Supporting Information

Z-scheme 2D/0D $ZnIn_2S_4$/ZnO heterostructure for efficient photocatalytic degradation of tetracycline: Energy band engineering and morphology modulation

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Characterization

The morphology of the synthesized samples was characterized by scanning electron microscopy (SEM) (Carl Zeiss Ultra Plus). Transmission electron microscopy (TEM, JOEL JEM-2100) and X-ray diffraction (XRD) measurements with Cu Kα radiation (λ = 0.15406 nm) (Bruker D8 Advance) were used to characterize the crystal structure. The surface chemical states and valence band of the samples were investigated by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250) and the binding energy of each element was calibrated by C 1s (284.6 eV). The work function of the XPS apparatus is 4.2 eV. The UV-vis diffuse reflectance spectra (DRS) of the samples were measured on a UV-vis spectrophotometer (UV-2600) with $BaSO_4$ as a reflectance standard. Ultraviolet photoelectron spectrum (UPS) was measured by a PHI5000 VersaProbe III (Scanning ESCA Microprobe) SCA (Spherical Analyzer), in which the photoelectron was generated using 21.2 eV ultraviolet light.

Photocatalytic activity tests

The light source of the photocatalytic degradation tests was performed by a mercury-

xenon lamp (Beijing NBET Technology, Mexe-500) at a distance of 10 cm from the reactor. The energy intensity is 180 mW/cm^2. Photocatalytic degradation of TC (25 mg/L, 40 mL) was conducted under different rates of magnetic stirring. Before the photocatalytic reaction, the sample powders (10 mg) were immersed in TC solution and stirred in the dark for 2 h to establish an adsorption-desorption balance. During the test, 2 mL of the sample solution was taken every 10 min and analyzed by a UV-vis spectrometer (UV-1750, Shimadzu). The maximum absorption intensity of TC located at 367 nm is regarded as the representative of TC concentration. The efficiency of degradation is specified as $1-C/C_0$. Here, C is the remaining concentration of TC solution at each irradiated time interval, and C_0 is the concentration of TC solution before irradiation.

Photoluminescence (PL) spectra and electrochemical measurements

PL spectra and electrochemical measurements were conducted to investigate the process of charge separation and transfer. PL spectra were recorded by a spectrophotometer (Hitachi, F4600) with an excitation wavelength of 350 nm. Photocurrent and electrochemical impedance spectroscopy (EIS) measurements were performed in a three-electrode quartz cell with an electrochemical workstation (Shanghai Chenhua). The counter electrode is Pt foil, and the reference electrode is Ag/AgCl. The working electrode of the sample was prepared as follows. The sample powder (2 mg) was dispersed in ethanol (500 μL) to form a suspension. Then the suspension was dropped with a coating area of 1 cm^2 on a fluorine-doped tin oxide (FTO) glass (1 cm×2 cm).

Density functional theory (DFT) calculations

To explore the charge transfer direction between the $ZnIn_2S_4$ and ZnO, the Fermi levels of $ZnIn_2S_4$ and ZnO were measured by DFT calculations using the Cambridge Sequential Total Energy Package (CASTEP) module. The geometry optimization of the bulk structures of $ZnIn_2S_4$ and ZnO was implemented by Perdew-Burke- Ernzerhof (PBE) of the Generalized Gradient Approximation (GGA). The $ZnIn_2S_4$ (102) surface

and ZnO (100) surface were cleaved from their bulk structures, respectively. The thickness of these surfaces was set to be around 8-10 Å, and a 30 Å of vacuum was introduced in the slad calculation. Monkhorst-Pack k-point mesh was 3x2x1 for ZnO (100) and 1x5x1 for $ZnIn_2S_4$ (102). A plane-wave cutoff energy of 310 eV was used, which converged total energy differences to under 1 meV/atom.

Reactive species trapping tests

Reactive species trapping was conducted to ensure the dominant species during the photocatalytic degradation of TC. Before mercury-xenon lamp irradiation, 5 mg of p-BQ, 5 mL of IPA, and 60 μL of TEOA as the scavenger of superoxide radical ($\cdot O_2^-$), hydroxyl radical (·OH), and hole (h^+) were added into TC (25 mg/L) solution, respectively. The real-time concentration of TC was determined by the same method as photocatalytic activity tests.

Electron spin resonance (ESR) measurements

ESR measurement was performed to estimate the amount of ·OH and $\cdot O_2^-$ created by photocatalysts. The catalyst (2 mg) was dispersed in deionized water or methanol (10 mL) with 1 mL 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) under xenon lamp irradiation for 10 min. DMPO was used to trap the real-timely generated ·OH in deionized water or $\cdot O_2^-$ in methanol by forming DMPO-·OH or DMPO-$\cdot O_2^-$, respectively. The ESR signals of DMPO-·OH and DMPO-$\cdot O_2^-$ were measured by Bruker EMXplus spectrometer.

High performance liquid chromatography (HPLC) and electrospray ionization-mass spectrometry (ESI-MS) tests

The photodegradation intermediates were investigated by HPLC and ESI-MS. HPLC purification was performed on a Shimazu UFLC system equipped with two LC-20AP pumps and an SPD-20A UV/vis detector using a Shimazu PRC-ODS column. HPLC analyses were performed on an Agilent 1260 HPLC system equipped with a G1322A

pump and inline diode array UV detector using an Agilent Zorbax 300SB-C18 RP column with CH3CN (0.1% of trifluoroacetic acid (TFA)) and water (0.1% of TFA) as the eluent. The spectra of ESI-MS were obtained on a Finnigan LCQ Advantage ion trap mass spectrometer (ThermoFisher Corporation) that was equipped with a standard ESI source.

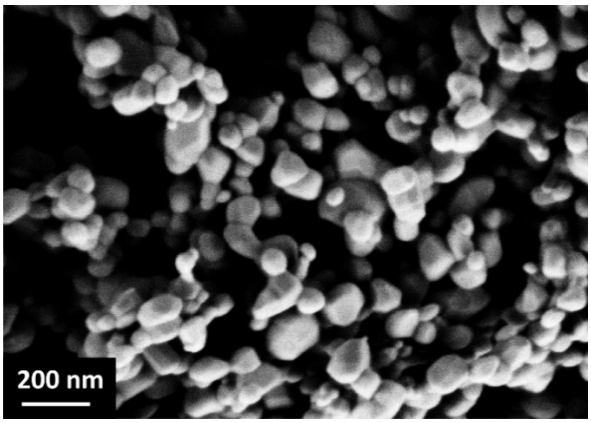

Fig. S1 SEM image of blank ZnO.

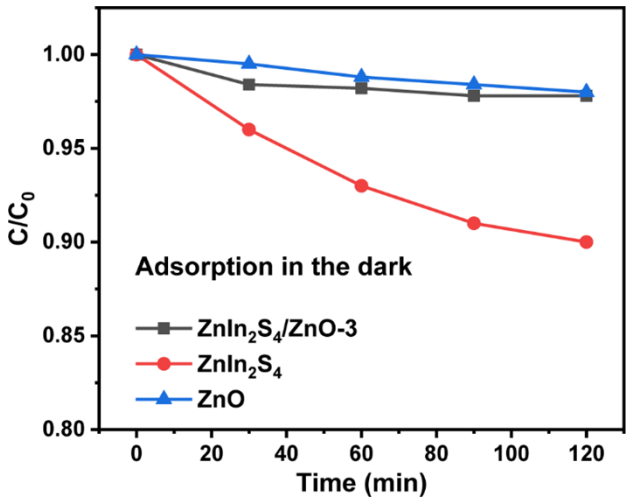

Fig. S2 TC adsorption plots over the $ZnIn_2S_4$, ZnO, and $ZnIn_2S_4$/ZnO-3 in the dark.

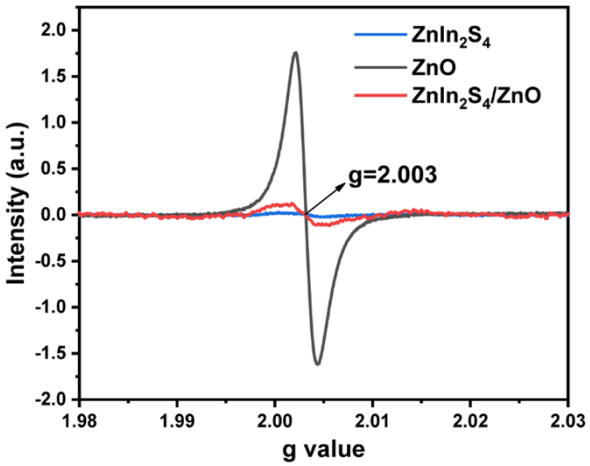

Fig. S3 Room temperature ESR spectra of $ZnIn_2S_4$, ZnO and $ZnIn_2S_4$/ZnO-3 samples oxygen for vacancy.

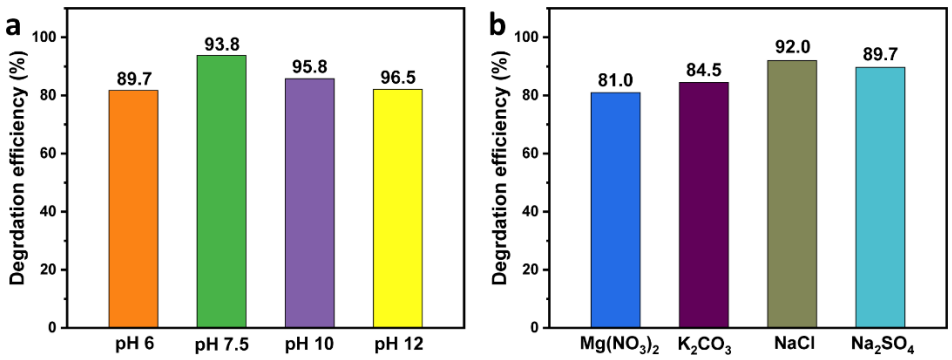

Fig. S4 TC (25 mg/L) degradation efficiencies over the $ZnIn_2S_4$/ZnO-3 photocatalyst (a) at different pH and (b) with different salts (salt concentration is 0.1 M).

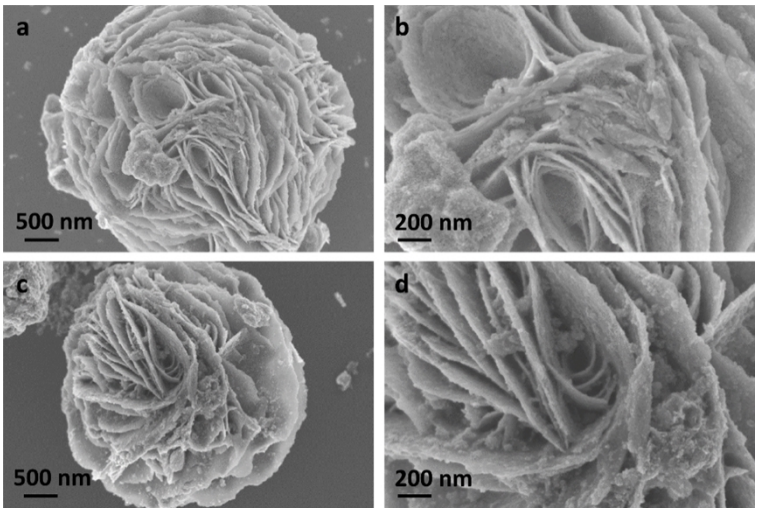

Fig. S6 SEM images of $ZnIn_2S_4$/ZnO-3 before and after catalysis.

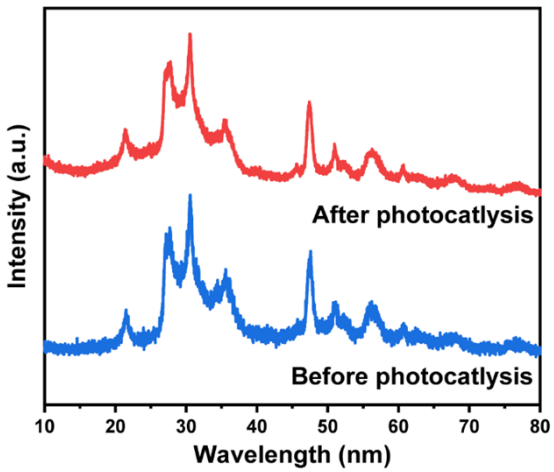

Fig. S7 XRD patterns of $ZnIn_2S_4$/ZnO-3 before and after catalysis.

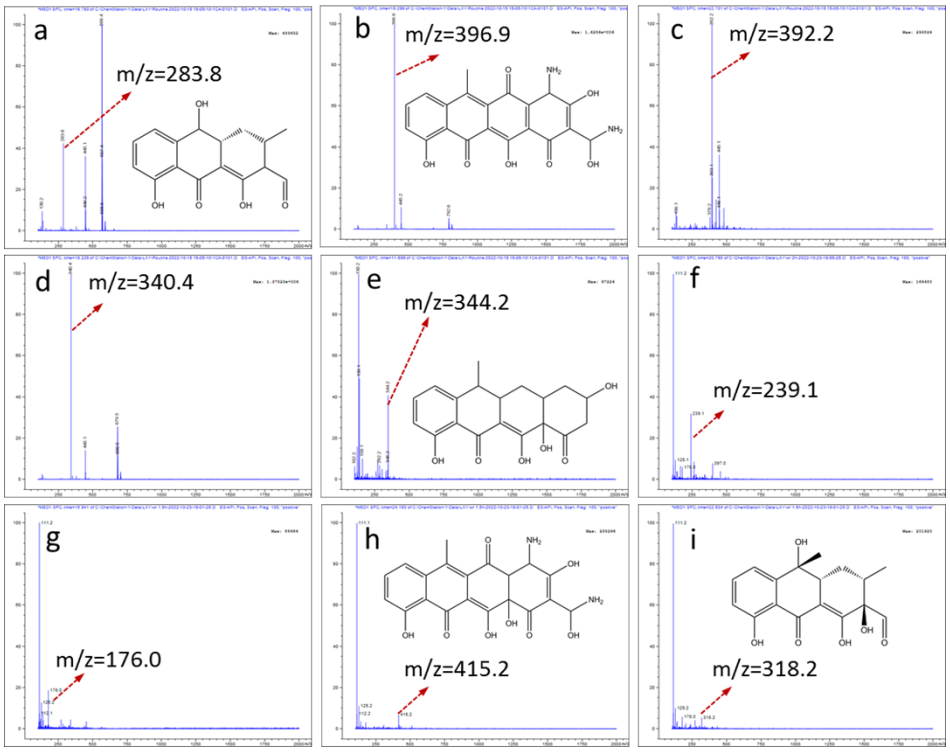

Fig. S8 Mass spectra of intermediate products during tetracycline degradation over $ZnIn_2S_4$/ZnO-3.

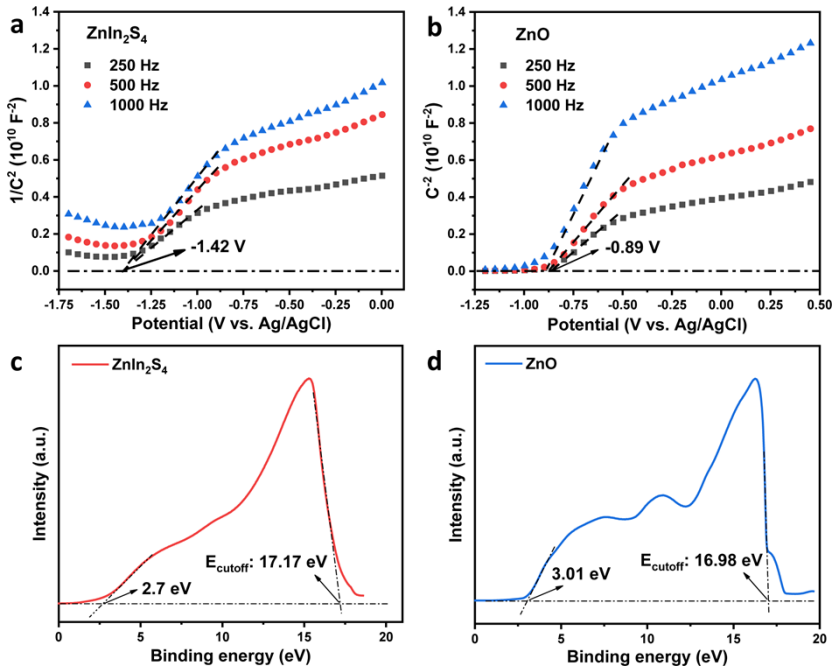

Fig. S9 Mott-Schottky curves and UPS of (a) $ZnIn_2S_4$ and (b) ZnO.

Table S1 PL lifetime of $ZnIn_2S_4$ and $ZnIn_2S_4$/ZnO-3.

Sample	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{ave} (ns)
$ZnIn_2S_4$	2.45	12.56	98.6	1.4	3.12
$ZnIn_2S_4$/ZnO-3	2.63	14.15	98.5	1.5	3.50

Table S2 Component parameters in the simulated circuit of impedance plots of $ZnIn_2S_4$, ZnO and $ZnIn_2S_4$/ZnO-3 electrodes under mercury-xenon lamp irradiation.

Sample	Rs (Ohm)	Rct (Ohm)	Cdl (10^{-5} F)	W (S $sec^{0.5}$)
$ZnIn_2S_4$	25.73	298	5.907	0.02258
ZnO	24.07	378.6	5.105	0.02037
$ZnIn_2S_4$/ZnO-3	20.24	186	8.697	0.02986