

## Electronic Supplementary Information

### C–H activation of methanol and ethanol and C–C coupling into diols by zinc-indium-sulfide under visible-light

Haikun Zhang,<sup>‡</sup> Shunji Xie,<sup>‡,\*</sup> Jinyuan Hu, Xuejiao Wu, Qinghong Zhang, Jun Cheng and Ye Wang\*

*State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.*

\*Corresponding authors: shunji\_xie@xmu.edu.cn, wangye@xmu.edu.cn

#### Experimental details

**Synthesis of  $Zn_mIn_2S_{m+3}$ .** The series of  $Zn_mIn_2S_{m+3}$  ( $m = 1-3$ ) were synthesized by a low-temperature hydrothermal method.<sup>1</sup> In brief, 2.0 mmol of  $InCl_3 \cdot 4H_2O$ ,  $m$  mmol of  $Zn(CH_3COO)_2 \cdot 2H_2O$ , and  $(m+3)$  mmol of thioacetamide were dissolved in 160 mL of deionized (DI) water, the mixture was heated to 90 °C and maintained at the same temperature for 5 h under vigorous stirring. After that, the solution was cooled to room temperature naturally. The suspension was sonicated continuously for 1 h. Then the precipitation was collected by centrifugation, rinsed with DI water and absolute ethanol, and dried under vacuum at 60 °C overnight.

**Preparation of  $In_2S_3$  and  $ZnS$ .**  $In_2S_3$  were synthesized by a low-temperature hydrothermal method. In brief, 2.0 mmol of  $InCl_3 \cdot 4H_2O$ , 3.0 mmol of thioacetamide were dissolved in 160 mL of DI water, the mixture was heated to 90 °C and maintained at the same temperature for 5 h under vigorous stirring. After that, the solution was cooled to room temperature naturally. The suspension was sonicated continuously for 1 h. Then the precipitation was collected by centrifugation, rinsed with DI water and

absolute ethanol and dried in vacuum at 60 °C overnight. ZnS was synthesized by similar method while  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was used as the precursor instead of  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ .

**Synthesis of CoP co-catalyst.**<sup>2</sup> The Cobalt(III) acetylacetonate ( $\text{Co}(\text{acac})_3$ , 400 mg) was dispersed into a mixed solution of 40 mL of ethylene glycol and 8 mL of DI water under vigorous stirring for 12 h in a 100 mL Teflon-lined stainless-steel autoclave. Then the mixture was treated at 190 °C for 48 h and cooled down naturally. The blue product was the CoO nanosheets. CoO was washed with ethanol and water several times and then dried under vacuum overnight. The as-prepared CoO nanosheets was heated to 400 °C at a rate of 5 °C  $\text{min}^{-1}$ , and kept at 400 °C for 3 h. Then cooled to room temperature and the obtained powders were the ultrathin porous  $\text{Co}_3\text{O}_4$  nanosheets. The ultrathin porous  $\text{Co}_3\text{O}_4$  nanosheets was washed with ethanol and water several times and then dried under vacuum overnight.  $\text{Co}_3\text{O}_4$  and  $\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$  (2 g) were put in two separate quartz boats with  $\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$  at the upstream side of the furnace. Subsequently, the samples were heated to 300 °C for 2 h in a static Ar atmosphere at a rate of 2 °C  $\text{min}^{-1}$ . After cooling to room temperature, the sample was washed with water and ethanol several times and naturally dried at 40 °C overnight.

**Synthesis of CoP/ $\text{Zn}_2\text{In}_2\text{S}_5$  catalysts.** The series of CoP/ $\text{Zn}_2\text{In}_2\text{S}_5$  nanocomposites were prepared by an ultrasonic method. CoP nanosheets was first ultrasonically dispersed in N,N-dimethylformamide (DMF, 10 mL) in a flask for 3 h at room temperature. Then,  $\text{Zn}_2\text{In}_2\text{S}_5$  (100 mg) was added to the suspension. The mixture was further subjected to ultrasonic treatment for another 2 h to achieve close contact between CoP and  $\text{Zn}_2\text{In}_2\text{S}_5$ . The CoP/ $\text{Zn}_2\text{In}_2\text{S}_5$  nanocomposite was collected by centrifugation and washed with deionized water and ethanol, followed by drying at 60 °C. The loading amount of CoP was controlled in the range from 0.125 wt% to 0.5 wt%.

**Preparation of  $\text{Ni}_2\text{P}/\text{Zn}_2\text{In}_2\text{S}_5$ .**<sup>3</sup> 200 mg of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 1 g of  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  were dissolved in 200  $\mu\text{L}$  and 1.0 mL of water, separately. Then these two solutions were mixed and stirred for 1 h. Water was removed by vacuum at 60 °C and the dry solid was heated in argon atmosphere for 1 h at 200 °C with a ramp of 5 °C  $\text{min}^{-1}$  and cooled naturally to room temperature. The resulting solid  $\text{Ni}_2\text{P}$  was washed several times with water/ethanol. 0.25 wt% $\text{Ni}_2\text{P}/\text{Zn}_2\text{In}_2\text{S}_5$  nanocomposites were prepared by an ultrasonic method the same to 0.25 wt%CoP/ $\text{Zn}_2\text{In}_2\text{S}_5$ .

**Preparation of Pt/ $\text{Zn}_2\text{In}_2\text{S}_5$ , and Pd/ $\text{Zn}_2\text{In}_2\text{S}_5$ .**<sup>4</sup> Pt were loaded onto  $\text{Zn}_2\text{In}_2\text{S}_5$  by a photoreduction technique. In brief, Pt was deposited by photoreduction of  $\text{H}_2\text{PtCl}_6$  in an aqueous solution containing methanol as a sacrificial agent under irradiation with a 300 W Xe lamp for 1 h.  $\text{PdCl}_2$  was used as the precursors instead of  $\text{H}_2\text{PtCl}_6$  for the preparation of Pd/ $\text{Zn}_2\text{In}_2\text{S}_5$ . The loading amount of Pt and Pd were controlled at 0.25 wt%.

**Preparation of  $\text{MoS}_2/\text{Zn}_2\text{In}_2\text{S}_5$ .**<sup>5</sup> For the synthesis of  $\text{MoS}_2$  nanofoam, 0.4 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and 1.6 g of  $\text{SiO}_2$  nanospheres (30 wt%  $\text{SiO}_2$  in EG, Alfa Aesar) were first dispersed in 20 mL of DI

water. After removing the solvent, the obtained powder reacted with 0.8 g of  $\text{CH}_4\text{N}_2\text{S}$  at  $400\text{ }^\circ\text{C}$  for 4 h. The obtained product was treated in hydrofluoric acid aqueous solution under room temperature, followed by washing with DI water and drying.  $\text{MoS}_2/\text{Zn}_2\text{In}_2\text{S}_5$  nanocomposites were prepared by an ultrasonic method.  $\text{MoS}_2$  nanofoam (5.0 mg) was first ultrasonically dispersed in  $\text{N,N}$ -dimethylformamide (DMF, 10 mL) in a flask for 3 h at room temperature. Then,  $\text{Zn}_2\text{In}_2\text{S}_5$  (100 mg) was added to the suspension. The mixture was further subjected to ultrasonic treatment for another 2 h to achieve close contact between  $\text{MoS}_2$  and  $\text{Zn}_2\text{In}_2\text{S}_5$ . The  $\text{MoS}_2/\text{Zn}_2\text{In}_2\text{S}_5$  nanocomposite was collected by centrifugation and washed with DI water and ethanol, followed by drying at  $60\text{ }^\circ\text{C}$ . The loading amount of  $\text{MoS}_2$  was controlled at 0.25 wt%.

**Evaluation of catalytic performances for methanol coupling to EG.** Photocatalytic reactions were carried out in a sealed quartz tube reactor (volume, 20 mL; inner diameter, 16 mm). Typically, the height of the reaction solution was 19 mm. The light source was a 300 W Xe lamp. Typically, 10 mg of solid catalyst was ultrasonically dispersed in  $4.0\text{ cm}^3$  methanol and  $1.0\text{ cm}^3$   $\text{H}_2\text{O}$ . Then, the reactor was evacuated and filled with nitrogen. Photocatalytic reactions were performed for 12 h. After the reaction, the liquid products were analyzed using a high-performance liquid chromatograph (HPLC, Shimadzu LC-20A) with refractive index (RI) and ultraviolet detectors together with a Shodex SUGARSH-1011 column ( $8\text{ mm} \times 300\text{ mm}$ ) using a dilute  $\text{H}_2\text{SO}_4$  aqueous solution as the mobile phase. Gaseous products including  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  were analyzed using an INFICON Micro GC Fusion equipped with a molecular sieve 5A column and a high-sensitivity thermal conductivity detector.

**Evaluation of catalytic performance for ethanol coupling to 2,3-BD.** Photocatalytic reactions were carried out in a sealed quartz tube reactor (volume, 20 mL; inner diameter, 16 mm). Typically, the height of the reaction solution was 19 mm. The light source was a 300 W Xe lamp. Typically, 10 mg of solid catalyst was ultrasonically dispersed in  $5.0\text{ cm}^3$  ethanol. Then, the reactor was evacuated and filled with nitrogen. Photocatalytic reactions were performed for 12 h. After the reaction, the liquid products were analyzed using an Agilent 7890A series gas chromatograph (GC) equipped with a DB-WAX column and a flame ionization detector (FID). Gaseous products including  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  were analyzed using an INFICON Micro GC Fusion equipped with a molecular sieve 5A column and a high-sensitivity thermal conductivity detector.

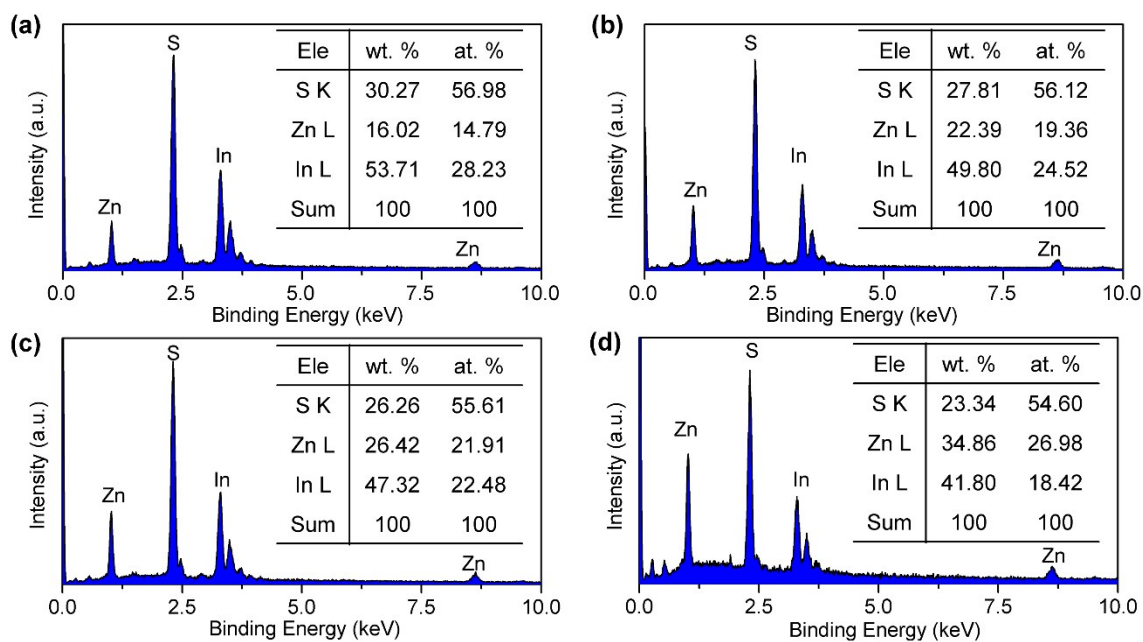
### **Characterization.**

The EDX analysis of the elemental contents were carried out on the HITACHI S4800 scanning electron microscope with 20 kV accelerating voltage. The powder XRD patterns were recorded on a Panalytical X'pert Pro diffractometer using  $\text{Cu K}_\alpha$  radiation (40 kV, 30 mA). The TEM measurements were performed using a Tecnai F20 electron microscope (Phillips Analytical) operated at an acceleration voltage of 200 kV. The AFM measurements were carried out on an AFM (Agilent SPM 5500) in air

using a Pt/Ir-coated Si tip (PPP-CONTPT-50, NANOSENSORS). The diffuse reflectance UV-vis spectroscopic measurements were performed on Varian Cary 5000 spectrophotometer equipped with a diffuse reflectance accessory. The spectra was collected with BaSO<sub>4</sub> as a reference. The steady-state photoluminescence (PL) spectra were recorded on a F4500 fluorescence spectrophotometer at an excitation wavelength of 380 nm.

The photoelectrochemical measurements were carried out with CHI 760E using a standard three-electrode cell with a working electrode, a Pt plate as the counter electrode, and an Ag/AgCl electrode as the reference electrode. A 0.5 M Na<sub>2</sub>SO<sub>4</sub> mixed solution (10% (v/v) methanol + 90% (v/v) water) was used as the electrolyte. The working electrode was prepared based on an F-doped SnO<sub>2</sub>-coated glass (FTO glass, 1 cm × 2 cm). The photocatalyst was dispersed in water, and the suspension was added dropwise directly onto the FTO by microsyringe with a gentle stream of air to speed drying. The film was dried at 60 °C for 1 h, and the typical surface density of the photocatalyst was 1 mg cm<sup>-2</sup>. The Mott-Schottky measurements were performed with the potential ranged from -0.3 to 1.0 V (vs NHE, pH = 7) and the frequency ranging from 500 to 1500 Hz. The electrochemical impedance spectra (EIS) were measured in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution and carried out under bias of -0.75 V, and the frequency ranges from 1 to 1000 kHz.

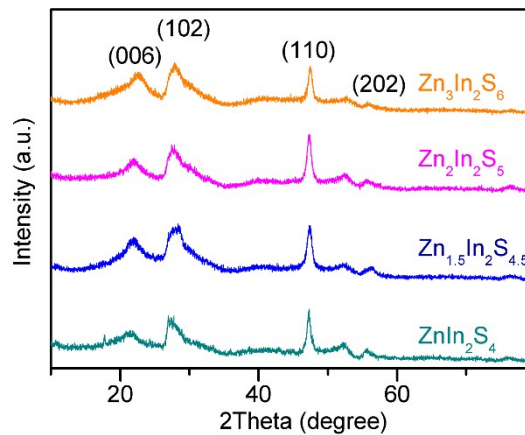
The ESR spectroscopic measurements were performed at room temperature using a Bruker EMX-10/12 ESR spectrometer operated at X-band frequency. The parameters for ESR measurements were as follows: microwave frequency 9.43 GZ, microwave power 20 mW, modulation frequency 100 kHz, attenuator 10 dB. For in-situ ESR measurements, Zn<sub>2</sub>In<sub>2</sub>S<sub>5</sub> powder was dispersed in a mixed solution of CH<sub>3</sub>OH/H<sub>2</sub>O or C<sub>2</sub>H<sub>5</sub>OH containing DMPO (4 mM), which was used as a spin-trapping agent, by ultrasonic treatment. Then, the suspension was injected into a glass capillary and the glass capillary was placed in a sealed glass tube under N<sub>2</sub> atmosphere. The sealed glass tube was placed in the microwave cavity of ESR spectrometer and was irradiated with Xe lamp ( $\lambda$  = 400-780 nm) during ESR measurements at room temperature.



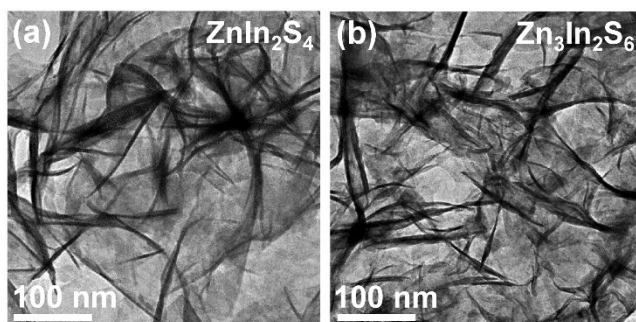
**Fig. S1** EDX and elemental contents (inset) of  $\text{Zn}_m\text{In}_2\text{S}_{m+3}$  samples. (a)  $\text{ZnIn}_2\text{S}_4$ , (b)  $\text{Zn}_{1.5}\text{In}_2\text{S}_{4.5}$ , (c)  $\text{Zn}_2\text{In}_2\text{S}_5$ , (d)  $\text{Zn}_3\text{In}_2\text{S}_6$ .

**Table S1** EDX composition of  $\text{Zn}_m\text{In}_2\text{S}_{m+3}$  ( $m = 1-3$ ) samples

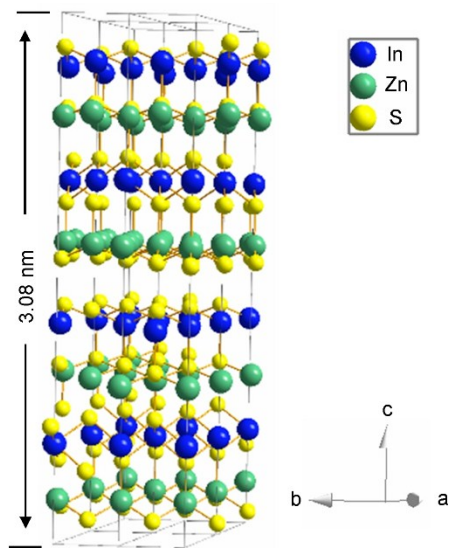
Catalyst	EDX composition
$\text{ZnIn}_2\text{S}_4$	$\text{Zn}_{1.04}\text{In}_2\text{S}_{4.04}$
$\text{Zn}_{1.5}\text{In}_2\text{S}_{4.5}$	$\text{Zn}_{1.58}\text{In}_2\text{S}_{4.58}$
$\text{Zn}_2\text{In}_2\text{S}_5$	$\text{Zn}_{1.95}\text{In}_2\text{S}_{4.95}$
$\text{Zn}_3\text{In}_2\text{S}_6$	$\text{Zn}_{2.93}\text{In}_2\text{S}_{5.93}$



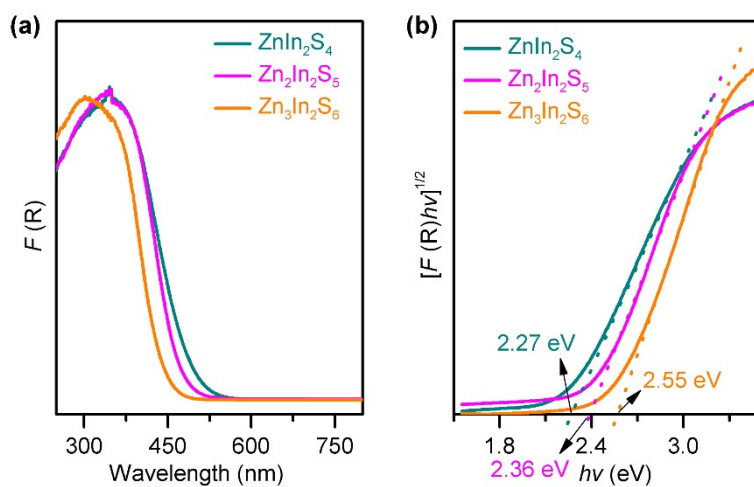
**Fig. S2** X-ray diffraction patterns of  $Zn_mIn_2S_{m+3}$  ( $m = 1-3$ ) samples.



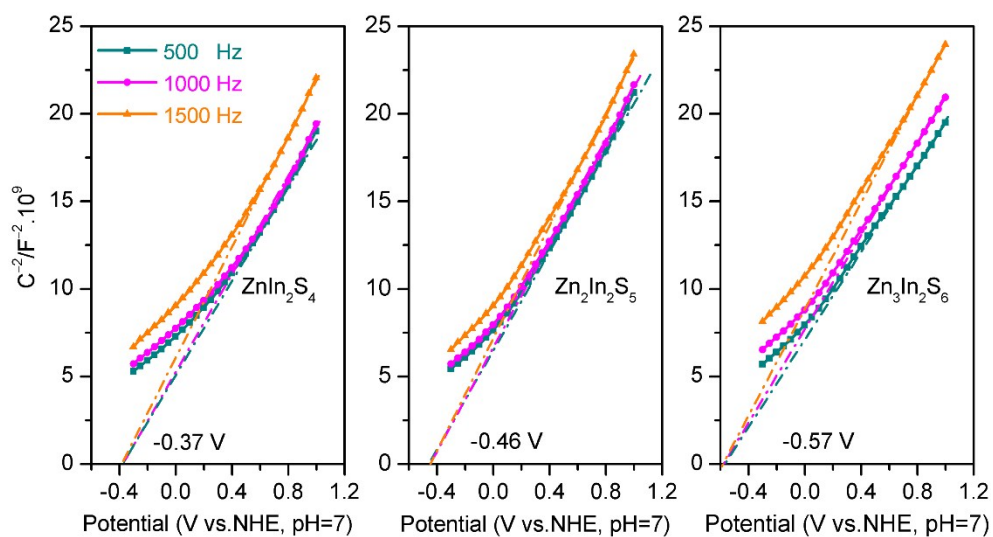
**Fig. S3** TEM images of  $ZnIn_2S_4$  and  $Zn_3In_2S_6$  nanosheets.



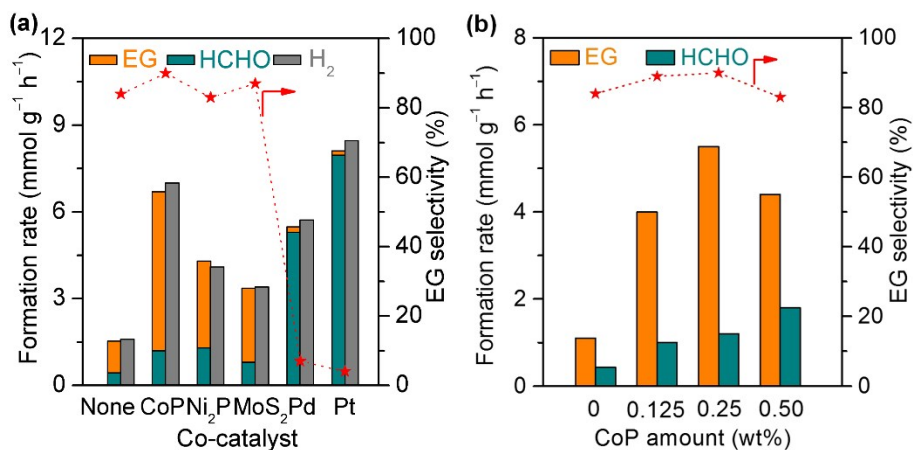
**Fig. S4** The structural model of the unit cell of the layered  $Zn_2In_2S_5$ .



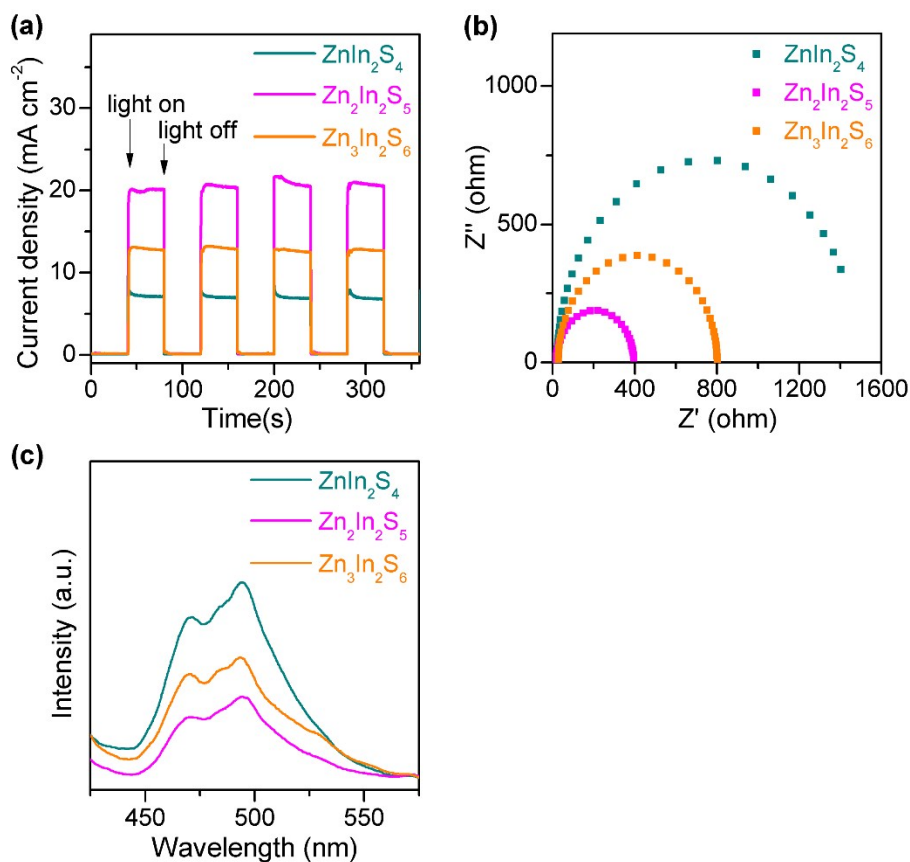
**Fig. S5** (a) Diffuse-reflectance UV-vis spectra and (b) the corresponding plots of modified Kubelka-Munk function versus the energy of exciting light of  $\text{Zn}_m\text{In}_2\text{S}_{m+3}$  ( $m = 1-3$ ).



**Fig. S6** Mott-Schottky plots of  $\text{Zn}_m\text{In}_2\text{S}_{m+3}$  ( $m = 1-3$ ).

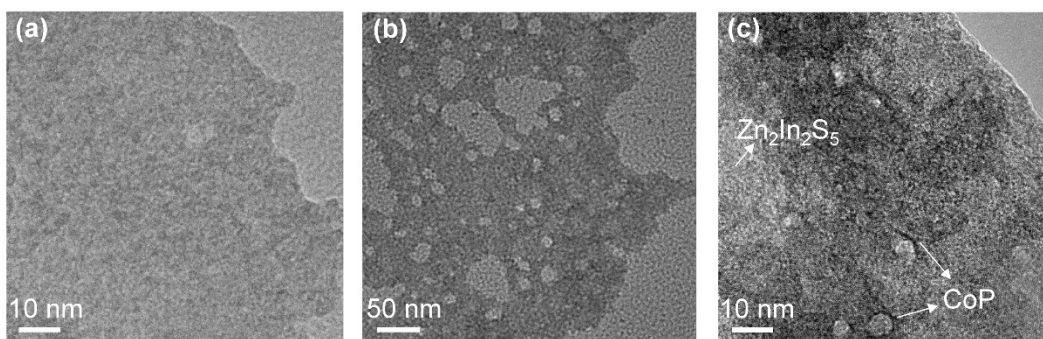


**Fig. S7** (a) Catalytic performances of different co-catalysts modified  $\text{Zn}_2\text{In}_2\text{S}_5$  for MTEG. (b) Catalytic performances of  $x$  wt%CoP/ $\text{Zn}_2\text{In}_2\text{S}_5$  for MTEG. Reaction conditions: solution, 76 wt%  $\text{CH}_3\text{OH}$  + 24 wt%  $\text{H}_2\text{O}$ , 5.0  $\text{cm}^3$ ; atmosphere,  $\text{N}_2$ ; light source, 300 W Xe lamp; visible light,  $\lambda = 400\text{-}780$  nm.

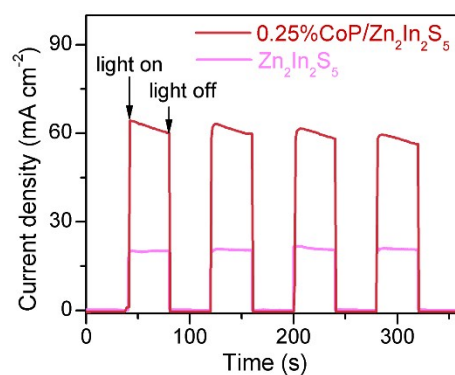


**Fig. S8** Characterization for  $\text{ZnIn}_2\text{S}_4$ ,  $\text{Zn}_2\text{In}_2\text{S}_5$ , and  $\text{Zn}_3\text{In}_2\text{S}_6$ . (a) Transient photocurrent responses. (b) Electrochemical impedance spectra. (c) Steady-state photoluminescence (PL) emission spectra under 380 nm light excitation.

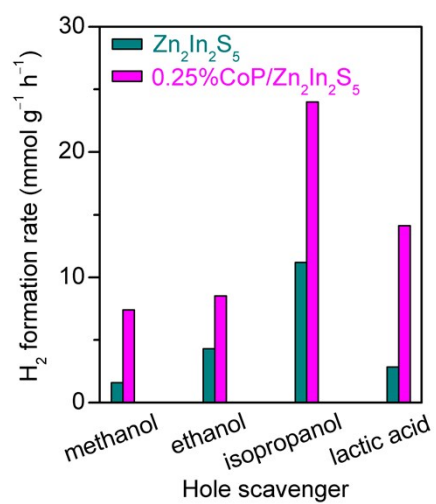




**Fig. S9** TEM image of Zn<sub>2</sub>In<sub>2</sub>S<sub>5</sub> (a), CoP (b), and 0.25 wt%CoP/Zn<sub>2</sub>In<sub>2</sub>S<sub>5</sub> (c).



**Fig. S10** Transient photocurrent responses for Zn<sub>2</sub>In<sub>2</sub>S<sub>5</sub> and 0.25 wt%CoP/Zn<sub>2</sub>In<sub>2</sub>S<sub>5</sub>.



**Fig. S11** H<sub>2</sub> evolution activity of Zn<sub>2</sub>In<sub>2</sub>S<sub>5</sub> and 0.25 wt%CoP/Zn<sub>2</sub>In<sub>2</sub>S<sub>5</sub> using different hole scavengers instead of methanol.

## References

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