Supporting Information

One-step facile synthesis and high H$_2$-evolution activity of suspensible Cd$_x$Zn$_{1-x}$S nanocrystal photocatalysts in a S$^{2-}$/SO$_3^{2-}$ system

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Table S1 Summary of physical and chemical properties for the prepared suspensible Cd$_x$Zn$_{1-x}$S nanocrystals.

<table>
<thead>
<tr>
<th>Initial $x$</th>
<th>Final $x$ (EDS)</th>
<th>Final $x$ (ICP-OES)</th>
<th>Crystallite size$^a$ (nm)</th>
<th>Band gap$^b$ (eV)</th>
<th>H$_2^-$ production rate (μmol·h$^{-1}$)</th>
<th>Quantum efficiency (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>6.9</td>
<td>2.25</td>
<td>320.99</td>
<td>12.84</td>
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<tr>
<td>0.8</td>
<td>0.72</td>
<td>0.79</td>
<td>6.0</td>
<td>2.44</td>
<td>518.61</td>
<td>20.74</td>
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<tr>
<td>0.6</td>
<td>0.58</td>
<td>0.60</td>
<td>5.5</td>
<td>2.53</td>
<td>717.19</td>
<td>28.69</td>
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<tr>
<td>0.4</td>
<td>0.32</td>
<td>0.41</td>
<td>5.2</td>
<td>2.64</td>
<td>570.25</td>
<td>22.81</td>
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<tr>
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<td>0.17</td>
<td>0.20</td>
<td>5.0</td>
<td>2.86</td>
<td>353.53</td>
<td>14.14</td>
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<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.7</td>
<td>3.52</td>
<td>5.89</td>
<td>0.24</td>
</tr>
</tbody>
</table>

$^a$ crystallite size is determined by the (111) diffraction peak of suspensible Cd$_x$Zn$_{1-x}$S nanocrystals using Scherrer equation.

$^b$ the band gaps of the suspensible Cd$_x$Zn$_{1-x}$S nanocrystals were calculated according to the UV-vis spectra.

$^c$ the quantum efficiency (QE) was calculated by using the following Eq:

\[
\text{QE} [%] = \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%
\]
Fig. S1. Photographs of Cd$_{0.6}$Zn$_{0.4}$S nanocrystals synthesized in (A) a sulfur-rich S$^{2-}$/SO$_3^{2-}$ solution with an atom ratio of M$^{2+}$(Cd$^{2+}$/Zn$^{2+}$):S$^{2-}$ = 1:81 and (B) a conventional solution with an atom ratio of M$^{2+}$(Cd$^{2+}$/Zn$^{2+}$):S$^{2-}$ = 1:1.
**Fig. S2.** FESEM images and their EDS spectra (inset) of suspensible Cd$_x$Zn$_{1-x}$S nanocrystals: (A) CdS, (B) Cd$_{0.8}$Zn$_{0.2}$S, (C) Cd$_{0.6}$Zn$_{0.4}$S, and (D) ZnS.
Fig. S3. Photographs of suspensible Cd$_{0.6}$Zn$_{0.4}$S nanocrystals (left) and its corresponding aggregates (right) in the sulfur-rich S$^{2-}$/SO$_3^{2-}$ solution.

To demonstrate the importance of pre-adsorption of S$^{2-}$/SO$_3^{2-}$ ions on the Cd$_x$Zn$_{1-x}$S nanocrystal surface, the above suspensible Cd$_{0.6}$Zn$_{0.4}$S nanocrystal suspension (left) was filtered and washed with deionized water several times to remove the adsorbed S$^{2-}$/SO$_3^{2-}$ ions. After drying at 60 °C for 12 h, the obtained Cd$_{0.6}$Zn$_{0.4}$S powder was re-dispersed into the sulfur-rich S$^{2-}$/SO$_3^{2-}$ solution, which shows a typical precipitation at the bottom of cuvette (right).
Fig. S4. Photographs of traditional hexagonal CdS (calcined at 550°C under N₂) before (a) and after (b) photocatalytic H₂-evolution reaction.
**Fig. S5.** Photocatalytic H₂-evolution activity of suspensible CdₓZn₁₋ₓS nanocrystals before and after loading Pt cocatalyst (1 wt%): (a) CdS, (b) Cd₀.₈Zn₀.₂S, (c) Cd₀.₆Zn₀.₄S, (d) Cd₀.₄Zn₀.₆S, (e) Cd₀.₂Zn₀.₈S and (f) ZnS.

The Pt-modified CdₓZn₁₋ₓS photocatalyst was obtained via a typical photodeposition method. Briefly, 134 μL of H₂PtCl₆ solution (10 g L⁻¹) was injected into the prepared suspensible CdₓZn₁₋ₓS nanocrystals suspension (the synthesis details are shown in Section 2.1), where the amount of metallic Pt to CdₓZn₁₋ₓS is controlled to be 1 wt%. After bubbled with N₂ for 15 min to remove the dissolved oxygen, the above suspension was irradiated by UV-light irradiation (a 3 W and 365 nm LED, Shenzhen Lamplic Science Co. Ltd.) for 30 min under vigorous stirring to induce the deposition of metallic Pt nanoparticles on CdₓZn₁₋ₓS surface. Finally, the suspension solution was bubbled with N₂ for 15 min to remove the generated hydrogen, and the system was directly used for the following H₂-evolution experiment.
Photoelectrochemical measurements were performed on a CHI 660E electrochemical work station (Chenhua Instrument, Shanghai, China) use a standard three-electrode system configuration in Na$_2$S(0.35 M)/Na$_2$SO$_3$(0.25 M) electrolyte solution, where the photocatalyst-coated FTO as the working electrode, Ag/AgCl as a reference electrode and platinum wire as the counter electrode. A 3 W and 365 nm LED (Shenzhen Lamplic Science Co. Ltd.) served as the irradiation light source. The photocatalyst-coated FTO working electrodes were prepared as follows. Briefly, the Cd$_x$Zn$_{1-x}$S powder (10 mg) was dispersed into the ethanol-Nafion solution (1 mL of anhydrous ethanol and 1 mL of D-520 Nafion (5%, w/w, in water and 1-propanol, Alfa Aesar)), and then ultrasonicated for 30 min to obtain the suspension solution. The resulting Cd$_x$Zn$_{1-x}$S suspension was coated on the FTO (the FTO washed with deionized water, ethanol and acetone for three times, respectively, and then was dried at 60 °C) surface with the side protected by Scotch tape and then dried at 40 °C for 24 h. The transient photocurrent responses ($i$-$t$ curve) were measured at the open circuit
voltage during repeated ON/OFF illumination cycles and EIS was measured in the frequency range of 0.001-10^6 Hz with an ac amplitude of 10 mV at the open circuit voltage.