

One-pot hydrothermal synthesis of noble-metal-free NiS on $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanosheets photocatalysts for high H_2 evolution from water under visible light.

Linfen Yang ^{a, b}, Yong Peng ^{a, b*} and Yuhua Wang ^{c*}

^a Department of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, China

^b School of Materials and Energy, or Electron Microscopy Centre of Lanzhou University, Lanzhou, 730000, China

^c School of Materials and Energy, Lanzhou University, Lanzhou, 730000, China

*Corresponding author: Prof. Yong Peng, or Prof. Yuhua Wang.

Tel: +86-931-8912772; Fax: +86-931-8913554

E-mail address: pengy@lzu.edu.cn, or wyh@lzu.edu.cn

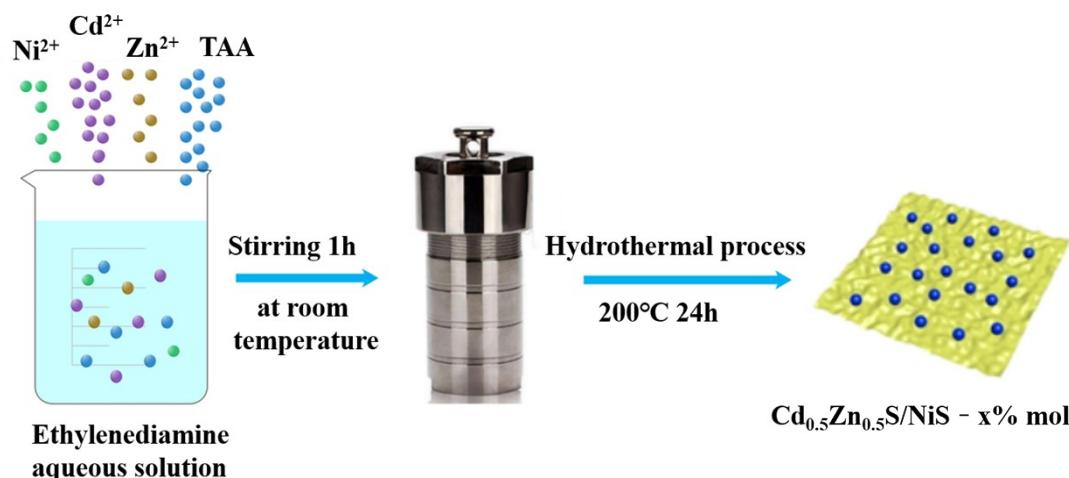


Fig. S1. Schematic illustration of the fabrication process of ZCS/NS.

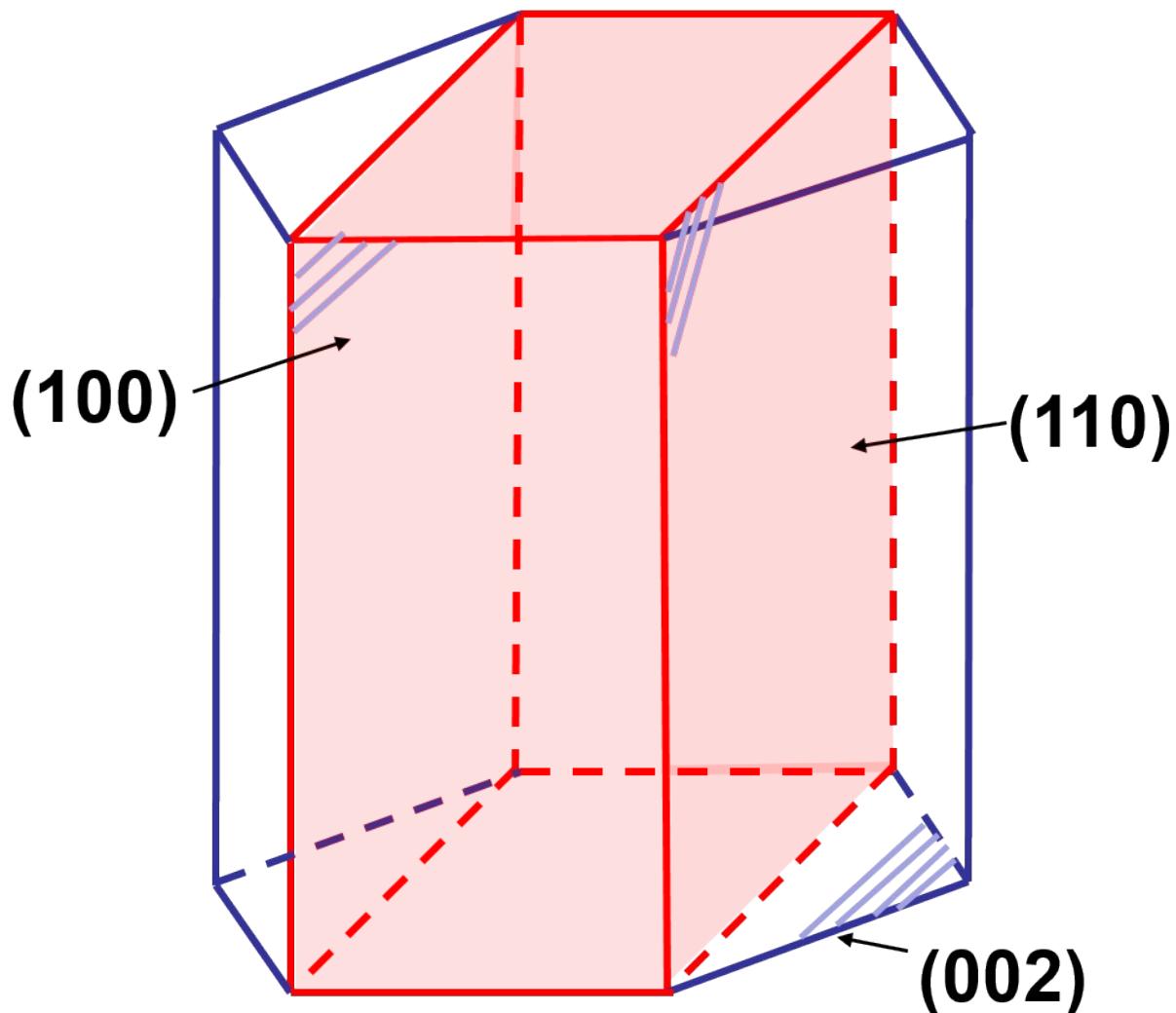


Fig. S2. Schematic diagram of formation of nanosheets in hexagonal crystal system.

Table S1. The relative intensity of different crystal faces in Zn_{0.5}Cd_{0.5}S sample and its PDF card

| Crystal faces | (100) | (002) | (101) |
|---|-------|-------|-------|
| Relative intensity of PDF card | 78.5 | 51.4 | 100 |
| Relative intensity of Zn _{0.5} Cd _{0.5} S | 73 | 144 | 85 |

Table S2. The relative intensity ratios of (101)/(100), (101)/(002) and (101)/(101) in Zn_{0.5}Cd_{0.5}S sample and its PDF card

| Crystal plane | (100) | (002) | (101) |
|---|-------|-------|-------|
| Relative intensity ratios of PDF card | 0.785 | 0.514 | 1 |
| Relative intensity of ratios Zn_{0.5}Cd_{0.5}S | 0.86 | 1.694 | 1 |

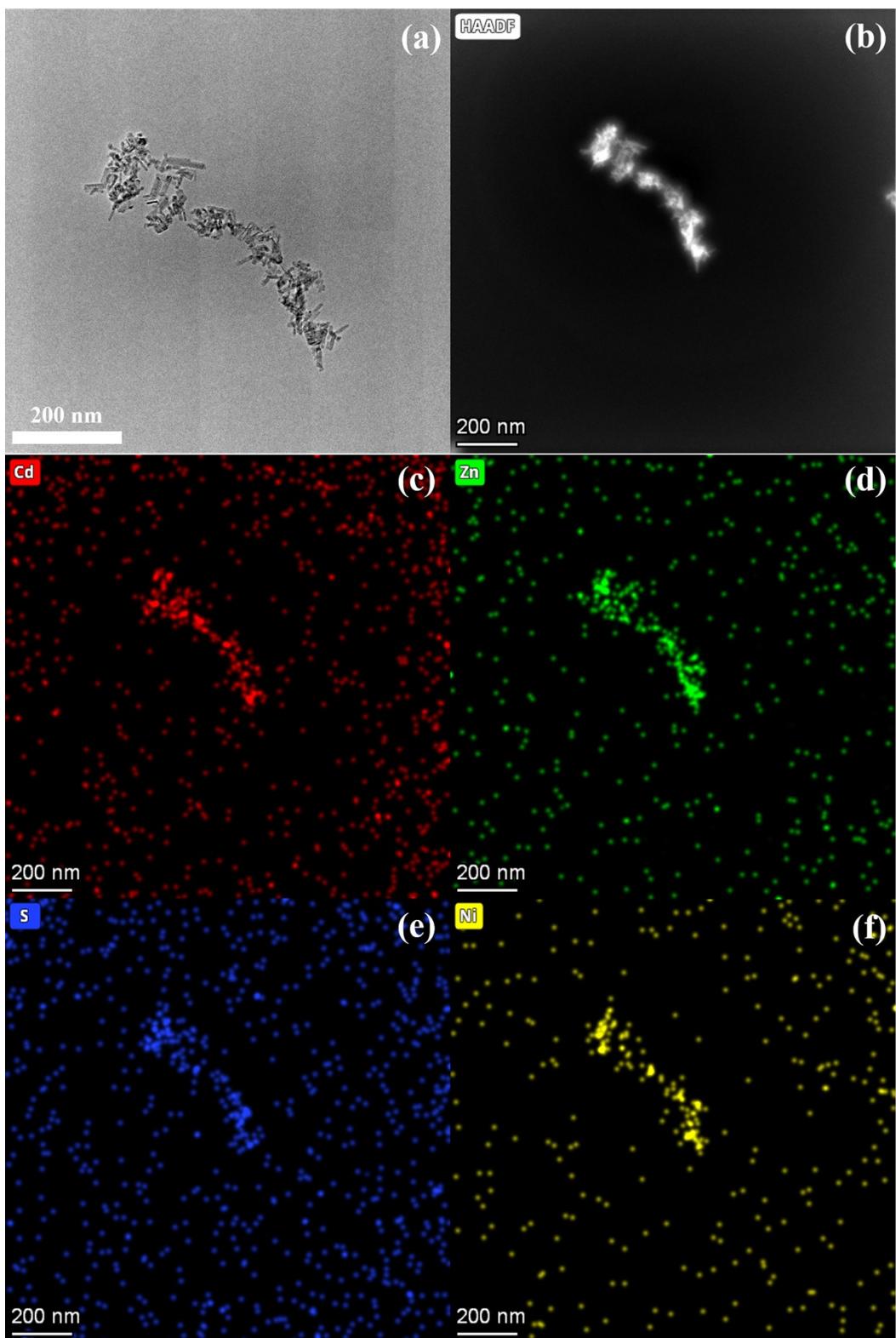


Fig. S3. (a) TEM image of ZCS-NS-5 composites. (b-f) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the elemental mappings of ZCS-NS-5

composites.

Table S3. The measured ICP concentration and the calculated mass and molar ratio of metal ions contained in ZCS/NS-5.

| Metal ion | C1(mg/L) | C2(mg/L) | m(mg) | n(Mmol) | Practical molar ratio | Ni/(Cd+Mn) |
|-----------|----------|----------|-------|---------|-----------------------|------------|
| Zn | 52.75 | 51.76 | 2.77 | 0.042 | 4.86% | |
| Cd | 88.72 | 89.36 | 4.72 | 0.0424 | | |
| Ni | 4.631 | 4.417 | 0.24 | 0.0041 | | |

Table S4 Performance comparison of typical sulfide based photocatalysts.

| Photocatalyst | Light source | Sacrificial reagent | Catalyst dosage (mg) | morphology | H ₂ evolution (mmol g ⁻¹ h ⁻¹) | Ref. |
|--|--|---|----------------------|---------------|--|------|
| MS/Cd _{0.4} Zn _{0.4} S(M = Mo, Cu, Pd) | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | nanoparticles | 1.2 | S1 |
| 1wt%Pt/ Cd _{0.4} Zn _{0.4} S | 300 W Xe lamp ($\lambda \geq 400$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | nanoparticles | 1.21 | S1 |
| Cd _{0.2} Zn _{0.8} S@UiO-66-NH ₂ | 300 W Xe lamp ($\lambda \geq 400$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | nanoparticles | 5.85 | S2 |
| Cu ₂ S/Zn _{0.5} Cd _{0.5} S | 300 W Xe lamp ($\lambda \geq 400$ nm) | Na ₂ S-Na ₂ SO ₃ | 100 | nanoparticles | 4.92 | S3 |
| CuS/Cd _{0.3} Zn _{0.7} S | high-pressure mercury lamp($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | nanoparticles | 3.52 | S4 |
| p-Cu ₂ S/n-Zn _x Cd _{1-x} S | solar simulator | Na ₂ S-Na ₂ SO ₃ | 50 | nanoparticles | 0.87 | S5 |

| Photocatalyst | Light source | Sacrificial reagent | Catalyst dosage (mg) | morphology | H_2 evolution (mmol g ⁻¹ h ⁻¹) | Ref. |
|--|--|---------------------|----------------------|---------------|---|------|
| $Cu_2(OH)_2CO_3/Zn_{0.5}Cd_{0.5}S$ | 300 W Xe lamp ($\lambda \geq 420$ nm) | $Na_2S-Na_2SO_3$ | 50 | nanoparticles | 5.51 | S6 |
| $CuS/Zn_{0.8}Cd_{0.2}S$ | 300 W Xe lamp($\lambda \geq 400$ nm) | $Na_2S-Na_2SO_3$ | 200 | nanoparticles | 2.79 | S7 |
| $MoS_2/Zn_{0.5}Cd_{0.5}S/g-C_3N_4$ | 300 W Xe lamp ($\lambda \geq 400$ nm) | $Na_2S-Na_2SO_3$ | 100 | particles | 4.91 | S8 |
| $CoFe_2O_4/Cd_{0.9}Zn_{0.1}S$ | 300 W Xe lamp ($\lambda \geq 400$ nm) | $Na_2S-Na_2SO_3$ | 100 | nanorods | 3.5 | S9 |
| $Zn_{0.5}Cd_{0.5}S-OLC$ | 300 W Xe lamp ($\lambda \geq 400$ nm) | $Na_2S-Na_2SO_3$ | 30 | nanosheets | 10.8 | S10 |
| $Zn_{0.7}Cd_{0.3}S/NiWO_4$ | 5 W LED ($\lambda \geq 420$ nm) | $Na_2S-Na_2SO_3$ | 10 | nanosheets | 15.95 | S11 |
| AuPd/ $Cd_{0.5}Zn_{0.5}S$ | 300 W Xe lamp ($\lambda \geq 400$ nm) | $Na_2S-Na_2SO_3$ | 50 | spheres | 3.65 | S12 |
| Bi^{3+} -doped $Cd_{0.5}Zn_{0.5}S$ | high-pressure mercury lamp($\lambda \geq 420$ nm) | $Na_2S-Na_2SO_3$ | 100 | particles | 0.56 | S13 |
| $MoS_2/Cd_{0.8}Zn_{0.2}S$ | 300 W Xe lamp ($\lambda \geq 400$ nm) | $Na_2S-Na_2SO_3$ | 35 | urchin-like | 1.3 | S14 |
| $Zn_{0.1}Cd_{0.9}S/NiS$ | 300 W Xe lamp ($\lambda > 300$ nm) | glucose | 10 | nanorods | 12.7 | S15 |
| NiS modified $Mn_xCd_{1-x}S$ | 300 W Xe lamp ($\lambda \geq 420$ nm) | $Na_2S-Na_2SO_3$ | 50 | nanoparticles | 8.39 | S16 |
| 1wt%Pt/ $Ni_{0.01}Mn_{0.56}Cd_{0.43}S$ | 300 W Xe lamp ($\lambda \geq 400$ nm) | $Na_2S-Na_2SO_3$ | 200 | nanoparticles | 0.33 | S17 |
| Cu_2S/CdS | 300 W Xe lamp ($\lambda \geq 420$ nm) | $Na_2S-Na_2SO_3$ | 200 | polyhedrons | 2.0 | S18 |

| Photocatalyst | Light source | Sacrificial reagent | Catalyst dosage (mg) | morphology | H ₂ evolution (mmol g ⁻¹ h ⁻¹) | Ref. |
|--|--|---|----------------------|--------------|--|------|
| CdS/NiTiO ₃ /CoS | 300 W Xe lamp ($\lambda \geq 420$ nm) | lactic acid | 50 | nanoflakes | 6.24 | S19 |
| NiS/TiO ₂ | 300 W Xe lamp ($\lambda > 300$ nm) | methanol | 50 | nanosheets | 0.31 | S20 |
| Co(OH) ₂ /CdS | 500 W Xe lamp | ethanol | 100 | nanorods | 0.061 | S21 |
| NiS/CDs/CdS | 350 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 100 | spheres | 1.44 | S22 |
| Cd _{0.5} Zn _{0.5} S/BiVO ₄ | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | certain amounts | spheres | 2.35 | S23 |
| Cd _{0.5} Zn _{0.5} S | 300 W Xe lamp ($\lambda \geq 420$ nm) | AgNO ₃ , benzoquinone and EDTA-2Na | 50 | dendritic | 0.15 | S24 |
| Mo doped Cd _{0.5} Zn _{0.5} S | 300 W Xe lamp ($\lambda \geq 420$ nm) | lactic acid | 20 | nanorods | 11.32 | S25 |
| NiS _x / Cd _{0.5} Zn _{0.5} S | 300 W Xe lamp ($\lambda \geq 430$ nm) | Na ₂ S-Na ₂ SO ₃ | 100 | nanorods | 4.46 | S26 |
| SiO ₂ /Ni ₂ P/rGO/Cd _{0.5} Zn _{0.5} S | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 30 | yolk-shell | 11.65 | S27 |
| PtPd decorated Zn _{0.5} Cd _{0.5} S | 300 W Xe lamp ($\lambda \geq 400$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | nanorods | 9.689 | S28 |
| Cd _{0.5} Zn _{0.5} S@Bi ₂ Fe ₄ O ₉ | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 20 | quantum dots | 0.8 | S 29 |
| Co _{0.85} Se/Cd _{0.5} Zn _{0.5} S | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 100 | nanorods | 0.76 | S30 |

| Photocatalyst | Light source | Sacrificial reagent | Catalyst dosage (mg) | morphology | H ₂ evolution (mmol g ⁻¹ h ⁻¹) | Ref. |
|---|--|---|----------------------|------------------|--|------------------|
| Cd _{0.5} Zn _{0.5} S@C ₃ N ₄ | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 20 | quantum dots | 33.4 | S31 |
| p-CuS/n-CdS | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 20 | nano particles | 7 | S32 |
| CoO _x -loaded TiO ₂ /CdS | 300 W Xe lamp ($\lambda \geq 400$ nm) | Na ₂ S-Na ₂ SO ₃ | 10 | nano particles | 0.66 | S33 |
| CuS/ZnS | 300 W Xe lamp ($\lambda \geq 400$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | hexagonal plates | 1.23 | S34 |
| Ni-doped ZnS | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-K ₂ SO ₃ | 1000 | particles | 0.28 | S35 |
| Cu-doped ZnIn ₂ S ₄ | 300 W Xe lamp ($\lambda \geq 430$ nm) | Na ₂ S-Na ₂ SO ₃ | 200 | microspheres | 0.76 | S36 |
| MoS ₂ -graphene/ZnIn ₂ S ₄ | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | microspheres | 4.17 | S37 |
| CdIn ₂ S ₄ | 450 W Xe lamp ($\lambda \geq 420$ nm) | methanol | 50 | nanotubes | 6.96 | S38 |
| Zn _{0.5} Cd _{0.5} S/NiS | 300 W Xe lamp ($\lambda \geq 420$ nm) | Na ₂ S-Na ₂ SO ₃ | 50 | nanosheets | 9.98 | This work |

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