Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information:

Construction of Core-Shell $CoSe_2/ZnIn_2S_4$ Heterostructures for Efficient Visible-Light-Driven Photocatalytic Hydrogen Evolution

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Materials

Cobalt chloride hexahydrate ($CoCl_2·6H_2O$, ≥ 99%), chloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$, ≥ 99%), zinc chloride ($ZnCl_2$, ≥ 98%), ethylenediamine (≥ 99%), triethanolamine (TEOA, ≥ 99%), and anhydrous ethanol (≥ 98%) and ethylene glycol (≥ 99.5%) were purchased from Sinopharm Chemical Reagent Co. Lot. (China). Indium chloride tetrahydrate ($InCl_3·4H_2O$, ≥ 99%) and selenium dioxide (SeO_2, ≥ 99%) were obtained from Shanghai Macklin Biochemical Technology Co. Ltd. Thioacetamide (TAA, ≥ 98%) was purchased from Aladdin Industrial Corporation. The above materials were used directly without further purification.

Characterizations

The composition of the synthesized catalysts was determined by using X-ray diffraction (XRD) with incident radiation Cu Kα (λ = 0.15406 nm) in the range of 10° - 80° at a scan speed of 15°/min. UV-vis spectrometer (UV2700) was used to observe the diffuse reflectance spectra of monomers and compounds with $BaSO_4$ as a reference. The morphology of the samples was characterized by scanning electron microscope

(SEM, FEI Inspect F50). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were obtained by FEIG220 microscope under 200 kV acceleration voltage, and energy dispersive X-ray spectroscopy (EDX) was also measured. To determine the elemental composition and the surface valence states, X-ray photoelectron spectroscopy (XPS) data were obtained by using a Thermo Scientific K-Alpha with Al Kα radiation as the X-ray source. Photoluminescence (PL) spectra were measured by Fluoromax-Plus fluorescence spectrometers (Horiba) and time-resolved photoluminescence (TRPL) spectra were measured by FLS1000 fluorescence spectrometer (Edinburgh).

Photoelectrochemical measurements

The photoelectrochemical properties were tested on the CHI660E electrochemical workstation by a standard three-electrode system, including an Ag/AgCl (3 M KCl) electrode, a platinum plate electrode, and a working electrode. The electrolyte was 0.5 M Na_2SO_4 aqueous solution. The electrical impedance spectroscopy (EIS), transient photocurrent, and the Mott-Schottky plots of the materials were characterized. The working electrode was prepared as follows. A small spoon of sample and a drop of terpineol were added into a mortar. It was ground into a paste and evenly smeared to the square area in the center of the conductive surface of the ITO conductive glass (the coating size is 5×5 mm). Then it was dried at 60 °C for 6 h. In the transient photocurrent test, the light source was still a 300 W xenon lamp with a UV-CUT filter ($\lambda \geq 420$ nm).

Additional Data

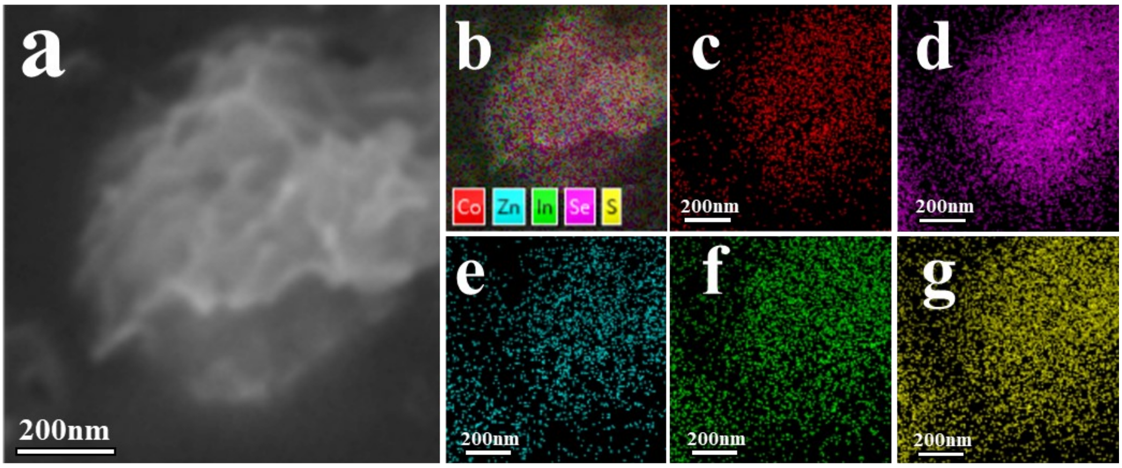
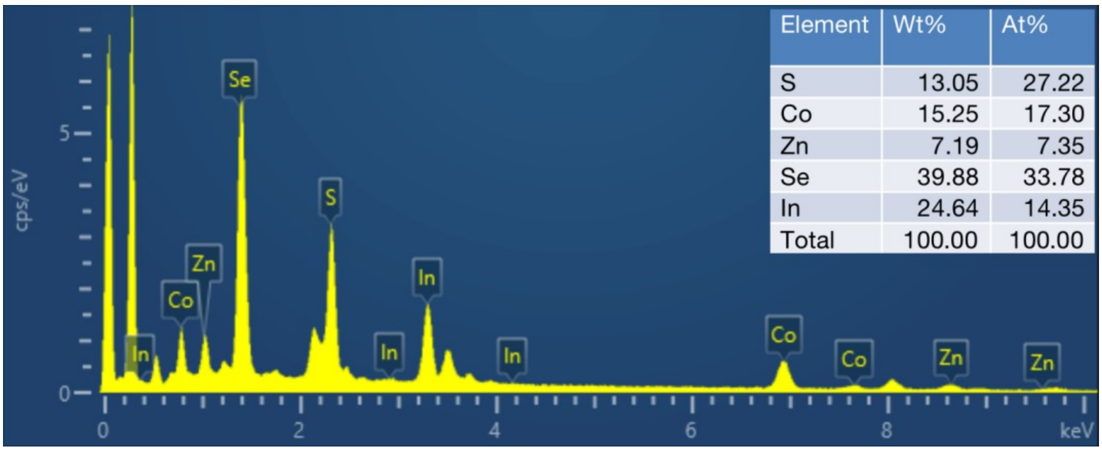


Fig. S1 SEM image of (a) $CoSe_2/ZnIn_2S_4$-20 core-shell heterostructure and (b) the corresponding EDS and elemental mapping images of (c) Co, (d) Se, (e) Zn, (f) In, and (g) S.



Element	Wt%	At%
S	13.05	27.22
Co	15.25	17.30
Zn	7.19	7.35
Se	39.88	33.78
In	24.64	14.35
Total	100.00	100.00

Fig. S2 EDS element analysis of $CoSe_2/ZnIn_2S_4$-20.

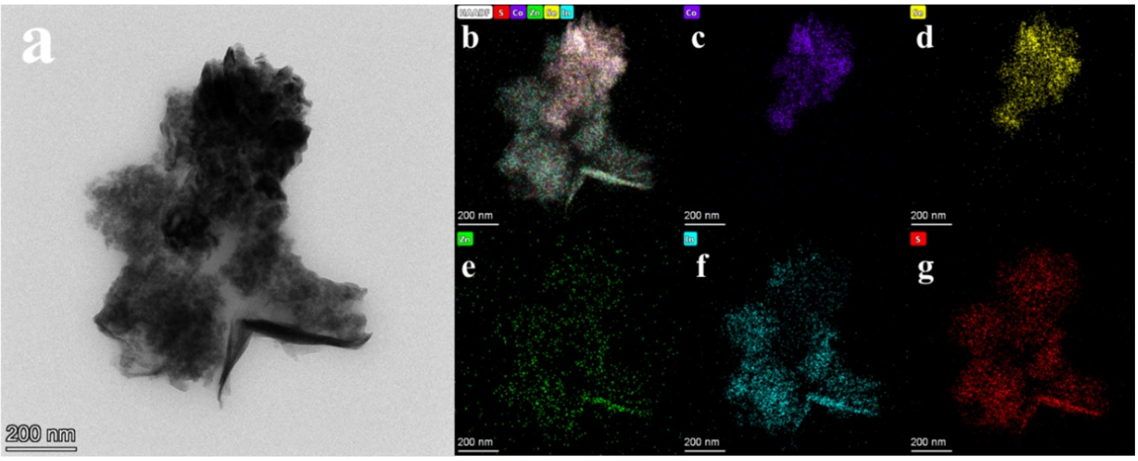


Fig. S3 TEM image of (a) $CoSe_2$@$ZnIn_2S_4$ physical mixture heterostructure and (b) the corresponding EDS and elemental mapping images of (c) Co, (d) Se, (e) Zn, (f) In, and (g) S.

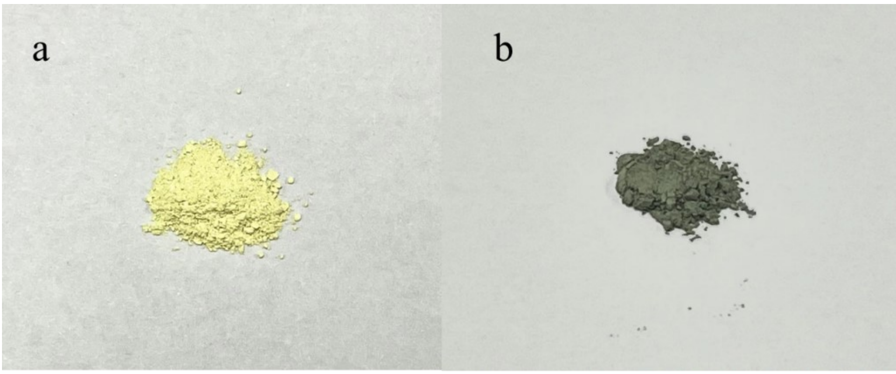


Fig. S4 the pictures of (a) $ZnIn_2S_4$ and (b) $CoSe_2/ZnIn_2S_4$-20 sample.

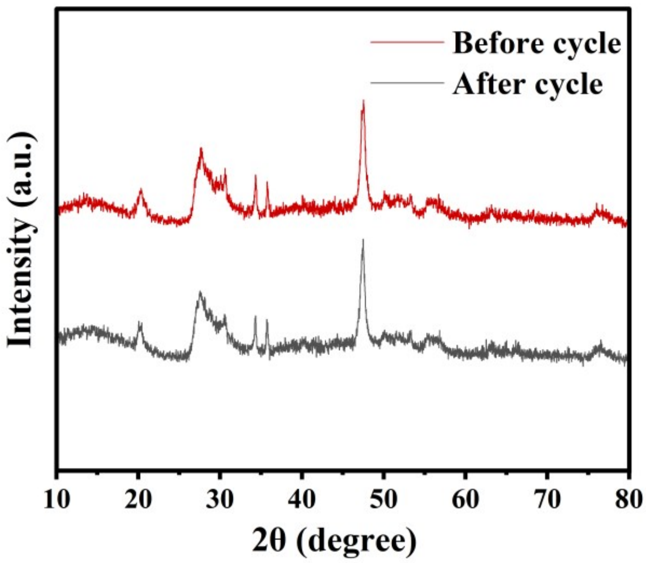


Fig. S5 XRD patterns comparison of $CoSe_2/ZnIn_2S_4$-20 before and after cycle.

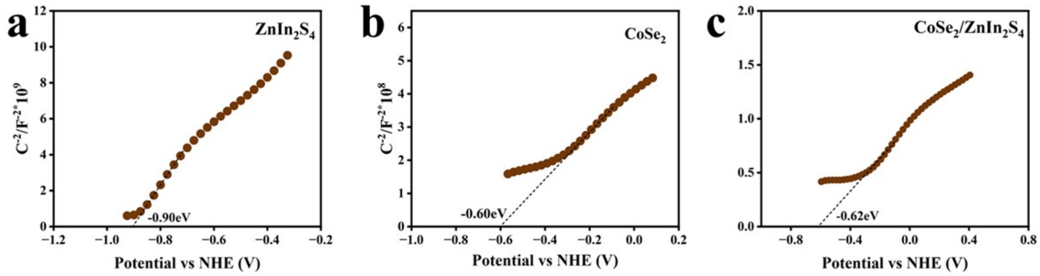


Fig. S6 Mott-Schottky plots of (a) $ZnIn_2S_4$, (b) $CoSe_2$ and (c) $CoSe_2/ZnIn_2S_4$-20.

Table S1 Comparison of photocatalytic H_2 evolution performance for different photocatalysts.

Photocatalysts	**Sacrificial agent**	**Light source**	**H_2 evolution rate (μmol g^{-1} h^{-1})**	**Ref.**
$CoSe_2/ZnIn_2S_4$	TEOA (10 vol%)	300 W Xe lamp ($\lambda \geq 420$ nm)	2199 μmol g^{-1} h^{-1}	**this work**
$ZnIn_2S_4/ZnSe$	0.25 M Na_2S and 0.35 M Na_2SO_3	300 W Xe lamp ($\lambda \geq 420$ nm)	1296.9 μmol g^{-1} h^{-1}	1
$ZnIn_2S_4/MoSe_2$	0.35 M Na_2S and 0.25 M Na_2SO_3	300 W Xe lamp ($\lambda \geq 420$ nm)	2228 μmol g^{-1} h^{-1}	2
$NiSe_2/ZnIn_2S_4$	TEOA (10 vol%)	visible light ($\lambda \geq 420$ nm)	1487 μmol g^{-1} h^{-1}	3
$MoSe_2/ZnIn_2S_4$	0.35 M Na_2S and 0.25 M Na_2SO_3	300 W Xe lamp ($\lambda \geq 420$ nm)	1226 μmol g^{-1} h^{-1}	4
$Co_3O_4/ZnIn_2S_4$	TEOA	300 W Xe lamp ($\lambda \geq 420$ nm)	3844.12 μmol g^{-1} h^{-1}	5
$ZnIn_2S_4@CoS_2$	TEOA	300 W Xe lamp ($\lambda \geq 350$ nm)	2768 μmol g^{-1} h^{-1}	6
$Co_9S_8@ZnIn_2S_4/CdS$	Acetonitrile, sodium sulfite	300 W Xe lamp ($\lambda \geq 420$ nm)	1419.14 μmol g^{-1} h^{-1}	7
$Sb_2S_3/ZnIn_2S_4$	TEOA	250 W Xe lamp ($\lambda \geq 420$ nm)	1685.14 μmol g^{-1} h^{-1}	8
$ZnIn_2S_4$/ WS_2	0.35 M Na_2S and 0.25 M Na_2SO_3	150 W Xe lamp	293.3 μmol g^{-1} h^{-1}	9
$CoSe_2/g\text{-}C_3N_4$	0.15 M Na_2S and 0.35 M Na_2SO_3	300 W Xe lamp	1386.8 μmol g^{-1} h^{-1}	10

Table S2 Comparison of the fluorescence decay time (τ) and the average lifetime (τ_{ave}) of the $ZnIn_2S_4$ and $CoSe_2/ZnIn_2S_4$-20 samples.

Materials	**τ_1(ns)**	**B_1(%)**	**τ_2(ns)**	**B_2(%)**	**τ_{ave}(ns)**
$ZnIn_2S_4$	1.28	69.9	8.6	30.1	3.48
$CoSe_2/ZnIn_2S_4$-20	1.09	62.6	6.09	37.4	2.96

References

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