

Electronic Supplementary Information

Photocatalytic production of C₁₂ liquid biofuel precursor and H₂ by Ni(OH)₂-ZnIn₂S₄ in anaerobic water

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Experimental section

1. Materials. Indium chloride tetrahydrate ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$), thioacetamide (CH_3CSNH_2), zinc chloride (ZnCl_2), sodium hydroxide (NaOH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), ammonium acetate ($\text{CH}_3\text{COONH}_4$), N, N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, DMF), isopropanol ($\text{C}_3\text{H}_8\text{O}$, IPA), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), thiourea ($\text{CH}_4\text{N}_2\text{S}$) and acetonitrile (CH_3CN , ACN) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium borohydride (NaBH_4) was supplied by Tianjin Comiou Chemical Reagent Co., Ltd. (Tianjin, China). Triethanolamine ($\text{C}_6\text{H}_{15}\text{NO}_3$, TEOA) was supplied by Tianli Chemical Reagent Co., Ltd. (Tianjin, China). Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was obtained from Tianjin Damao Chemical Reagents Factory (Tianjin, China). 5-hydroxymethyl-2-furancarboxylic acid ($\text{C}_6\text{H}_6\text{O}_4$, HMFCA), 2,5-diformylfuran ($\text{C}_6\text{H}_4\text{O}_3$, DFF), 5-formylfuran-2-carboxylic acid ($\text{C}_6\text{H}_4\text{O}_4$, FFCA) and 4-chloro-2-nitrophenol ($\text{C}_6\text{H}_4\text{ClNO}_3$, CN) were supplied by Maclin Biochemical Technology Co., Ltd. (Shanghai, China). 5-hydroxymethyl-2-furaldehyde ($\text{C}_6\text{H}_6\text{O}_3$, HMF) and 2,5-furandicarboxylic acid ($\text{C}_6\text{H}_4\text{O}_5$, FDCA) were supplied by Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Deionized water (18 $\text{M}\Omega \cdot \text{cm}$) from a YL-100BU (V5) system was produced in the lab. All the above chemicals were analytically pure. Methanol (CH_3OH , MeOH) and acetonitrile (CH_3CN) supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were chromatographically pure.

2. Preparation of the catalysts.

2.1. Preparation of ZnIn_2S_4 nanosheets (ZIS): In a typical experiment, 0.4 mmol ZnCl_2 , 0.8 mmol $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and 3.2 mmol thioacetamide were first dissolved in the mixture of 15 mL water and 15 mL ethanol. After vigorous stirring for 30 min, the mixture was transferred into a 50 mL Teflon-lined autoclave, sealed and heated at 180 °C for 24 h. After cooling to room temperature naturally, the obtained products were collected by centrifugation. After being washed with distilled water and ethanol for several times, and dried in freezer dryer, the ZIS catalyst was obtained.

2.2. Preparation $\text{Ni}(\text{OH})_2$ -modified ZnIn_2S_4 ($\text{Ni}(\text{OH})_2$ -ZIS): Typically, as-prepared ZIS (0.4 g) was dispersed in NaOH aqueous solution (30ml, 0.25 M) and stirred for 30 minutes, then $\text{Ni}(\text{NO}_3)_2$ (0.05 M) with different volume was added dropwise under stirring. And then the resulting mixture was stirred for 6 h at room temperature. After that, the final product was washed by deionized water and ethanol with centrifugation for three times respectively, and then dried in a vacuum oven at 60 °C for 12 h. By adjusting the volume of $\text{Ni}(\text{NO}_3)_2$ added into the solution, $\text{Ni}(\text{OH})_2$ -ZIS with different amounts of $\text{Ni}(\text{OH})_2$ was obtained. Different nominal molar ratios of $\text{Ni}(\text{OH})_2$ to (ZIS + $\text{Ni}(\text{OH})_2$) with $R=0, 1, 2, 3,$ and 4% were prepared and characterized.

3. Characterizations. Transmission electron microscopy (TEM) images were obtained using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns of the samples were collected on a Bruker D8 Advance X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA in the 2θ ranging from 15° to 85° with a scan rate of 4° per minute. The optical properties of the samples were analyzed by UV-vis diffuse reflectance spectroscopy (DRS)

using a UV-vis spectrophotometer (Cary 500, Varian Co.), in which BaSO₄ was employed as the internal reflectance standard. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCA Lab 250 spectrometer which consists of monochromatic Al K α as the X-ray source, a hemispherical analyser, and a sample stage with multiaxial adjustability to obtain the surface composition of the samples. All of the binding energies were calibrated by the C 1s peak at 284.8 eV. The electron paramagnetic resonance (EPR) signal of the radical spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was measured on a Bruker EPR A300 spectrometer. The sample powders (10 mg) were dispersed in a mixed solution of 10 mL water containing 0.1 mmol HMF and 0.1 mmol dimethylpyridine nitrogen oxide (DMPO) and placed in a sealed glass tube under argon (Ar) atmosphere. The mixture was oscillated to obtain a well-blending suspension. A 300 W Xe arc lamp (PLS-SXE 300D, Beijing Perfectlight Technology Co., Ltd.) with a filter to cut off light of wavelength $\lambda < 420$ nm was used as the irradiation source. The structures of HMF oxidation products were further confirmed on the LC-MS system (Agilent 1290II-6460 series) using ESI techniques. The LC-MS system equipped with an Agilent Technologies, Inc. SB-C₁₈ column (1.8 μ m, 2.1 mm \times 100 mm). Inductively coupled plasma mass-spectrometry (ICP-MS, NexION 1000G) was utilized to quantify the leaching of Ni(OH)₂ from ZIS surface by testing the final reaction mixture.

4. Photoactivity testing: The photocatalytic activities of the as-prepared materials were evaluated by the photocatalytic redox of HMF with a 300 W Xe lamp (PLS-SXE 300/300UV, Beijing Perfectlight Co., Ltd.) with a filter to cut off light of wavelength $\lambda \geq 420$ nm was used as the light source. In a typical process, 0.01 g of the as-prepared sample and 10 mL of 10 mM HMF with different solvents were added into a quartz reactor. Before irradiation, the mixture sonicated for 30 min to guarantee the probability of adsorption or reactivity and then in the air or purged with N₂ gas for 30 min to remove air. Photoactivity of quenching experiments with addition of different scavengers. The reaction was sustained for 4 h under illumination and agitation. (TEOA as scavenger for photogenerated holes, IPA as scavenger for hydroxyl radicals, and K₂S₂O₈ as scavenger for photogenerated electrons, were carried out similar to the above photoredox-catalyzed HMF conversion integrated with DFF selectivity except that scavengers (0.1 mmol) were added to the reaction system. After the reaction, the gas product was analyzed by a gas chromatograph (Shimadzu GC-2014C, MS-5 A column, TCD, argon (Ar) carrier). The liquid products were analyzed as followed: 10 μ l sample was collected, and then analyzed by high-performance liquid chromatography (HPLC) on a Waters 1525. The HPLC was equipped with an ultraviolet-visible (UV) detector set at $\lambda = 263$ nm and a C₁₈ column (4.6 mm \times 250 mm Agilent ZORBAX SB - Aq 5 μ m) at 40 °C of column temperature. A mixture of eluting solvents (A: 5 mM ammonium acetate aqueous solution and B: methanol) was utilized. For the HMF related chemicals, the elution is composed of 85% A and 15% B for 22 min run time and the flow rate was set at 1 mL min⁻¹. HMF and the corresponding products were identified and quantified by comparison to genuine samples, except for BHMF and DHMF. Since a commercial sample was not available for BHMF and DHMF, the calibration was estimated as twice that of HMF,

consistent with the previous reports.^{1, 2} The conversion efficiency of HMF to the oxidation products were quantified using the following equations³ :

$$\text{HMF Conversion (\%)} = \frac{\text{mol of HMF consumed}}{\text{mol of initial HMF}} \times 100\% \quad (1)$$

$$\text{Product yield (\%)} = \frac{\text{mol of product formed}}{\text{mol of initial HMF}} \times 100\% \quad (2)$$

$$\text{Product selectivity (\%)} = \frac{\text{mol of product formed}}{\text{mol of HMF consumed}} \times 100\% \quad (3)$$

The apparent quantum efficiency (AQE) was calculated from the ratio of twice the number of H₂ molecules to the number of incident photons by using the following expression: AQE = (2 × Number of H₂ molecules formed in 4 h / Number of incident photons in 4 h) × 100%. The “Number of incident photons” was measured using a PLD MOPM-I Multifunctional optical power meter. Only the incident light intensity in the range of 420-550 nm was considered for the calculation of quantum yield, based on the UV-Vis absorption of the catalysts.

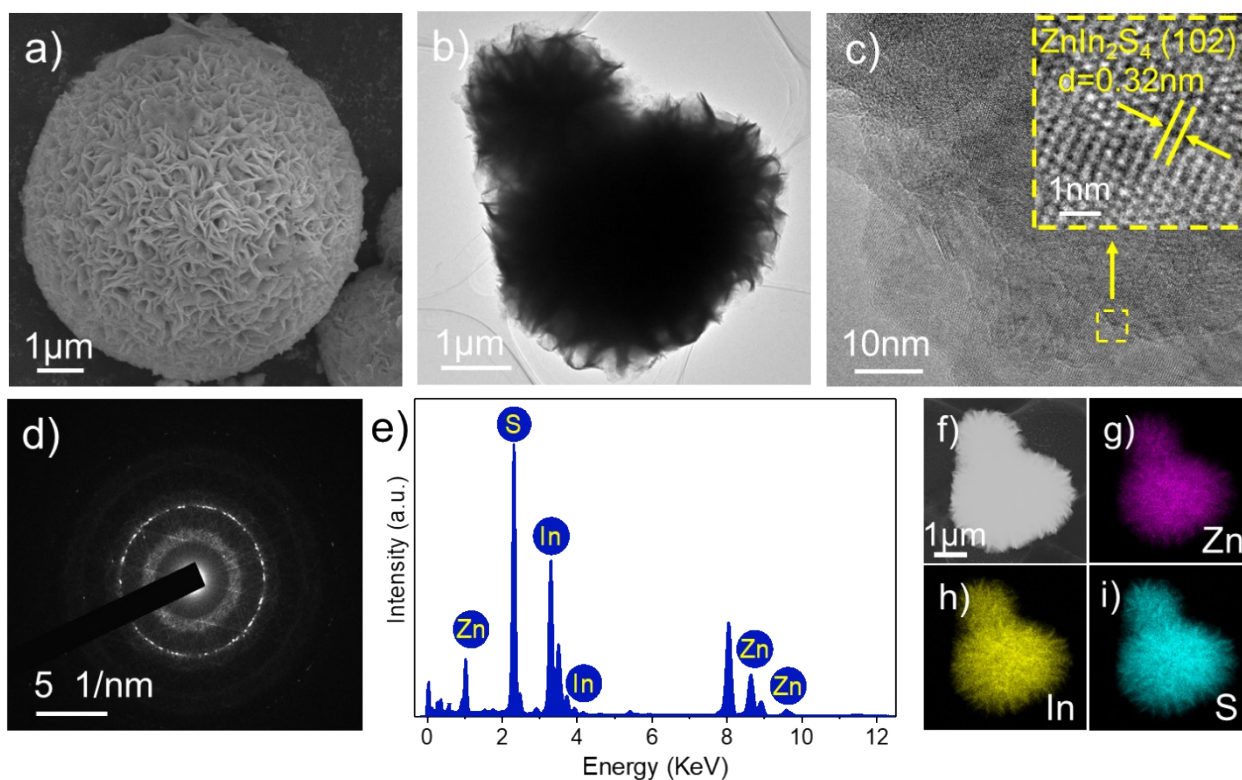


Figure S1. (a) SEM image, (b) TEM image, (c) HRTEM image and (d) the selected area electron diffraction (SAED) pattern of ZIS. (e) The energy-dispersive X-ray spectroscopy (EDX) spectrum of ZIS. (f) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of ZIS, and (EDX) mapping images of its (g) Zn, (h) In and (i) S elements.

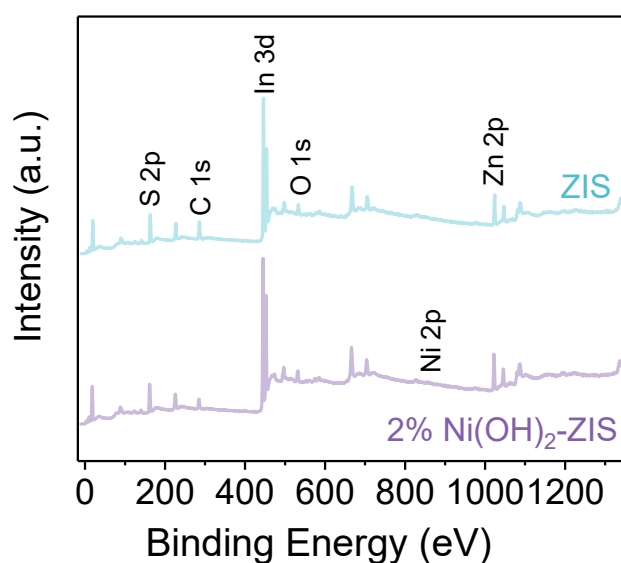


Figure S2. Survey XPS spectra for ZIS and 2% Ni(OH)₂-ZIS.

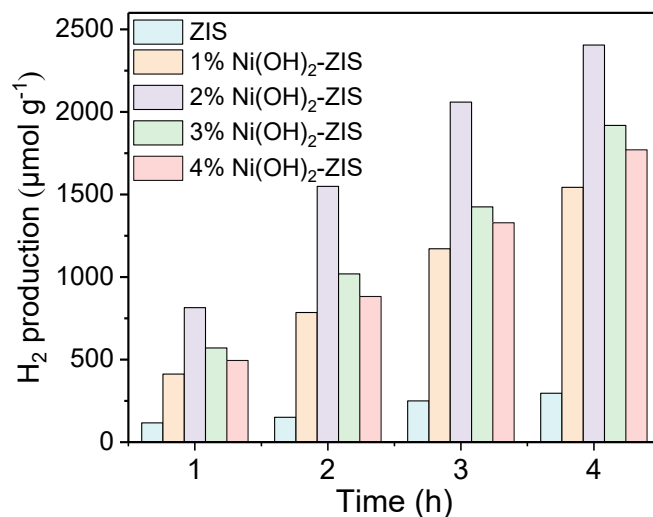


Figure S3. H₂ evolution over bare ZIS of various Ni(OH)₂-ZIS samples in various time within 4-h photocatalytic HMF transformation under N₂.

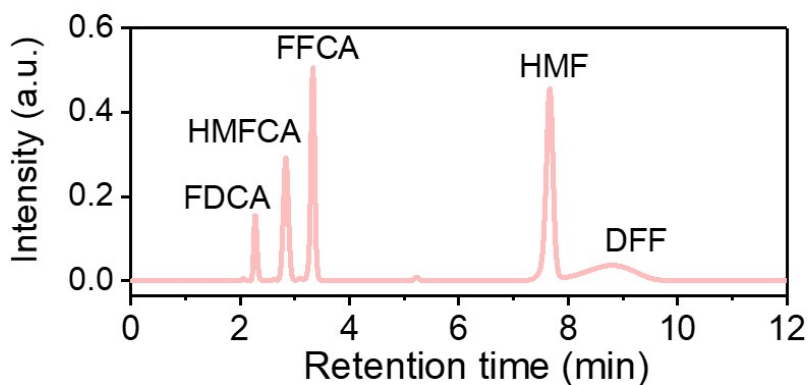


Figure S4. Exemplary HPLC chromatogram of mixed standard samples of possible product of HMF oxidation.

Note: The liquid products for the samples are measured by the high-performance liquid chromatography (HPLC) and no peak related to the mostly reported oxidative products of HMF, including standard samples of FDCA, FFCA, HMFCA and DFF, can be detected.

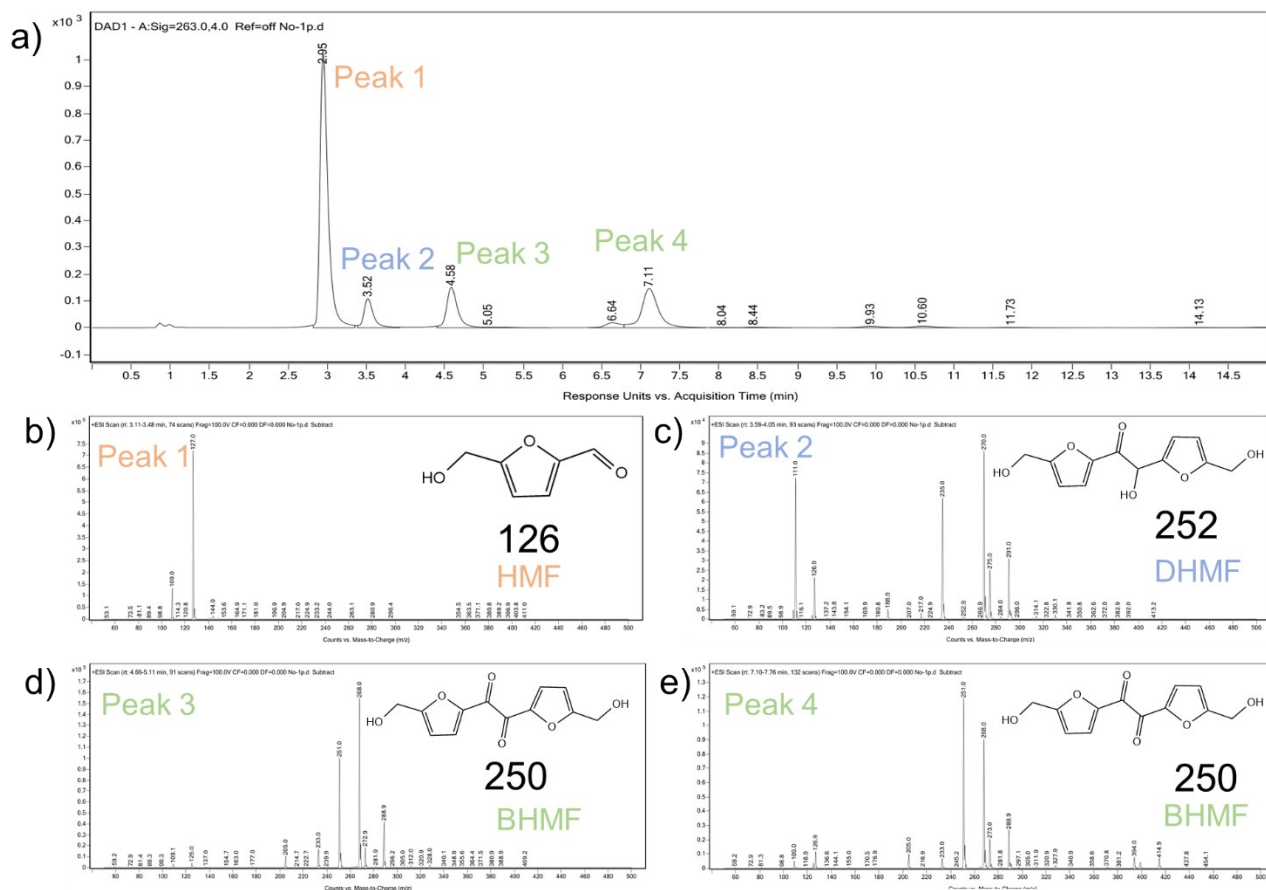


Figure S5. (a) LC-MS spectra recorded in the solution after photocatalytic reaction over 2% Ni(OH)₂-ZIS catalyst, and the corresponding positive ESI-MS spectra for the identification of (b) HMF and two main products: (c) DHMF and (d, e) BHMF.

Note: In positive scan the peaks could give coupling with proton (m/z 1), NH₄ (m/z 18), sodium (m/z 23), potassium (m/z 39).⁴ (b) The peak with $m/z = 127 - 1 = 126$ corresponds to HMF; (c) The peaks with $m/z = 270 - 18 = 252$, $m/z = 275 - 23 = 252$, $m/z = 291 - 39 = 252$ corresponds to DHMF; (d, e) the peaks with $m/z = 251 - 1 = 250$, $m/z = 268 - 18 = 250$, $m/z = 273 - 23 = 250$, $m/z = 289 - 39 = 250$ corresponds with the mass of BHMF.

The spectra reveals the presence of three intense peaks corresponding to DHMF and BHMF, which are the C-C coupling product of HMF, and the BHMF was composed of dl-, meso-diastereoisomers.

Table S1. Comparison of recent researches for photocatalytic transformation of HMF.

Catalyst (amount)	Reaction medium (Concentration of HMF)	Light	Atmos phere	H ₂ evolution ($\mu\text{mol/g h}$)	DFF yield (AQE)	Ref.
Ni(OH) ₂ -ZnIn ₂ S ₄ (10 mg)	10 mL water (10 mM)	Xe lamp, $\lambda >$ 420 nm	Ar	601	30% yield for C ₁₂ products in 4h (0.14%)	This work
NiS/Zn ₃ In ₂ S ₆ (100 mg)	50 mL water (0.1 M)	Xe lamp, $\lambda >$ 400 nm	N ₂	120	129 $\mu\text{mol/g h}$	[5]
Pt/ZnIn ₂ S ₄ /Nb ₂ O ₅ (15 mg)	40 mL water (1.25 mg/mL)	Xe lamp	N ₂	429	21.6% in 3h	[6]
Cd _{0.7} Zn _{0.3} S/NiSe ₂ (10 mg)	3 mL MeCN (100 μmol)	Xe lamp, $\lambda >$ 400 nm	Ar	1690	1728 $\mu\text{mol/g h}$	[7]
Ni/CdS (10 mg)	5 mL water (10 mM)	blue LED, 450 nm	N ₂	280	20% in 22h	[8]
Pt/CdS (10 mg)	1 mL MeAN+1 mL water (0.2 mmol)	blue LED	N ₂	429	94.3% in 12h	[9]
MAPbBr ₃ (40 mg)	10 mL MeCN (5 mM)	blue LED, 450 nm	O ₂	none	85% in 10h (0.123%)	[10]
CD-ZnIn ₂ S ₄ (20 mg)	20 mL MeCN (20 mM)	Xe lamp, $\lambda >$ 400 nm	O ₂	none	298 $\mu\text{mol/g h}$	[11]
Ti ₃ C ₂ /CdIn ₂ S ₄ (20 mg)	5 mL water (10 mM)	Xe lamp, $\lambda >$ 400 nm	O ₂	none	60.3% in 12h	[12]

Abbreviations: MeCN = acetonitrile, HMF = 5-hydroxymethylfurfural, DFF = 2,5-diformylfuran, CD = carbon dots, AQE = apparent quantum efficiency (only provided when the value was calculated by the authors).

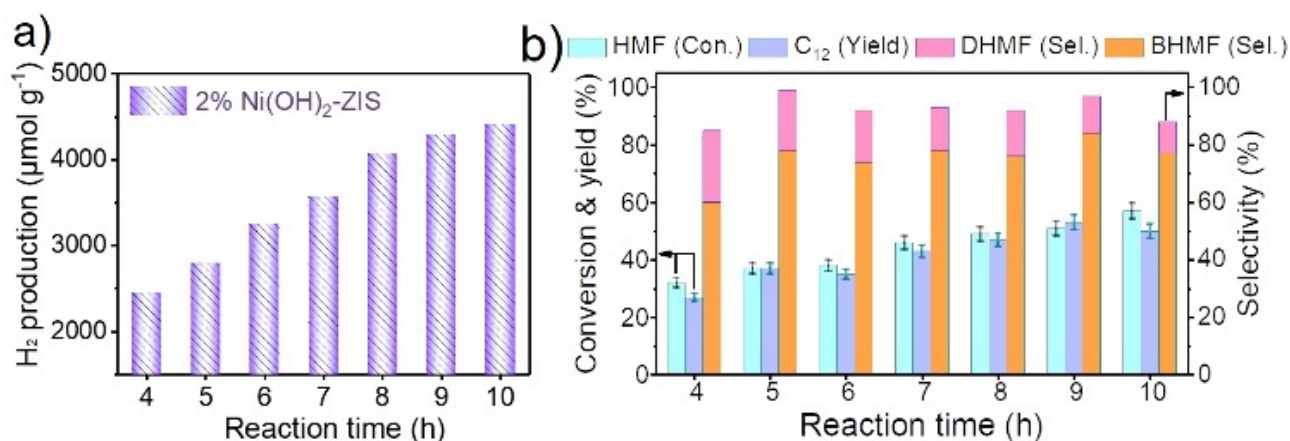


Figure S6. Time-dependent photoactivity tests over 2% Ni(OH)₂-ZIS under N₂ atmosphere. (a) H₂ evolution and (b) conversion of HMF, yield of C₁₂ products and selectivity of the DHMF and BHMF.

Table S2. Controlled experiments for photocatalytic upgrading of 5-hydroxymethylfurfural under nitrogen atmosphere.

Entry	Atmosphere	Additive ^a	H ₂ (μmol·g ⁻¹)	HMF Conversion (%)	Selectivity (%)				Yield (%)	
					DHMF	BHMF	C ₁₂	DFF	C ₁₂	DFF
1 ^b	N ₂	--	--	--	--	--	--	--	--	--
2 ^c	N ₂	--	--	--	--	--	--	--	--	--
3 ^d	N ₂	--	257	--	--	--	--	--	--	--
4	N ₂	IPA	2340	35	24	74	98	--	34	--
5	N ₂	K ₂ S ₂ O ₈	--	45	--	10	10	27	5	12
6	N ₂	TEOA	2576	9	51	7	58	--	5	--
7	N ₂	FA ^e	2310	--	--	--	--	--	--	--
8	Air	TEOA	--	5	22	3	25	--	1	--
9	Air	CN	--	22	--	--	--	86	--	20
10	Air	BQ	--	24	--	--	--	--	--	--

Reaction condition (unless specified): Catalysts (10 mg), HMF (10 mM), solvent (10 mL), reaction 4 h, 300 W Xe lamp (λ > 420 nm). ^a0.1 mmol, ^bWithout light, ^cWithout catalyst, ^dWithout HMF, ^eWith FA as the substrate.

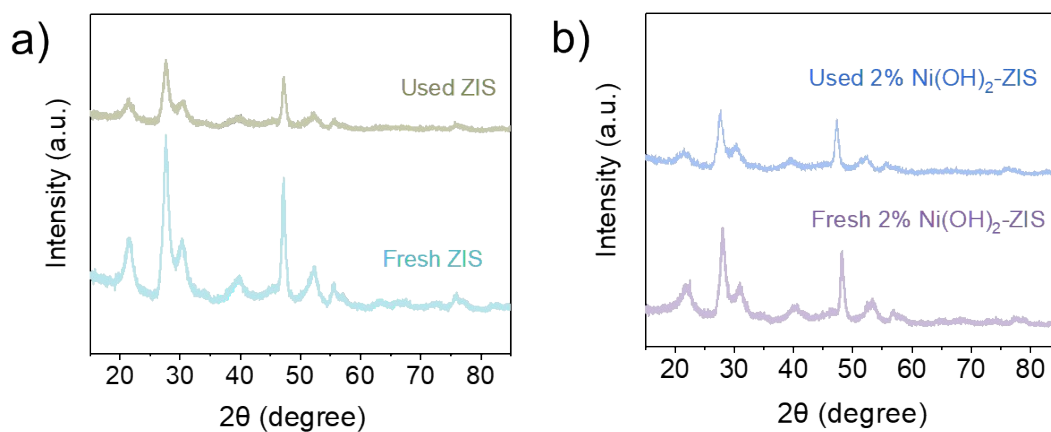


Figure S7. Compared XRD patterns of the catalysts before and after the 5-run recycle reaction: (a) bare ZIS and (b) 2% Ni(OH)₂-ZIS.

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