$ZnIn_2S_4$ with oxygen atom doping and surface sulfur vacancies for overall water splitting under visible light irradiation

Haitong Jing [a,c,d,#], Jun Ren [a,#], Jianyong Yue [a,c,d], Shiyan Liu [a], Qifeng Liang [a], Rong Wu [c,d], Yawei Wang [e], Zebo Fang [a,*], Huili Li [b,*], Shunhang Wei [a,*]

[a] Zhejiang Engineering Research Center of MEMS, Shaoxing University, Shaoxing 312000, China

[b] College of Chemistry and Materials Science, Shanghai Normal University, Shanghai 200234, China.

[c] School of Physics Science and Technology, Xinjiang University, Urumqi 830017, China

[d] Xinjiang Key Laboratory of Solid State Physics and Devices, Xinjiang University, Urumqi 830017, China

[e] School of Chemistry and Chemical Engineering, Jiujiang University, Jiujiang 332005, China.

[#] Equal contributions

*Corresponding author. E-mail addresses: csfzb@usx.edu.cn (Z. Fang); li_huili@shnu.edu.cn (H. Li); wshusx@163.com (S. Wei).

Chemicals

Zinc acetate dihydrate (Aladdin; AR), Indium(III) chloride tetrahydrate (Macklin; AR), Thioacetamide (Macklin; AR), Citric acid (Aladdin; AR), Chromium(III) nitrate nonahydrate (Aladdin; AR), Ethanol absolute (SCR; AR), Chloroplatinic acid hexahydrate (Aladdin; AR).

Characterization

An X-ray powder diffractometer (XRD, Empyrean) was used to measure the crystalline phases of the prepared samples. A SIGMA 300 field emission scanning electron microscope (FESEM) and a JEM-2100F high-resolution transmission electron microscope (HRTEM) were used to record their morphology and elemental distributions. Their elemental chemical states were examined using an X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+), and the binding energies calibrated to the C1s peak at 284.8 eV. A Shimadzu UV-3600 plus uv-vis spectrophotometer was used to obtain their diffuse reflection spectra (DRS). A Hitachi F-7000 fluorescence spectrophotometer was used to measure their photoluminescence (PL) spectra at room temperature (the excitation wave length was 360 nm). The time-resolved PL (TRPL) decay spectra were recorded using a FLUOROLOG-3-11 spectrofluorometer (the excitation wavelength was 370 nm; detection wavelength was 518 nm; bandwidth was 1.5 nm)). Electron paramagnetic resonance (EPR) spectra were recorded using a Bruker EMXPLUS at room temperature. The molecular structural information in the range of 400 - 4000 cm^{-1} was measured using a NEXUS870 fourier transform infrared spectrophotometer (FTIR). The Brunauer-Emmett-Teller (BET) surface area was measured using a Micromeritics ASAP2460 analyzer.

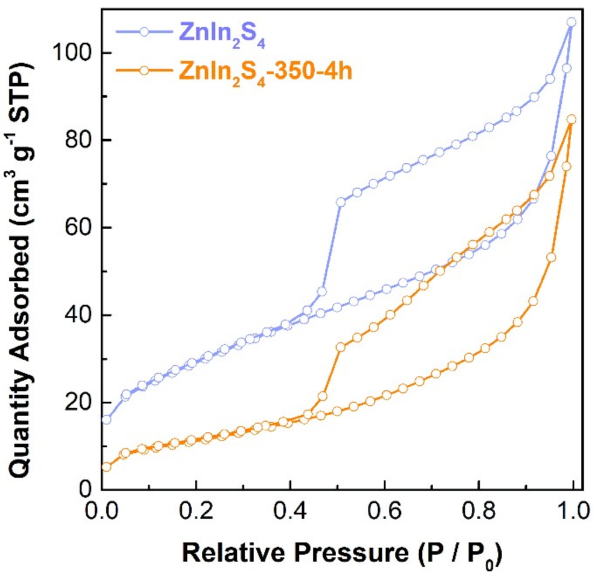

Fig. S1 Nitrogen adsorption-desorption isotherms of the initial $ZnIn_2S_4$ and $ZnIn_2S_4$-350-4h samples.

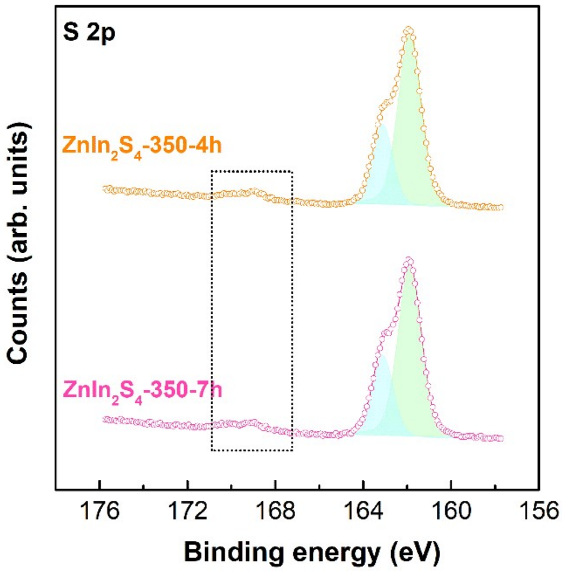

Fig. S2 S 2p spectra of the $ZnIn_2S_4$-350-4h and $ZnIn_2S_4$-350-7h samples.

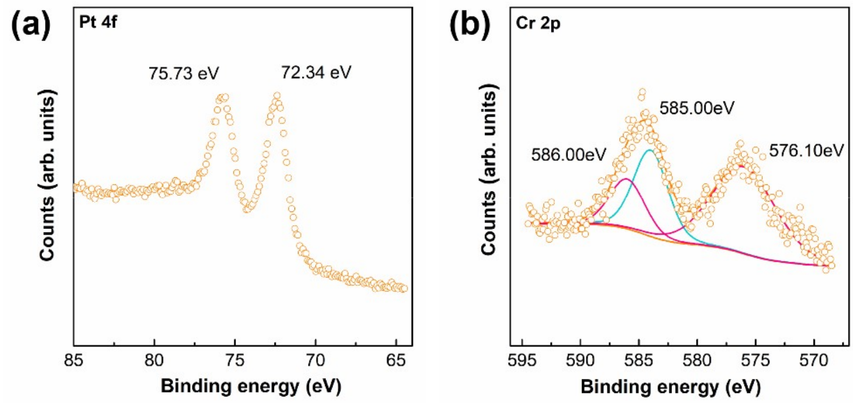

Fig. S3 XPS spectra of Pt 4f peaks (a) and Cr 2p peaks (b).

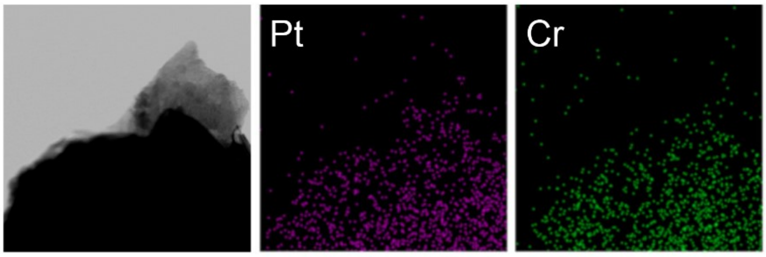

Fig.S4 TEM elemental mappings of Pt/Cr cocatalysts loaded on the $ZnIn_2S_4$-350-4h sample.

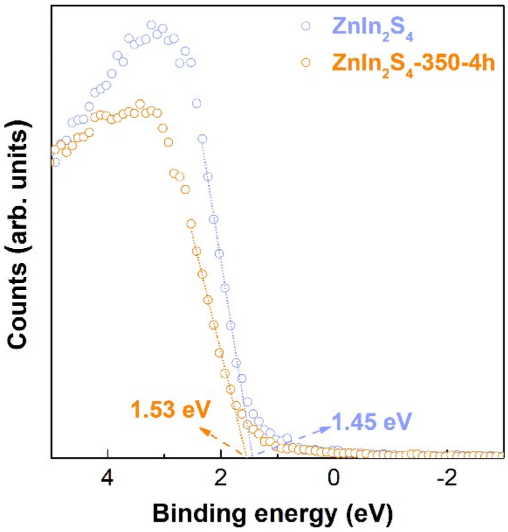

Fig. S5 XPS valence band spectra of samples

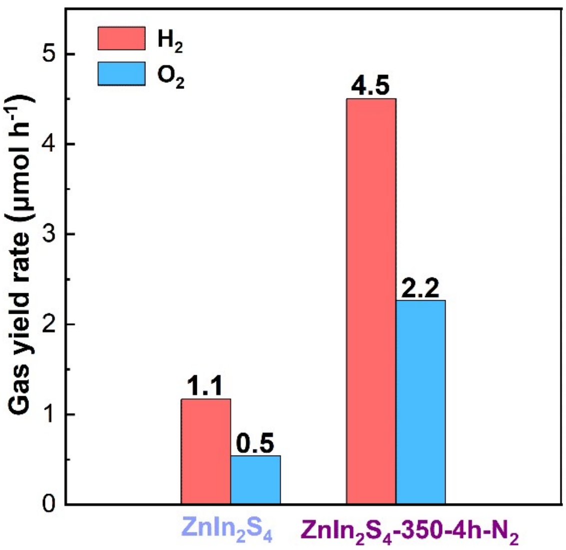

Fig. S6 Photocatalytic overall water splitting rates of the as-prepared samples.

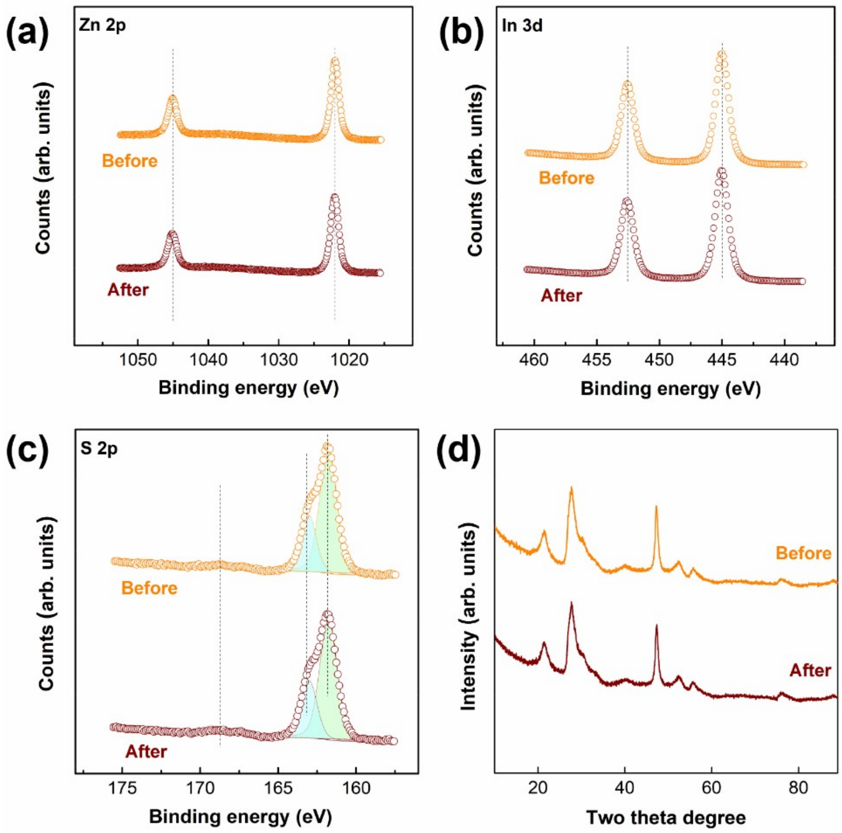

Fig. S7 XPS spectra ((a) Zn 2p peaks, (b) In 3d peaks, (c) S 2p peaks) and XRD patterns (d) of the samples before and after photocatalytic overall water splitting.

Table S1 STH efficiency of single-phase $ZnIn_2S_4$ reported in literatures.

Photocatalysts	Activity measurement				Ref.
	Illumination	H_2 (μmol/g/h)	O_2 (μmol/g/h)	STH efficiency	
d_{Zni}-$ZnIn_2S_4$	300W Xe lamp (≥ 420 nm)	74.3	35.4	/	[1]
Al-$ZnIn_2S_4$	300W Xe lamp (≥ 420 nm)	77.2	35.3	/	[2]
Ag-$ZnIn_2S_4$	300W Xe lamp (> 420 nm)	56.6	29.1	0.003%	[3]
$ZnIn_2S_4$-800	300W Xe lamp (≥ 420 nm)	68.0	31.0	0.021%	[4]
$ZnIn_2S_4$-350-4h	300W Xe lamp (≥ 420 nm)	270.2	130.0	**0.035%**	**This work**

References:

1 B. Sun, J. Bu, X. Chen, D. Fan, S. Li, Z. Li, W. Zhou and Y. Du, *Chem. Eng. J.*, 2022, **435**, 135074.

2 B. Sun, D. Fan, X. Chen, Z. Li, W. Zhou and Y. Du, *Mater. Chem. Front.*, 2022, **6**, 1795-1802.

3 R. Pan, M. Hu, J. Liu, D. Li, X. Wan, H. Wang, Y. Li, X. Zhang, X. Wang and J. Jiang, *Nano Lett.*, 2021, **21**, 6228-6236.

4 H. Jing, G. Xu, B. Yao, J. Ren, Y. Wang, Z. Fang, Q. Liang, R. Wu and S. Wei, *ACS Appl. Energy Mater.*, 2022, **5**, 10187-10195.