Electronic Supplementary Information

Noble-metal-free Cu$_2$S-modified photocatalysts for enhanced photocatalytic hydrogen production by forming nanoscale p-n junction structure

Yubin Chen*, Zhixiao Qin, Xixi Wang, Xu Guo, Liejin Guo*

Synthesis of ZnIn$_2$S$_4$ and Cu$_2$S/ZnIn$_2$S$_4$ photocatalysts

Zinc sulphate heptahydrate (ZnSO$_4$·7H$_2$O), Indium nitrate tetrahydrate (In(NO$_3$)$_3$·4H$_2$O), cetyltrimethylammonium bromide (CTAB), thioacetamide (C$_2$H$_5$NS), and ethanol (C$_2$H$_6$O) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as purchased without further purification.

ZnIn$_2$S$_4$ photocatalysts were synthesized by a reported hydrothermal method.$^1$ Briefly, 0.735 g of ZnSO$_4$·7H$_2$O, 1.615 g of In(NO$_3$)$_3$·4H$_2$O, 0.65 g of CTAB, and a double excess of TAA were respectively dissolved in 50 mL of distilled water. The mixed solution was transferred into a 70-mL Teflon-lined autoclave, which was then sealed and kept at 160 °C for 12 h. After the autoclave cooled naturally in air, the produced ZnIn$_2$S$_4$ photocatalysts were washed with ethanol and deionized water several times and dried in vacuum at 80°C for 5 h. Cu$_2$S/ZnIn$_2$S$_4$
photocatalysts were prepared by an in-situ deposition of Cu$_2$S onto ZnIn$_2$S$_4$. The preparation process is the same as that for Cu$_2$S/CdS. The Cu/Zn molar ratio of Cu$_2$S/ZnIn$_2$S$_4$ was controlled to be 0.05.

**Synthesis of Cu$_2$S/TiO$_2$ photocatalysts**

TiO$_2$ photocatalysts used in the present study were commercial P25 TiO$_2$ (Sigma Aldrich). Cu$_2$S/TiO$_2$ photocatalysts were prepared according to the following process. Typically, appropriate amounts of Cu(NO$_3$)$_2$ solution were added into 190 mL of 0.25 M Na$_2$SO$_3$/0.35 M Na$_2$S aqueous solution containing 1.0 g of TiO$_2$ powders. The suspension was stirred for 0.5 h with nitrogen purged. The obtained Cu$_2$S/TiO$_2$ photocatalysts were washed with ethanol and deionized water several times and dried in vacuum at 80°C for 5 h. The Cu/Ti molar ratio of Cu$_2$S/TiO$_2$ was controlled to be 0.05.

**Photocatalytic hydrogen production over ZnIn$_2$S$_4$, Cu$_2$S/ZnIn$_2$S$_4$, TiO$_2$ and Cu$_2$S/TiO$_2$ photocatalysts**

The reaction conditions for photocatalytic hydrogen production over ZnIn$_2$S$_4$ and Cu$_2$S/ZnIn$_2$S$_4$ photocatalysts were the same as those for CdS and Cu$_2$S/CdS photocatalysts. Photocatalytic reaction conditions for TiO$_2$ and Cu$_2$S/TiO$_2$ photocatalysts were a little different. The hydrogen production was tested with stirring under white light irradiation in a side irradiation Pyrex cell. 0.2 g of photocatalysts were added into 190 mL of aqueous solution containing 38 mL of methanol as sacrificial reagents. Nitrogen was purged through the cell before reaction to remove oxygen. A 300 W Xe lamp was used as the light source, and the temperature was kept at 35 ± 0.2 °C for the photocatalytic reaction.

**References**

The number of incident photons for the apparent quantum yield test can be calculated by the following equation.

\[ n_i = \frac{PS\lambda}{hc} \]

\( n_i \) —— the number of incident photons;

\( P \) —— light intensity / W·m\(^{-2}\);

\( S \) —— irradiation area / m\(^2\);

\( \lambda \) —— wavelength / nm;

\( h \) —— Planck constant / J·s;

\( c \) —— speed of light / m·s\(^{-1}\);

\( t \) —— reaction time / s.

**Table S1.** The Cu/Cd molar ratios determined by EDX of different Cu\(_2\)S/CdS samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>the Cu/Cd molar ratio determined by EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)S/CdS-0.01</td>
<td>0.015</td>
</tr>
<tr>
<td>Cu(_2)S/CdS-0.02</td>
<td>0.028</td>
</tr>
<tr>
<td>Cu(_2)S/CdS-0.05</td>
<td>0.056</td>
</tr>
<tr>
<td>Cu(_2)S/CdS-0.1</td>
<td>0.114</td>
</tr>
<tr>
<td>Cu(_2)S/CdS-0.2</td>
<td>0.248</td>
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</tbody>
</table>
Fig. S1. The schematic diagram of the photocatalytic reactor for hydrogen production.

Fig. S2. XRD patterns of Cu$_x$S (Na$_2$S) sample and Cu$_2$S (Na$_2$SO$_3$/Na$_2$S) sample (Cu$_2$S achieved by adding Cu$^{2+}$ into Na$_2$SO$_3$/Na$_2$S solution).
Fig. S3. Illustration of the deposition process of Cu$_2$S nanoparticles on CdS polyhedrons.

Fig. S4. Cu 2p XPS spectra of Cu$_2$S/CdS-0.05 sample before and after long-time photocatalytic reaction.
Fig. S5. Mott-Schottky plot of Cu$_2$S film. The Mott-Schottky measurement was carried out at the frequency of 5 kHz in a conventional three-electrode cell with Ag/AgCl reference electrode and a platinum wire as the counter electrode. A 0.5 M aqueous solution of Na$_2$SO$_4$ was used as the electrolyte. The Cu$_2$S film was prepared by dripping the suspension of 250 µL of water, 250 µL of ethanol, 10 µL of Nafion solution (DuPont), and 1.0 mg of Cu$_2$S powders onto a platinized-carbon electrode and leaving the solvent evaporating in air.