Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information:

Methylthio-functionalized-UiO-66 to promote the electron-hole separation of $ZnIn_2S_4$ for boosting hydrogen evolution under visible light illumination

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Chemicals

Zirconium tetrachloride ($ZrCl_4$), Zinc chloride ($ZnCl_2$), acetic acid, thioacetamide, N,N-dimethyl formamide (DMF), dichloromethane were purchased from Nanjing Wanqing, which was manufactured by Sinopharm Chemical Reagent Co., Ltd. 2,5-dimercaptoterephthalic acid (H_2BDC-$(SH)_2$)，1,4-bezenedicarboxylate (H_2BDC), Indium chloride ($InCl_3$)， $Na_2S{\cdot}9H_2O$ and Na_2SO_3 were obtained from Nanjing Jingge, which was manufactured by Shanghai Aladdin Bio-Chem Technology Co., Ltd. The reagents employed in this work were all of analytical grade.

Synthesis of the ligand H_2BDC-$(SCH_3)_2$

The H_2BDC-$(SCH_3)_2$ precursor was synthesized following the previous report with some modifications.[1] Typically, 460 mg 2, 5-dimercaptoterephthalic acid H_2BDC-$(SH)_2$ (2 mmol) were dissolved in 80 mL acetone, Then 1656 mg K_2CO_3 (6 mmol) was added. Iodomethane (685 μL, 11 mmol) was added dropwise to the mixed solution while magnetically stirring. After stirred for 1 h at room temperature, the solvent was removed by rotary evaporator vacuum and the residue was dissolved in water (80 mL) and cooled to 0 °C using the ice water bath. The pH of the solution approximately was adjusted to 1 with 2 M HCl. The precipitated solids was alienated via centrifugation, and washed with H_2O for several times. The resulting powder was dried at 60 °C overnight, and the obtained yellow solid was H_2BDC-$(SCH_3)_2$ precursor.

Synthesis of UiO-66

Normally, 41.5 mg H_2BDC, 58.3 mg $ZrCl_4$ were dissolved in a mixed solution of 15 mL DMF and 1.8 mL acetic acid with stirring for 30 min. Transfered the mixed solution to a 25 mL high temperature Teflon-lined autoclave. Then heated it to 120 °C, and maintained for 24 h. After cooled to room temperature, poured the products into centrifuge tube for centrifugal separation, washing and precipitation. Finally, UiO-66 was obtained by vacuum drying overnight at 60 °C.

Synthesis of Pt/ZIS

Pt/UIOS composites were achieved by photodeposition. Specifically, 30 mg of ZIS and 1 mg of $H_2PtCl_6{\cdot}6H_2O$ were added to the preprepared aqueous solution, which was sonicated for 20 min and stirred for another 30 min to obtain the homogeneous mixture. The suspension was then exposed to visible light produced by a Xe lamp with a 420 nm cutoff filter and photodeposited in Ar atmosphere for 2 h. The entire process was maintained at 25 °C via a cooling water system.

Synthesis of UiO-66/ZIS

The synthesis process of UiO-66/ZIS is similar to that of UiOSC/ZIS, except the addition of UiOSC changes to UiO-66, and was labeled as UiO-66/ZIS.

Characterization and measurement

The crystalline structure of as-prepared photocatalysts was identified by combined multifunctional horizontal X-ray diffractometer (Ultima IV, Rigaku, Japan).

The morphologies and structures of samples were detected by scanning electron microscopy (SEM, FEI Inspect F50A) and transmission electron microscopy (TEM, Talos F200XA). To investigate the surface elemental composition, chemical states and valence band spectrum of samples, X-ray photoelectron spectroscopy (XPS) data was performed by using a PerkinElmer PHI 5000C ESCA using a monochromatic Al Kα source (Mono Al Kα) with energy of 1486.6 eV. Ultraviolet and visible spectrophotometer (UV 2600) with $BaSO_4$ as the reference was applied to characterize the optical properties of samples. Photoluminescence (PL) spectra for power samples were realized on an F-4700A FL spectrophotometer. Time-resolved photoluminescence (TRPL) spectra were observed using a PluoroLog-3-TCSPC fluorescence spectrometer (Horiba Jobin Yvon Inc).

Photoelectrochemical tests

All photoelectrochemical measurements including mott-schottky curves, transient photocurrent and electrochemical impedance spectroscopy (EIS) were carried out on a CHI-660E electrochemical workstation with a typical three electrode electrochemical system. The as-prepared samples were directly used as working electrode, a Pt electrode was utilized as counter electrode and the KCl saturated Ag/AgCl electrode was used as reference electrode. The 0.5 M Na_2SO_4 solution was used as the electrolyte. The working electrode was prepared by the following steps: The indium tin oxide (ITO) conductive glass was sonicated in water and ethanol for 10 min. Then dried it and set aside. 20 mg of catalyst was poured into a small mortar and added into a drop of terpineol, ground it for 2 min to form a homogeneous paste. Sequentially, the paste was coated on the ITO conductive surface with a blade, controlling the square area coated with 0.25 cm^2. Finally, the coated conductive glass was placed in a vacuum drying oven at 60 °C for 6 h to dry.

Formulas:

The apparent quantum efficiency (AQE) was estimated by the formula as following.

$$AQE\ (\%) = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100$$

$$= \frac{rate\ of\ evolved\ H_2\ molecules \times 2}{number\ of\ incident\ photons} 100$$

$$= \frac{v(H_2) \times N_0 \times 2}{IS\lambda/(hc)} \times 100$$

Where N_0 is Avogadro's constant (6.022×10^{23} mol^{-1}), I is the average irradiation intensity per unit area (100 mW cm^{-2}), S is the irradiation area (25.84 cm^2), λ is the selected incident wavelength (420 nm), h is Planck's constant (6.626×10^{-34} J s), c is the speed of light (3.0×10^8 m s^{-1}).

The Scherrer equation:

$$D_{h,\ k,\ l} = \frac{K\lambda}{\beta_c cos\theta}$$

From the equation, $D_{h,k,l}$ is the crystallite size perpendicular to the reflected crystallite plane. Here K is the shape factor of the crystallite size, and its value is 0.9 for all base peaks. β is the half width of the diffraction intensity peaks, λ is the X-ray wavelength, and θ is the Bragg angle in degrees.

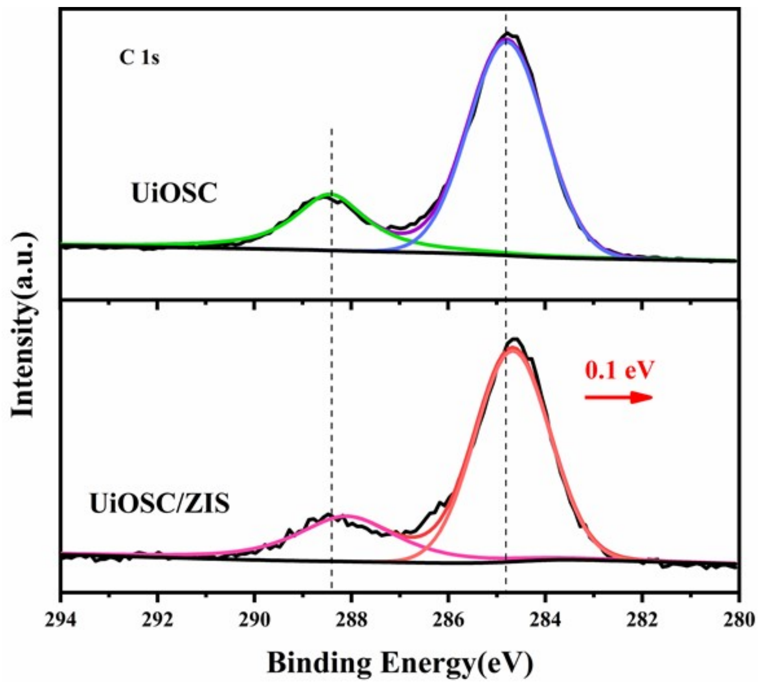

Fig. S1. High resolution XPS spectra of C 1s for UiOSC and UiOSC/ZIS.

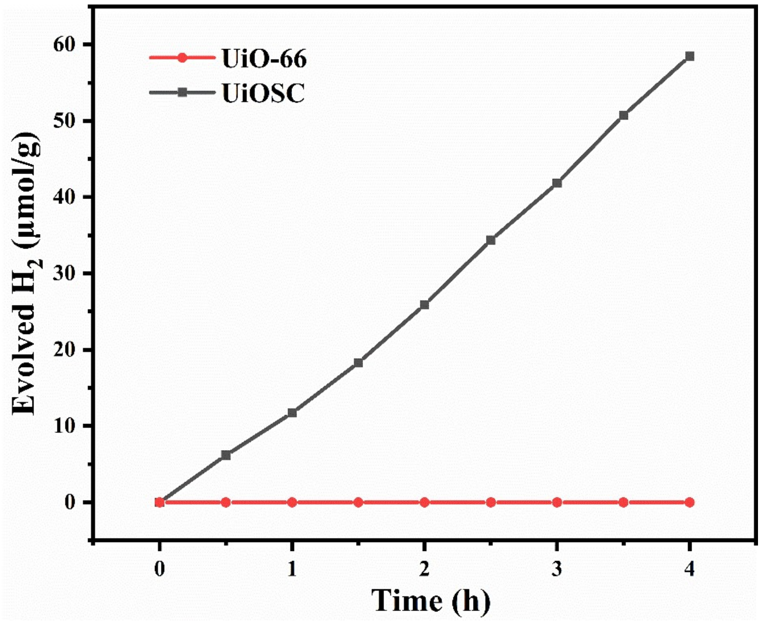

Fig. S2. Photocatalytic hydrogen evolution curves of UiOSC and UiO-66

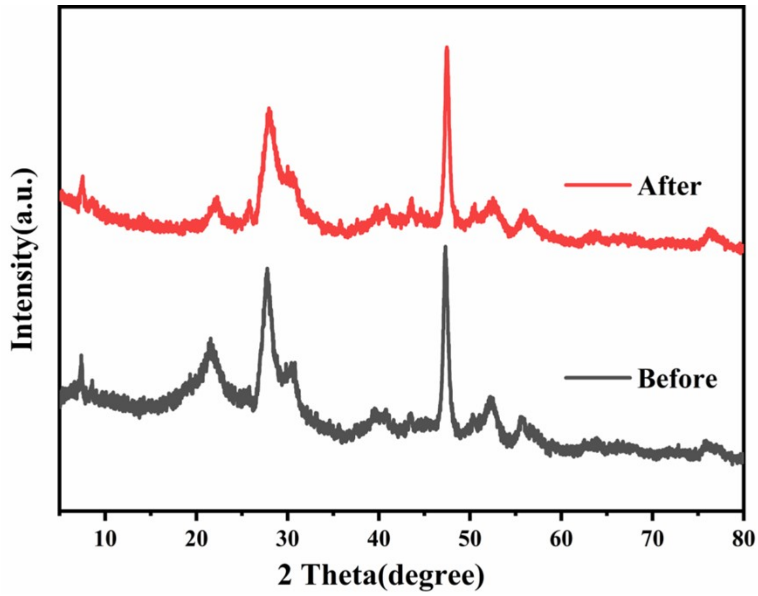

Fig. S3. XRD patterns of UiOSC/ZIS before and after photocatalytic H_2O splitting reaction

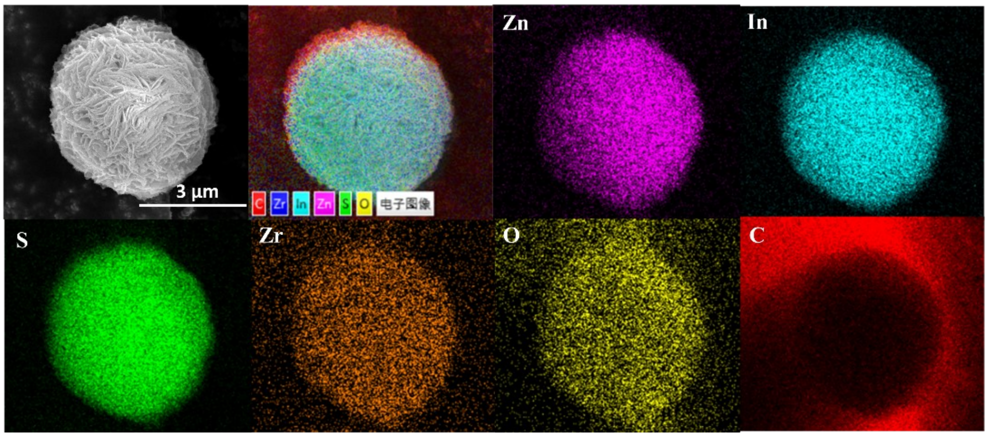

Fig. S4. SEM images of UiOSC/ZIS after 16 h photocatalytic reaction and the corresponding EDX elemental mapping images of Zn, In, S, C, O and Zr.

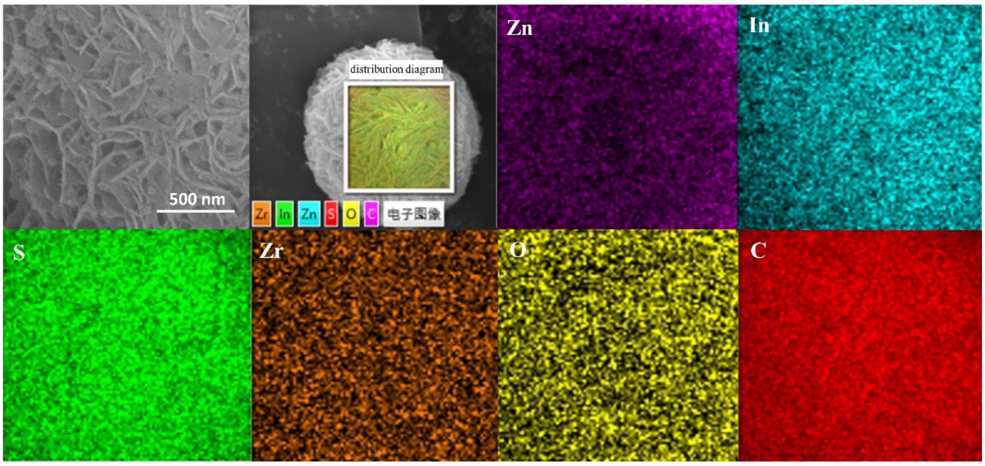

Fig. S5. SEM images of partial UiOSC/ZIS after 16 h photocatalytic reaction and the corresponding EDX elemental mapping images of Zn, In, S, C, O and Zr.

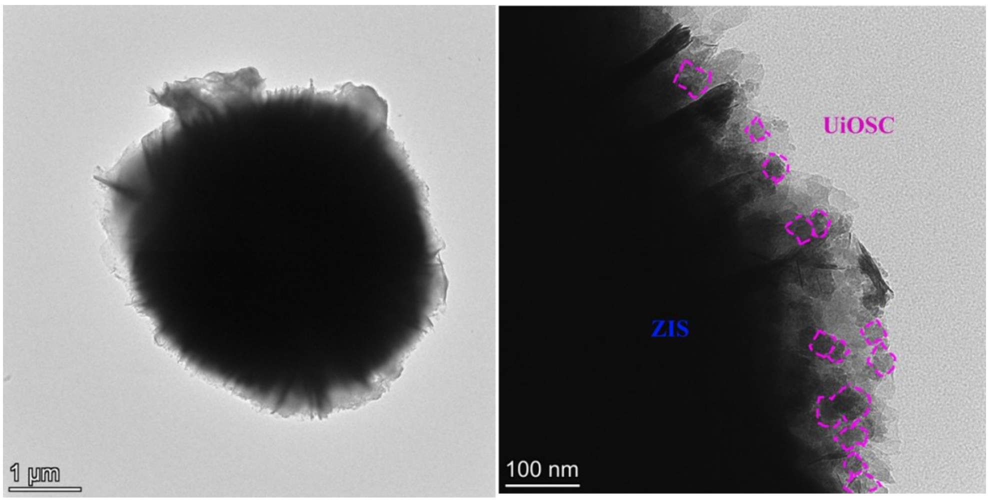

Fig. S6. TEM images of UiOSC/ZIS after 16 h photocatalytic reaction

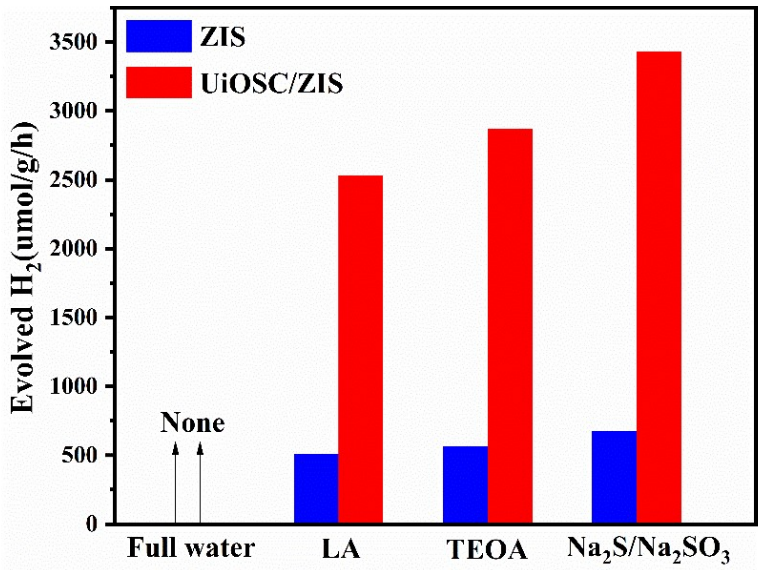

Fig. S7. Photocatalytic hydrogen evolution curves of UiOSC/ZIS and ZIS in different sacrificial agent.

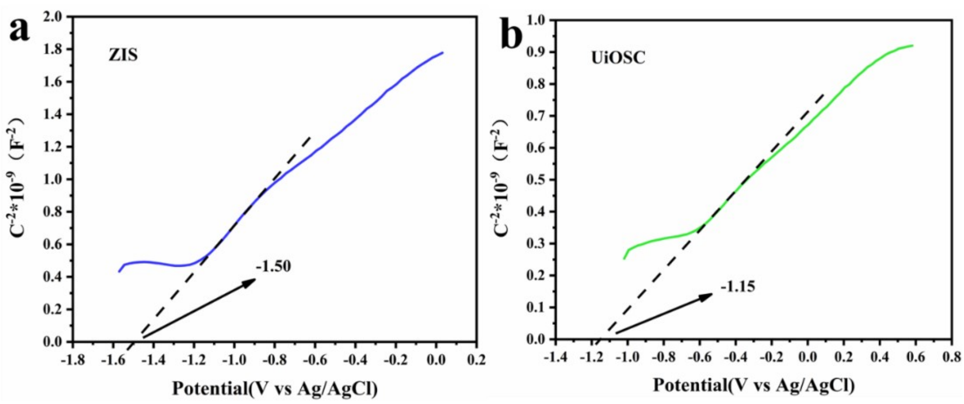

Fig. S8. Mott–Schottky plots of UiOSC and ZIS

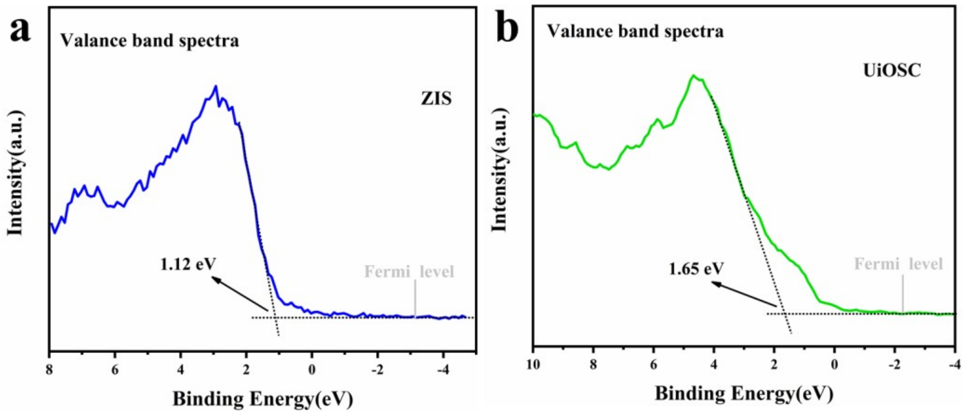

Fig. S9. XPS-VB of UiOSC and ZIS

Table S1. Crystallite size of pristine ZIS and UiOSC/ZIS ($D_{1,1,0}$)

name of the photocatalysts	crystallite size (nm)
pristine ZIS	15
10-UiOSC/ZIS	15
20-UiOSC/ZIS	16
30-UiOSC/ZIS	16
40-UiOSC/ZIS	16
50-UiOSC/ZIS	15

Table S2 Comparison of the fluorescence decay time (τ) and the average lifetime (τ_{avg}) of the ZIS and UiOSC/ ZIS hybrid samples.

Materials	**τ_1(ns)**	**B_1(%)**	**τ_2(ns)**	**B_2(%)**	**τ_3(ns)**	**B_3(%)**	**τ_{avg}(ns)**
Pure ZIS	1.34	820.90	4.61	278.90	13.96	45.60	5.38
UiOSC/ZIS	0.92	860.25	3.76	214.51	15.98	26.53	5.21

Table S3 The comparison of the photocatalytic hydrogen production rate of UiOSC/ZIS with those reported Photocatalysts.

Photocatalyst	Light source (λ in nm)	Sacrificial agents	Maximum rate (μmol·g^{-1}·h^{-1})	Reference
Pure ZIS	300 W Xe lamp (λ ≥ 420 nm)	Na_2S/Na_2SO_3	673	**This work**
UiOSC/ZIS	300 W Xe lamp (λ ≥ 420 nm)	Na_2S/Na_2SO_3	3433	**This work**
Pt/ZIS	300 W Xe lamp (λ ≥ 420 nm)	Na_2S/Na_2SO_3	1205	**This work**
UiOSC	300 W Xe lamp (λ ≥ 420 nm)	Na_2S/Na_2SO_3	15	**This work**

Pt/UiO-66-$(SCH_3)_2$	300 W Xe lamp (λ ≥ 420 nm)	Ascorbic acid	1290	1
$ZnIn_2S_4$@NH_2-MIL-125(Ti)	300 W Xe lamp (λ > 400 nm)	Na_2S/Na_2SO_3	2204.2	2
$WS_2/ZnIn_2S_4$	300 W Xe lamp (λ ≥ 420 nm)	Lactic acid	2550	3
Au@UiOS@ZIS	300 W Xe lamp (420<λ<780 nm)	Na_2S/Na_2SO_3	39160	4
$ZnIn_2S_4/Ni_{12}P_5$	300 W Xe lamp (λ ≥ 420 nm)	Na_2S/Na_2SO_3	2263	5
UiO-66-$(SH)_2$/CdS	225 W Xe lamp (λ> 420 nm)	Na_2S/Na_2SO_3	15320	6
$Co_9S_8/ZnIn_2S_4$	300 W Xe lamp (λ ≥ 420 nm)	TEOA	9039	7
$ReS_2/ZnIn_2S_4$	300 W Xe lamp (λ ≥ 420 nm)	TEOA	1858	8
UiO-66/$CdIn_2S_4$	150W Xe lamp (λ > 420 nm)	methanol	2950	9
$MoS_2/ZnIn_2S_4$	300 W Xe lamp (λ> 420 nm)	Na_2S/Na_2SO_3	3891	10
UiO-66@$ZnIn_2S_4$	300 W Xe lamp (λ > 400 nm)	TEOA	3061	11
NH_2-UiO-66/$ZnIn_2S_4$	300 W Xe lamp (λ > 420 nm)	Na_2S/Na_2SO_3	2199	12
Pt@UiO-66-NH_2	300 W Xe lamp (λ> 380 nm)	Triethylamine acetonitrile	378	13

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