Supporting information

Interfacial S−O bonds specifically boost Z-scheme charge separation in $CuInS_2/In_2O_3$ heterojunction for efficient photocatalytic activity

Xiaofei Fu[1,*], Junwu Tao[1], Zizhou Zhao[1], Siwen Sun[1], Lin Zhao[1], Zuming He[2], Yong Gao[1] and Yongmei Xia[3]

[1] *School of Resources and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, China*

[2] *School of Microelectronics and Control Engineering, Changzhou University, Changzhou 213164, China*

[3] *School of Materials and Engineering, Jiangsu University of Technology, Changzhou 213001, China*

** Corresponding author: Xiaofei Fu; fuxiaofei@jsut.edu.cn*

Supplementary Material 1 (SM1)

Sample characterization

The crystal structure and phases of the as-prepared materials were performed on X-ray diffraction diffraction (XRD, Shimadzu-3A) with Cu Kα radiation at 0.15418 nm. Scanning electron microscopy (SEM) images were characterized by Hitachi 4800. The details of the morphology were further observed by transmission electron microscope (TEM) and high-resolution TEM (FEI Tecnai G2 F20) with an accelerating voltage of 200 kV. Fourier Transform Infrared (FT-IR) spectra were observed on a Tensor 27 spectrometer (Bruker, Germany). Elemental compositions were measured with a X-ray photoelectron spectrometer (XPS, ULVAC-PHI 5000, Japan) operated at 12.5 kV and 16 mA with the Al Kα irradiation as exciting source (1486.6 eV). The UV-vis diffuse reflectance spectra were measured on a Shimadzu UV-3600 spectrophotometer using $BaSO_4$ as a reference. The photoluminescence (PL) spectra of samples were obtained from an F-4600 spectrophotometer (Hitachi) with a laser excitation at 320 nm. The photocurrent and Mott-schottky curves were measured on an electrochemical station (CHI660D, Chenhua Instruments, China) in the standard three-electrode system. Electron spin resonance (ESR) signals of the active radicals were performed on a Bruker model ESR JES-FA200 spectrometer with 5,5-dimethyl-l-pyrroline N-oxide (DMPO) as the spin-trapping agent to detect $\bullet O_2^-$ and •OH.

Computational details

Density functional theory (DFT) calculations were carried out using the Vienna ab initio Simulation Package (VASP) on a plane-wave code with projector augmented wave potential (PAW). The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) described the exchange-correlation interactions.The lattice parameters and atomic coordinates were relaxed using the cutoff energy of 450 eV and Monkhorst-pack grids of 7×7×1 and 5×5×1 k-points for $CuInS_2$ and In_2O_3, respectively. All structures were fully relaxed until the maximum force at each atom was less than 0.01eV/Å.

SM2

Table S1

Comparison of the photocatalytic performance of $CuInS_2/In_2O_3$ with those of previously reported photocatalysts

Material	Light source	Catalyst concentration	Pollutant concentration	Catalyst performance/ irradiation time	Refs.
$CdS/CuInS_2$	300 W Xe lamp	30 mg in 150 mL	Cr(VI) (10 mg/L)	98% in 60 min	[1]
$ZnFe_2O_4/BiVO_4/$ g-C_3N_4	300 W Xe lamp	150 mg in 300 mL	lomefloxacin (25 mg/L)	96% in 105 min	[2]
$MgTiO_3$	30 W LED	30 mg in 75 mL	lomefloxacin (10 mg/L)	83% in 150 min	[3]
In_2O_3/BiOBr	300 W Xe lamp lamp	100 mg in 200 mL	Cr(VI) (10 mg/L)	56% in 30 min	[4]
Cu_2WS_4	20 W LED	20 mg in 50 mL	lomefloxacin (20 mg/L)	60% in 120 min	[5]
TiO_2/AC-AEMP	300 W UV lamp	250 mg in 500 mL	Cr(VI) (40 mg/L)	93% in 180 min	[6]
$CuInS_2/In_2O_3$	350 W Xe lamp	200 mg in 500 mL	lomefloxacin (30 mg/L), Cr(VI) (50 mg/L)	99% in 90 min, 98% in 90 min	This work

1 F. Deng, X. Lu, Y. Luo, J. Wang, W. Che, R. Yang, X. Luo, S. Luo, and D. D. Dionysiou, *Chem. Eng. J.*, 2019, **361**, 1451−1461.

2 H. B. Truong, B. T. Huy, S. K. Ray, G. Gyawali, Y. I. Lee, J. Cho, and J. Hur, *Chemosphere*, 2022, **299**, 134320.

3 Y. Sneha, S. R. Yashas, T. Thinley, S. Prabagar Jijoe, and H. Puttaiah Shivaraju, *Environ. Sci. Pollut. Res.*, 2022, **29**, 67969−67980.

4 T. Xian, H. Li, X. Sun, Y. Huo, L. Di, C. Sun, and H. Yang, *ACS Appl. Nano Mater.*, 2022, **5**, 15260–15271.

5 S. M. Abhishek, N. K. Swamy, S. R. Yashas, H. P. Shivaraju, and N. A. Chamaraja, *J. Mater. Sci. Mater. Electron.*, 2022, **33**, 12359−12370.

6 Z. Gao, H. Yang, X. Fu, Q. Jin, Q. Wu, L. Kang, and J. Wu, *Environ. Sci. Pollut. Res.*, 2020, **27**, 17446−17457.

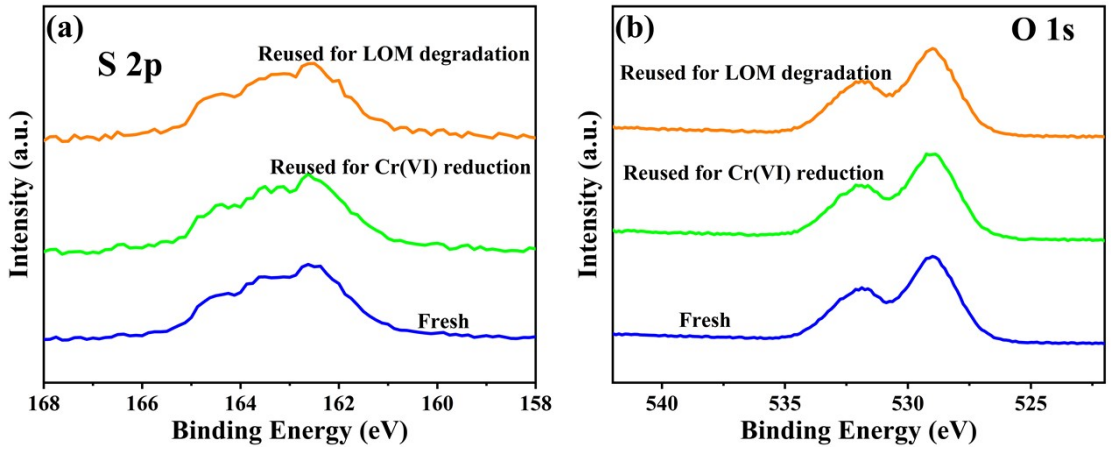

Fig. S1 High-resolution XPS spectra of (a) S 2p and (b) O 1s on the fresh and used 17-$CuInS_2/In_2O_3$.

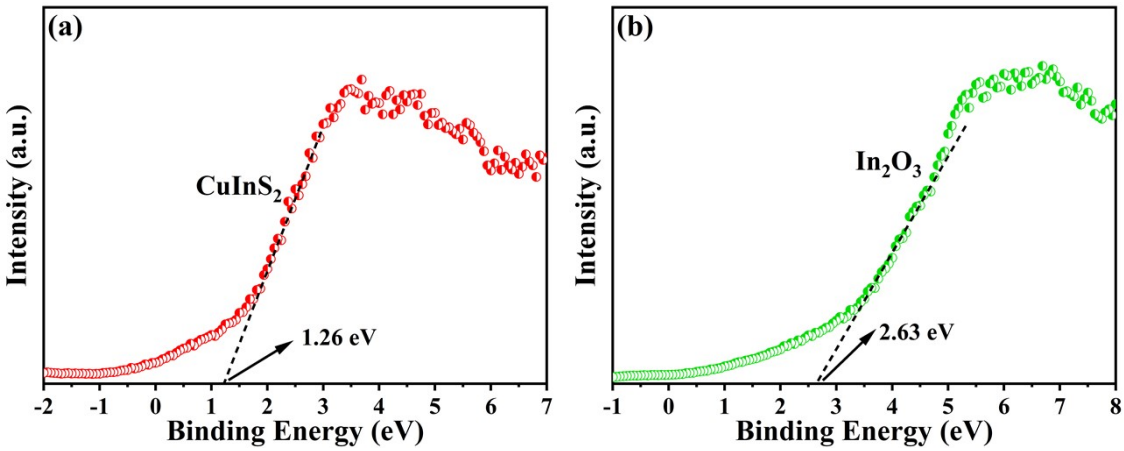

Fig. S2 XPS valence band spectra of $CuInS_2$ (a) and In_2O_3 (b).

Fig. S2 shows the XPS valence band (VB) spectra on the bare $CuInS_2$ and In_2O_3. The tangent extrapolation method was used to determine the VB position, and the VB values of $CuInS_2$ and In_2O_3 were obtained at 1.26 and 2.63 eV, respectively.