. Anal. Cal., 2008, 94, 151–155.

[2] S. C. Yan, Z. S. Li and Z. G. Zou. *Langmuir*, 2009, **25** (17), 10397–10401.



Fig. S7 UV-vis absorption spectra of pure g- C_3N_4 (a) and sulfur-mediated g- C_3N_4 with different sublimed sulfur contents of (b, c, d) corresponding to 0.5:1, 1:1, 1.5:1 respectively. The sulfur-mediated g- C_3N_4 with different sublimed sulfur contents display enhanced absorption over pure g- C_3N_4 .

Table S1. Radiative fluorescence lifetimes and their relative percentages of photoexcited chargecarriers for pure $g-C_3N_4$ and sulfur-mediated $g-C_3N_4$ (1:1)

sample	$\tau_1(ns)$ –Rel %	$\tau_2(ns)$ -Rel %	τ ₃ (ns)–Rel %
pure g-C ₃ N ₄	0.83–26.46	3.41-42.32	16.72–31.22
sulfur-mediated g-C ₃ N ₄ (1:1)	1.19–24.11	4.74-43.87	19.08-32.02