Supporting Information

Improved activity and stability of $ZnIn_2S_4$ for H_2 production under visible light through Cerium UiO-66

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Experimental procedure for the synthesis of Zr-based UiO-66 (Zr-U66)

Zirconium UiO-66 (denoted as Zr-U66) was synthesized by following the previous report.[1] $ZrCl_4$ (233 mg), and terephthalic acid (166 mg) were dispersed in DMF (50 mL), followed by addition of 150 μL CH_3COOH. After heating at 120 °C for 24 h, the solid was collected, washed with DMF and ethanol several times, and dried in a vacuum oven at 60 °C overnight. Then Zr-U66/ZIS was prepared with the same procedure used for Ce-U66/ZIS (see details in the text).

Table S1. Recipe for the synthesis of 20–50% Ce-U66/ZIS samples

Reagents	20%	30%	40%	50%	ZIS
Ce-U66 (mg)	20.0	30.0	40.0	50.0	0
$ZnCl_2$ (mg)	43.9	38.4	32.9	27.4	54.8
$InCl_3 \cdot 4H_2O$ (mg)	163.2	142.8	122.4	102	204
TAA (mg)	85.7	75.0	64.3	53.5	107

Table S2. XPS analysis for Ce^{3+} and Ce^{4+} species in different samples[a]

Species	Ce-U66			30 Ce-U66/ZIS			30% Ce-U66/ZIS [b]		
	BE (eV)	*A*	*Y* (%)	BE (eV)	*A*	*Y* (%)	BE (eV)	*A*	*Y* (%)
Ce^{3+}	881.2	14307		881.2	6427		881.2	16917	
	885.7	160971		885.6	136080		885.6	120649	
			44.0			44.3			49.0
	899.2	28785		899.1	18083		899.1	17050	
	904.4	122772		904.2	85960		904.2	91493	
Ce^{4+}	882.9	88519		882.9	72630		882.9	65314	
	887.5	63659		887.4	50128		887.4	42962	
	898.4	2272		898.3	600		898.3	3424	
			56.0			55.7			51.0
	901.5	78414		901.3	49018		901.2	47154	
	907.2	101342		907.1	82254		907.0	60017	
	917.1	81330		917.0	56194		917.0	37728	

[a]BE, binding energy; *A*, peak area; *Y*, the relative content. [b]after photoreaction for 8 h.

Table S3. Literature survey for H_2 production on different photocatalysts[a]

Samples	H_2 (μmol/h)	Cat. (mg/mL)	Sacrifices	Light source	Ref.
ZIS/Ce-U66	273.5	0.50	Na_2S/Na_2SO_3	LED/λ = 420 nm	This
Au/UiOS/ZIS	391.6	0.40	Na_2S/Na_2SO_3	Xe/420−780 nm	[2]
ZIS/UiO-66	122.5	0.47	15% TEOA	Xe/λ > 400 nm	[3]
ZIS/MIL-125-NH_2	110.2	0.50	Na_2S/Na_2SO_3	Xe/λ > 420 nm	[4]
CdS/Ce-UiO-66-NH_2	103	0.50	Na_2S/Na_2SO_3	LED/λ = 420 nm	[5]
CdS/UiOS	153.2	0.50	Na_2S/Na_2SO_3	Xe/λ > 420 nm	[6]
Pt/ZnCdS/Ti-MIL-125-NH_2	391	0.20	20% TEOA	Xe/λ > 420 nm	[7]
ZIS/CdS/Ti-MIL-125-NH_2	923	1.0	20% MeOH	Xe/λ > 400 nm	[8]
PdS/ZnCdS/Zr-UiO66-SH	461	0.50	Na_2S/Na_2SO_3	Xe/λ > 420 nm	[9]

[a]SH, 2,5-disulfanyl; TEOA, triethanolamine; MeOH, methanol; LED, 4 W light emitting diode.

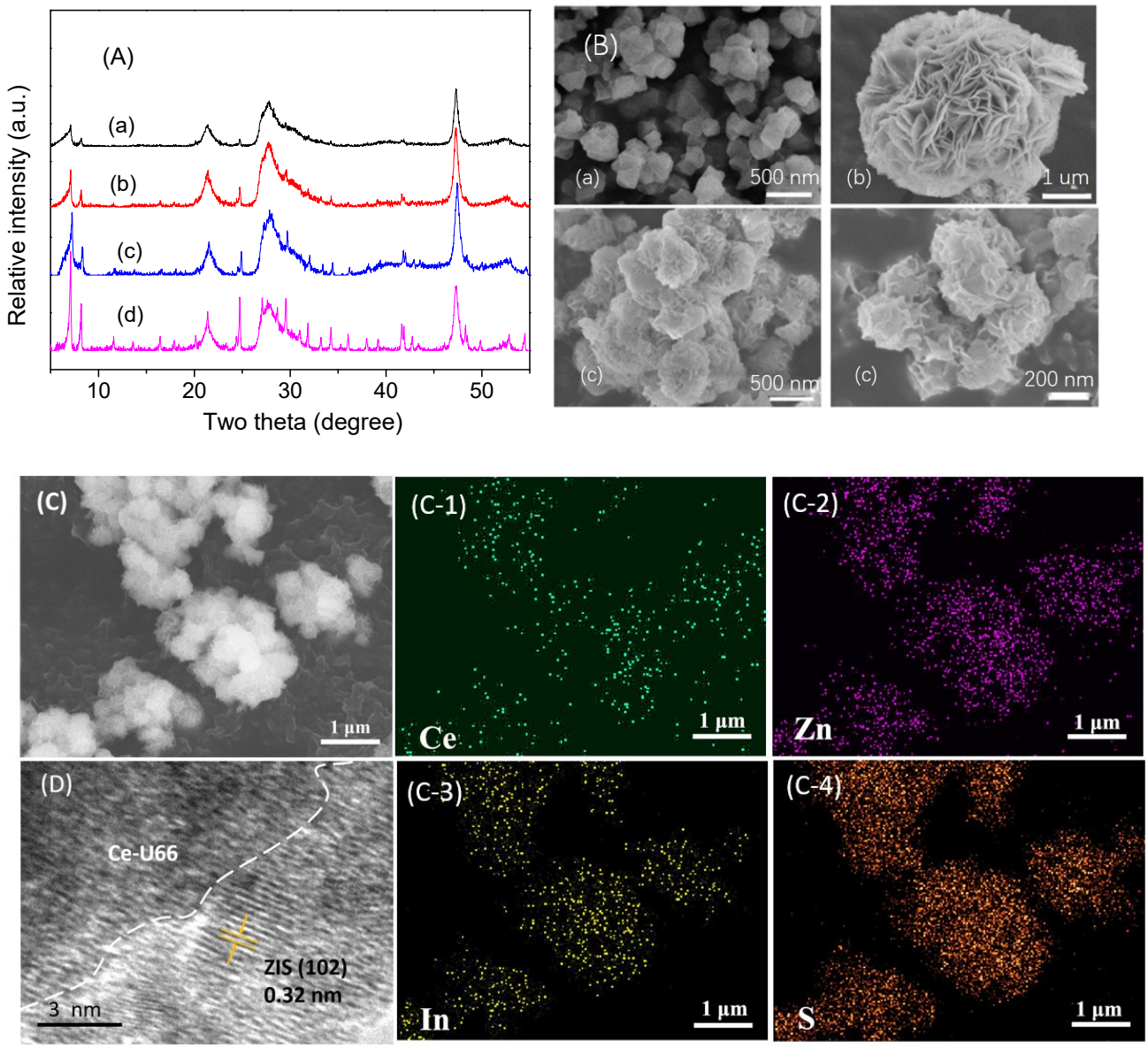

Fig. S1 (A)XRD patterns for *x* Ce-U66/ZIS, where *x* (wt%) was (a) 20, (b) 30, (c) 40, and (d) 50. (B, C) SEM images and for Elemental mapping (a) Ce-U66, (b) ZIS, and (c) 30% Ce-U66/ZIS, and (D) HRTEM image for 30% Ce-U66/ZIS.

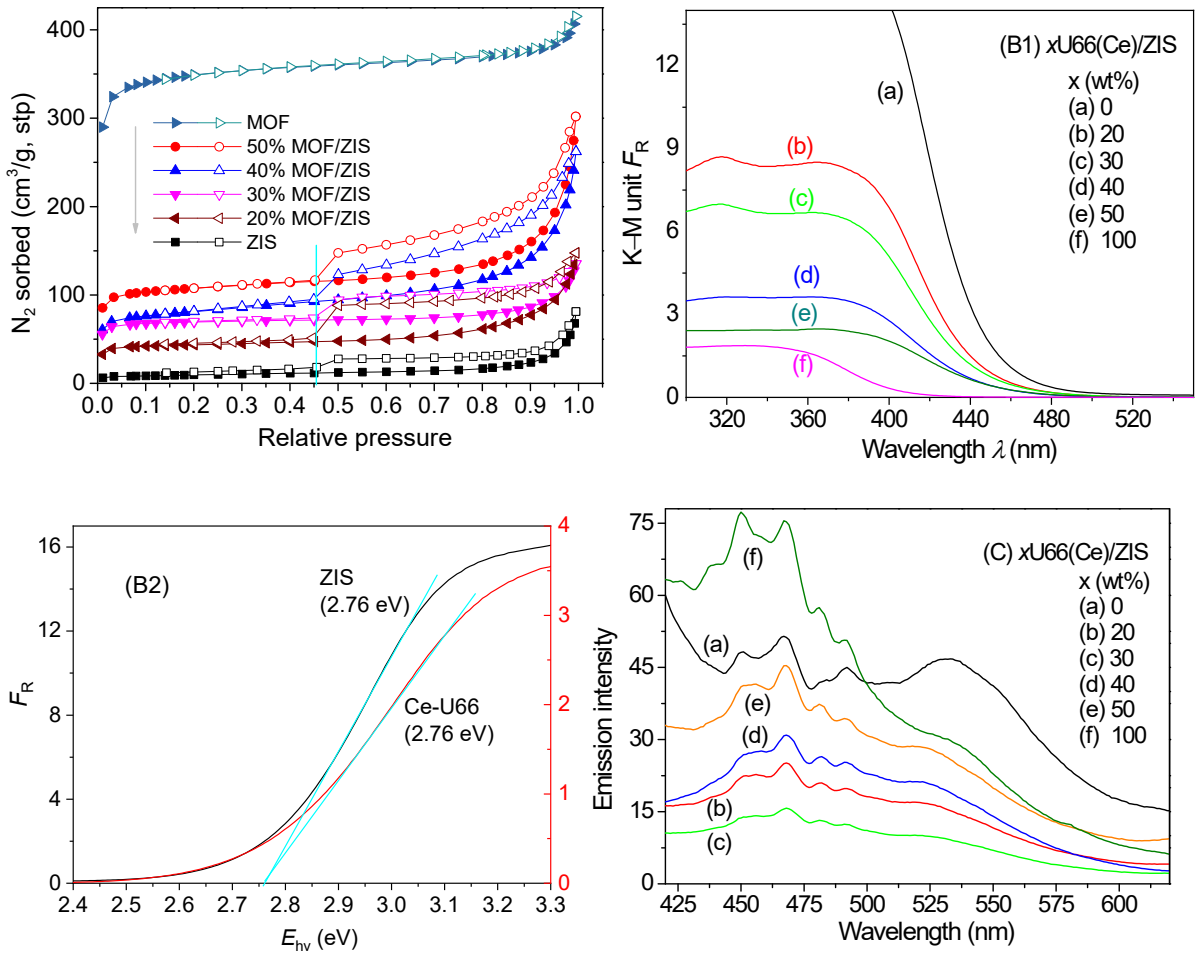

Fig. S2 (A) Isotherms of N_2 adsorption (solid symbols) and desorption (open symbols) on solids as indicated by the legends. (B1) Absorption and (C) photoluminescence spectra for *x*Ce-U66/ZIS, and (B2) the calculation of band energy for ZIS and Ce-U66.

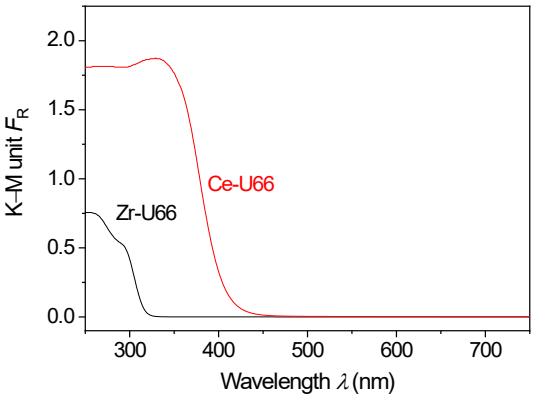

Fig. S3 Absorption spectra for Zr-U66 and Ce-U66.

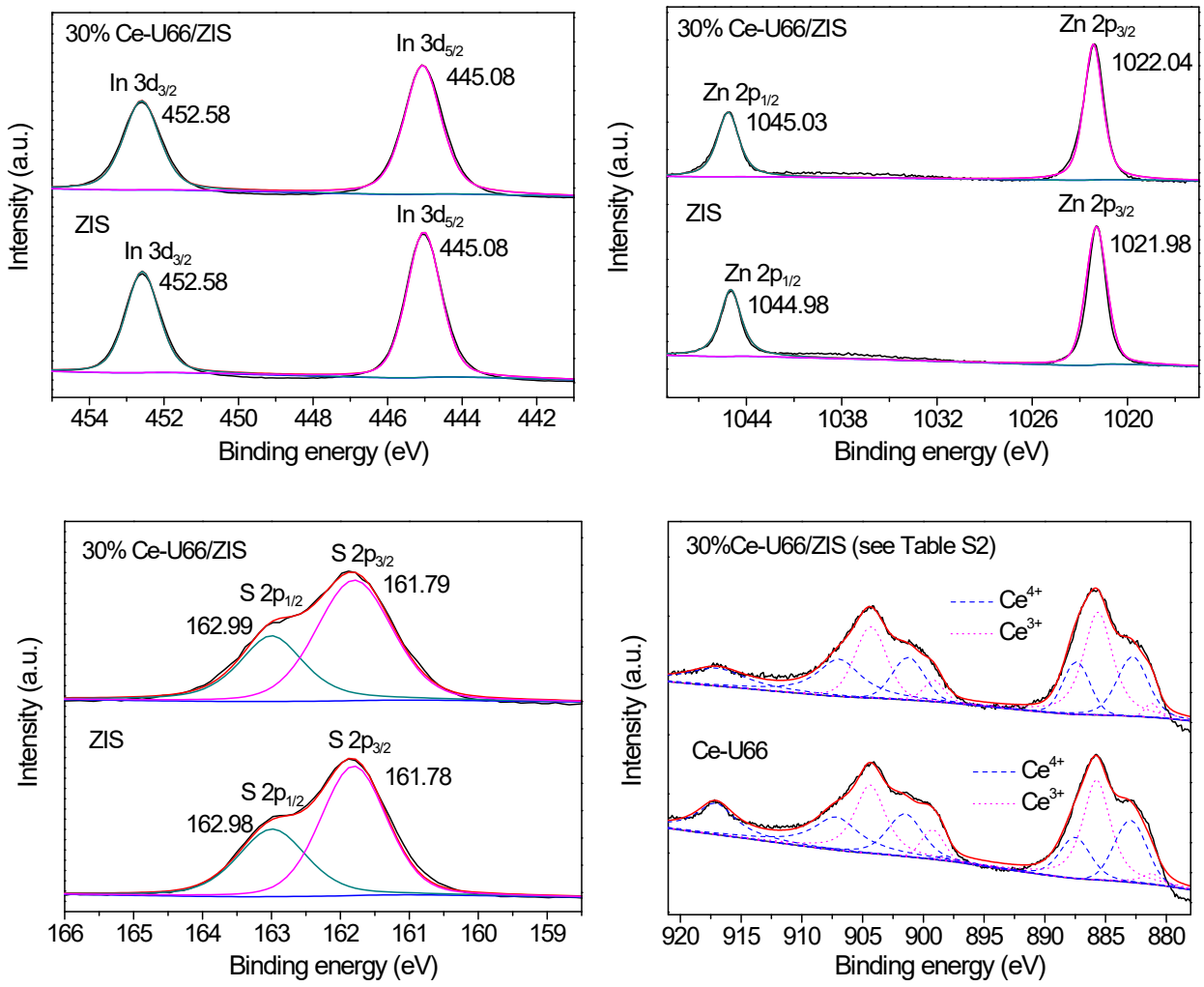

Fig. S4 XPS spectra of In 3d, Zn 2p, S 2p, and Ce 3d, for the samples as indicated by the legends

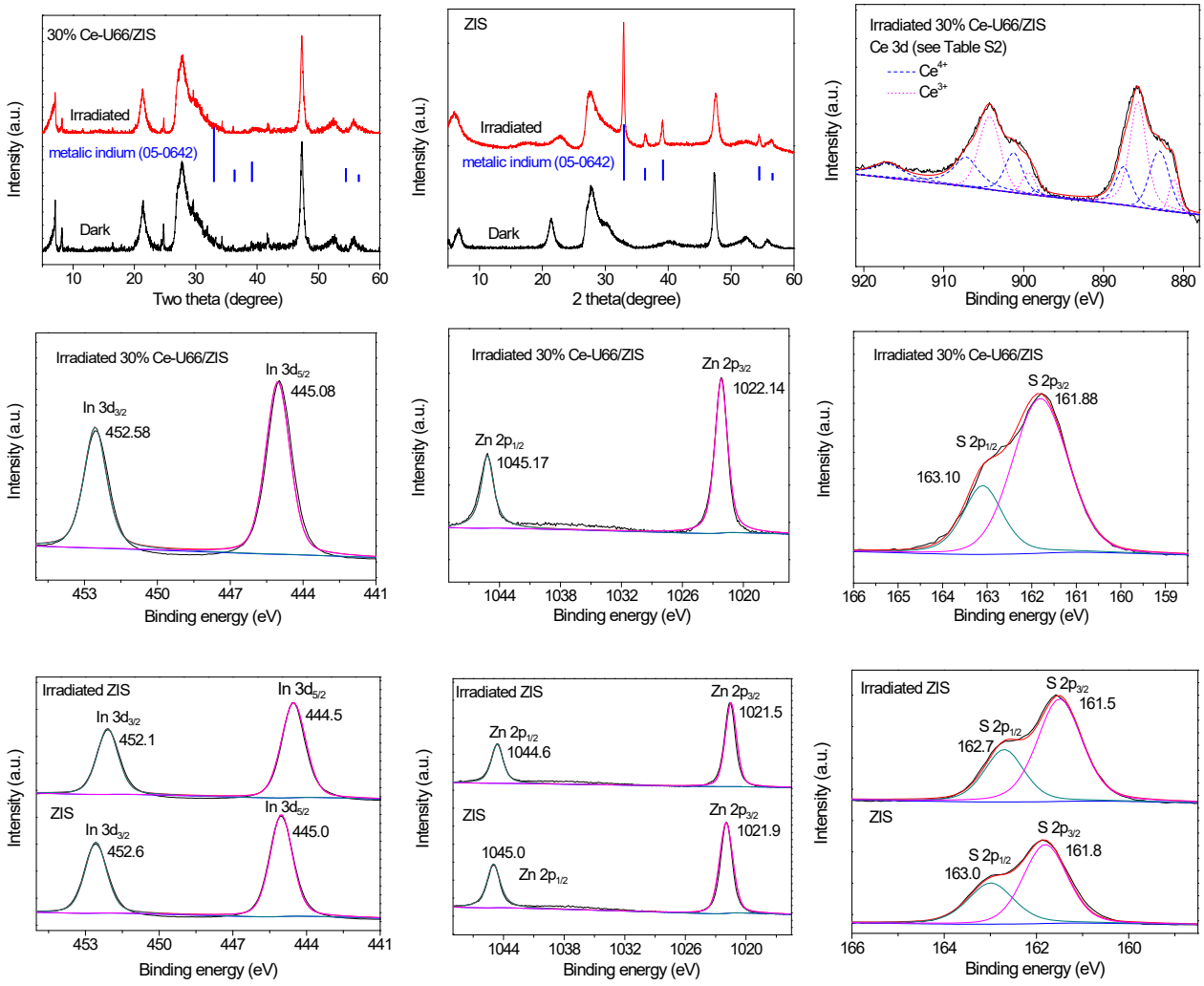

Fig. S5 XRD patterns and XPS spectra for the dark and 8 h-irradiated samples

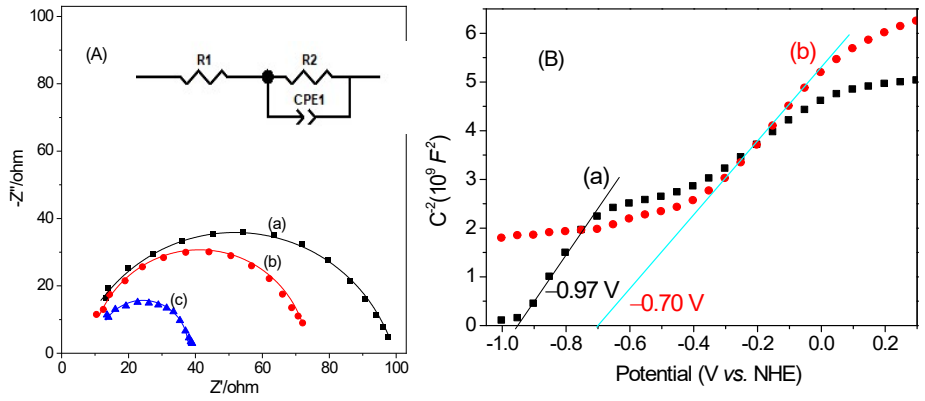

Fig. S6 (A) Nyquist plots for a film electrode of (a) ZIS, (b) Ce-U66, and (c) 30% Ce-U66/ZIS, measured in the dark at a potential of 0.2 V (NHE) in 0.5 M $NaClO_4$ under N_2. (B) The corresponding Mott–Schottky plots, measured in the dark at 1–1 × 10^6 Hz.

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