# Visible-light-driven valorization of biomass-derived furfuryl alcohol to diesel precursors with simultaneous $H_2$ evolution over dual functional $In_2S_3$-$Zn_5In_2S_8$ photocatalysts

Yibei Zhang, Hongyun Lu, Xuekai-Qu, Lunan Wu, Zhenghao Song, Xinyi Ding, Peng Li, Xiu-Jie Yang*, Dong Liu

*State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, China*

*** Corresponding author**

Mailing Address: State Key Laboratory of Heavy Oil Processing, College of Chemistry and Chemical Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, China.

E-mail: yangxiujie@upc.edu.cn (X.-J. Yang)

Tel.: +86-532-86984615

# Methods



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## Method

### Synthesis of $In_2S_3$

A mixture of $InCl_3$ (2 mmol) and $CH_3CSNH_2$ (6 mmol) was dissolved in 80 mL of deionized water under continuous stirring until complete dissolution. Subsequently, CTAB (1 mmol) was added, and the solution was stirred for an additional 1 h. The resulting mixture was transferred to a Teflon-lined autoclave and heated at 180°C for 12 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed three times with deionized water and ethanol, and finally dried in a vacuum oven at 50°C for 12 h.

### Synthesis of $Zn_5In_2S_8$ ($ZIS_8$)

A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (5 mmol), $InCl_3$ (2 mmol), and $CH_3CSNH_2$ (16 mmol) was dissolved in 80 mL of deionized water under continuous stirring until complete dissolution. Subsequently, CTAB (1 mmol) was added, and the solution was stirred for an additional 1 h. The resulting mixture was transferred to a Teflon-lined autoclave and heated at 180°C for 12 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed three times with deionized water and ethanol, and finally dried in a vacuum oven at 50°C for 12 h.

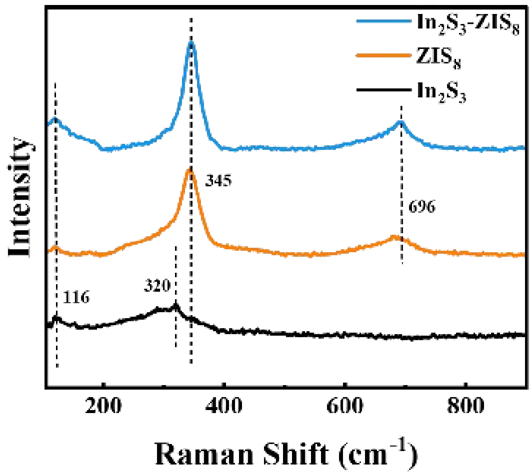


**Figure S1** The Raman spectra of $In_2S_3$-$ZIS_8$ catalysts.

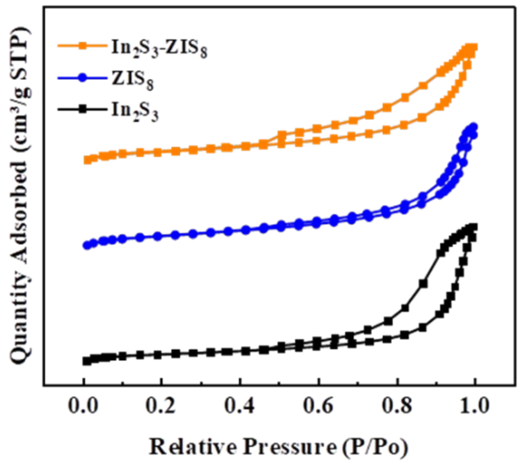


**Figure S2** $N_2$ adsorption/desorption isotherms of $In_2S_3$, $ZIS_8$ and $In_2S_3$-$ZIS_8$.

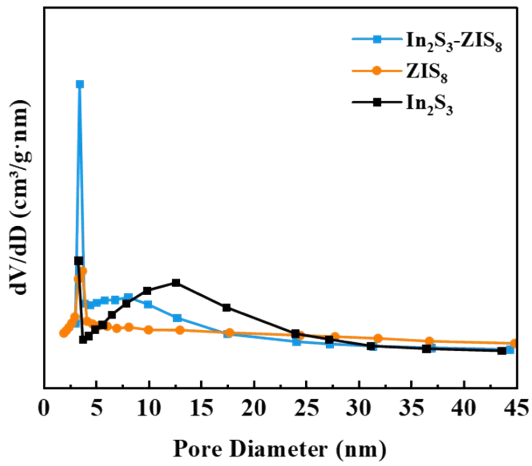


**Figure S3** Pore size distribution of $In_2S_3$, $ZIS_8$ and $In_2S_3$-$ZIS_8$.

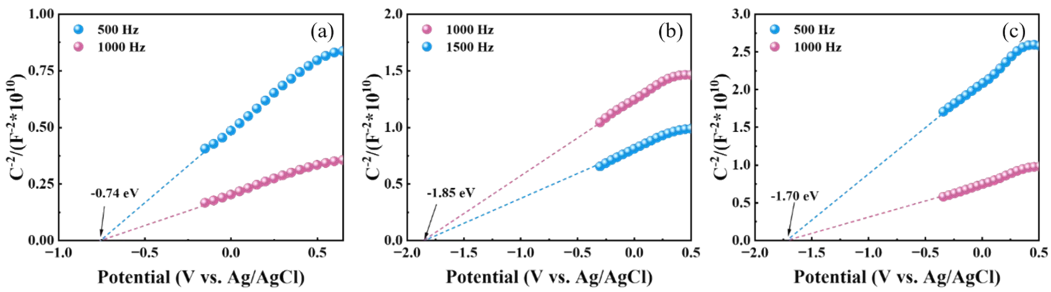


**Figure S4** The Mott-Schottky measurement of (a) $In_2S_3$, (b) $ZIS_8$ and (c) $In_2S_3$-$ZIS_8$.

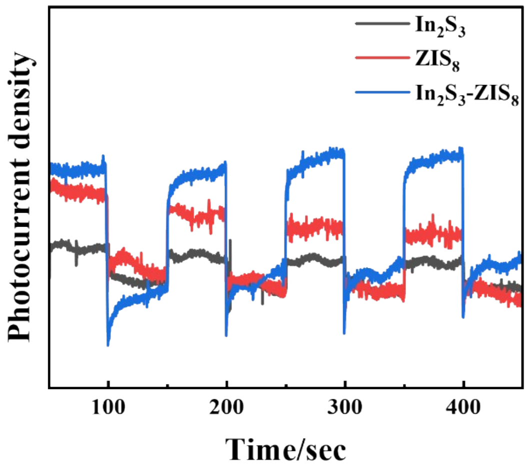


**Figure S5** photocurrent spectra of $In_2S_3$, $ZIS_8$ and $In_2S_3$-$ZIS_8$.

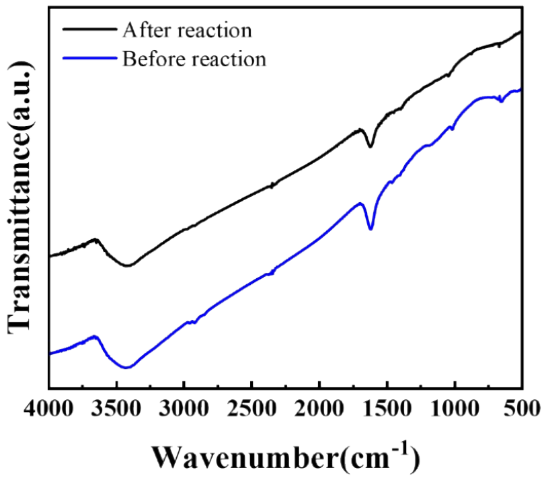


**Figure S6** FT-IR spectra of $In_2S_3$-$ZIS_8$ catalyst before and after recycling.

**Table S1** Different surface atom contents derived from XPS analysis for the $In_2S_3$, $ZIS_8$ and $In_2S_3$-$ZIS_8$.

| Sample | Zn/ at.% | In/ at.% | S/ at.% | Zn:In:S |
|---|---|---|---|---|
| $In_2S_3$ | —— | 43.36 | 56.64 | 3:4 |
| $ZIS_8$ | 25.68 | 19.31 | 55.00 | 4:3:9 |
| $In_2S_3$-$ZIS_8$ | 24.43 | 22.46 | 53.11 | 12:11:26 |

**Table S2** ICP-OES results of $ZIS_8$ and $In_2S_3$-$ZIS_8$.

| Sample | Zn/ wt.% | In/ wt.% | Zn:In |
|---|---|---|---|
| $ZIS_8$ | 22.7 | 13.00 | 0.35:0.11 |
| $In_2S_3$-$ZIS_8$ | 15.25 | 18.05 | 0.23:0.16 |

**Table S3** Physicochemical properties of $In_2S_3$, $ZIS_8$ and $In_2S_3$-$ZIS_8$.

| Catalyst | BET surface area ($m^2 \cdot g^{-1}$) | Pore volume ($cm^3 \cdot g^{-1}$) | Pore size (nm) |
|---|---|---|---|
| $In_2S_3$ | 22.38 | 0.145 | 12.035 |
| $ZIS_8$ | 34.97 | 0.129 | 12.317 |
| $In_2S_3$-$ZIS_8$ | 30.51 | 0.124 | 8.785 |

**Table S4** Photocatalytic coupling of furfuryl alcohol under different experimental condition[a].

| Entry | solvent | C-C coupling Product | |
|---|---|---|---|
| | | **Conv./%[b]** | **Select./%[c]** |
| 1[d] | $CH_3CN$ | 6.6 | —— |
| 2[e] | $CH_3CN$ | 12.4 | 9.5 |
| 3[f] | $CH_3CN$ | 90.3 | 67.3[g] |
| 4 | $CH_3CN$ | 88.6 | 87.1 |
| 5[h] | $CH_3CN$ | 61.5 | 91.1 |
| 6 | $H_2O$ | 35.7 | 92.6 |
| 7 | Acetone | 23.3 | 91.2 |
| 8 | Methanol | 66.2 | 87.7 |
| 9 | DCM | 55.8 | 29.1 |
| 10 | Toluene | 85.7 | 68.3 |

[a] Light source: LED (blue, 460 nm); room temperature; substrate amount: 0.46 mmol; 1 atm $N_2$; 5 mL $CH_3CN$; 24h. [b] Conversion of furfuryl alcohol were determined by GC analysis; [c] Selectivity of hydrofuroin were determined by GC analysis; [d] Without photocatalyst; [e] Without irradiation; [f] Using 1 atm $O_2$ instead of $N_2$; [g] Selectivity for furfural; [h] Without CTAB.

**Table S5** Photocatalytic performance of $In_2S_3$-$ZIS_8$ with various substrates[a].

| Entry | Substrate | C-C coupling Product | |
|---|---|---|---|
| | | **Conv./%[b]** | **Select./%[b]** |
| 1 | 5-Methyl-2-furanmethanol | 82.2 | 78.1 |
| 2 | benzyl alcohol | ≈ 100 | 61.5 |
| 3 | 4-Bromobenzyl alcohol | ≈ 100 | 78.3 |
| 4 | 4-Methylbenzyl alcohol | 89.8 | 65.4 |
| 5 | 4-Fluorobenzyl alcohol | ≈ 100 | 75.0 |
| 6 | 4-Methoxybenzyl alcohol | ≈ 100 | 80.9 |
| 7 | benzaldehyde | 76.3 | 63.3 |

[a] Light source: LED (blue, 460 nm); room temperature; substrate amount: 0.46 mmol; 1 atm $N_2$; 5 mL $CH_3CN$; [b] Determined by gas chromatograph with n-dodecanol as internal standard.

**Table S6** Photocatalytic coupling of furfuryl alcohol under different synthesis method[a].

| Entry | solvent | C-C coupling Product | |
|---|---|---|---|
| | | **Conv./%[b]** | **Select./%[c]** |
| 1[d] | $CH_3CN$ | 12.1 | 62.9 |
| 2[e] | $CH_3CN$ | 25.2 | 70.2 |
| 3[f] | $CH_3CN$ | 88.6 | 87.1 |

[a] Light source: LED (blue, 460 nm); room temperature; substrate amount: 0.46 mmol; 1 atm $N_2$; 5 mL $CH_3CN$; 24h. [b] Conversion of furfuryl alcohol were determined by GC analysis; [c] Selectivity of hydrofuroin were determined by GC analysis; [d] Mechanically mixed sample; [e] Low-temperature solvothermal sample; [f] Hydrothermal sample.

**Table S7** Comparison of $In_2S_3$-$ZIS_8$ and previously reported photocatalytic systems.

| Photocatalysts | Reaction conditions | Conv./% | Select./% | $H_2$ rate | Reference |
|---|---|---|---|---|---|
| $In_2S_3$-$ZIS_8$ | LED (blue, 460 nm), 0.46 mmol FA, 5 mL $CH_3CN$ | 88.6 | 87.1 | 14408.6 μmol·g$^{-1}$ | This work |
| ZIS/Ni | 300 W Xe lamp, 76.9 μmol BA, 5 mL $CH_3CN$ | 86 | 99 | 42.24 μmol | 2 |
| Mo/MCS/Co | 300 W Xe lamp, 50 0.48 mmol BA, 10 mL $CH_3CN$ | 90 | 98 | 1.83 mmol g$^{-1}$h$^{-1}$ | 3 |
| Ni-ZIS | 300 W Xe lamp, 5 mM FA | 90 | 12 | 583 μmol g$^{-1}$h$^{-1}$ | 4 |
| $Zn_3In_2S_6$-STAB | 300 W Xe lamp, 0.35 mmol FA, 5 mL $CH_3CN$ | 96.6 | 74.8 | —— | 5 |
| $ZnIn_2S_4$ | 300 W Xe lamp, 0.1 mmol BA, 10 mL $CH_3CN$ | 80 | ~80 | —— | 6 |
| $Zn_{0.6}Cd_{0.4}S$ | 300 W Xe lamp,10 mM BA, 10 mM scavenger, 7 mL of $CH_3CN$, 3 mL of deionized water | 77.14 | 81.19 | 22 μmol | 7 |
| In(0.1)-ZnS | 365 nm LED light, 192 mol BA, 4.0 mL $CH_3CN$ | 73 | 100 | 60 μmol | 8 |
| CdS | 365 nm LED light, 192 mol BA, 4.0 mL $CH_3CN$ | 23 | 76 | —— | 8 |
| CdS/TNS | 300 W Xe lamp, 0.1 mmol BA, 5 mL $CH_3CN$ | 16.2 | 89.7 | 69.5 μmol g$^{-1}$ | 9 |
| $Ni(OH)_2$–ZIS | 300 W Xe lamp, 10 mM HMF, 10 mL $H_2O$ | 20 | 79 | 2405 μmol g$^{-1}$ | 10 |

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