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

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Haikun Zhang,[‡] Shunji Xie,[‡],* Jinyuan Hu, Xuejiao Wu, Qinghong Zhang, Jun Cheng and Ye Wang*

Herein, an environmentl-friendly CoP/Zn₂In₂S₅ catalyst is reported as a visible-light photocatalyst for selective activation of the α -C–H bond in methanol to generate ethylene glycol with selectivity as high as 90%. The catalytic sysmtem also illustrated the first exmaple of visible-light-driven dehydrogenative coupling of ethanol to 2,3butanediol.

Selective activation of the inert sp³ α -C–H bond within an alcohol and direct formation of C–C bond with the coupling partners is a promising way to produce multi-carbon alcohol or polyalcohol.¹ Among various reactions in this field, the direct coupling of methanol to ethylene glycol (Eq. 1, denoted as MTEG) is known as a "dream catalytic reaction", which is expected to be solved in the 21st century.

(1)

 $2CH_3OH \rightarrow HOCH_2CH_2OH + H_2$

Ethylene glycol (EG) is the world's largest diol in demand, underpins almost every aspect of our daily life, such as chemical manufacturing, and transportation.² In current industrial process, EG is primarily produced from petroleum-derived ethylene via epoxidation and subsequent hydrolysis of ethylene epoxide, which suffers from high price of ethylene, low yield of EG, and high energy consumption.² In contract, the MTEG utilizes methanol, which can be produced on a large scale from a wide range of carbon resources, such as natural gas, coal, biomass, and CO_2 .³ The direct coupling of methanol to EG and H₂ is also an economic process with high atom utilization.

This direct synthesis of EG from methanol has not been achieved through thermocatalysis, because of the thermodynamic limitations.⁴ However, photocatalysis has been found to be able to make up for the incapability of theromocatalysis in many cases,⁵⁻⁷ among which the photocatalytic MTEG has shown some preliminary success.^{4,8} Yanagida and co-workers have reported that EG could be formed on ZnS (bandgap energy 3.6 eV) under ultraviolet (UV) irradiation, yet with low activity. ⁸ In the solar spectrum, UV light only makes up ~3% of the total solar energy, whereas visible-light makes up ~44%.⁵ Therefore, it is very attractive to develop a visible-light-responsive catalyst to improve the utilization of solar energy. In our previous work, methanol was photocatalytically converted to EG under visible-light irradiation for the first time with high efficiency and selectivity using a MoS₂/CdS photocatalyst.⁴ However, the toxicity of CdS has motivated us to develop a more environmentally friendly visible-light photocatalyst.

Metal sulfide is a class of photocatalyst with good visiblelight response and hydrogen evolution activity, especially ternary metal sulfides, which have shown richer variability in properties and higher activity than binary metal sulfides.⁹ Therefore, it is possible to develop an environmentally friendly ternary metal sulfide catalyst for efficient photocatalytic conversion of methanol to EG and H₂ under visible-light irradiation, which has not been realized in previous literatures.

Herein, a series of environmentally friendly ternary metal sulfide photocatalysts, zinc-indium-sulfide ($Zn_mIn_2S_{m+3}$, m = 1-3), were synthesized by a simple method. We found that the few-layer $Zn_2In_2S_5$ nanosheets showed higher activity and selectivity for EG production than $ZnIn_2S_4$ and $Zn_3In_2S_6$ under visible-light irradiation. The modification of $Zn_2In_2S_5$ with cobalt phosphide (CoP) could significantly enhance the formation of EG and H₂. We also demonstrated the first example of the visible-light-driven dehydrogenative coupling of ethanol to 2,3-butanediol over CoP/Zn_2In_2S_5 catalyst.

The fabrication of a series of ternary metal sulfides $Zn_mIn_2S_{m+3}$ (m = 1-3) is schematically illustrated in Fig. 1a. Initially, the multi-layer $Zn_mIn_2S_{m+3}$ was prepared at 90 °C via a facile low-temperature hydrothermal method using $Zn(CH_3COO)_2$, $InCl_3$, and thioacetamide as the precursors.

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. E-mail: shunji_xie@xmu.edu.cn, wangye@xmu.edu.cn

Electronic Supplementary Information (ESI) available: Experimental details, catalytic performances, EDX results, XRD patterns, TEM images, Mott-Schottky plots, UV-vis spectra, PL spectra. See DOI: 10.1039/x0xx00000x
 These authors contributed equally to this work.

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Fig. 1 (a) Schematic must atom of the low-temperature hydromermal and ultrasonic process for $Zn_m ln_2S_{m+3}$ synthesis. (b) TEM image and HRTEM image (inset) of $Zn_2ln_2S_5$. (c) AFM image of $Zn_2ln_2S_5$. (d) The AFM-measured height profiles of $Zn_2ln_2S_5$ for lines in c. (e) Energy levels of several related redox couples and band-edge positions of some semiconductors.

The few-layer $Zn_m In_2 S_{m+3}$ was then generated by ultrasonic treatment. The stoichiometries of each element in $Zn_mIn_2S_{m+3}$ (m = 1-3) were tuned by altering the Zn/In ratio in the feedstock. The energy-dispersive X-ray spectroscopy (EDX) analysis was applied to confirm that the elemental compositions of Zn, In, and S in all of the $Zn_m In_2 S_{m+3}$ samples were corresponding with the stoichiometric compositions (Fig. S1 and Table S1, ESI⁺). XRD patterns of $Zn_m In_2 S_{m+3}$ samples present similar profiles (Fig. S2, ESI⁺), which correspond to a hexagonal wurtzite crystal phase.¹⁰ The morphology of $Zn_m In_2 S_{m+3}$ was identified by transmission electron microscopy (TEM) (Fig. 1b and Fig. S3, ESI⁺), from which ZnIn₂S₄, Zn₂In₂S₅, and Zn₃In₂S₆ present similar sheet-like nanostructure. Taking Zn₂In₂S₅ for example, the HRTEM image of Zn₂In₂S₅ displays a few-layer structure (Fig. 1b, inset). The AFM image confirms that $Zn_2In_2S_5$ present a 2D structure with a smooth surface morphology (Fig. 1c). The corresponding height profiles in Fig. 1d show that the typical thickness of the $Zn_2In_2S_5$ nanosheets are ~3.07, 6.17, and 9.25 nm. Considering that the c parameter of the unit cell of Zn₂In₂S₅ is 30.85 Å (Fig. S4, ESI⁺) according to JCPDS card (No. 89-1906), the Zn₂In₂S₅ thickness is well in agreement with 1-3 times of the thickness of a unit cell along the [001] axis, validating the fewlayer structure of the Zn₂In₂S₅ nanosheets.

The UV-vis spectra shows that the absorption edge of $Zn_mIn_2S_{m+3}$ shifts slightly to a shorter wavelength with increased Zn/In atomic ratio (Fig. S5, ESI[†]). The bandgap energy (E_g) can be evaluated from the modified Kubelka-Munk plots (Fig. S5, ESI[†]), which were 2.27, 2.36, and 2.55 eV for ZnIn₂S₄, Zn₂In₂S₅, and Zn₃In₂S₆, respectively. The flat-band potential (E_{fb}) of Zn_mIn₂S_{m+3} could be obtained from Mott-Schottky measurement (Fig. S6, ESI[†]). The conduction-band minimum (E_{cb}) is ~0.15 V more negative than E_{fb} , $E_{cb} = E_{fb} - 0.15$ V.¹¹ Thus,

Table 1 Photocatalytic performances of $Zn_m ln_2 S_{m+3}$ (m = 1-3) in comparison with View Article Online some binary metal sulfides for MTEG

| , | | | | | 00 | 1. 10.1 | 0007000 | 0001001 |
|----------------------------------|---|------|-------|----------------|------------------------------|---------|---------|---------|
| | Formation rate (mmol g _{cat} ⁻¹ h ⁻¹) | | | e⁻/ | Selectivity ^b (%) | | | |
| Catalyst | EG | нсно | нсоон | H ₂ | h+a | EG | нсно | нсоон |
| ZnIn ₂ S ₄ | 0 | 0.46 | 0 | 0.46 | 1.0 | 0 | 100 | 0 |
| $Zn_{1.5}In_2S_{4.5}$ | 0.44 | 0.42 | 0 | 0.83 | 0.97 | 68 | 32 | 0 |
| $Zn_2In_2S_5$ | 1.1 | 0.43 | 0 | 1.6 | 1.04 | 84 | 16 | 0 |
| $Zn_3In_2S_6$ | 0.90 | 0.36 | 0 | 1.3 | 1.03 | 83 | 17 | 0 |
| In_2S_3 | 0 | 0 | 0 | 0 | - | - | - | - |
| ZnS | 0 | 0 | 0 | 0 | - | - | - | - |
| ZnS(UV) | 1.3 | 2.2 | 0.067 | 3.4 | 0.92 | 54 | 43 | 1.3 |
| CdS^d | 0.46 | 0.38 | 0 | 0.75 | 0.90 | 71 | 29 | 0 |

Reaction conditions: solution, 76 wt% CH₃OH + 24 wt% H₂O, 5.0 cm³; atmosphere, N₂; light source, 300 W Xe lamp; UV-vis light, λ = 320-780 nm; visible light, λ = 400-780 nm. ^{*a*} The ratio of electrons and holes consumed in product formation was calculated by the equation of e⁻/h⁺ = [2 × *n*(H₂) + 2 × *n*(CH₄)]/[2 × *n*(EG) + 2 × *n*(HCHO) + 4 × *n*(HCOOH) + 4 × *n*(CO) + 6 × *n*(CO₂]. Only trace amount of CO, CO₂, CH₄ were observed on ZnS, which were not listed in Table 1. ^{*b*} Selectivity was calculated on a molar carbon basis. ^{*c*} Reaction was carried out under UV-vis light irradiation. ^{*d*}

the E_{cb} of ZnIn₂S₄, Zn₂In₂S₅, and Zn₃In₂S₆ were calculated to be -0.52, -0.61, and -0.72 V (vs. NHE, pH = 7), respectively, all more negative than the redox potential of H₂O/H₂ (-0.42 V vs. NHE, pH = 7) (Fig. 1e). Moreover, the valence-band maximum (E_{vb}) can be calculated according to $E_{vb} = E_g + E_{cb}$. The E_{vb} of ZnIn₂S₄, Zn₂In₂S₅, and Zn₃In₂S₆ were 1.75, 1.75, and 1.83 V (vs. NHE, pH = 7), respectively, which were all significantly lower (more positive) than the redox potential of EG/CH₃OH (-0.37 V vs. NHE, pH = 7) (Fig. 1e). These results indicate that the energy band positions of Zn_mIn₂S_{m+3} could provide sufficient redox ability for the photocatalytic conversion of methanol to EG and H₂, thermodynamically speaking.

The $Zn_m In_2 S_{m+3}$ (*m* = 1-3) catalysts were exploited for the photocatalytic coupling of methanol to EG under visible-light irradiation, and the reaction selectivity was found to be significantly influenced by the chemical composition of the catalysts. As shown in Table 1, HCHO was formed as the major carbon-based product over ZnIn₂S₄, and no EG was detected. Meanwhile, H₂ was formed along with HCHO. In contrast, Zn₂In₂S₅ displayed a very high selectivity towards EG production (84%). The estimated ratio of photogenerated electrons and holes according to Eqs. 2-4 was close to 1.0, which indicates that HCHO was the major byproduct along with EG and H_2 . The formation rate of EG over $Zn_2In_2S_5$ could reach 1.1 mmol g_{cat}^{-1} h⁻¹, which was more than two times higher than that over CdS nanorods reported in our previous work.4 Moreover, the $Zn_{1.5}In_2S_{4.5}$ with lower Zn/In atomic ratio than $Zn_2In_2S_5$ showed lower EG formation rate and selectivity than Zn₂In₂S₅. The Zn₃In₂S₆ with higher Zn/In atomic ratio than Zn₂In₂S₅ showed almost the same EG selectivity as Zn₂In₂S₅, but with slightly lower photocatalytic activity than Zn2In2S5. Thus, the photocatalytic activity of Zn_mIn₂S_{m+3} for MTEG strongly depended on the Zn/In atomic ratio.

| • | | |
|---|--|-----|
| 2CH ₃ OH + 2h ⁺ - | \rightarrow HOCH ₂ CH ₂ OH + 2H ⁺ | (2) |

| $CH_3OH + 2h^+ \rightarrow HCHO + 2H^+$ | (3) |
|---|-----|
| $2H^+ + 2e^- \rightarrow H_2$ | (4) |

| | | (* | 4) |
|--|--|----|----|
| | | | |

For comparison, In_2S_3 and ZnS were also examined for this reaction. In_2S_3 showed poor photocatalytic performance for EG and H_2 formation. ZnS was inactive under visible-light

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Fig. 2 (a) Time course process of $Zn_2ln_2S_5$ for MTEG within 12 h under visible light. (b) Repeated use of $Zn_2ln_2S_5$ under visible light (12 h for each cycle). (c) Photocatalytic performances of $Zn_2ln_2S_5$, 0.25 wt%CoP/Zn_2ln_2S_5 for MTEG under visible light and AM 1.5 light. Reaction conditions: solution, 76 wt% CH₃OH + 24 wt% H₂O, 5.0 cm³; atmosphere, N₂; light source, 300 W Xe lamp; visible light, λ = 400-780 nm; AM 1.5 filter.

irradiation, with EG formed only under UV light irradiation. Hence, $Zn_2In_2S_5$ shows great superiority over its binary counterparts (In_2S_3 and ZnS) for photocatalytic coupling of methanol to EG. On the other hand, $Zn_2In_2S_5$ showed good stability under the catalytic condition, with the steady formation of EG, HCHO, and H₂ over 12 h (Fig. 2a) and no obvious deactivation was observed in the six recycling experiments (Fig. 2b).

Co-catalysts are known to play crucial roles in photocatalysis. The Zn₂In₂S₅ nanosheets was further modified by some typical co-catalysts, including CoP, Ni₂P, MoS₂, Pt, and Pd. Our results suggested that most co-catalysts could enhance the H₂ formation rate, but Pt and Pd co-catalysts significantly increased the HCHO formation rate, which may due to their ability for O-H bond scission and sequential hydrogen abstraction (Fig. 2c and Fig. S7, ESI⁺).¹² Only CoP, Ni₂P, and MoS₂ co-catalysts were capable of promoting the EG formation rate. CoP was the most effective co-catalyst on Zn₂In₂S₅ for MTEG. Under visible-light irradiation, with a loading of 0.25 wt%CoP, the selectivity towards EG formation was enhanced to 90% along with a ~5 fold increase in its formation rate (5.5 mmol $g_{cat}^{-1} h^{-1}$) compared to $Zn_2In_2S_5$ alone (Fig. 2c). The CoP/Zn₂In₂S₅ also showed the same high EG selectivity to MoS₂/CdS reported in our previous work,⁴ while the activity still not as high as the best performance of MoS₂/CdS under similar reaction conditions. Moreover, under



Fig. 3 Photocatalytic performances for the coupling of ethanol to 2,3-BD under visible light irradiation. (a) $ZnIn_2S_4$, $Zn_2In_2S_5$, and $Zn_3In_2S_6$. (b) Different co-catalysts modified $Zn_2In_2S_5$ (co-catalyst loading amount 0.25 wt%). Reaction conditions:

solution, 100 wt% C₂H₅OH, 5.0 cm³; atmosphere, N₂; light source 300 W Xe Jampse visible light, $\lambda = 400-780$ nm. DOI: 10.1039/C9CC09205F the simulated sunlight irradiation (Xe lamp with AM 1.5 filter), the CoP co-catalyst also showed remarkable promoting effect, the EG formation rate over 0.25 wt%CoP/Zn₂In₂S₅ could reach 18.9 mmol g_{cat}⁻¹ h⁻¹ (Fig. 2c). The EG yield could reach 4.5% after 12 h reaction.

Ethanol is another simple primary alcohol, which has been used as a sustainable fuel and versatile building block for the production of various chemicals. 2,3-Butanediol (2,3-BD) is an important chemical that has a number of applications.¹³ Here, we demonstrated that ethanol could be directly transformed into 2,3-BD driven by visible-light for the first time. As shown in Fig. 3a, ethanol could be mainly oxidized to 2,3-BD and acetaldehyde over $Zn_2ln_2S_5$. The CoP co-catalyst also showed significant promoting effect in ethanol-to-2,3-BD reaction (Fig. 3b). Under visible light irradiation, the 2,3-BD selectivity and formation rate over 0.25 wt%CoP/Zn_2ln_2S_5 were 53% and 3.2 mmol $g_{cat}^{-1} h^{-1}$, respectively.

Photocatalysis is a complex reaction process, and in order to better evaluate the photocatalytic efficiency for MTEG, the following processes are considered: the efficiencies of light harvesting, charge separation, and surface reaction. The photocurrent density under periodic irradiation of visible light increased in the following sequence: $ZnIn_2S_4 < Zn_3In_2S_6 <$ $Zn_2In_2S_5$ (Fig. S8a, ESI⁺), with $Zn_2In_2S_5$ showing the highest overall efficiency of light harvesting and charge separation. Furthermore, the electrochemical impedance spectrum of $Zn_2In_2S_5$ shows the smallest semicircle in the Nyquist plot (Fig. S8b, ESI[†]), indicating the lowest charge-transfer resistance that guarantees efficient charge separation and transfer. Moreover, the photoluminescence (PL) intensity of the emission band at ~494 nm due to the recombination of photogenerated electrons and holes decreased in the following sequence: ZnIn₂S₄ > $Zn_3In_2S_6 > Zn_2In_2S_5$ (Fig. S8c, ESI⁺), confirming that $Zn_2In_2S_5$ has the highest efficient for charge separation. These results confirm that Zn₂In₂S₅ exhibited the best performance in the separation and transfer of photogenerated excitons, which contribute to its high activity in the MTEG reaction. However, the effect of Zn/In atomic ratio on surface reaction and EG selectively requires further studies in the future.

The CoP has been demonstrated to be an efficient catalyst in electrochemical H_2 evolution and also an outstanding cocatalyst in water spliting, benefiting from its rich active sites for H_2 evolution and high ability for charge separation.¹⁴ From our TEM images (Fig. S9, ESI[†]), the CoP displayed an ultra-thin porous nanosheet morphology, and kept an intimate contact with $Zn_2In_2S_5$ nanosheets, which would facilitate the charge transfer. Our photocurrent density results showed that the incorporation of CoP significantly increased the charge separation (Fig. S10, ESI[†]). Furthermore, the CoP co-catalyst also displayed a promoting effect on photocatalytic H_2 evolution when using other hole scavenger (ethanol, isopropanol, or lactic acid) (Fig. S11, ESI[†]). Thus, we speculated that CoP improves EG formation in MTEG reaction by promoting charge separation and H_2 production.

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The *in situ* electron spin resonance (ESR) spectroscopic study on MTEG reaction using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a spin-trapping agent revealed the generation of the



Fig. 4 (a) *In situ* ESR spectra for systems containing $Zn_2ln_2S_5$ and $CoP/Zn_2ln_2S_5$ catalysts in methanol aqueous solution in the presence of DMPO (a spin-trapping agent) with or without light irradiation. (b) *In situ* ESR spectra for systems containing $Zn_2ln_2S_5$ and $CoP/Zn_2ln_2S_5$ catalysts in ethanol solution in the presence of DMPO. (c) Illustration of photocatalytic conversion of methanol and ethanol to diols over $CoP/Zn_2ln_2S_5$.

hydroxymethyl radical (•CH₂OH) on Zn₂In₂S₅ and CoP/Zn₂In₂S₅ catalysts (Fig. 4a).⁴ The •CH₂OH radical should be the intermediate by selective activation of the C-H bond within methanol for the formation of EG. The modification of CoP on Zn₂In₂S₅ could significantly increase the generation of •CH₂OH radicals, and thus promoted EG formation. On the other hand, the in situ ESR spectra for systems of ethanol conversion also observed strong signals which could be attribute to the generation of α -hydroxyethyl radicals (•CH(OH)CH₃) on Zn₂In₂S₅ and CoP/Zn₂In₂S₅ catalysts (Fig. 4b).¹⁵ The selectively activated α -C–H bond of ethanol would result in the formation of •CH(OH)CH₃ radical, and enabled the subsequent C-C coupling to 2,3-BD (Fig. 4c). As shown in Fig. 4c, the H₂ evolution may occur on the CoP surface, while the dehydrogenative coupling of alcohols to diols may occur on the surface of $Zn_2In_2S_5$. Thus, $Zn_2In_2S_5$ is quite unique in the preferential activation of the α -C–H bond in alcohols without affecting the O-H group. The thiol group (-SH) on the surface of sulfide semiconductor has been proposed to be the active sites for selective activation of the C-H bond.¹⁶ In our case, the thiol groups on Zn₂In₂S₅ surface may trap holes to generate thiyl radicals for abstracting hydrogen from α -C–H bond of alcohols to form the radical intermediates for subsequent C-C coupling to diols.

In conclusion, we found that the few-layer $Zn_2ln_2S_5$ nanosheets was an environmentally friendly visible-light photocatalyst for coupling methanol to EG. The modification of $Zn_2ln_2S_5$ nanosheets with CoP nanosheets could significantly enhance EG formation. We also demonstrated the first visible-

light-driven dehydrogenative coupling of ethanol to 2.3 RD OMAE CoP/Zn₂In₂S₅ catalyst. Mechanism studies show that the CDH bond within methanol was activated to form •CH₂OH radical without affecting the O-H group for subsequent coupling to EG, and the α -C-H bond within ethanol was selectively activated to form •CH(OH)CH₃ radical for subsequent coupling to 2,3-BD. The present work would offer an environmentally friendly visible-light-driven strategy for preferential activation of α -C-H bond in the present of O-H group under mild conditions.

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Conflicts of interest

There are no conflicts to declare.

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