

Supplementary information

Spatial Charge Separation on (110)/(102) Facets of Cocatalyst-Free ZnIn₂S₄ for Selective Conversion of 5-Hydroxymethylfurfural to 2,5-Diformylfuran

Heng Zhao,^{*a} Dhwanil Trivedi,^a Morteza Roostaeinia,^a Xue Yong,^b Jun Chen,^c Pawan Kumar,^a Jing Liu,^c Bao-Lian Su,^{c, d} Steve Larter,^c Md Golam Kibria,^{*a} Jinguang Hu^{*a}

^a Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive, NW, Calgary, Alberta T2N 1N4, Canada.

^b Department of Chemistry, The University of Sheffield, Western Bank, Sheffield S10 2TN, United Kingdom.

^c State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 122 Luoshi Road, 430070 Wuhan, Hubei, China.

^d Laboratory of Inorganic Materials Chemistry (CMI), University of Namur, 61 rue de Bruxelles, B-5000 Namur, Belgium.

^e Department of Geosciences, University of Calgary, 2500 University Drive, NW, Calgary, Alberta T2N 1N4, Canada.

*Corresponding authors.

E-mail addresses: heng.zhao1@ucalgary.ca (H. Zhao), md.kibria@ucalgary.ca (M.-G. Kibria), jinguang.hu@ucalgary.ca (J.-G. Hu)

Experimental section

g-C₃N₄: Graphitic carbon nitride was prepared by traditional calcination method. Typically, 7.2 g melamine was put in a boat crucible which was covered by another boat crucible. Melamine was annealed at 550 °C for 2 h in Ar atmosphere with a ramp rate of 2 °C/min. The yellow sample was obtained and grounded into fine powder to get the final g-C₃N₄ photocatalyst.

NiTiO₃: Nickel titanate was prepared by sol-gel process. Typically, 10 mmol nickel acetate tetrahydrate was dissolved into 60 mL ethylene glycol until green and transparent solution was formed. 10 mmol titanium (IV) isopropoxide was added dropwise and the mixture was stirred for 2 h at room temperature. The precipitate was collected and washed with 70% isopropanol for three times. Then final photocatalyst was obtained after calcination at 600 °C for 2 h in air with a ramp rate of 2 °C/min.

BiVO₄: Bismuth vanadate was prepared by chemical bath deposition method. Typically, 2 mmol Bi(NO₃)₃·5H₂O was added into 20 ml ethylene glycol solution and stirred until a clear solution was formed, labeled as solution A. Then 2 mmol NH₄VO₃ was added into the 20 ml deionized water and concentrated HNO₃ was added until transparent solution was formed as solution B. Solution B was quickly added into solution A and stirred for about 1h. The precipitate was filtered, washed with deionized water and absolute ethanol several times, and dried at 60 °C for 10 h in air. Finally, the yellow powder was calcined in air at 300 °C for 2 h to get pure BiVO₄ photocatalyst.

TiO₂ and ZnS: TiO₂ (anatase, nanopowder, <25 nm particle size, 99.7% trace metals

basis) and ZnS (powder, 10 μm , 99.99% trace metals basis) were purchased from Millipore Sigma without further purification.

In₂S₃ and CdS: Indium sulfide and cadmium sulfide were prepared by hydrothermal method. Typically, 1.0 mmol InCl₃•4H₂O or 1.5 mmol Cd(NO₃)₂•4H₂O and 1.5 mmol thioacetamide were dissolved in 50 mL deionized water. The transparent solution was transferred into 80 mL Teflon-lined autoclave and kept at 180 °C for 2 h. The In₂S₃ or CdS photocatalyst was finally obtained after washed with 70% isopropanol for three times and dried at 40 °C overnight.

CdIn₂S₄ and NiIn₂S₄: Min₂S₄ (M=Cd and Ni) was prepared in the same procedure as ZnIn₂S₄. The only difference was the change of precursor of 0.5 mmol ZnCl₂ to 0.5 mmol Cd(NO₃)₂•4H₂O or 0.5 mmol Ni(NO₃)₂•6H₂O.

Supporting Figures

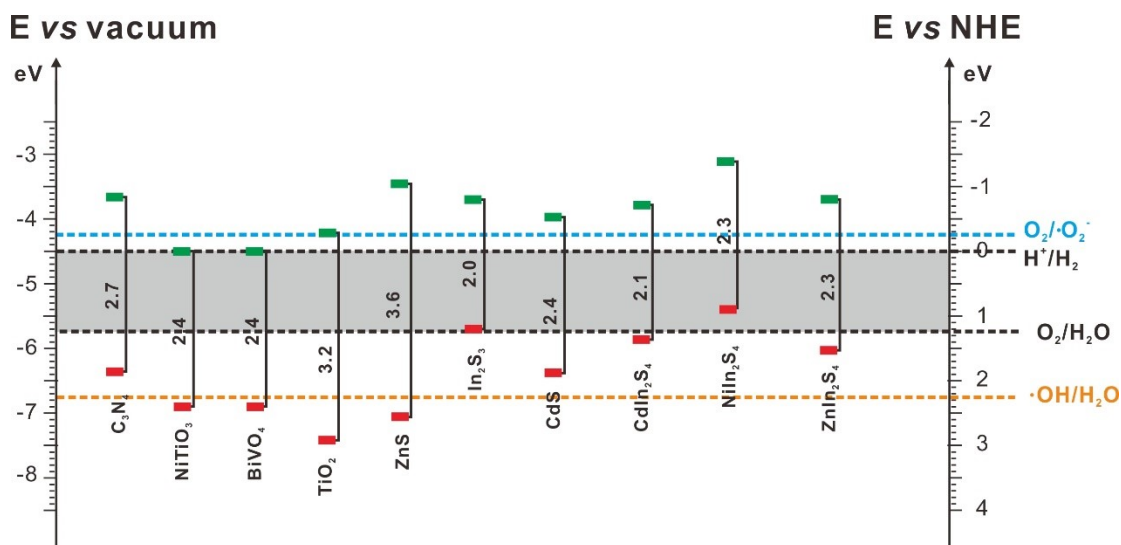


Fig. S1. Band gap structures of different photocatalysts used in this work.

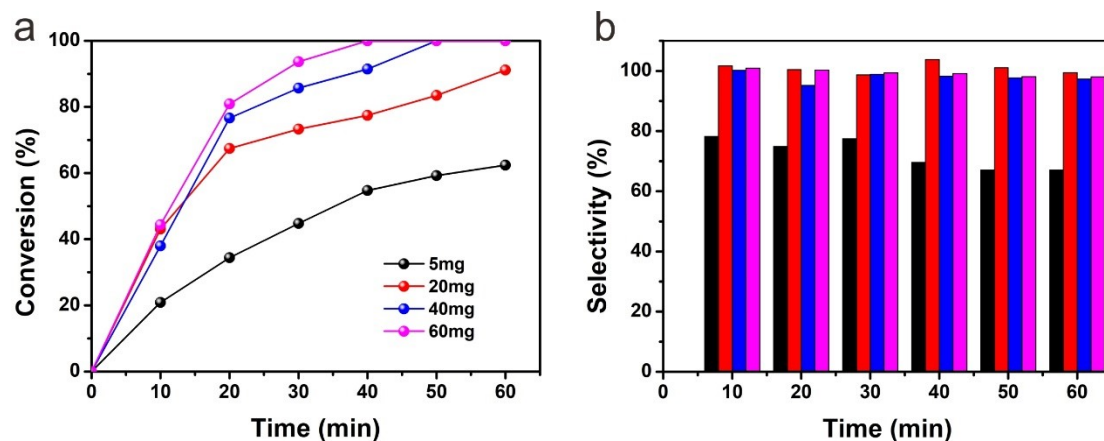


Fig. S2. The effect of catalyst loading on (a) HMF conversion and (b) DFF selectivity.

Reaction condition: 5 mM HMF, 10 mL CH₃CN, O₂, simulated solar light.

Higher photocatalyst loading exhibited higher HMF conversion rate. For the cases of 40 mg and 60 mg of ZnIn₂S₄, all the 5 mM HMF was completely converted within 50 min and 40 min with almost 100% DFF selectivity respectively. While 5 mg of ZnIn₂S₄ only showed ~60% HMF conversion with ~65% DFF selectivity. Herein, 20 mg of ZnIn₂S₄ was chose as the optimized photocatalyst loading.

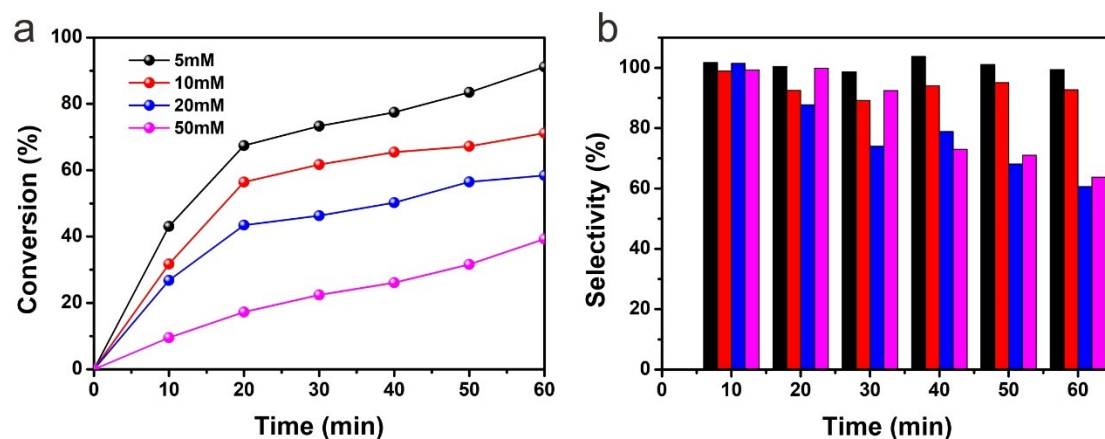


Fig. S3. The effect of HMF concentration on (a) HMF conversion and (b) DFF selectivity. Reaction condition: 20 mg ZnIn_2S_4 , 10 mL CH_3CN , O_2 , simulated solar light.

20 mg ZnIn_2S_4 showed lower HMF conversion and lower DFF selectivity when the concentration of HMF increased. Herein, 5 mM of HMF was finally chose as the optimized substrate concentration.

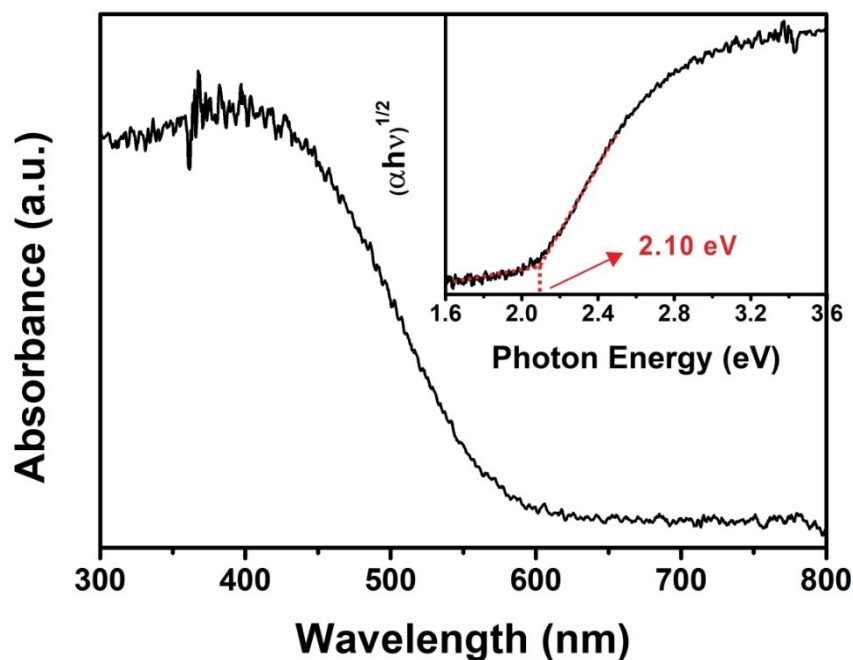


Fig. S4. Light absorption spectrum and corresponding Tauc plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$).

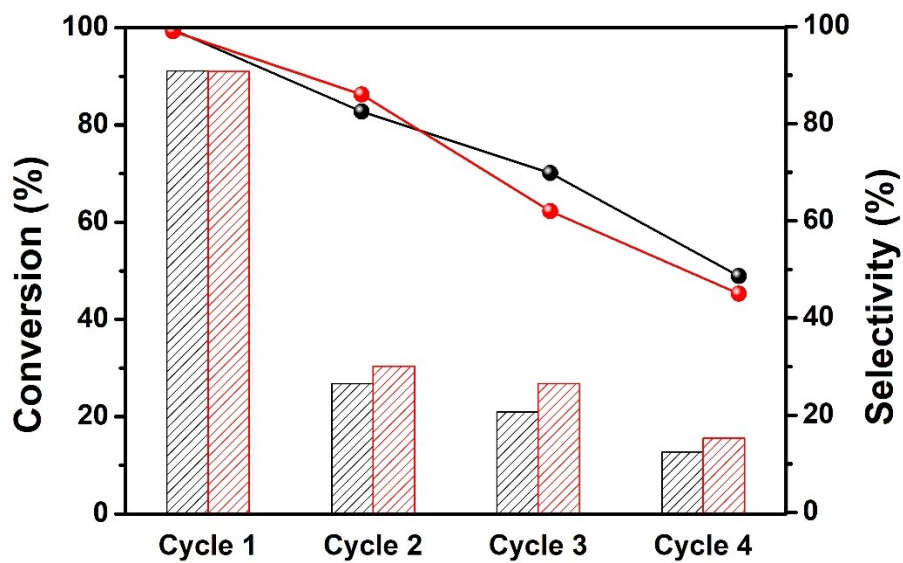


Fig. S5. Cycling tests of ZnIn_2S_4 for HMF conversion (histograms) and DFF selectivity (dotted lines) under simulated solar light (black color) and visible light (red color).

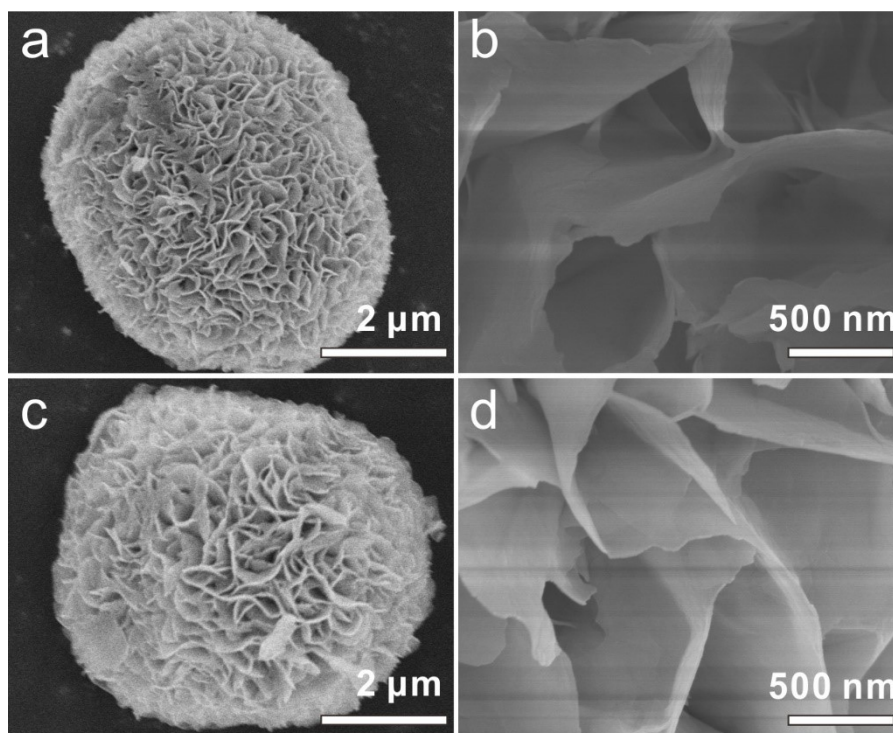


Fig. S6. SEM images of ZnIn_2S_4 before (a, b) and after (c, d) photocatalytic reaction.

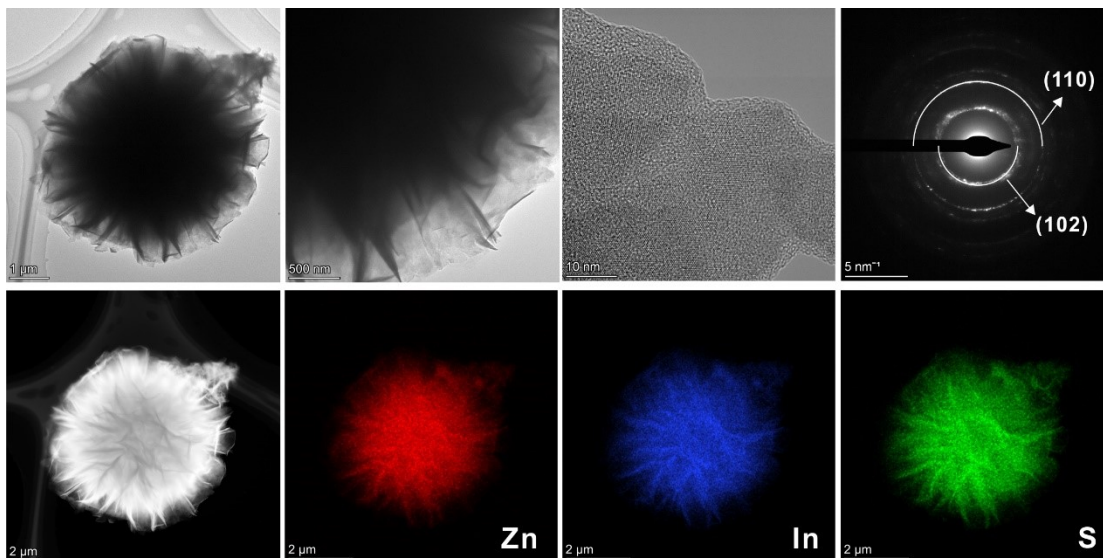


Fig. S7. TEM images in low and high resolutions along with SAED and elemental mappings of the as-fabricated ZnIn_2S_4 .

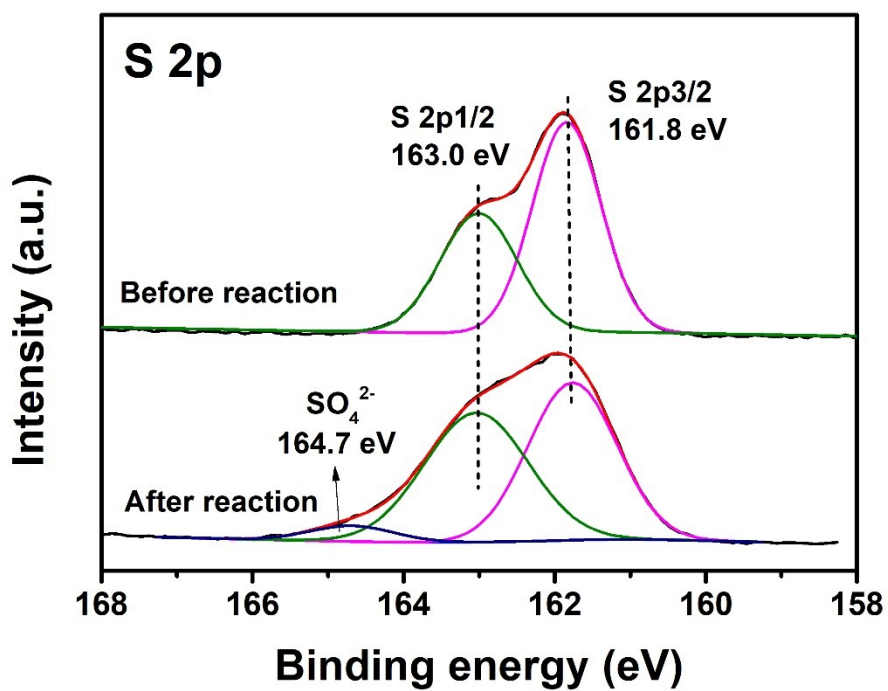


Fig. S8. High resolution XPS spectra of S 2p of ZnIn_2S_4 before and after photocatalytic reaction.

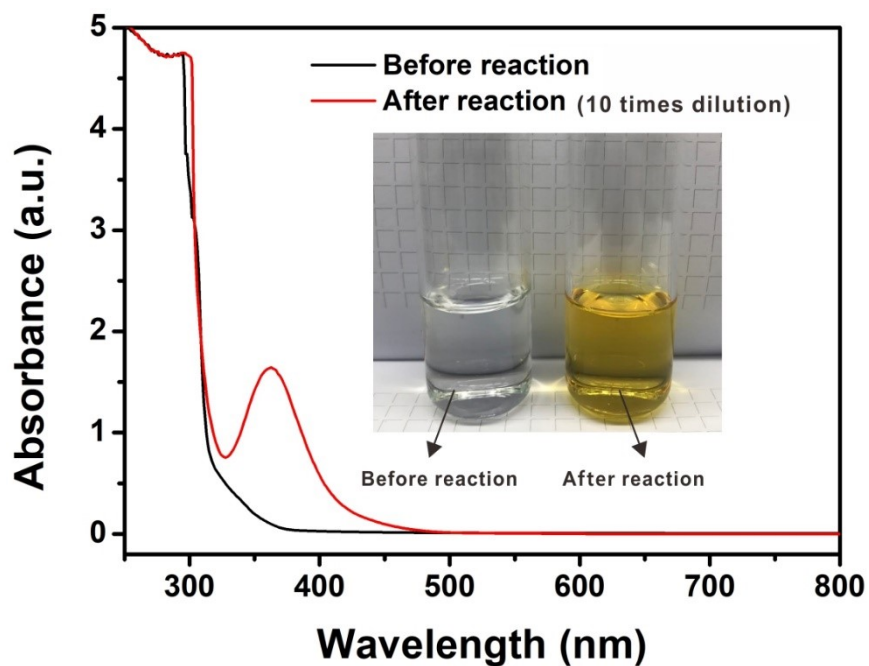


Fig. S9. Light absorption of the solution before and after photocatalytic reaction with addition of excess KI to detect the produced H_2O_2 . Inset is the corresponding photograph.

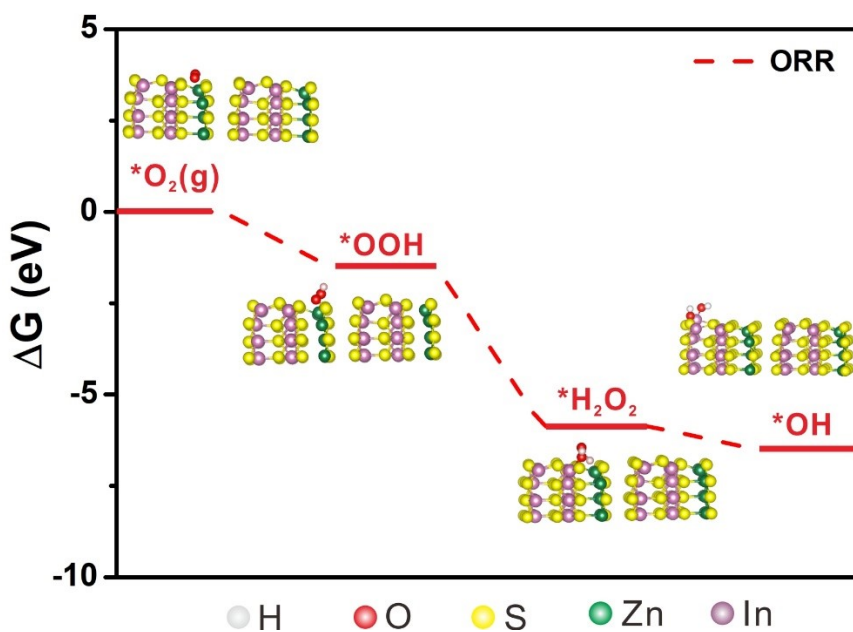


Fig. S10. Reaction energy profiles of O_2 reduction reaction on (110) crystal facet.

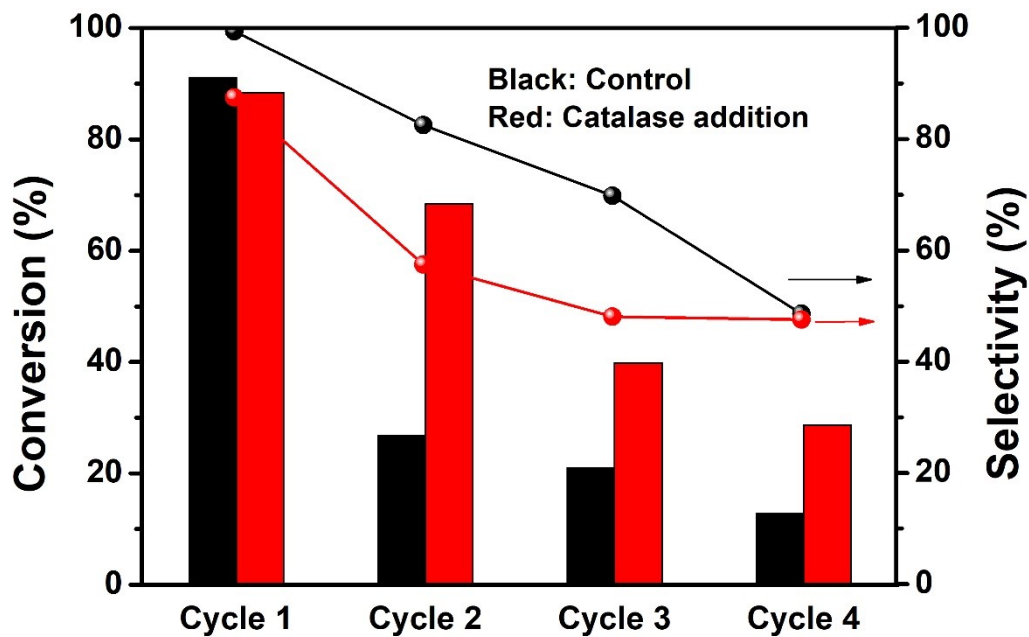


Fig. S11. Comparison of ZnIn_2S_4 for HMF conversion (histograms) and DFF selectivity (dotted lines) between control experiment (black color) and the one with catalase (red color).

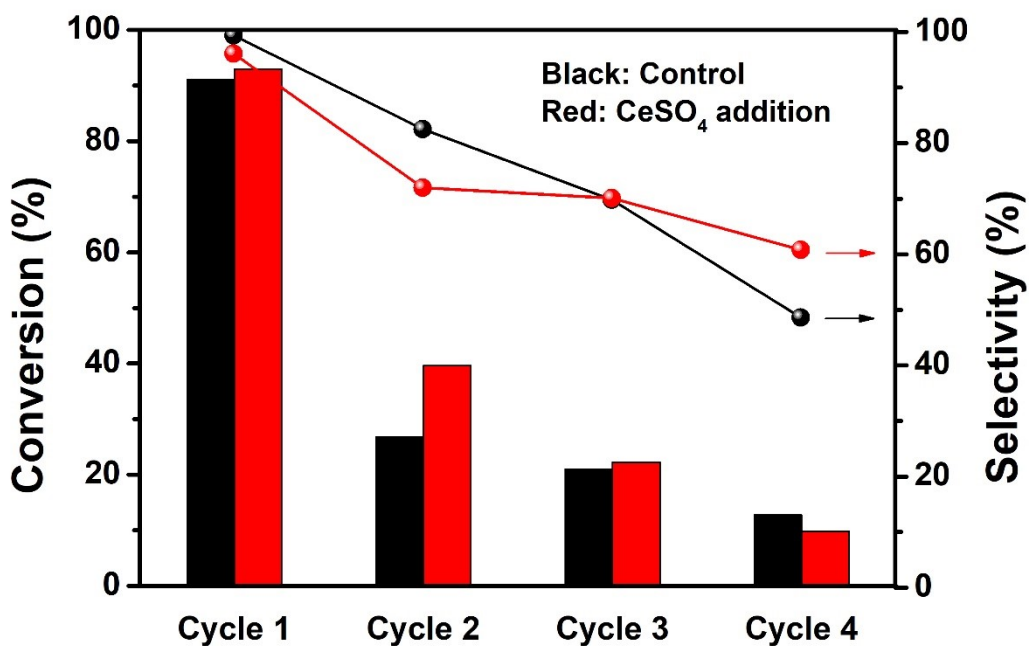


Fig. S12. Comparison of ZnIn_2S_4 for HMF conversion (histograms) and DFF selectivity (dotted lines) between control experiment (black color) and the one with CeSO_4 (red color).

Supporting tables

Table S1. Comparison of literatures on HMF to DFF by photocatalysis.

Photocatalyst	Solvent	HMF (mM)	Tim e (h)	Conv. (%)	Sel. (%)	yield (%)	Ref.
ZnIn ₂ S ₄	MeCN	5	1	91.1	99.4	90.6	This work
MAPbBr ₃	MeCN	5	10	100	90	90	1
CdS	MeCN/Mn(NO ₃) ₂	25	48	99	99	99	2
SGH-TiO ₂	MeCN	1	0.5	59	87	52	3
Fe(III)-Bi ₂ MoO ₆	Water	20	8	32.6	95.3	31.1	4
WO ₃ /g-C ₃ N ₄	MeCN/PhCF ₃	0.1	6	48.3	67.7	32.7	5
P-Zn _x Cd _{1-x} S	Water	16	8	40	65	26	6
Zn _{0.5} Cd _{0.5} S/MnO ₂	Water	16	24	46.6	100	46.6	7
Nb ₂ O ₅	PhCF ₃	0.1	6	19.2	90.6	17.4	8
Au-Ru/rGO	Toluene	50	8	95.7	95	90.9	9

Table S2. The intensity ratio of three major XRD diffraction peaks of ZnIn₂S₄ before and after cycling reactions.

Photocatalyst	I ₍₀₀₆₎	I ₍₁₀₂₎	I ₍₁₁₀₎	I _{(102)/I₍₀₀₆₎}	I _{(110)/I₍₀₀₆₎}	I _{(110)/I₍₁₀₂₎}
ZnIn ₂ S ₄	244	386	457	1.58	1.87	1.18
ZnIn ₂ S ₄ -C1	212	692	468	3.26	2.11	0.68
ZnIn ₂ S ₄ -C2	140	461	300	3.29	2.24	0.65
ZnIn ₂ S ₄ -C3	210	626	384	2.98	1.83	0.61

References

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