

Supporting Information

Highly crystalline sulfur and oxygen co-doped g-C₃N₄ nanosheets as an advanced photocatalyst for efficient hydrogen generation

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1. Experimental Section

1.1 Characterizations

The X-ray powder diffraction (XRD) patterns were conducted on Siemens D5005 Diffractometer at 40 kV and 40 mA using Cu K α radiation ($\lambda=1.5418\text{\AA}$). The scanning electron microscopy (SEM) and the Energy Dispersive Spectrometer (EDS) analyses were performed on XL30 ESEM FEG microscope. Transmission electron microscopic (TEM), high-resolution transmission electron microscopy (HRTEM) and elemental mapping images were obtained on JEM-2100F microscope. X-ray photoelectron spectroscopy (XPS), ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) and Photoluminescence (PL) spectra were measured on Thermo ESCALAB 250 XPS instrument, Cary 7000 spectrometer and FLSP920 Edinburgh fluorescence spectrometer, respectively. Brunauer–Emmett–Teller (BET) surface area of the samples were determined by a Micromeritics Tristar 3000 analyzer at 77.4 K. Electrochemical analyses were carried out on an electrochemical workstation (CHI660E, China) with a three-electrode system using 0.1 M Na₂SO₄ solution as electrolyte.

1.2 Computational methods

All density functional theory (DFT) calculations in this work were performed using Vienna *ab initio* simulation package (VASP).^{1,2} The Perdew-Burke-Ernzerhof (PBE) exchange–correlation functional of the generalized gradient approximation (GGA) was utilized for describing the electron interactions,^{3,4} while the projector augmented wave (PAW) pseudopotential was used to treat the core electrons.⁵ The van der Waals interactions were described by using Grimme’s DFT-D3 method.⁶ The energy cutoff and convergence criteria for the energy and force were set to 500 eV, 1×10^{-5} eV, and 0.02 eV/Å, respectively.

1.3 Apparent quantum efficiency (AQE) calculation method

The AQE was measured by using a Pyrex top-irradiation-type reaction vessel and a 300 W Xe lamp fitted with different band-pass filters of 420, 450, 475, 500, 550, and 560 nm (FWHM = 15 nm), the average intensity of monochromic light was determined by using CEL-NP 2000 photo-radiometer. For the AQE at 420 ± 15 nm, the average intensity of irradiation was determined to be 9.77 mW and the irradiation area was 1.0 cm². The AQE value was calculated by the following Equation:

$$\begin{aligned} \text{AQE (\%)} &= \frac{\text{number of reacted electrons}}{\text{number of incident electrons}} \times 100\% \\ &= \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident electrons}} \times 100\% \end{aligned}$$

2. Results

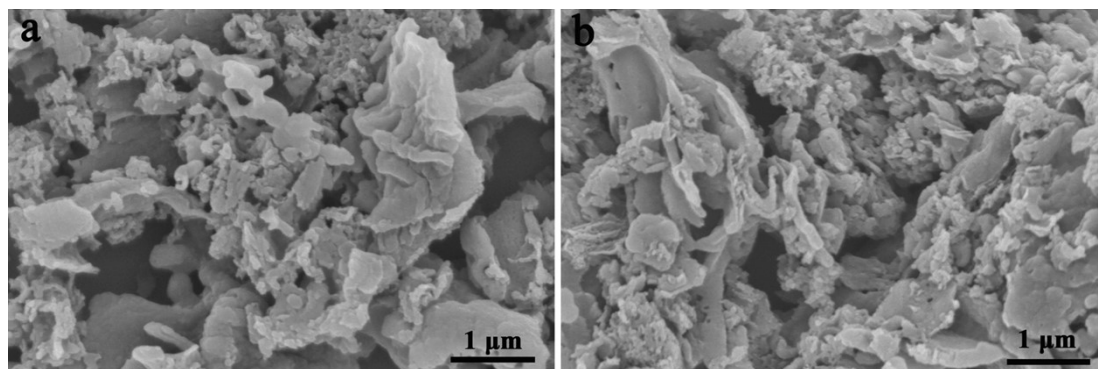


Figure S1. TEM images of (a) CNS and (b) SOCNS samples.

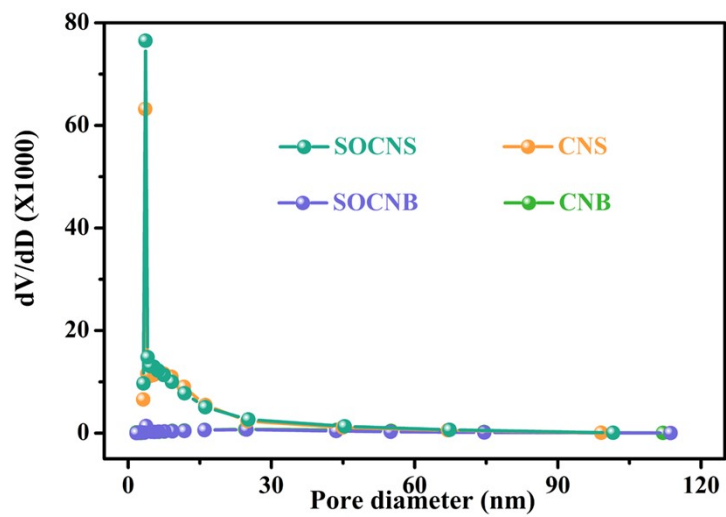


Figure S2. Pore size distribution curves of CNB, CNS, SOCNB and SOCNS.

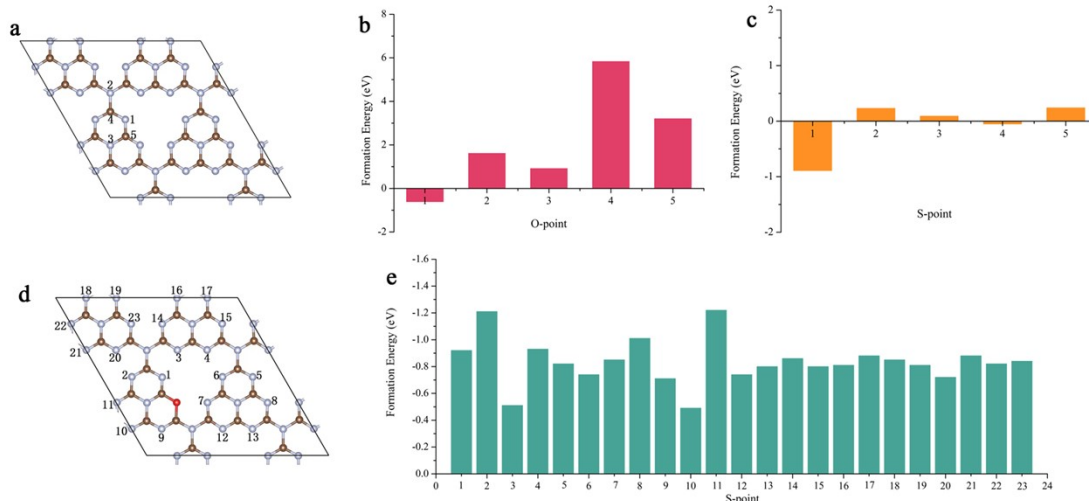


Figure S3. (a) Structure of g-C₃N₄ (brown: C; gray: N), the numbers 1-5 are the selected sites that O/S replaces; formation energies for (b) the 5 O doped g-C₃N₄ and (c) 5 S doped g-C₃N₄ configurations; (d) structure of O and S co-doped g-C₃N₄ (brown: C; gray: N; red: O), the numbers 1-23 are the selected sites that S replaces, (e) formation energies for the 23 S, O co-doped g-C₃N₄ configurations.

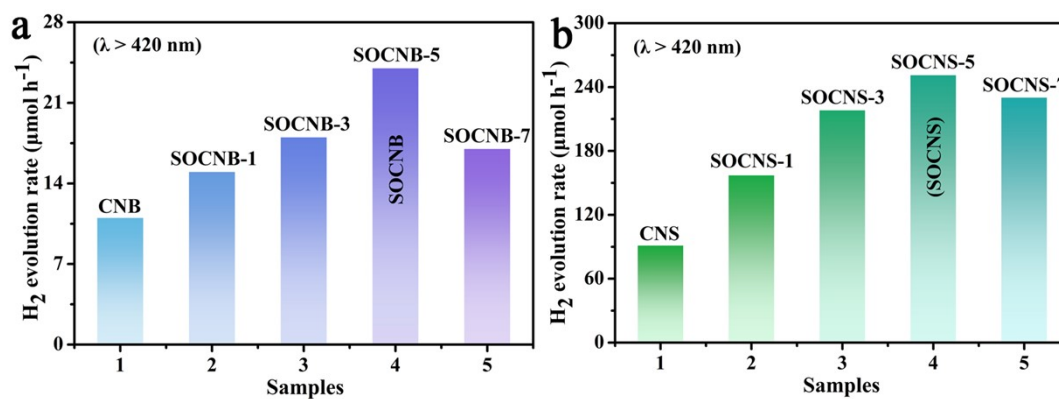


Figure S4. Hydrogen evolution rate of (a) SOCNB-X and (b) SOCNS-X samples.

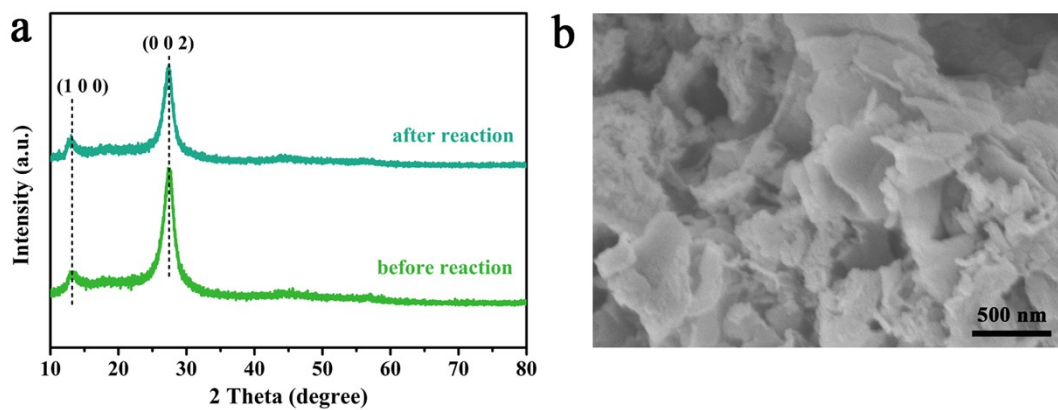


Figure S5. (a) XRD pattern and (b) SEM image of SOCNS after the photocatalytic H₂ evolution reaction.

Table S1. Comparison of the full width at half maximum of as-prepared samples at the main XRD signal.

Sample	FWHM (nm)
CNB	2.25
CNS	2.68
SOCNB	1.73
SOCNS	2.14

Table S2. The wavelength dependent AQE for photocatalytic H₂ evolution reactions over the SOCNS photocatalyst.

Wavelengths (λ , nm)	H ₂ evolved ($\mu\text{mol h}^{-1}$)	Catalyst mass (mg)	Light power (mW)	AQE (%)
420 \pm 15	101	10	9.77	23.75
450 \pm 15	53	10	13.42	17.29
475 \pm 15	30	10	21.89	6.00
500 \pm 15	9	10	27.15	1.45
550 \pm 15	4	10	16.72	1.04
600 \pm 15	2	10	12.11	0.72

Table S3. Comparison of photocatalytic H₂ evolution performance of SOCNS with some previous doped g-C₃N₄-based photocatalysts in recent years.

Photocatalyst	Amount (mg)	Light source (nm)	H ₂ evolution (μmol/h)	AQE (420 nm)	Ref.
S doped g-C ₃ N ₄	10	λ ≥ 400	31.7	3.02%	S7
S doped g-C ₃ N ₄	50	λ ≥ 420	311.27	10%	S8
S doped g-C ₃ N ₄	50	λ ≥ 400	567.7	13.69%	S9
S doped g-C ₃ N ₄	50	λ ≥ 420	26.275	3.02%	S10
O doped g-C ₃ N ₄	20	λ ≥ 420	73.84	4.22%	S11
O doped g-C ₃ N ₄	30	λ ≥ 420	31.51	13.04%	S12
O doped g-C ₃ N ₄	10	λ ≥ 420	136.1	24.7%	S13
B doped g-C ₃ N ₄	5	λ ≥ 420	19	10.6%	S14
S, K co-doped g-C ₃ N ₄	30	λ ≥ 420	263.4	70%	S15
Na, O co-doped g-C ₃ N ₄	50	λ ≥ 400	110	22.3%	S16
C, P co-doped g-C ₃ N ₄	50	λ ≥ 420	74.67	2.14%	S17
C, N co-doped g-C ₃ N ₄	5	λ ≥ 420	91.9	9.83%	S18
B, O co-doped g-C ₃ N ₄	50	λ ≥ 420	487.6	8.1%	S19
Mo, S co-doped g-C ₃ N ₄	25	λ ≥ 420	7.35	0.24%	S20
C, O co-doped g-C ₃ N ₄	20	λ ≥ 420	51.9	16.6%	S21
SOCNS	10	λ ≥ 420	251	23.75%	This work

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