Supporting Information

Spatially Separated Catalytic Sites Supplied with CdS-MoS$_2$-In$_2$O$_3$
Ternary Dumbbell S-scheme heterojunction For Enhanced Photocatalytic Hydrogen Production

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1. Experimental details Supplement

1.1 Characterization methods

The morphology and crystal structure of the photocatalyst is understood by Zeiss evo10 scanning electron microscope, FEI tecnai G2 transmission electron microscope, and HORIBA Scientific X-ray diffractometer. The valence state analysis of the surface elements of the photocatalyst was performed on the ESCALAB Xi+ X-ray Photoelectron Spectrometer instrument. In-situ irradiated XPS measurements of samples with external light source irradiation ($\lambda = 310$ nm, Shenzhen Lamplicc Technology Co., Ltd.) UV-Vis-NIR diffuse reflectance spectroscopy (UV-Vis-NIR DRS) was measured using Shimadzu UV-2550 spectrometer, with BaSO$_4$ as the background. ASAP2460M was used to obtain the nitrogen adsorption-desorption isotherm of the sample at 77 K. Electron paramagnetic resonance (EPR) testing of hydroxyl and superoxide radicals was performed using a German Bruker A300-10/12. Use FLUOROMAX-4 spectrophotometer for photoluminescence spectrum test. The photoelectrochemical test was carried out in 0.2 M NaSO$_4$ solution using VersaStat4-400 electrochemical workstation.

1.2 Hydrogen production experiments
The PCX-50B multi-channel photochemical reaction system of Beijing Perfectlight is used to test the performance of photocatalytic hydrogen production. A quartz bottle with a flat window at the bottom was used as the reaction vessel. The simulated solar light source is a white light 5 W LED lamp and 300 W Xe lamp (with 420 nm cut-off filter, \( \lambda \geq 420 \text{ nm} \)), and 10 mg photocatalyst is dispersed in 10 vol% lactic acid aqueous solution. After using ultrasonic dispersion, the system air is replaced by nitrogen. Finally, a Tianmei GC7900 gas chromatograph was used to detect hydrogen. The chromatographic column is 13X, the carrier gas is \( \text{N}_2 \), and it is equipped with a TCD detector. The \( \text{H}_2 \) output is determined by the external standard method. The containers and experimental procedures used in the hydrogen production experiment under the natural sun are the same as those operated under the simulated solar light source. The apparent quantum efficiency (AQE) is calculated according to the following formula:

\[
AQE = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%
\]

\[
= \frac{2 \times \text{number of evolved } \text{H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100\%
\]
2. Supporting Figures and Table

**Figure S1.** XRD patterns of the (a) MoS$_2$; (b) In$_2$O$_3$; (c) CdS-Mx (x=1, 2, 3, 4.) and (d) CdS-Inx (x= 10%, 20%, 30%, 40%, 50%) samples.

**Figure S2.** (d, e) N$_2$ adsorption-desorption isotherms of CdS, MoS$_2$, In$_2$O$_3$, CdS-M2, CdS-In30% and CdS-M2-In30%.

**Figure S3.** The pore size distribution curves of CdS, CdS-M2, CdS-In30% and CdS-M2-In30%.

**Figure S4.** SEM morphologies of the MoS$_2$ (a); Element mapping test of CdS-M2 (b); In-MOFs (c); In$_2$O$_3$ (d).

**Figure S5.** XRD comparison of CdS-M2-In30% photocatalyst before and after illumination.

**Figure S6.** SEM comparison of the CdS-M2-In30% photocatalyst before and after the reaction.

**Figure S7.** Comparison of fine spectra of S 2p XPS before and after the CdS-M2-In30% photocatalyst reaction.

**Figure S8.** Photocatalyst coated electrode schematic.

**Figure S9.** UV-Vis-NIR diffuse reflectance curves of MoS$_2$ (a) and In$_2$O$_3$ (b). Kubelka-Munk function and energy graph of In$_2$O$_3$ (c) and CdS (d).

**Figure S10.** The schematic diagram of the scattering/reflection effect for the incident light on the surface of a Hollow structure.

**Figure S11.** CdS(a) and In$_2$O$_3$ (b) Mott-Schottky curve.

**Figure S12.** CdS and In$_2$O$_3$ Schematic diagram of the energy band.

**Figure S13.** Schematic diagram of photo-generated electron flow between semiconductors before and after CdS-In$_2$O$_3$ catalyst is illuminated.

**Table S1.** Parameters of CdS, MoS$_2$, In$_2$O$_3$, CdS-M$_2$(CdS-MoS$_2$), CdS-In30%(CdS-In$_2$O$_3$), and CdS-M2-In30%(CdS-MoS$_2$-In$_2$O$_3$) were obtained from the analysis of N$_2$.

**Table S2.** Attenuation parameters of the catalyst.
Figure S1. XRD patterns of the (a) MoS$_2$; (b) In$_2$O$_3$; (c) CdS-M$_x$ (x=1, 2, 3, 4) and (d) CdS-In$_x$ (x=10%, 20%, 30%, 40%, 50%) samples.
Figure S2. (a, b) N$_2$ adsorption-desorption isotherms of CdS, MoS$_2$, In$_2$O$_3$, CdS-M2(CdS-MoS$_2$), CdS-In30%(CdS-In$_2$O$_3$) and CdS-M2-In30%(CdS-In$_2$O$_3$-MoS$_2$).
Figure S3. The pore size distribution curves of CdS, CdS-M2, CdS-In30% and CdS-M2-In30%.
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Figure S6. SEM comparison of the CdS-M2-In30% photocatalyst before and after the reaction.
Figure S7. Comparison of fine spectra of S 2p XPS before and after the CdS-M2-In30% photocatalyst reaction.
Area: 2cm × 6cm

Figure. S8. Photocatalyst coated electrode schematic.
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**Table S1.** Parameters of CdS, MoS$_2$, In$_2$O$_3$, CdS-M$_2$(CdS-MoS$_2$), CdS-In$_{30\%}$(CdS-In$_2$O$_3$), and CdS-M$_2$-In$_{30\%}$(CdS-MoS$_2$-In$_2$O$_3$) were obtained from the analysis of N$_2$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{\text{BET}}$</th>
<th>Pore volume</th>
<th>Average pore size</th>
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<tr>
<td>CdS</td>
<td>5 m$^2$g$^{-1}$</td>
<td>0.01 cm$^3$g$^{-1}$</td>
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<td>MoS$_2$</td>
<td>12 m$^2$g$^{-1}$</td>
<td>0.04 cm$^3$g$^{-1}$</td>
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<td>In$_2$O$_3$</td>
<td>49 m$^2$g$^{-1}$</td>
<td>0.15 cm$^3$g$^{-1}$</td>
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<td>CdS-MoS$_2$</td>
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<td>0.06 cm$^3$g$^{-1}$</td>
<td>27 nm</td>
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<td>CdS-In$_2$O$_3$</td>
<td>33 m$^2$g$^{-1}$</td>
<td>0.20 cm$^3$g$^{-1}$</td>
<td>24 nm</td>
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<td>CdS-M$<em>2$-In$</em>{30%}$O$_3$</td>
<td>23 m$^2$g$^{-1}$</td>
<td>0.13 cm$^3$g$^{-1}$</td>
<td>23 nm</td>
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**Table S2.** Attenuation parameters of the catalyst.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pre-exponential factors A</th>
<th>Lifetime</th>
<th>Average lifetime</th>
<th>$\chi^2$</th>
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<td>1.952 ns</td>
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<td>$\tau_2 = 128.5$ ns</td>
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<td>$\tau_3 = 0.972$ ns</td>
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<td>$A_4 = 34.39$</td>
<td>$\tau_1 = 5.271$ ns</td>
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<td>CdS-M2</td>
<td>$A_2 = 23.00$</td>
<td>$\tau_2 = 133.1$ ns</td>
<td>2.116 ns</td>
<td>1.55</td>
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<td>$\tau_3 = 1.051$ ns</td>
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<tr>
<td></td>
<td>$A_4 = 42.66$</td>
<td>$\tau_1 = 1.069$ ns</td>
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<tr>
<td>CdS-In30%</td>
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<td>2.158 ns</td>
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