Hexagonal Microsphere/Cubic Particle $ZnIn_2S_4$ Heterojunctions: A Robust Photocatalyst for Visible-Light-Driven Conversion of 5-Hydroxymethylfurfural to 2,5-Diformylfuran under Ambient Air Conditions

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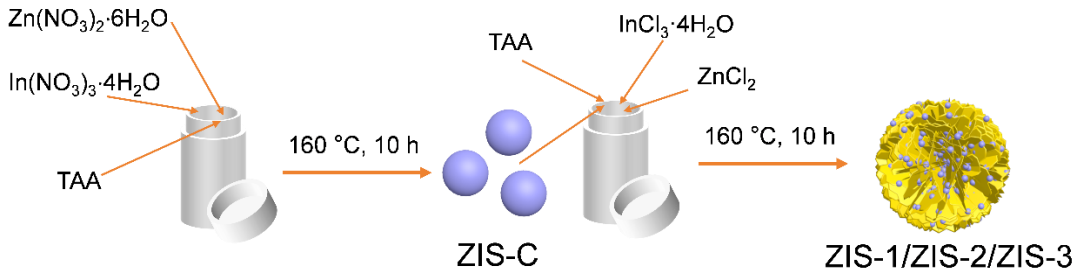
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Supporting Information

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I. Experimental and Characterization Results



Scheme S1. Illustration of the preparation of ZIS composite.

Under aerobic photocatalytic conditions, 5-hydroxymethylfurfural (HMF) underwent selective oxidation to yield 2,5-diformylfuran (DFF) as the product. Reaction mixtures were analyzed using high-performance liquid chromatography (HPLC; Shimadzu LC-20AD system equipped with a C18AQ column, 250 × 4.6 mm, 5 μm). As demonstrated in Figure S1, the chromatographic analysis revealed exclusive detection of HMF and DFF, with no observable byproducts, confirming the high selectivity of the transformation.

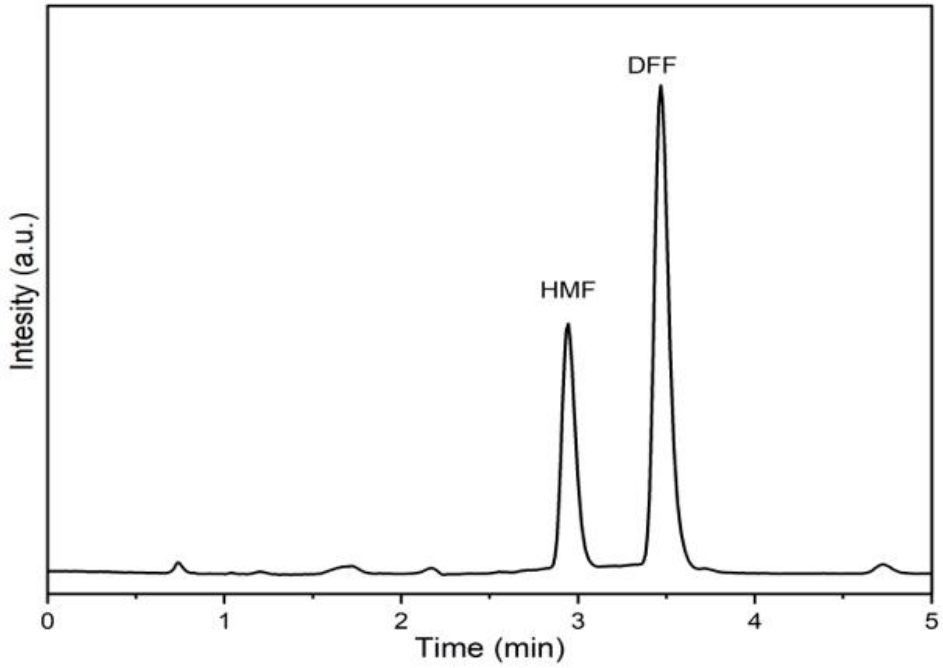


Figure S1. HPLC analysis of HMF and DFF.

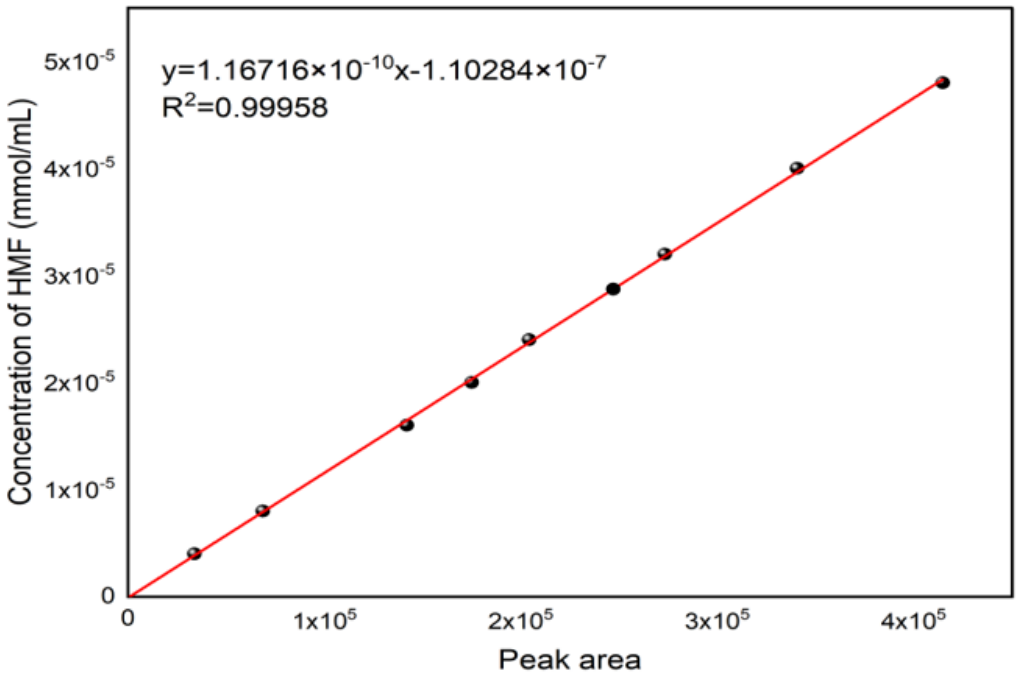


Figure S2. Standard curve of HMF.

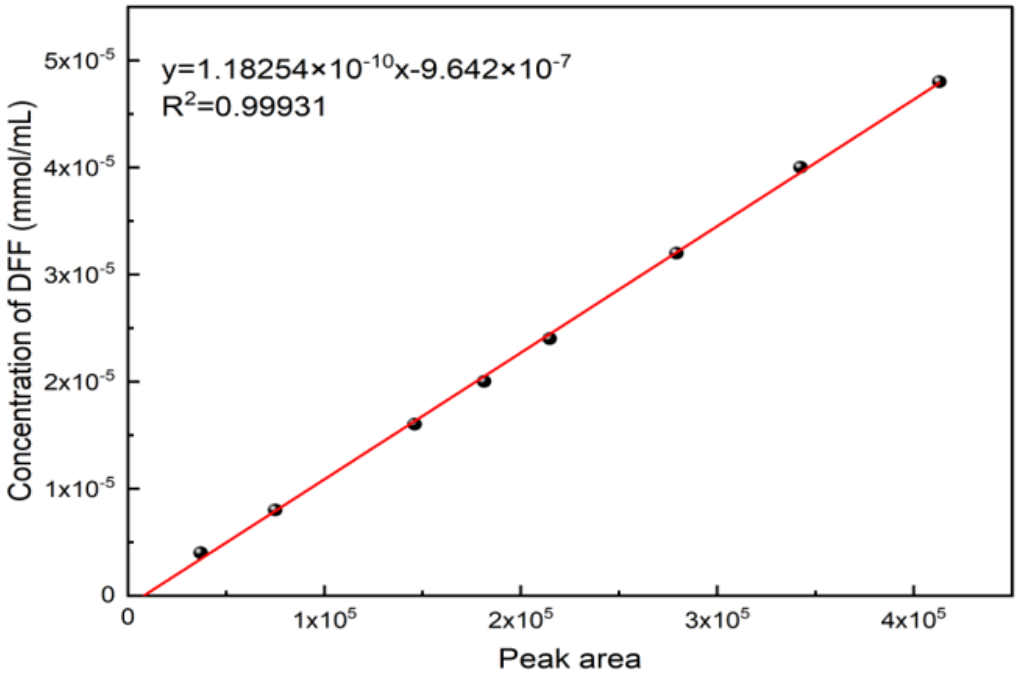


Figure S3. Standard curve of DFF.

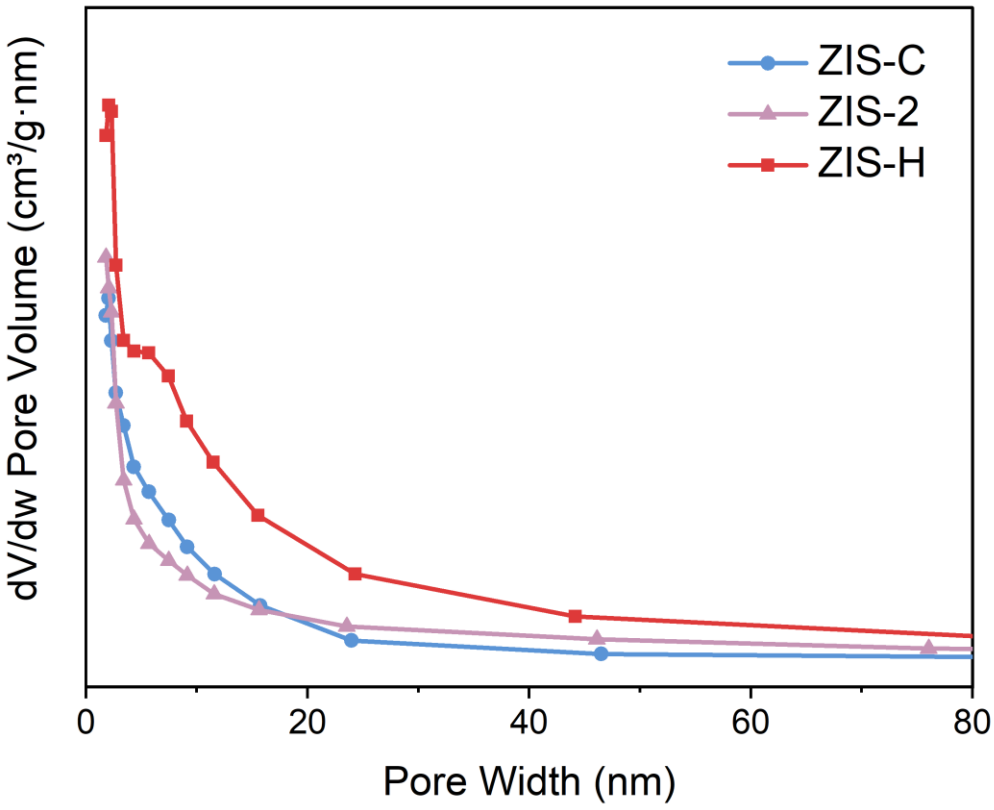


Figure S4. Pore size distribution plots of ZIS-H, ZIS-C, and ZIS-2.

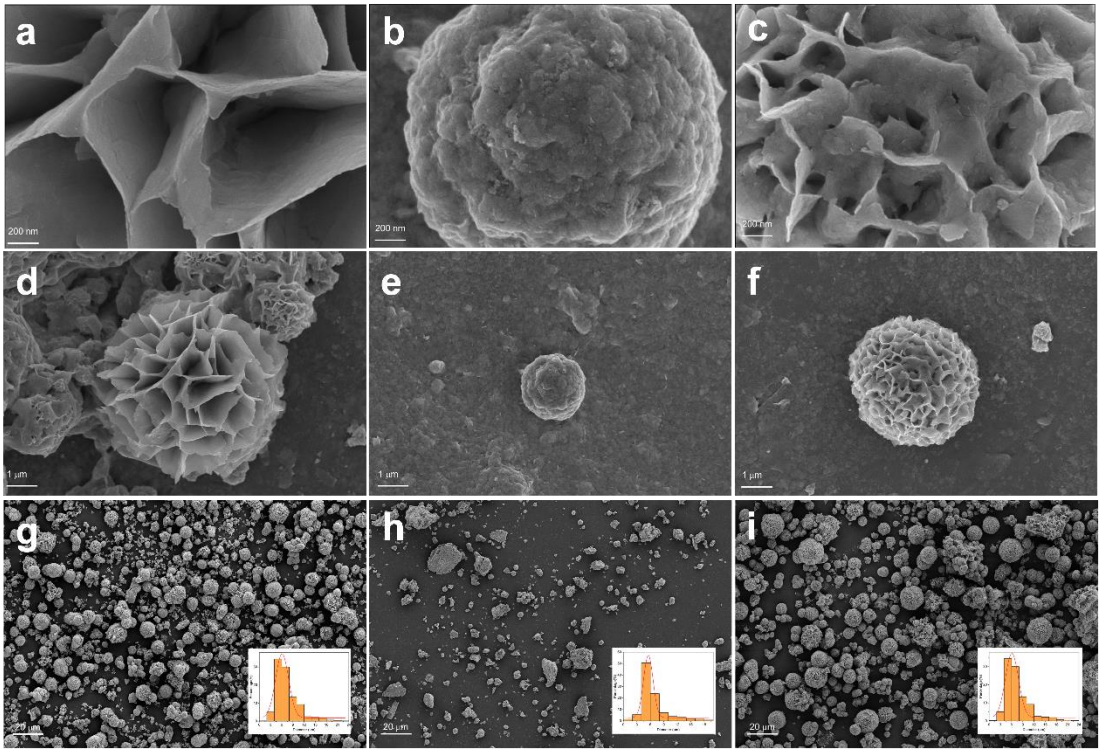


Figure S5. Different magnification SEM images of ZIS-H (**a** and **d**), ZIS-C (**b** and **e**), and ZIS-2 (**c** and **f**). Size distribution of the ZIS-H (**g**), ZIS-C (**h**), and ZIS-2 (**i**).

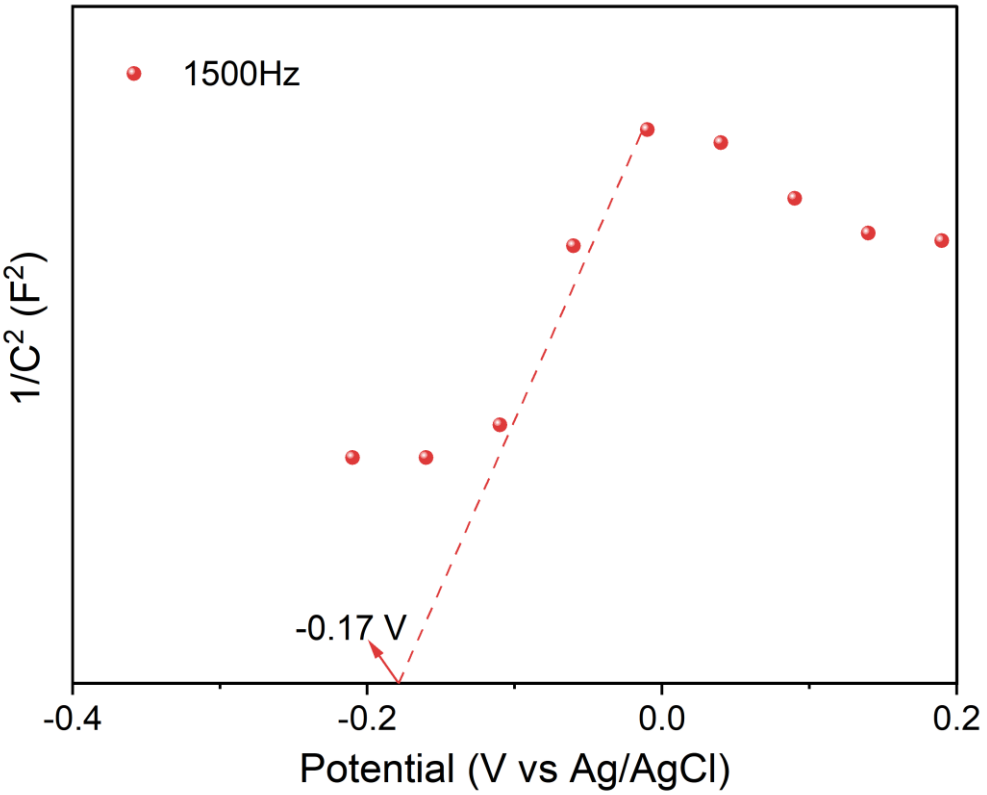


Figure S6. Mott-Schottky curves of ZIS-H.

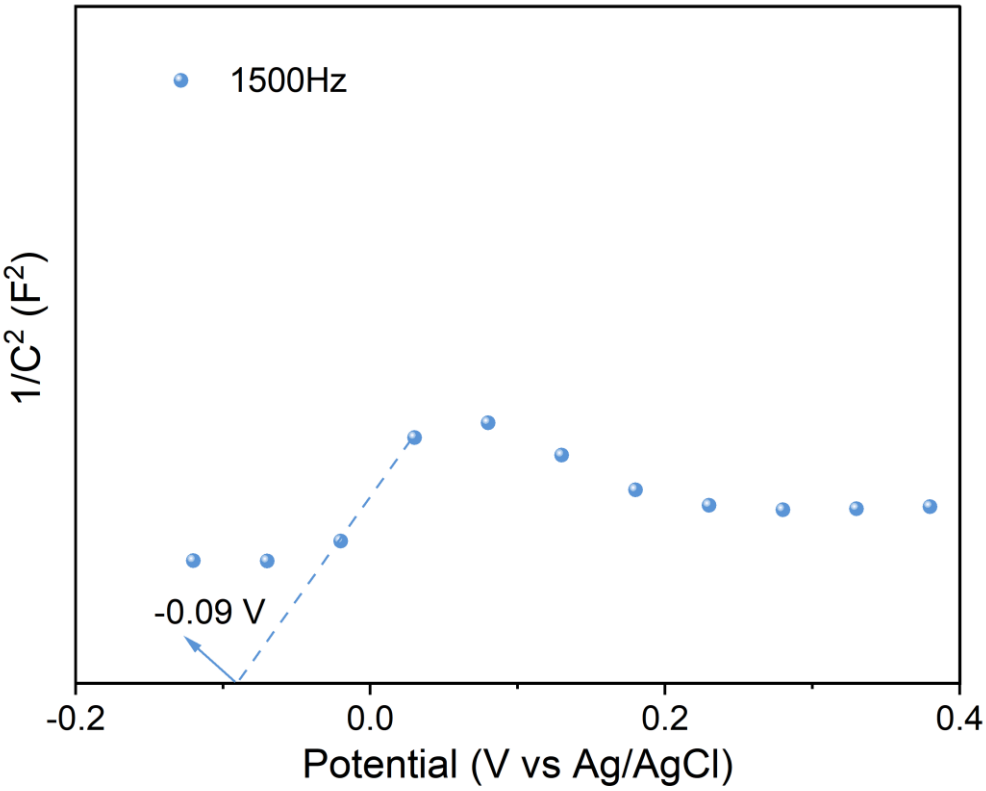


Figure S7. Mott-Schottky curves of ZIS-C.

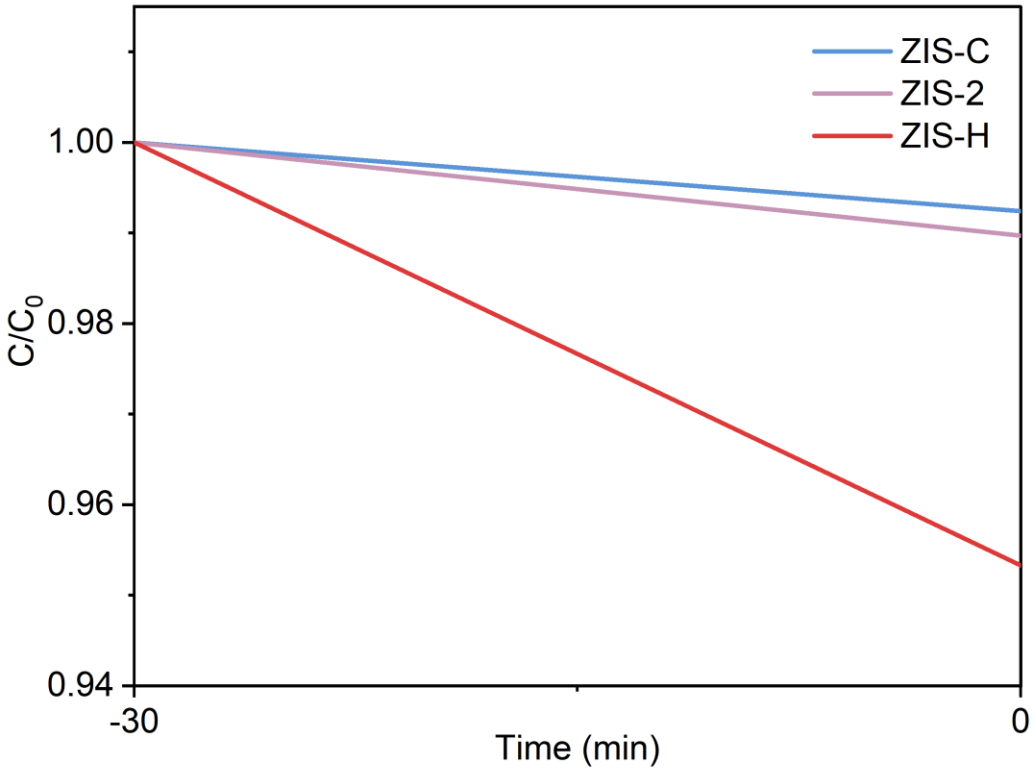


Figure S8. Dark reaction of different catalysts.

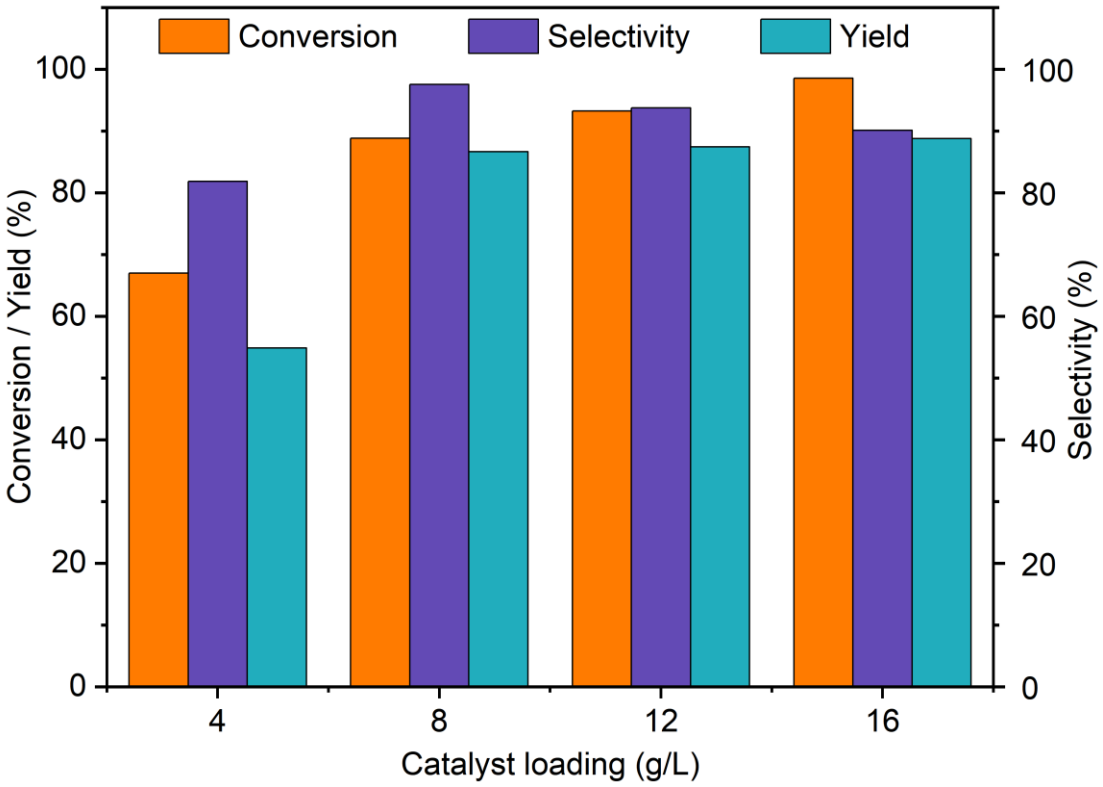


Figure S9. Influence of catalyst loading on photocatalytic oxidation of HMF

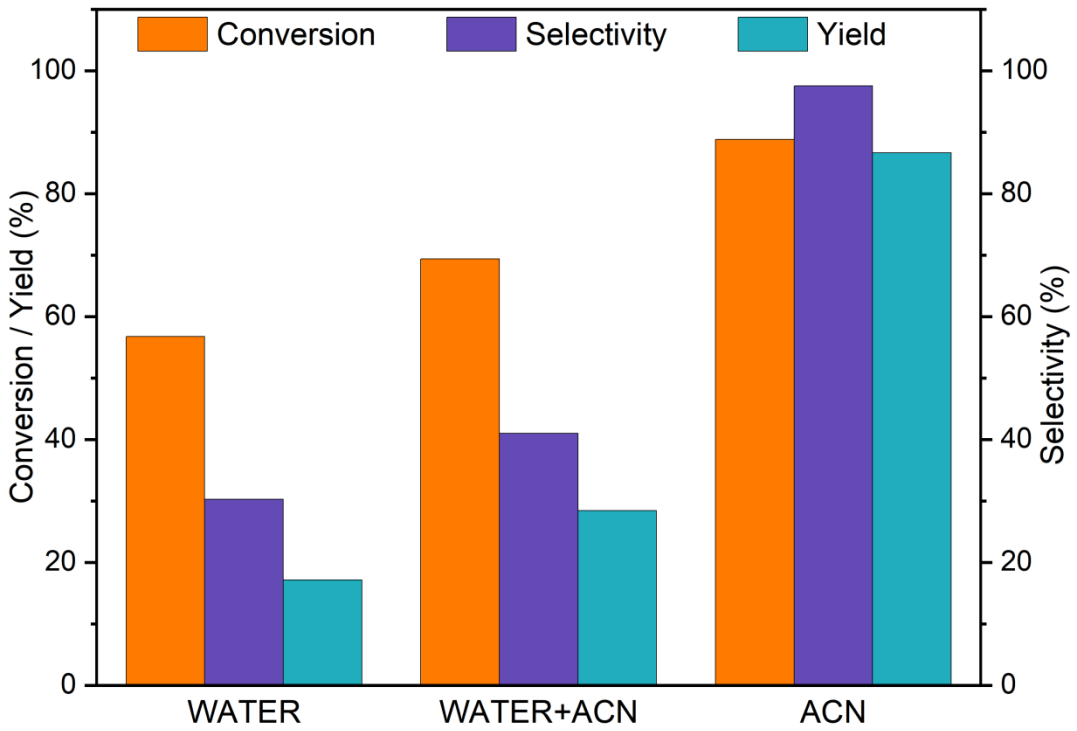


Figure S10. Influence of solvents on photocatalytic oxidation of HMF.

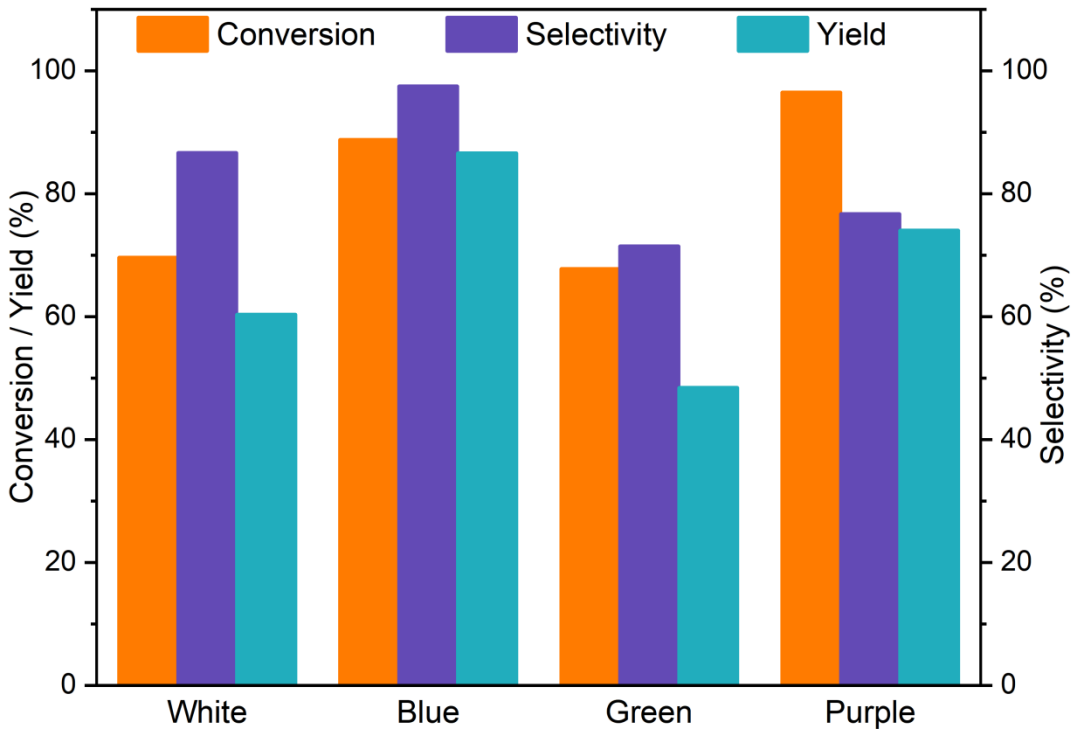


Figure S11. Influence of wavelengths on photocatalytic oxidation of HMF.

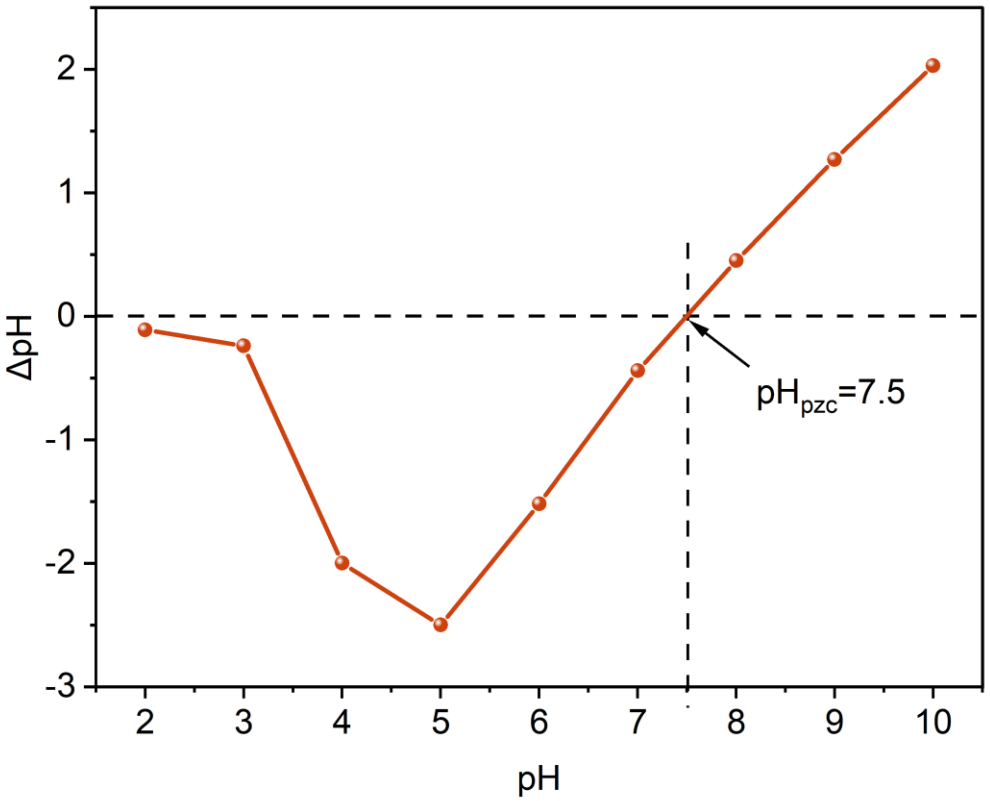


Figure S12. The point of zero charge (PZC) of ZIS-2.

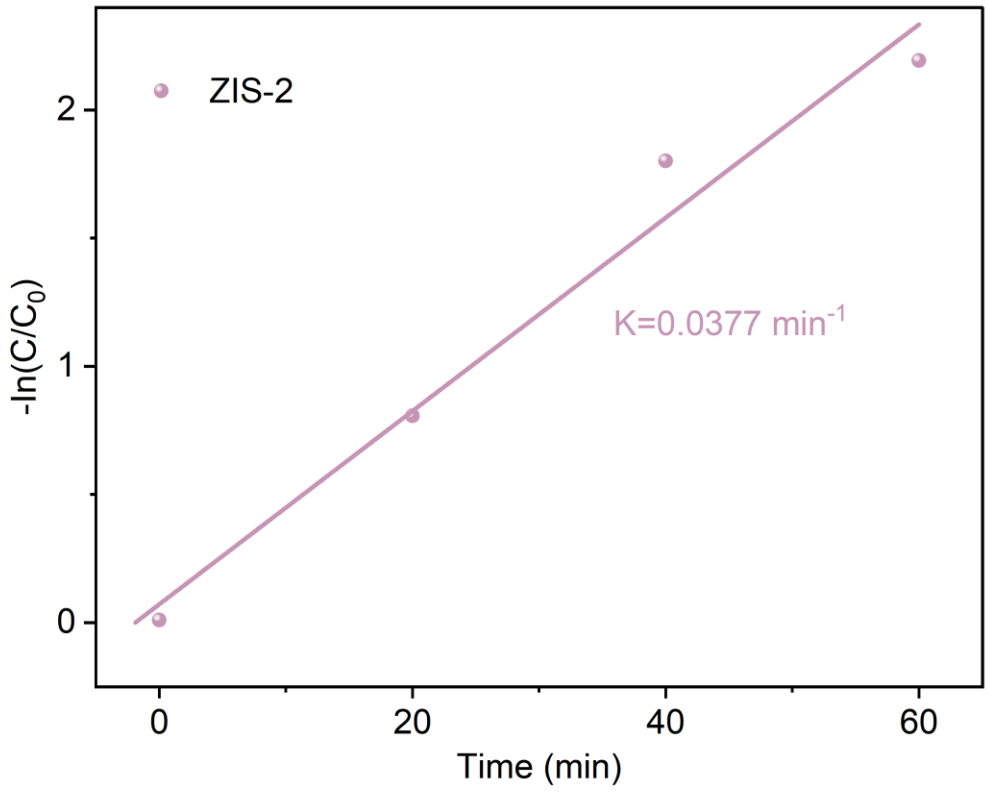


Figure S13. Apparent rate constants of the reaction.

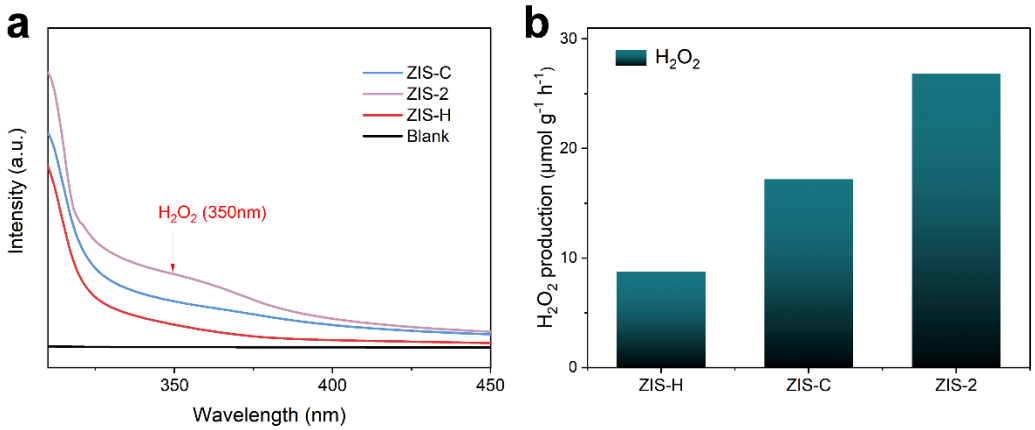


Figure S14. (**a**) UV–Vis spectra of H_2O_2 production. (**b**) The H_2O_2 production of different catalysts.

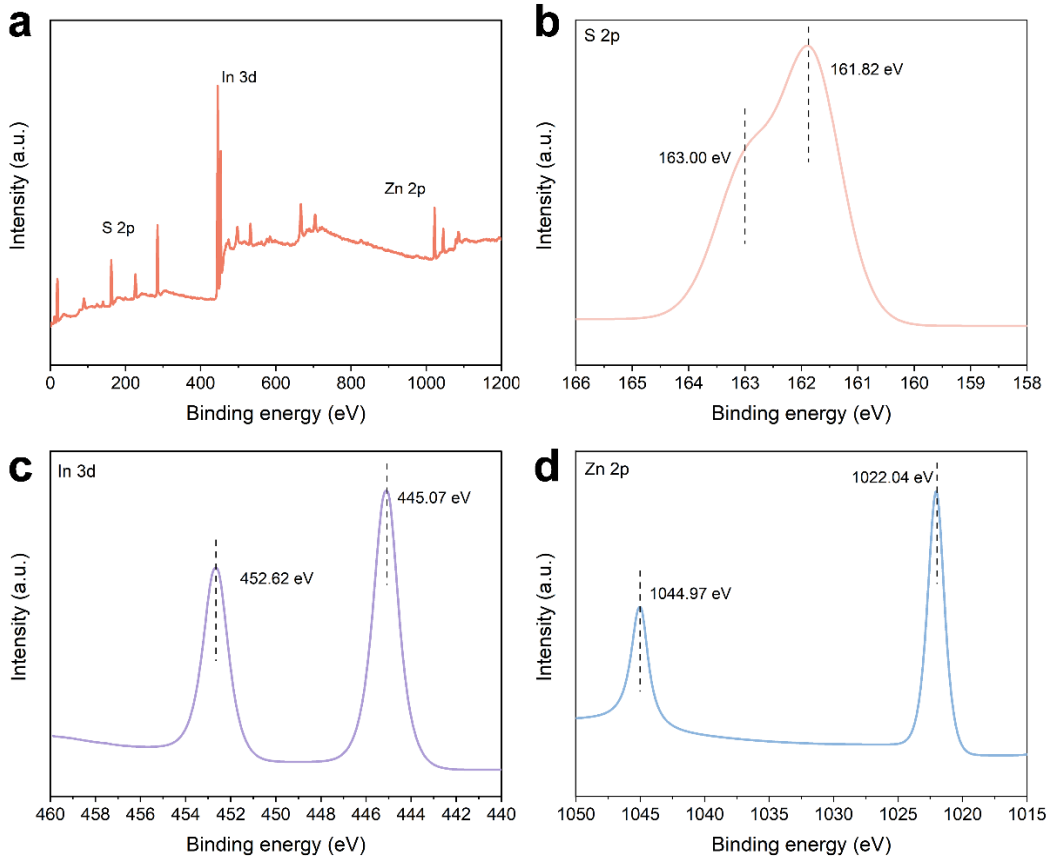


Figure S15. (a) XPS survey spectra and the high resolution XPS spectra of **(b)** Zn 2p, **(c)** In 3d, **(d)** S 2p of ZIS-2 after the cyclic reaction.

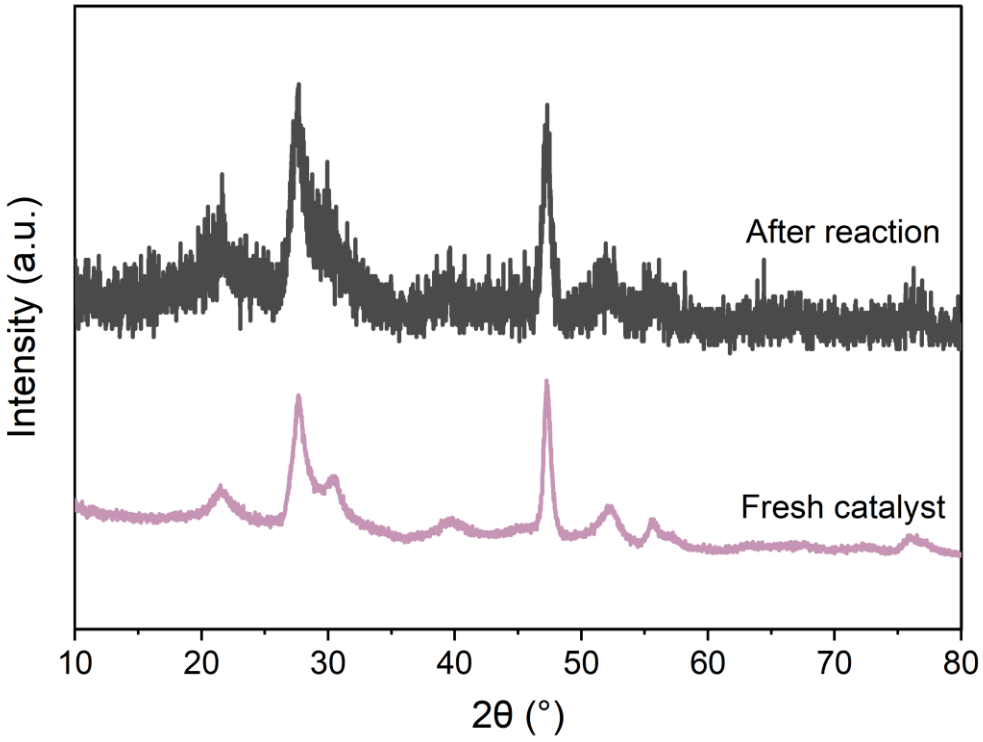


Figure S16. XRD diffraction patterns of ZIS-2 before and after the catalysis.

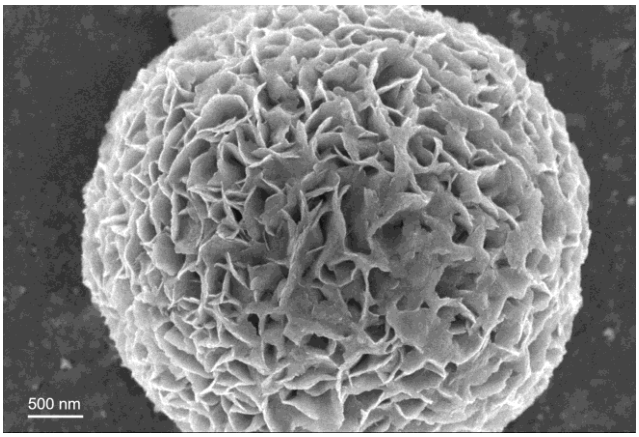


Figure S17. SEM of ZIS-2 after the catalysis.

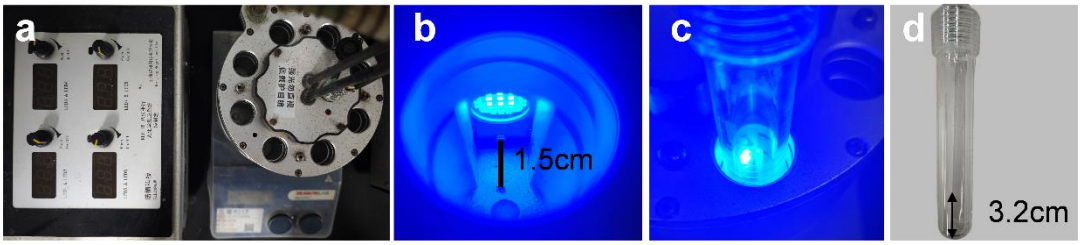


Figure S18. (**a**) Top view of photoreactor. (**b**) The distance from the light source to the bottom of the reaction tube. (**c**) Photo of the under blue LED. (**d**) Photo of the reaction tube.

Table S1. Conversion of HMF to DFF using ZIS-2 catalyst under varied conditions.

Entry	Catalyst	Light	Atmosphere	Conv. (%)	Select. (%)	Yield. (%)
1	ZIS-2	–	Air	traces	–	–
2	–	10 W 455 nm	Air	–	–	–
3	ZIS-2	10 W 455 nm	N_2	73.5	77.1	56.7
4	ZIS-2	10 W 455 nm	Air	88.8	97.5	86.6

Reaction conditions: 10 mM of HMF, 40 mg of catalyst, 25 °C, 1 h.

Table S2. Specific surface area, pore volume, and pore size of ZIS-H, ZIS-C, and ZIS-2.

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
ZIS-H	72.46	0.19	5.45
ZIS-C	38.88	0.06	4.16
ZIS-2	44.84	0.09	5.28

Table S3. Technical specifications of the RLH-18 parallel photoreactor.

Specifications	Parameters
Operating voltage	220 V, 50 Hz
Wavelength Options	275 nm (max 10 W), 455 nm (max 10 W), 525 nm (max 10 W)
Irradiance of the light	150 mW/cm^2 (455 nm ,10 W)

Table S4. Equivalent circuit fitting parameters of ZIS-H, ZIS-C, and ZIS composites.

Catalyst	Rs (Ω)	Rct (Ω)
ZIS-H	290.8	14518
ZIS-C	107.8	13816
ZIS-1	105.2	7486
ZIS-2	38.31	5825
ZIS-3	110.7	9859

II. Comparison of Reaction Results in Recent Studies

Table S5. Comparative of photocatalytic HMF-to-DFF conversion in recent studies.

Catalyst	Synthesis method	Morphological	Light source	HMF (mM)	Catalyst load (g/L)	Atmos-phere	Conv. (%)	Select. (%)	Yield. (%)	Refs
ZIS-2	Solvothermal	Microsphere	10 W blue LED (455 nm)	10	8	Air	88.8	97.5	86.6	This work
MCN	Thermal condensation	Bulk	Fluorescent lamp (340–420 nm)	0.5	0.7	O_2	50.0	35.0	17.5	45
Bi_2WO_6	Hydrothermal	Rose-like	300 W Xe lamp	30	4	O_2	58.3	99.5	58.0	46
Ni/CdS	Simple chemical reduction	Nanosheet	8 W blue LED (440–460 nm)	5	1	N_2	24.6	100	24.6	47
NiS_2/CdS	Solvothermal	Particles	300 W Xe lamp	10	0.5	N_2	54.5	95.2	51.9	48
SGH-TiO_2	Sol-gel-assisted	Nanoparticles	Green LED lamp (515 nm)	1	1	Air	59.0	87.0	51.3	49
S-vacancy $ZnIn_2S_4$	Hydrothermal	Flower-shaped nanosheets	20 W blue LED (445 ± 10 nm)	5	0.7	Air	96.5	79.9	77.1	35
Co_3O_4/ZIS	Solvothermal	Nanosheets	300 W Xenon lamp	1	1	Air	78.4	70.4	55.2	50

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