Supplemental Information

Reagents and chemicals

In the experiments, the related reagents are analytical reagents and can be used without further purifification, which are described as follows: acetone (CH_3COCH_3, Tianjin, FengChuan, 99.7%), isopropanol ($(CH_3)_2CHOH$, Tianjin, FengChuan, 99.7%), absolute ethanol (CH_3CH_2OH, Tianjin, FengChuan, 99.7%), zinc chloride hexahydrate ($ZnCl_2·6H_2O$, Tianjin, GuangFu, 99%), cupric chloride dihydrate ($CuCl_2·2H_2O$, Tianjin, GuangFu, 99%), indium chloride tetrahydrate ($InCl_3·4H_2O$, Tianjin, GuangFu, 99%), Thioacetamide (CH_3CSNH_2 Tianjin, GuangFu, 99%), absolute ethanol (C_2H_6O, Tianjin, GuangFu, 99.8%) sodium sulfate (Na_2SO_4, Tianjin, GuangFu, 99%). The specifications of fluorine-doped tin oxide (FTO) glass are described as follows: The manufacturer is South China Science and Technology Ltd. The production size and experimental size are 10 cm×10 cm×0.22 cm and 1 cm×1 cm×0.22 cm, respectively. The square resistance is less than 7 Ω. The film thickness is 500 nm. The transmittance is more than 80%.

Preparation of n-type $ZnIn_2S_4$ and p-type $CnInS_2$

The n-type $ZnIn_2S_4$ nanosheets were prepared on fluorine-doped tin oxide (FTO) substrate through hydrothermal method, and the precursor solution is composed of 0.01 M Zinc chloride ($ZnCl_2$), 0.02 M Indium chloride tetrahydrate ($InCl_3·4H_2O$) and 0.08 M Thioacetamide (CH_3CSNH_2). Subsequently, the solution was poured into the prepared Teflon-lined stainless steel and heated at 160 °C for 12 h. The p-type $CnInS_2$ nanosheets were fabricated via alcohothermal method, 0.04 M $CuCl_2·2H_2O$, 0.08 M $InCl_3·4H_2O$ and 0.08 M CH_3CSNH_2 were dissolved in 12 mL absolute ethanol, stirring for 30 min to obtain precursor solution, which was poured into the Teflon lined stainless steel autoclave with FTO for 16 h at 180 °C.

Preparation of $ZnIn_2S_4/CnInS_2$ and $CnInS_2/ZnIn_2S_4$ photoelectrodes

Typically, the obtained $ZnIn_2S_4$/FTO substrate is placed in a Teflon lined stainless steel autoclave and the $ZnIn_2S_4/CuInS_2$ heterojunction is prepared by the alcohothermal method as with the preparation of pure $CuInS_2$. Similarly, the as-obtained $CuInS_2$/FTO substrate is placed in a Teflon lined stainless steel autoclave with the conductive surface facing down at an angle of 45°, and the $CuInS_2/ZnIn_2S_4$ heterojunction was prepared by the hydrothermal method as with the preparation of pure $ZnIn_2S_4$.

Characterization

The crystalline structures of samples were characterized by the data from X-ray diffractometer (XRD, Rigaku-D/max-2500; Cu Kα radiation; □λ = 0.154059 nm; working

voltage with 40 kV and working current with 150 mA). The morphology and microstructure of samples were carried out on Scanning electron microscopy (SEM, JEOL JSM-7800F) and JEOL JEM-2100 transmission electron microscopy (TEM). Incidentally, energy dispersive spectro-meter (EDS, AZtec from Oxford) element mapping was conducted to analyze the chemical composition and stoichiometry of obtained samples. The optical absorption performance of samples was examined via a DU-8B UV-Vis double-beam spectrophotometer (UV-visible absorption spectrometer). A series of PEC performances of the as-prepared samples were probed using a three-electrode device with the prepared films as working electrode, a platinum electrode as counter electrode and Ag/AgCl (saturated KCl) as reference electrode in 0.2 M Na_2SO_4 (pH=6.8) aqueous solution via an electrochemical workstation and irradiated with a Xenon lamp (AM 1.5 G, 100 $mW \cdot cm^{-2}$). The collected Ag/AgCl potential values were converted to the reversible hydrogen electrode (RHE) potential via using the equation: $E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.1976$ V. A 300 W Xenon lamp was used to generate simulated sun light irradiation (AM 1.5 G, 100 mW/cm^2). The electrochemical impedance spectra (EIS) measurements were collected on a three-electrode configuration with AC amplitude of 5 mV and frequency range of 10-100 kHz. Moreover, the surface photovoltage (SPV) measurements can characterization of the separation of photoinduced charge in photoelectrodes through the surface photovoltage spectrometer (PL-SPS/IPCE1000) indirectly. More importantly, the band energy level of $ZnIn_2S_4$ and $CuInS_2$ can be calculated via Ultraviolet photoelectron spectroscopy (UPS). the calculation was according to the following equations:

$VBM = h\upsilon - (E_{cutoff} - E_{onset})$

Where VBM is valence band maximum, $h\upsilon$ (nonmonochromatized He-Iα radiation, $h\upsilon$ = 21.22 eV), the Ecutoff and Eonset is the secondary electron cut-off and binding energy onset, respectively.

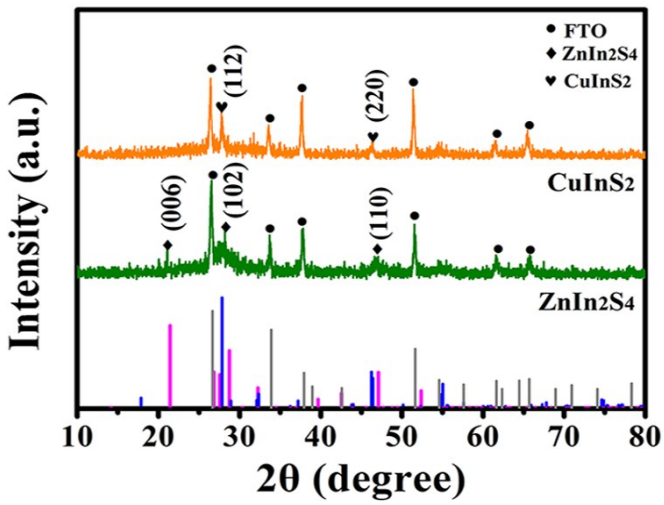

Fig. S1 XRD pattern of $ZnIn_2S_4$ and $CuInS_2$. The bottom peaks are standard position of $ZnIn_2S_4$ (JCPDS 72-0773, pink solid), $CuInS_2$ (JCPDS 82-1702, blue solid) and SnO_2 (JCPDS 77-0452, black solid)

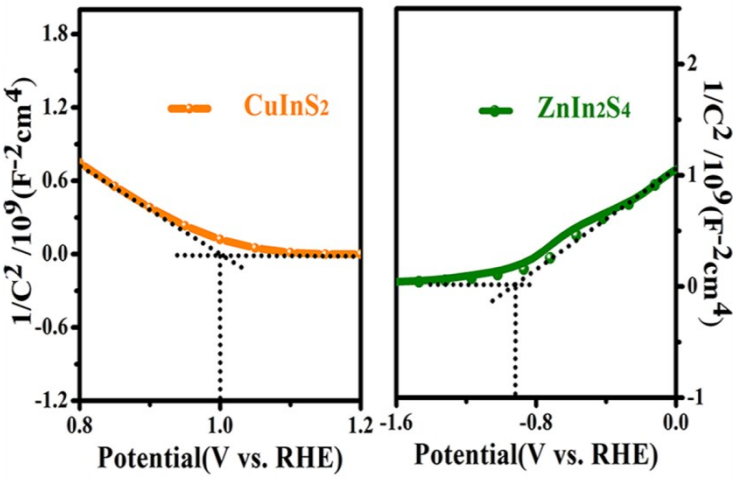

Fig. S2 Mott−Schottky plots of $ZnIn_2S_4$ and $CuInS_2$

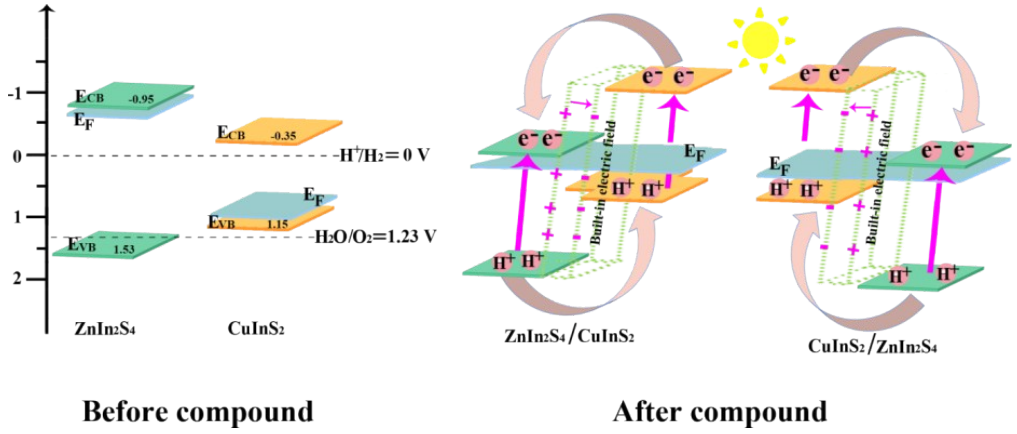

Fig. S3 Schematic diagram of $ZnIn_2S_4$ and $CuInS_2$ before and after forming bidirectional p-n heterojunction ($ZnIn_2S_4/CuInS_2$ p-n heterojunction and $CuInS_2/ZnIn_2S_4$ p-n heterojunction)

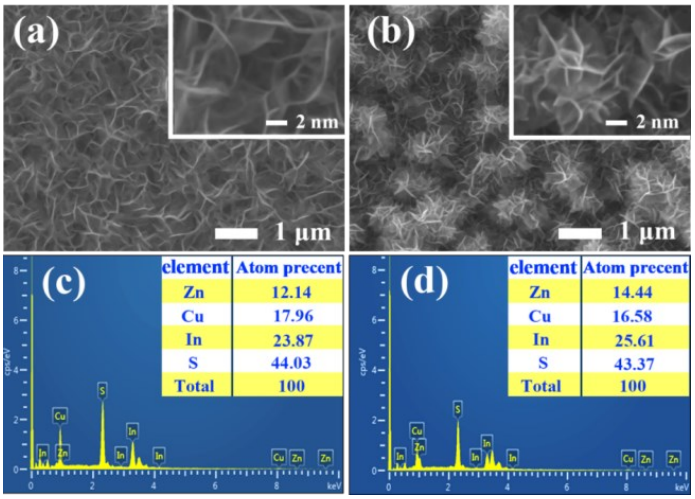

Fig. S4 The SEM images of (a) $ZnIn_2S_4/CuInS_2$ p-n heterojunction and (b) $CuInS_2/ZnIn_2S_4$ p-n heterojunction, the EDS spectrum of (c) $ZnIn_2S_4/CuInS_2$ p-n heterojunction and (d) $CuInS_2/ZnIn_2S_4$ p-n heterojunction

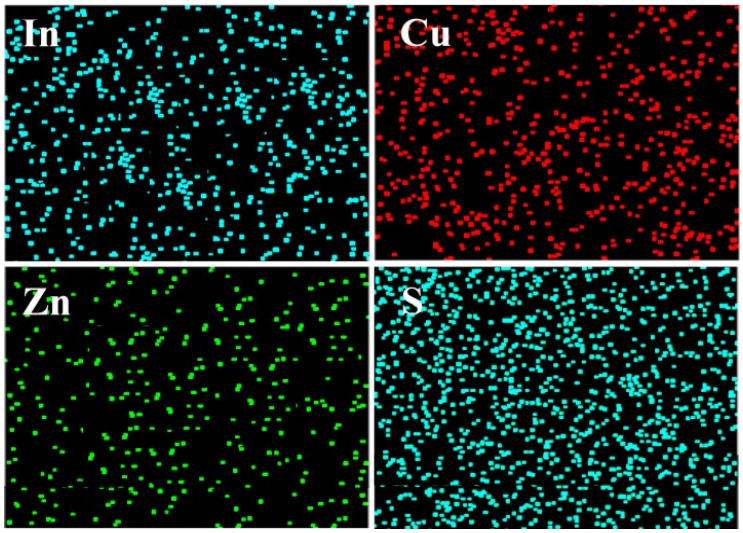

Fig. S5 Element distribution mapping

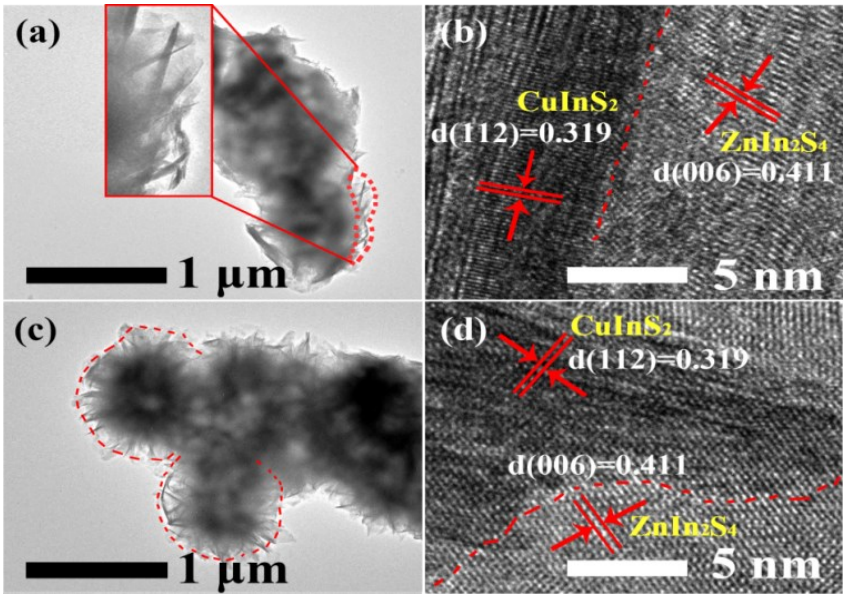

Fig. S6 TEM image (a) and HRTEM image (b) of $ZnIn_2S_4/CuInS_2$ p-n heterojunction, TEM image (c) and HRTEM image (d) of $CuInS_2/ZnIn_2S_4$ p-n heterojunction

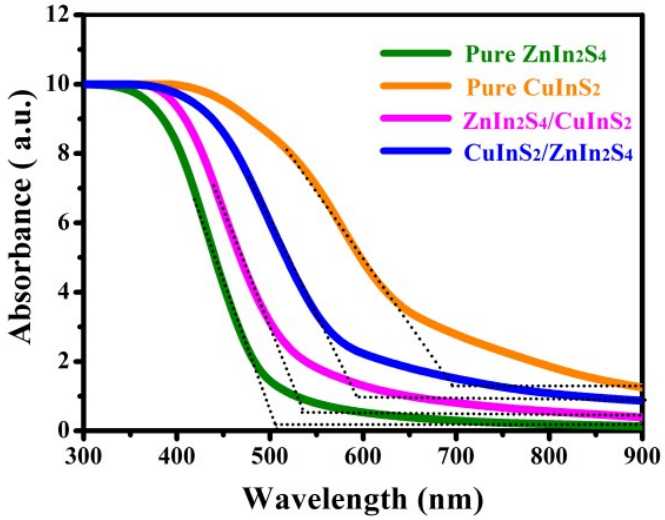

Fig. S7 UV-vis spectra of $ZnIn_2S_4$, $CuInS_2$, $ZnIn_2S_4/CuInS_2$ p-n heterojunction and $CuInS_2/ZnIn_2S_4$ p-n heterojunction

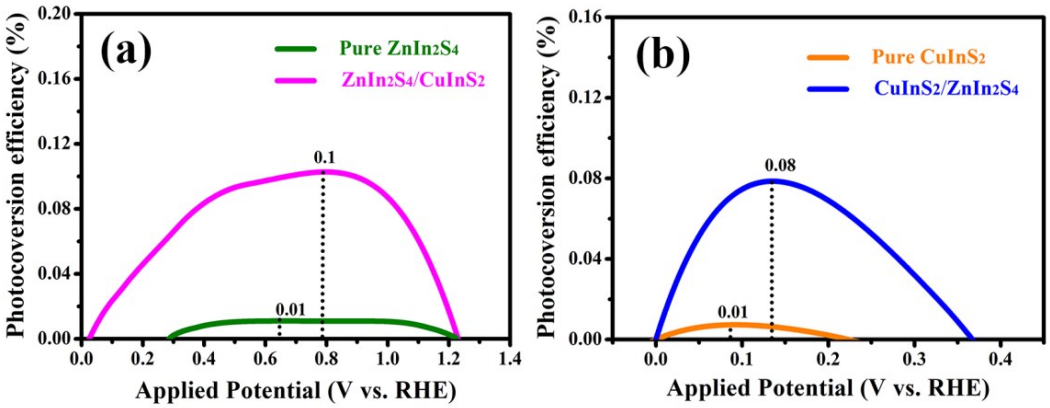

Fig. S8 Calculated applied bias photon-to-current efficiency (ABPE) curves of $ZnIn_2S_4$, $CuInS_2$, $ZnIn_2S_4/CuInS_2$ p-n heterojunction and $CuInS_2/ZnIn_2S_4$ p-n heterojunction

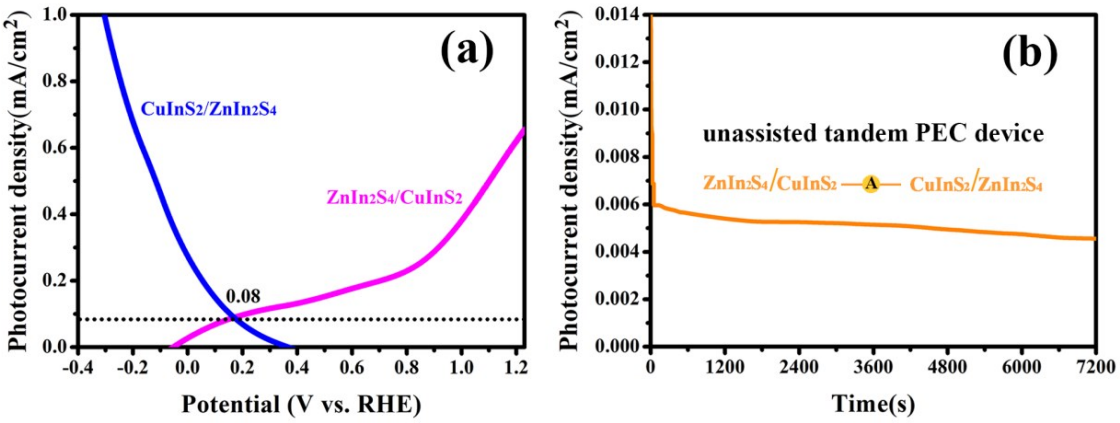

Fig. S9 (a) I−V curves of bidirectional p-n heterojunction photoelectrodes ($ZnIn_2S_4/CuInS_2$ photoanode and $CuInS_2/ZnIn_2S_4$ photocathode); (b) the I-T curve measured in unassisted tandem PEC cell device