Supporting Information

Construction of ZnS-In$_2$S$_3$ Nanonests and Its Heterojunction Boosted Visible-light Photocatalytic/Photoelectrocatalytic Performance

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Experimental

0.1 g ZIF-8 and 1.2 g In(NO$_3$)$_3$$\cdot$xH$_2$O 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-In$_2$S$_3$ 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-In$_2$S$_3$.

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(NO$_3$)$_3$, 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-In$_2$S$_3$) 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.

Table S1 The concentration and mass ratio of Zn and In based on ICP of ZnS-In$_2$S$_3$

<table>
<thead>
<tr>
<th>Elements</th>
<th>Measured Concentration</th>
<th>Correction Coefficient</th>
<th>Measured Mass Ratio</th>
<th>Measured Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.236 mg/L</td>
<td>0.998028</td>
<td>10.4288</td>
<td>5.941</td>
</tr>
<tr>
<td>In</td>
<td>12.89 mg/L</td>
<td>0.998680</td>
<td></td>
<td></td>
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</table>
Figure S6 XPS total spectrogram of as-prepared ZnS-In$_2$S$_3$ material.

Figure S7 the catalytic performance of the sulfides.
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$_2$S$_3$, In$_2$S$_3$ and ZnS are 68.4, 21.2 and 58.8 m$^2$/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-In$_2$S$_3$ heterojunction.

Figure S11. structural formula of MO.

Figure S12. structural formula of BPA.
In order to estimate the impact of dye-sensitization on the photocatalytic performance of ZnS-In$_2$S$_3$, 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.
The charge transfer was studied via electrochemical impedance spectroscopy. As Figure S14 shows, the Nyquist plot of ZnS-In$_2$S$_3$ heterojunction has a smaller arc radius in comparison to pure ZnS and pure In$_2$S$_3$, manifesting the higher electronic conductivity of ZnS-In$_2$S$_3$ due to electron transfer between ZnS and In$_2$S$_3$. The low charge transfer resistance/high electronic conductivity favored more efficient charge separation, which can also demonstrate the superiority of ZnS-In$_2$S$_3$ nanosized heterojunction.
Table S2 Examples of photocatalytic materials employed for MO degradation applications.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Light source</th>
<th>Concentration (ppm)</th>
<th>Time (min)</th>
<th>Degradation rate (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/ZSM-5</td>
<td>550 W Max Lamp</td>
<td>20</td>
<td>180</td>
<td>99.55</td>
<td>1</td>
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<tr>
<td>MIL-100(Fe)-RT</td>
<td>150 W UV lamp</td>
<td>5</td>
<td>420</td>
<td>64</td>
<td>2</td>
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<tr>
<td>PS-C$_3$N$_4$</td>
<td>Visible light by a 300 W Xe lamp</td>
<td>10</td>
<td>60</td>
<td>85.85</td>
<td>3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>300 W UV light</td>
<td>10</td>
<td>105</td>
<td>~100</td>
<td>4</td>
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<tr>
<td>In$_2$S$_3$</td>
<td>Visible light by a 500W Xe lamp</td>
<td>10</td>
<td>120</td>
<td>97</td>
<td>5</td>
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<tr>
<td>In$_2$S$_3$/In(OH)$_3$</td>
<td>300 W Xe-arc lamp</td>
<td>5</td>
<td>100</td>
<td>~94</td>
<td>6</td>
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<tr>
<td>ZnS-In$_2$S$_3$</td>
<td>Visible light by a 220W lamp</td>
<td>10</td>
<td>20</td>
<td>98</td>
<td>This work</td>
</tr>
</tbody>
</table>
Reference


