Supporting Information

Fabrication of a ternary CdS/ZnIn$_2$S$_4$/TiO$_2$ heterojunction for enhancing photoelectrochemical performance: Effect of cascading electron-hole transfer

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Table S1
Elemental composition of the CdS/ZnIn$_2$S$_4$/TiO$_2$ architecture film obtained from TEM-EDX data.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>24.06</td>
</tr>
<tr>
<td>S K</td>
<td>25.16</td>
</tr>
<tr>
<td>Ti K</td>
<td>23.82</td>
</tr>
<tr>
<td>Zn K</td>
<td>0.29</td>
</tr>
<tr>
<td>Cd L</td>
<td>23.45</td>
</tr>
<tr>
<td>In L</td>
<td>3.22</td>
</tr>
</tbody>
</table>
Reaction mechanism of CdS formation

The aqueous ammonia solution was reacted with Cd(NO$_3$)$_2$ to produce the white precipitate of Cd(OH)$_2$. The excess amount of aqueous ammonia solution dissolves the Cd (OH)$_2$ and forms the tetra amine cadmium $[\text{Cd}((\text{NH}_3)_4]^2$. Addition of thiourea to this solution, the CN$_2$H$_2$ and SH$^-$ products could be formed. Then, SH$^-$ reacts with $[\text{Cd}((\text{NH}_3)_4]^2$ and form the CdS. The reaction mechanism is given below (reaction 1 to 4).

\[
\begin{align*}
\text{Cd(NO}_3\text{)}_2(aq) + 2\text{NH}_4\text{OH}(aq) & \rightarrow \text{Cd(OH)}_2 + 2(\text{NH}_4\text{)}(\text{NO}_3\text{)} \quad (1) \\
\text{Cd(OH)}_2 + 4\text{NH}_4\text{OH} & \leftrightarrow [\text{Cd}((\text{NH}_3)_4]^2 + 2\text{OH}^- + 4\text{H}_2\text{O} \quad (2) \\
\text{CS(NH}_2\text{)}_2 + \text{OH}^- & \leftrightarrow \text{CN}_2\text{H}_2 + \text{SH}^- + \text{H}_2\text{O} \quad (3) \\
[\text{Cd(NH}_3\text{)}_2]^2 + \text{SH}^- & \leftrightarrow \text{CdS} + \text{NH}_4^+ + 3\text{NH}_3 \quad (4)
\end{align*}
\]
**Figure S1** XPS survey spectra for ZnIn$_2$S$_4$/TiO$_2$/FTO and CdS/ZnIn$_2$S$_4$/TiO$_2$/FTO films
Figure S2 (a) SEM top view and (b) cross section view of CdS/TiO$_2$
Figure S3 Surface and cross-sectional morphologies of (a-b) ZnIn$_2$S$_4$ and (c-d) CdS deposited on FTO substrate
Figure S4 Plot of $(\alpha h \nu)^2$ vs. $h \nu$ for CdS and ZnIn$_2$S$_4$ samples