

Supporting Information

Coordination polymer derived NiS@g-C₃N₄ composite photocatalyst for sulfur vacancy and photothermal effect synergistic enhanced H₂ production

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Experimental section

Material and characterization

All chemicals were of reagent grade and used for synthesis without further purification. The structure of **CP** was characterized on a diffractometer at 293 K (AXS SMART APEX II CCD, Bruker). PXRD patterns were recorded on X-ray diffractometer with CuK α ($\lambda=1.5418$ Å) radiation (X'Pert Pro Super, Philips). The Fourier transform infrared (FTIR) spectra were recorded on a FTIR spectrometer (Nicolet 6700). The electron paramagnetic resonance (EPR) spectrum was monitored using a digital X-band spectrometer (EMX-220, Bruker). The morphology was observed on a transmission electron microscopy (TEM, JEOL, JEM-2100F). XPS was performed with MgK α radiation (1253.6 eV) as an excitation source (ESCALab MKII, Thermo Scientific, and Waltham, MA). N₂ sorption analysis was conducted using an ASAP 2020 instrument (Micromeritics, Norcross, GA), equipped with an automated surface area, at 77 K using Barrett-Emmett-Teller (BET) calculations for the surface area. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu-2501PC spectrometer using BaSO₄ as a standard. Photoluminescence (PL) spectra were measured by using a FL-2T2 instrument (SPEX, USA) with 450-W xenon lamp monochromatized by double grating (1200 gr μ m⁻¹). Electrochemical experiments were conducted on CHI 660E electrochemical workstation.

Synthesis of CP, NCP and NiS@g-C₃N₄

CP was prepared from the mixture of Ni(OAc) \cdot 4H₂O (0.025 g, 0.1 mmol), MPPI (0.031 g, 0.2 mmol) and 8 mL H₂O. The pH value of this solution was adjusted to 5.0 with NaOH (1 mol \cdot L⁻¹). The mixture was stirred for 30 min, then transferred to a 25 mL Teflon-lined stainless steel bomb and kept at 150 °C under autogenously pressure for 120 h. The reaction system was cooled to room temperature during 24 h. A large

amount of green crystals was obtained. Yield: 82 % (based on Ni). The crystals of **CP** (0.6 g) were ground for 2.5 h with an agate mortar and pestle. Obtained powders were dissolved in methanol (20 mL) and placed in a Teflon autoclave, which were heated in a microwave oven at 300 W for 3 h. The resulted **NCP** were separated by centrifugation, rinsed with water, and dried in a vacuum drier at 80 °C for overnight. **NCP** were put in a tube furnace and heated at the rate of 2 °C·min⁻¹ to 500 °C under the protection Ar gas flow. The obtained results were collected, washed with water for several times, and then dried in a vacuum oven at 70 °C for 24 h. The product was named as **NiS@g-C₃N₄(A)**. The photocatalysts obtained at 550 and 600 °C were donated as **NiS@g-C₃N₄(B)** and **NiS@g-C₃N₄(C)**.

Electrochemical measurements

To prepare the electrode, **NiS@g-C₃N₄** (10 mg) was dispersed into 3 mL ethanol to give homogeneous suspension upon bath sonication. The suspension (5 µL) was dip-coated onto FTO and the electrode was dried at room temperature. Photoelectrochemical tests were carried out with a conventional three-electrode system in quartz cell filled with 0.5 M Na₂SO₄ electrolyte (50 mL), with the **NiS@g-C₃N₄/FTO** electrode serving as the working electrode, a Pt plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A 300 W Xe lamp (Beijing Perfect Co. Ltd., PLS-SXE-300UV) with a cutoff filter ($\lambda \geq 420$ nm) was used as the excitation light source for visible irradiation. Electrochemical impedance spectra (EIS) were recorded in potentiostatic mode. The amplitude of sinusoidal wave was 10 mV, and the frequency of the sinusoidal wave ranged from 100 kHz to 0.01 Hz.

Photocatalytic H₂ production

The photocatalytic reactions were conducted in a 100 mL quartz reactor at room

temperature and the visible light source is 8 cm away from this reactor. **NiS@g-C₃N₄** (20 mg) was dispersed in 60 mL lactic acid solution (10 %, as sacrificial agent) with stirring. At first, the system was deaerated by bubbling N₂ for 20 min, and then irradiated with above mentioned lamp equipped with a cut off filter ($\lambda \geq 420$ nm). The generated H₂ were measured through the online gas chromatograph (GC 7900) equipped with a TCD detector. The apparent quantum yield (AQY) was measured using the same light source equipped with a monochromatic filter (450 nm). The photo flux of the light was determined with a radiometer (Photoelectric instrument factory of Beijing normal university). The apparent quantum yield was calculated using the following equation.

$$\begin{aligned} \text{AQY (\%)} &= (\text{number of reacted electrons/number of incident photons}) \times 100\% \\ &= (2 \times \text{number of evolved H}_2 \text{ molecules/number of incident photons}) \times 100\% \end{aligned}$$

Table S1 the contents of different C in **NiS@g-C₃N₄**.

NiS@g-C₃N₄	A	B	C
N-C=N (%)	82.6	90.3	71.9
C-C (%)	17.4	9.7	28.1

Table S2 the contents of different N in **NiS@g-C₃N₄**.

NiS@g-C₃N₄	A	B	C
N-Ni (%)	12.3	8.4	0
C=N-C (%)	43.2	45.3	48.1
N-(C) ₃ (%)	44.5	46.3	51.9

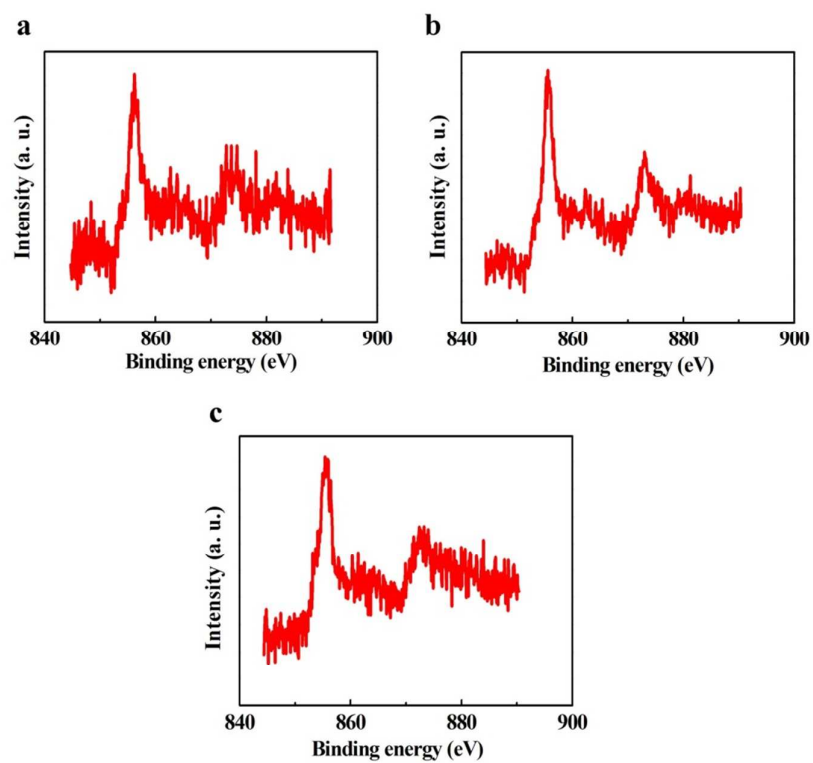


Figure S1 XPS spectra of Ni 2p, (a) **NiS@g-C₃N₄(A)**; (b) **NiS@g-C₃N₄(B)**; (c) **NiS@g-C₃N₄(C)**.

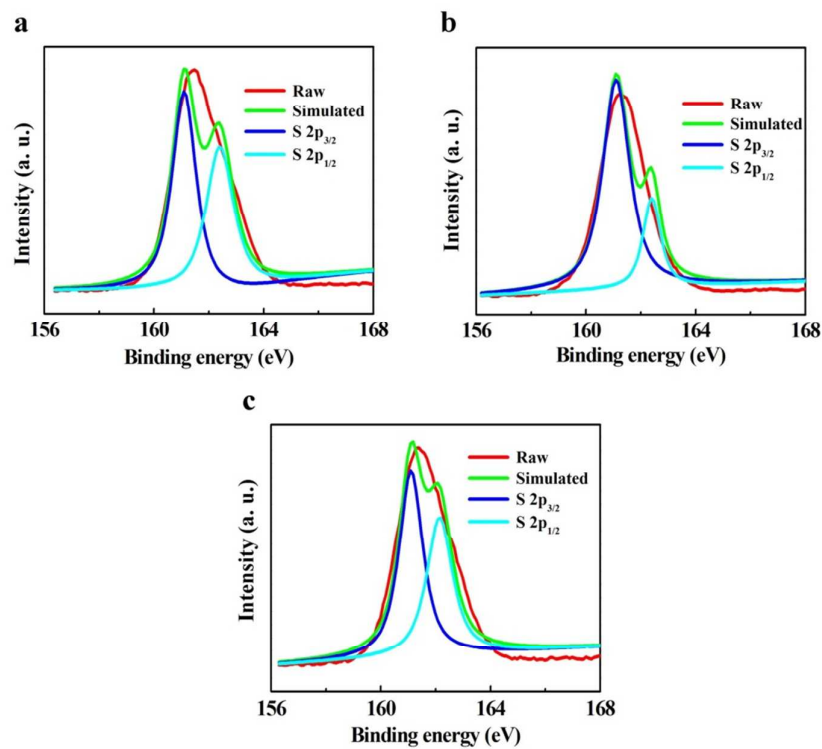


Figure S2 XPS spectra of S 2p, (a) NiS@g-C₃N₄(A); (b) NiS@g-C₃N₄(B); (c) NiS@g-C₃N₄(C)

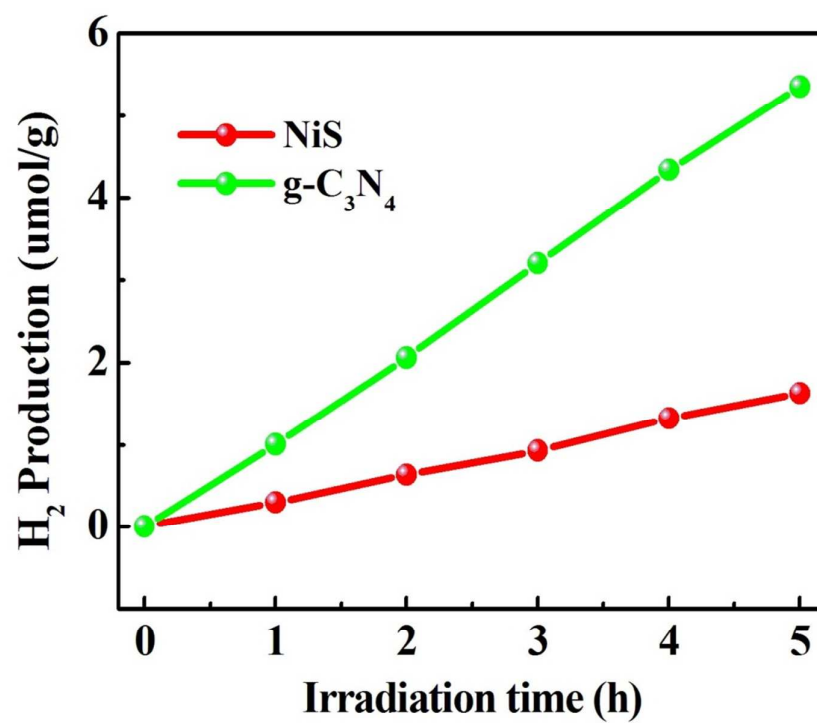


Figure S3 Time courses of H₂ production for NiS and g-C₃N₄