

Supporting information

***Surface Active Site Modulation of the S-scheme Heterojunction toward Exceptional
Photocatalytic Performance***

*Jing Wang,^{‡a} Zhongliao Wang,^{‡a} Jinfeng Zhang,^{‡a} Siang-Piao Chai,^c Kai Dai,^{*a} and
Jingxiang Low^{*b,c}*

^aKey Laboratory of Green and Precise Synthetic Chemistry and Applications, Ministry of Education, Huaibei Normal University, Huaibei, 235000, P. R. China. Email: daikai940@chnu.edu.cn

^bHefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. Email: jxlow@ustc.edu.cn

^cMultidisciplinary Platform of Advanced Engineering, Chemical Engineering Discipline, School of Engineering, Monash University, Bandar Sunway 47500, Selangor, Malaysia

[‡]These authors contributed equally to this work.

1. Materials

Sodium trithiocyanurate ($C_3N_3Na_3S_3$), cadmium nitrate hydrate ($Cd(NO_3)_2 \cdot 5H_2O$), nickel nitrate hydrate ($Ni(NO_3)_2 \cdot 6H_2O$), thiourea (CH_4N_2S), absolute ethanol (C_2H_6O), sodium sulfide (Na_2S), sodium sulfite ($NaSO_3$), chloroplatinic acid (H_2PtCl_6), thiourea (CH_4N_2S). Deionized water (18.25 M Ω) was used throughout the experiment.

2. Experimental details

2.1 Fabrication of CdCNS. 2.313 g $Cd(NO_3)_2 \cdot 5H_2O$ and 1.216 g $C_3N_3Na_3S_3$ were separately dissolved in 100 mL DI water and stirred violently until the color of the mixture turned transparent. Then, $C_3N_3Na_3S_3$ solution was added dropwise to the $Cd(NO_3)_2 \cdot 5H_2O$ solution. Subsequently, the mixture was aged with stirring at room temperature for 24 h. Finally, the CdCNS can be obtained by washing, and drying.

2.2 Synthesis of CdCNS/CdS porous composites. The CdCNS/CdS composite was prepared via calcination. Specifically, 0.5 g CdCNS was added to the crucible and calcined in a muffle furnace at varying temperatures of 300 °C, 400 °C, and 500 °C, and the obtained products were denoted as CdCNS/CdS300, CdCNS/CdS400, and CdCNS/CdS500, respectively.

2.4 Synthesis of X%NiS-CdCNS/CdS porous composites. The NiS was loaded on the CdCNS/CdS via light irradiation in the presence of $Ni(NO_3)_2 \cdot 6H_2O$ as Ni source. For instance, 60 mg obtained CdCNS/CdS400 was mixed with 10 mL $Ni(NO_3)_2 \cdot 6H_2O$ (0.0002 g/mL), 2.5 mL CH_4N_2S (0.0002 g/mL), 12 mL absolute ethanol and 12 mL DI mixture mixed. The mixture was then added in a three-necked flask and bubbled with N_2 for 30 min to remove air. Subsequently, the mixture was irradiated under 300 W Xe

lamp for 15 min. After irradiation, the sample was washed via centrifugation for 6 times with DI water. Finally, the NiS-CdCNS/CdS can be obtained by freeze-drying. By dropping numbers Ni(NO₃)₂·6H₂O solution by 6, 10 and 14, the NiS-CdCNS/CdS with NiS mass ratios of 0.6% (0.6% NiS-CdCNS/CdS400), 1% (1% NiS-CdCNS/CdS400) and 1.4% (1.4% NiS-CdCNS/CdS400) can be respectively prepared. 1% Pt-CdCNS/CdS400 was also prepared by substituting Ni(NO₃)₂·6H₂O and CH₄N₂S with H₂PtCl₆.

3. Characterization

The crystal phase structures of prepared samples were examined via X-ray diffraction diffractometer (XRD RIGAKU) with Cu K α radiation. The surface morphology and the composition of prepared samples were studied by field emission scanning electron microscope (FESEM, Hitachi S5500) with energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM JEOL JEM-2010). The surface structures of the prepared samples were analyzed using Fourier transform infrared spectroscopy (FT-IR Nicolet 6700) and X-ray photoelectron spectroscopy (XPS Thermo ESCALAB 250). The specific surface area of the prepared samples was determined by Brunauer-Emmett-Teller (BET) method, using a surface analytical instrument (ASAP 2010) by N₂ gas adsorption. The diffuse reflectance absorption spectra (DRS) and photoluminescence (PL) of the prepared samples were measured by a UV-vis spectrophotometer (PerkinElmer Lambda 950) with BaSO₄ reference and a FLS920 fluorescence spectrometer at room temperature, respectively. The electrochemical measurements were recorded by a Shanghai Chenhua CHI-660D

workstation in a 3-electrode cell. A Pt electrode and a calomel electrode were used as the counter and reference electrode, respectively.

4. Photocatalytic activity evaluation

The photocatalytic H₂ experiments were performed in a 250 mL Pyrex flask. Typically, 20 mg photocatalyst was dispersed in 50 mL aqueous solution of 0.35 M Na₂S·9H₂O and 0.25 M Na₂SO₃. The photoreactor was irradiated by a 300 W Xenon lamp (CEL-HXF300, Ceaulight, China) equipped with a 420 nm cut-off filter. The irradiation distance between the flask and the lamp was set to 20 cm. The generated H₂ was determined with gas chromatography (Ceaulight GC-7900, TCD). In addition, the apparent quantum efficiency (QE) for H₂ evolution was measured under the same photocatalytic reaction condition. The intensity and number of photons of the light source at 420 nm were measured by a light intensity meter. The QE was finally calculated according to Eq. (S1):

$$\text{QE}(\%) = \frac{\text{number of evolved hydrogen atoms } (N_H)}{\text{number of incident photons } (N_P)} \times 100\% \quad (\text{S1})$$

$$N_P = \frac{A \cdot I}{E} \cdot t = \frac{A \cdot I}{(hc/\lambda)} \cdot t$$

$$N_P = 2 \times n_{H_2} \times L$$

where n_{H_2} is the moles of evolved hydrogen; L is the Avogadro constant, $6.02 \times 10^{23} \text{ mol}^{-1}$; I is the light intensity at 420 nm; A is the illumination area; E is the photon energy; h is the Plank Constant, $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$; c is the speed of light, $3 \times 10^8 \text{ m/s}$.

5. Computational detail

The materials calculations were performed using optimized interface contact structures

of CdCNS/CdS and NiS/CdCNS shown in Fig. 10a and b, respectively. The charge distributions of the CdCNS/CdS and NiS/CdCNS heterostructures were analyzed by differential charge density. The calculation of the differential charge density difference was based on Density function theory (DFT) calculations through the CP2K-9.1 package. Perdew-Burke-Ernzerh (PBE) of functional was applied to describe the system. Unrestricted Kohn-Sham DFT was used as the electronic structure method in the Gaussian and Plane Waves (GPW) approach. The Goedecker-Teter-Hutter (GTH) pseudopotentials and Double- ζ molecularly optimized basis sets (DZVP-MOLOPT-GTH) were used for all elements. A plane-wave energy cutoff of 400 Ry has been employed. The geometries were optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm and the convergence criterion for the forces was set to 4.5×10^{-4} bohr/hartree. A vacuum layer of 15 Å was constructed to eliminate interactions between periodic structures of surface models. The van der Waals (vdW) interaction was complemented by Grimme's DFT-D3 method.

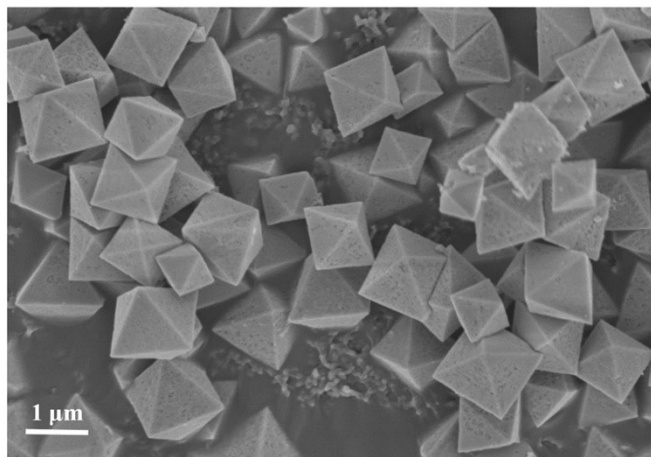


Fig. S1. SEM image of CdCNS/CdS400.

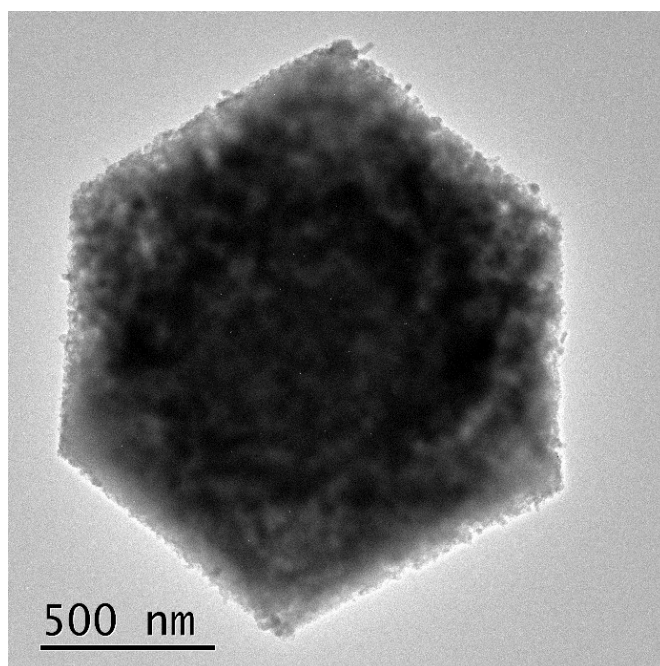


Fig. S2. TEM image of CdCNS/CdS400.

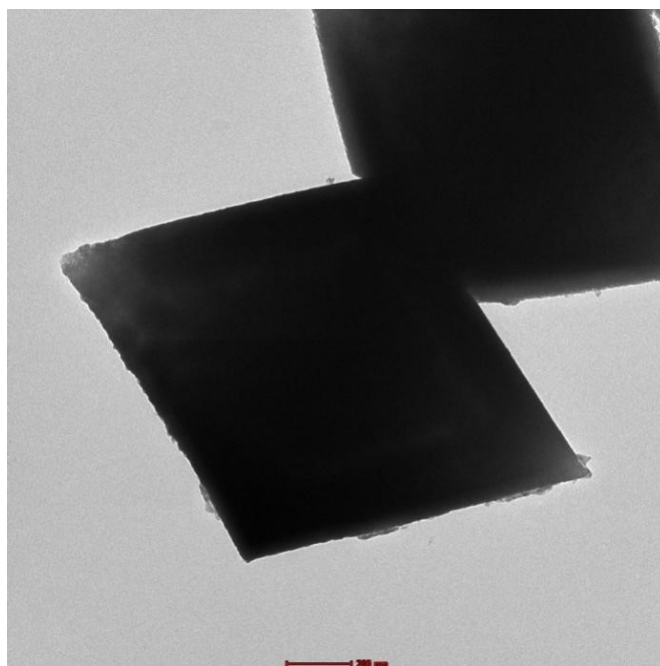


Fig. S3. TEM image of CdCNS.

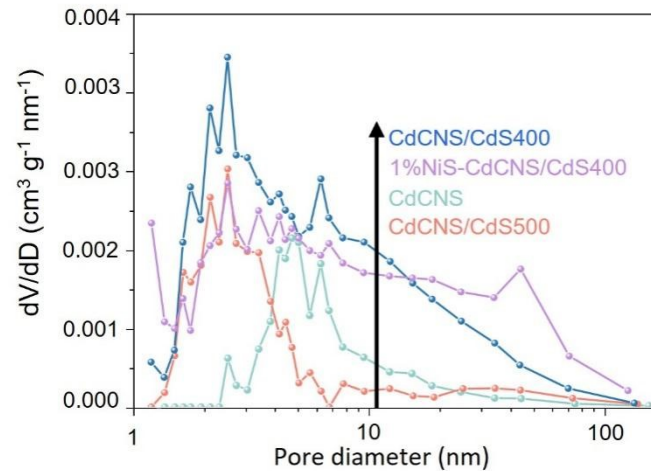


Fig. S4. Pore size distribution curves of as-prepared photocatalysts.

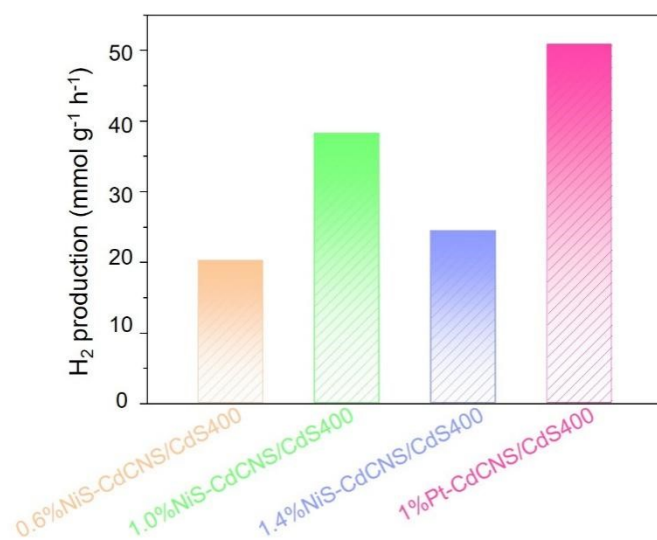


Fig. S5. Comparison of photocatalytic H₂ generation performance of a series of photocatalysts.