

## Supporting information

### **Construction of $\text{CoS}_x\text{-ZnIn}_2\text{S}_4$ hollow nanocages derived from metal organic frameworks for efficient photocatalytic hydrogen production**

Hongyu Ma, Yaqi Tan, Zhifei Liu, Jianhong Wei\*, Rui Xiong\*

Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education and School of Physics and Technology, Wuhan University, Luojiashan Road, Wuhan, 430072, P. R. China

\* Corresponding author: [jhwei@whu.edu.cn](mailto:jhwei@whu.edu.cn); [xiongrui@whu.edu.cn](mailto:xiongrui@whu.edu.cn).

## **Experimental Section**

### **Materials:**

Cobaltous nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), 2-methylimidazole ( $\text{C}_4\text{H}_6\text{N}_2$ ), methanol ( $\text{CH}_3\text{OH}$ ), indium chloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ), zinc chloride ( $\text{ZnCl}_2$ ), thioacetamide (TAA), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and glycerol (GL) were provided by Sinopharm Chemical Reagent Company, Ltd. All chemicals were obtained from commercial suppliers without further purification.

### **Synthesis of ZIF-67 polyhedrons**

The typical synthetic route of ZIF-67 polyhedrons is as follows: 2 mmol of cobalt nitrate hexahydrate and 8 mmol of 2-methylimidazole were dissolved in 50 ml methanol to form a transparent solution, and then the cobalt nitrate solution was quickly poured into 2-methylimidazole solution. After thorough mixing, the mixed solution was incubated for 24h at room temperature. The obtained precipitate was centrifuged and cleaned several times with methanol, and finally dried in  $80^\circ\text{C}$  oven for 12 h to obtain purple ZIF-67 polyhedrons.

### **Synthesis of $\text{CoS}_x$ hollow nanocages**

0.1 g of ZIF-67 polyhedron was dissolved in 25 ml of absolute ethanol and ultrasonically dispersed. Then 5 ml of absolute ethanol containing 50 mg of thioacetamide was added dropwise to the above solution and stirred for 5 minutes. Next, the mixed solution was transferred to a Teflon-lined autoclave and reacted at  $180^\circ\text{C}$  for 3 hours. After cooling to

room temperature, the precipitates were centrifuged and cleaned several times with absolute ethanol, and finally dried in an oven at 60 °C for 12 hours to obtain CoS<sub>x</sub> hollow nanocages.

### **Synthesis of CoS<sub>x</sub>-ZnIn<sub>2</sub>S<sub>4</sub> hollow nanocages**

The CoS<sub>x</sub>-ZnIn<sub>2</sub>S<sub>4</sub> hollow nanocages were synthesized by a low-temperature solvothermal reaction. Typically, a certain amount of the CoS<sub>x</sub> hollow nanocages were dissolved in 24 ml of water (pH = 2.5) and 6 ml of glycerol with stirred thoroughly, followingly, 81.6 mg of ZnCl<sub>2</sub>, 175.8 mg of InCl<sub>3</sub> • 4H<sub>2</sub>O, and 90 mg of TAA were added slowly into the above suspension one by one under strong stirring. After that, the resulting mixture was transferred into an oil bath and heated at 80 °C for 2 h. After cooling, the finally product was washed with ethanol several times, and then dried at 60 °C in a vacuum drying oven for 12 h. The as-synthesized samples with 10 wt%, 20 wt%, 30 wt% and 40wt% CoS<sub>x</sub> hollow nanocages were labeled as CZIS-1, CZIS-2, CZIS-3, and CZIS-4 respectively. For comparison, the pure ZnIn<sub>2</sub>S<sub>4</sub> was synthesized by the same solvothermal process without addition of CoS<sub>x</sub> hollow nanocages.

### **Characterization**

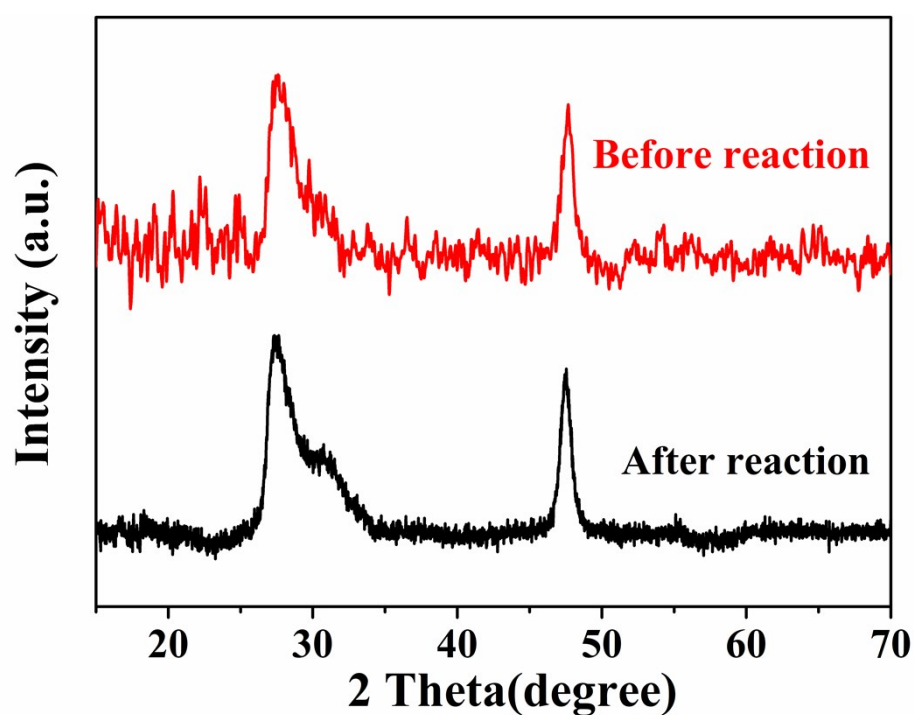
The phase composition of the as-prepared samples were characterized by X-ray diffraction (XRD) using a Burker D8 Advance X-ray diffractometer with a Cu K $\alpha$  radiation. The morphologies of the as-prepared samples were examined by scanning electron microscopy (SEM, Shimadzu SSX-550) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan). High-resolution transmission electron microscopy

(HRTEM) was carried out at room temperature on a Tecnai G2 F20 field emission transmission electron microscopy (America) at the accelerating voltage of 200 kV. The Energy dispersive X-ray (EDS) spectroscopy and Element mapping of samples were also investigated during the FE-SEM measurement. The surface compositions and the valence band spectra of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, with a monochromatic Al K $\alpha$  X-ray source). All binding energies were referenced to the C 1s peak (284.8 eV) arising from adventitious carbon. The UV-vis diffuse reflectance spectra (DRS) were analyzed by a U-4100 solid spectrophotometer with the wavelength range of 300-800 nm. Photoluminescence (PL) spectra of all the samples were recorded at room temperature using a Hitachi F-4600 fluorescence spectrometer (PerkinElmer). The specific surface areas of the catalysts were determined by applying the Brunauer Emmett Teller (BET) method to the adsorption of nitrogen at 77 K. All the samples were degassed at 180°C prior to nitrogen adsorption measurements. The photocurrents, electrochemical impedance spectroscopy (EIS) and Mott-Schottky were measured by an electrochemical analyzer (CHI660A, CH Instruments Co.) at room temperature. The electron spin resonance spectra the samples were conducted on a Paramagnetic Resonance Spectrometer (Bruker A300, Germany) at 77K.

### **Photocatalytic Testing.**

H<sub>2</sub> production experiments were performed at ambient temperature in a Labsolar-III(AG) photocatalytic reactor which was connected to a closed gas circulation system. The photocatalyst (20 mg) was suspended in an aqueous solution (100 ml) containing 10 vol%

triethanolamine (TEOA). The reactant solution was maintained at room temperature by a flow of cooling water during the reaction. After that, the above solution was illuminated by a 300W xenon arc lamp through a UV cutoff filter ( $\lambda > 420\text{nm}$ ) at room temperature. The evolved gases were sampled and analyzed by gas chromatography once an hour. The apparent quantum yield (AQY) for the  $\text{H}_2$  evolution was measured using a similar experimental process only with a band pass filter.



**Figure S1** The XRD of CZIS-3 before and after reaction.

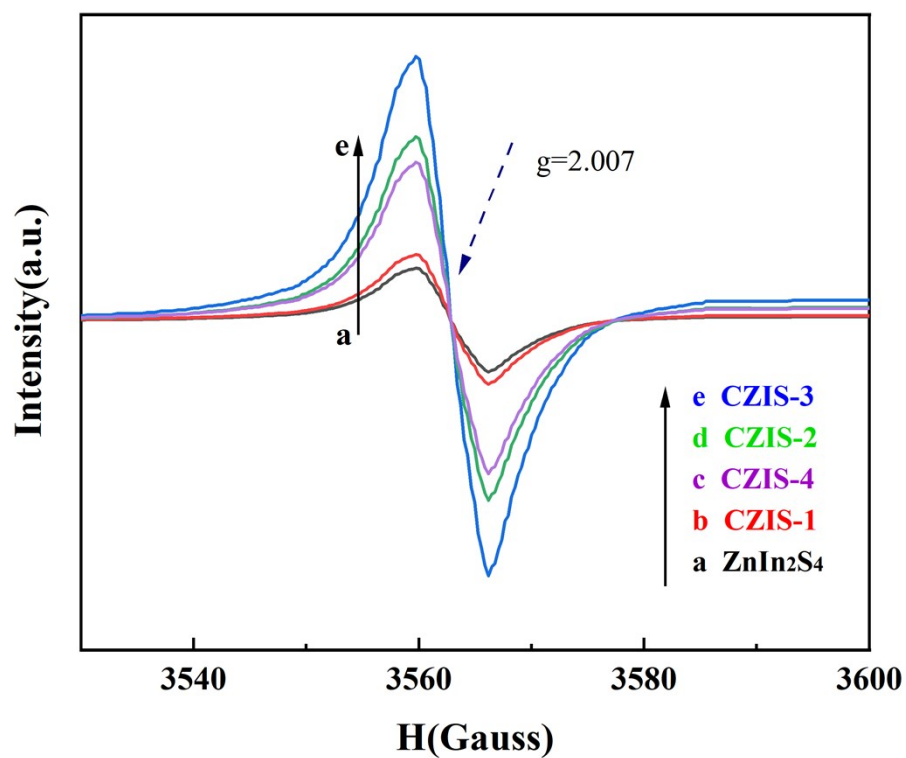


Figure S2 ESR spectra of different samples

Table S1 Comparison of photocatalytic H<sub>2</sub> generation performance

Catalyst	Hole scavenger Cocatalyst	H <sub>2</sub> evolution rate ( $\mu\text{mol h}^{-1} \text{g}^{-1}$ )	Ref.
CoS <sub>x</sub> -ZnIn <sub>2</sub> S <sub>4</sub>	TEOA	1538.4	This work
	/		
SiO <sub>2</sub> @ZnIn <sub>2</sub> S <sub>4</sub>	Methanol	730	1

---

	/		
ZnIn <sub>2</sub> S <sub>4</sub> @CuInS <sub>2</sub>	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	292	2
	/		
ZnIn <sub>2</sub> S <sub>4</sub> @SiO <sub>2</sub> @TiO <sub>2</sub>	TEOA	618.3	3
	/		
WS <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	199.1	4
	/		
AgIn <sub>5</sub> S <sub>8</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	949.9	5
	/		
g-C <sub>3</sub> N <sub>4</sub> /Ag:ZnIn <sub>2</sub> S <sub>4</sub>	TEOA	597.47	6
	/		
RGO/ZnIn <sub>2</sub> S <sub>4</sub>	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	1210	7
	/		
NiSe <sub>2</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	TEOA	1487	8
	/		

---

## References

1. A. R. Gunjal, Y. A. Sethi, U. V. Kawade, R. P. Panmand, C. K. Ugale, J. D. Ambekar, A. V. Nagawade, B. B. Kale, RSC Adv., 2021, **11**, 14399.
2. X. Guo, Y. Peng, G. Liu, G. Xie, Y. Guo, Y. Zhnag, J. Yu, J. Phys. Chem. C 2020, **124**, 5934–5943.
3. L. Wang, H. Zhou, H. Zhang, Y. Song, H. Zhang, X. Qian, Inorg. Chem. 2020, **59**, 2278–2287.

4. J. Zhou, D. Chen, L. Bai, L. Qin, X. Sun, Y. Huang, *Int. J. Hydrogen Energy*, 2019, **250**, 163-170.
5. Z. Guan, Z. Xu, Q. Li, P. Wang, G. Li, J. Yang, *Appl. Catal., B: Environ.*, 2018, **227**, 512-518.
6. Y. Gao, K. Qian, B. Xu, F. Ding, V. Dragutan, I. Dragutan, Y. Sun, Z. Xu, *RSC Adv.*, 2020, **10**, 32652.
7. F. Tian, R. Zhu, J. Zhong, P. Wang, F. Ouyang, G. Cao, *Int. J. Hydrogen Energy*, 2016, **41**, 20156-20171.
8. L. Lai, F. Xing, C. Cheng, C. Huang, *Adv. Mater. Interfaces*, 2021, **8**, 2100052.