Supporting Information

Construction of ZnS-In₂S₃ Nanonests and Its Heterojunction Boosted

Visible-light Photocatalytic/Photoelectrocatalytic Performance

Long-Zhen Zhang^a, Ya-Nan Li^a, Minqiang Wang^a, Heng Liu^a, Hao Chen^a, Yanhua Cai^b, Tianhao Li^a, Maowen Xu^a, Shu-Juan Bao^{a,*}

^a Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, Institute for Clean Energy and Advanced Materials, School of Materials and Energy, Southwest University, Chongqing 400715, PR China
^b Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, PR China

*Corresponding authors. *E-mail* addresses: <u>baoshj@swu.edu.cn</u> (S.J. Bao)

Experimental

0.1 g ZIF-8 and 1.2 g $In(NO_3)_3 \cdot xH_2O$ were dispersed and mixed in 20 mL ethanol under vigorous stirring. When the milky white suspension became clear, it was transferred it into a 100-mL Teflon-lined stainless-steel autoclave and heated at 120 °C for different hours. After cooling down, the medium products were obtained by filtering.



Figure S1 SAED of ZnS-In₂S₃ heterojunction.



Figure S2 The experimental phenomenon of the initial cation-exchange process with different time.



Figure S3 The FE-SEM images of a) ZIF-8, b) medium products of 4 h and c) ZnS-In₂S₃.

As shown in Figure S2 and S3, uniform dodecahedron, ZIF-8, was used as the zinc source (Fig. S3). After a cation-exchange reaction with In(NO₃)₃, the milky white ZIF-8 suspension became clear (Fig. S2). After growth for 4 h under solvothermal conditions, a slack network consisting of nanowires was obtained as the intermediate, which is shown in Fig. 3b. After further sulfuration, the product (ZnS-In₂S₃) in Fig. 3c retained a fluffy network structure textured by nanowires, very similar to that of the solvothermal intermedium.



Figure S4 the FE-SEM images of a) medium products of 5 h and b) its corresponding sulfide.



Figure S5 the XRD patterns of medium products.

| Elements | Measured Correction | | Measured | Measured | |
|----------|---------------------|-------------|------------|--------------|--|
| | Concentration | Coefficient | Mass Ratio | Atomic Ratio | |
| Zn | 1.236 mg/L | 0.998028 | 10 4200 | F 041 | |
| In | 12.89 mg/L | 0.998680 | 10.4288 | 5.941 | |

Table S1 The concentration and mass ratio of Zn and In based on ICP of ZnS-In₂S₃



Figure S6 XPS total spectrogram of as-prepared ZnS-In₂S₃ material.





Figure S8 the nitrogen adsorption-desorption isotherms and the corresponding pore size distributions of the as-prepared photocatalysts.

The specific surface areas of $ZnS-In_2S_3$, In_2S_3 and ZnS are 68.4, 21.2 and 58.8 m²/g, respectively. And the isotherms of as-prepared photocatalysts are displayed in **Figure S8**.



Figure S9. the liquid chromatograms of bisphenol A.



Figure S10. Photocatalytic degradation of tetracycline with time of ZnS-In₂S₃ heterojunction.



Figure S11. structural formula of MO.



Figure S12. structural formula of BPA.



Figure S13. structural formula of TC.

In order to estimate the impact of dye-sensitization on the photocatalytic performance of $ZnS-In_2S_3$, colorless tetracycline (TC) and bisphenol A (BPA) were chosen as the target pollutant. As shown in **Figure S9** and **S10**, about 73% of TC and 74% of BPA was degraded after a 20-min visible light irradiation. The different degradation rate of TC, BPA and MO should result from their different molecular structure (**Figure S11-S13**), of course, dye photosensitization should also help to increase the degradation efficiency of our designed materials, but the main reason should ascribe to the heterojunction structure of material itself.



Figure S14. EIS Nyquist plots of $ZnS-In_2S_3$, In_2S_3 and ZnS samples.

The charge transfer was studied via electrochemical impedance spectroscopy. As Figure S14 shows, the Nyquist plot of ZnS-In₂S₃ heterojunction has a smaller arc radius in comparison to pure ZnS and pure In₂S₃, manifesting the higher electronic conductivity of ZnS-In₂S₃ due to electron transfer between ZnS and In₂S₃. The low charge transfer resistance/high electronic conductivity favored more efficient charge separation, which can also demonstrate the superiority of ZnS-In₂S₃ nanosized heterojunction.

| Catalysts | Light source | Concentratio n (ppm) | Time (min) | Degradation rate (%) | Refereces |
|----------------------------------|--------------------|-------------------------|------------|-------------------------|-----------|
| TiO ₂ /ZSM-5 | 550 W Max | 20 | 180 | 99.55 | 1 |
| | Lamp | | | | |
| MIL-100(Fe)-RT | 150 W UV lamp | 5 | 420 | 64 | 2 |
| PS-C ₃ N ₄ | Visible light by a | 10 | 60 | 85.85 | 3 |
| | 300 W Xe lamp | | | | |
| TiO ₂ | 300 W UV light | 10 | 105 | ~100 | 4 |
| In_2S_3 | Visible light by | 10 | 120 | 97 | 5 |
| | 500W Xe lamp | | | | |
| $In_2S_3/In(OH)_3$ | 300 W Xe-arc | 5 | 100 | ~94 | 6 |
| | lamp | | | | |
| $ZnS-In_2S_3$ | Visible light by | 10 | 20 | 98 | This work |
| | 220W lamp | | | | |

Table S2 Examples of photocatalytic materials employed for MO degradation

applications.

Reference

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