# Supporting Information

## One-step synthesis of CdS/CdSe/CuS hollow nanospheres in aqueous solution for enhanced photocatalytic hydrogen evolution

Guotai Sun, Jian-Wen Shi*, Yajun Zou, Siman Mao, Dandan Ma, Yixuan Lv, Lvwei Sun, Zhihui Li, Yonghong Cheng

*State Key Laboratory of Electrical insulation and Power Equipment, Center of Nanomaterials for Renewable Energy, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China.*

**Corresponding author:**

Jian-Wen Shi, E-mail: jianwen.shi@mail.xjtu.edu.cn

## 1. Materials

Sodium sulfite ($Na_2SO_3$), sodium sulfate ($Na_2SO_4$), sodium hydroxide (NaOH) and Copper chloride ($CuCl_2·2H_2O$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Polyvinyl pyrrolidone (PVP) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Sodium sulfide ($Na_2S·9H_2O$) was received from Tianjin Tianli Chemical Reagent Co., Ltd. Thioacetamide (TAA) was obtained from Tianjin Guangfu fine chemical research institute. Cadmium chloride ($CdCl_2·2.5H_2O$) and selenium powders were ordered from Tianjin Kermel Chemical Reagent Co., Ltd. As a selenium resource, the $Na_2SeSO_3$ solution was prepared by refluxing selenium powders in a sodium sulfite ($Na_2SO_3$) solution. The concrete process is summarized as follows. Firstly, 78.9 mg of selenium powder and 315.1 mg of $Na_2SO_3$ were dispersed into 50 mL of distilled water under magnetic stirring for 0.5 h. Then, the mixed solution was heated at 90 $^oC$ and refluxed under vacuum for 2 h, resulting in $Na_2SeSO_3$ solution. All the reagents were analytically pure and used directly without further purification. Distilled water with a resistivity of 18.2 MΩ·cm was used throughout the experiments.

**2. The calculation of apparent quantum efficiency**

The apparent quantum efficiency (AQE) over the $CdSe_{30}Cu_2S$ sample was carried out under the photocatalytic reaction condition (20 mg of catalysts in 50 mL aqueous solution containing 0.35 M $Na_2S$ and 0.25 M $Na_2SO_3$) using 225 W Xenon lamp assembled with band-pass filters of different wavelengths. The AQE was calculated by the formula as follows:

$$AQE = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100\%$$

$$= \frac{number\ of\ evolved\ H_2\ molecules \times 2}{number\ of\ incident\ photons} \times 100\%$$

$$= \frac{n_{H_2} \times N_A \times 2}{E\lambda/hc} \times 100\%$$

For example, the above equation can be employed to make the following calculation for the AQE at the wavelength of 365 nm with the corresponding experimental parameters, including the power density of Xenon lamp at 365 nm (1.834 $mW/cm^{-2}$), the effective area under irradiation light (28.26 $cm^2$) and the amount of produced hydrogen in 3 h (113.93 μmol).

$$AQE = \frac{113.93 \times 10^{-6} \times 6.02 \times 10^{23} \times 2}{1.834 \times 10^{-3} \times 28.26 \times 3600 \times 3 \times 365 \times 10^{-9} / \left(6.626 \times 10^{-34} \times 3 \times 10^{8}\right)} \times 100\%$$

$$= 13.35\%$$

## 3. Figures

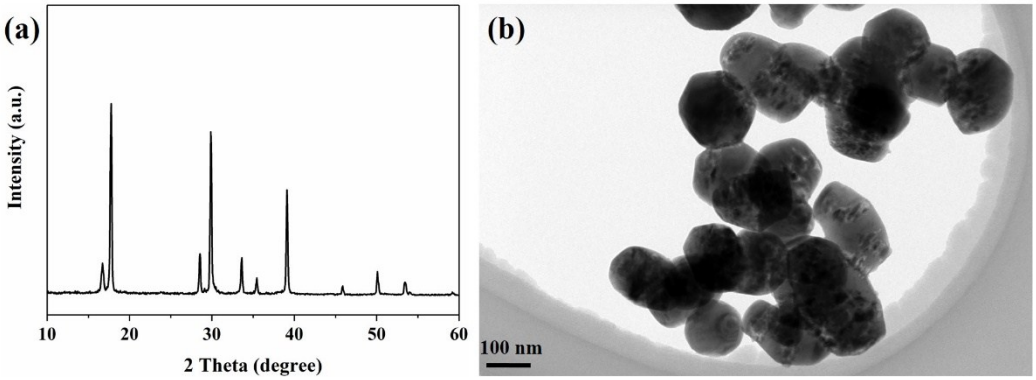


**Fig. S1.** The XRD pattern (a) and TEM image (b) of the as-prepared Cd(OH)Cl nanospheres.

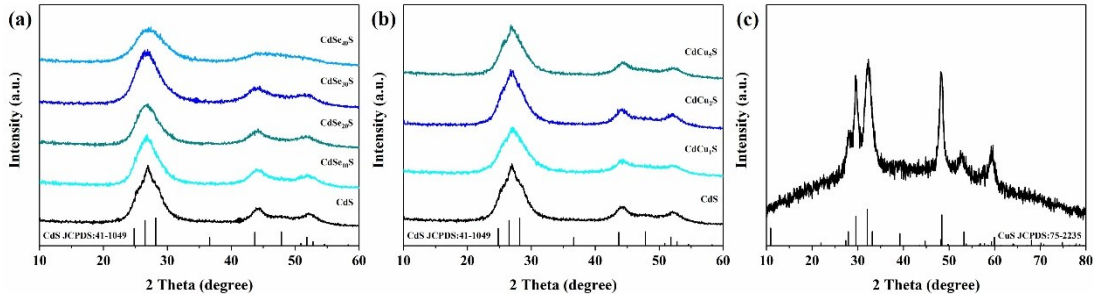


**Fig. S2.** The XRD patterns of CdS/CdSe HNPs (a), CdS/CuS HNPs (b), CuS nanoparticles (c).

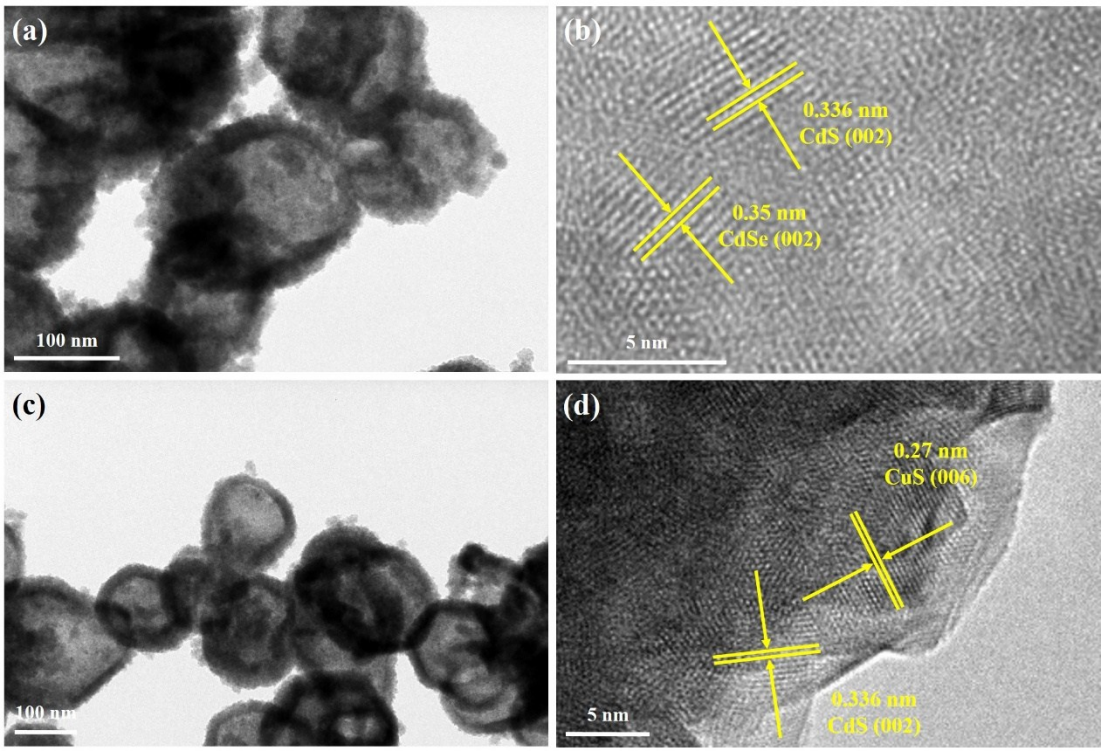

**Fig. S3.** TEM images of $CdSe_{30}S$ HNPs (a, b) and $CdCu_2S$ HNPs (c, d).

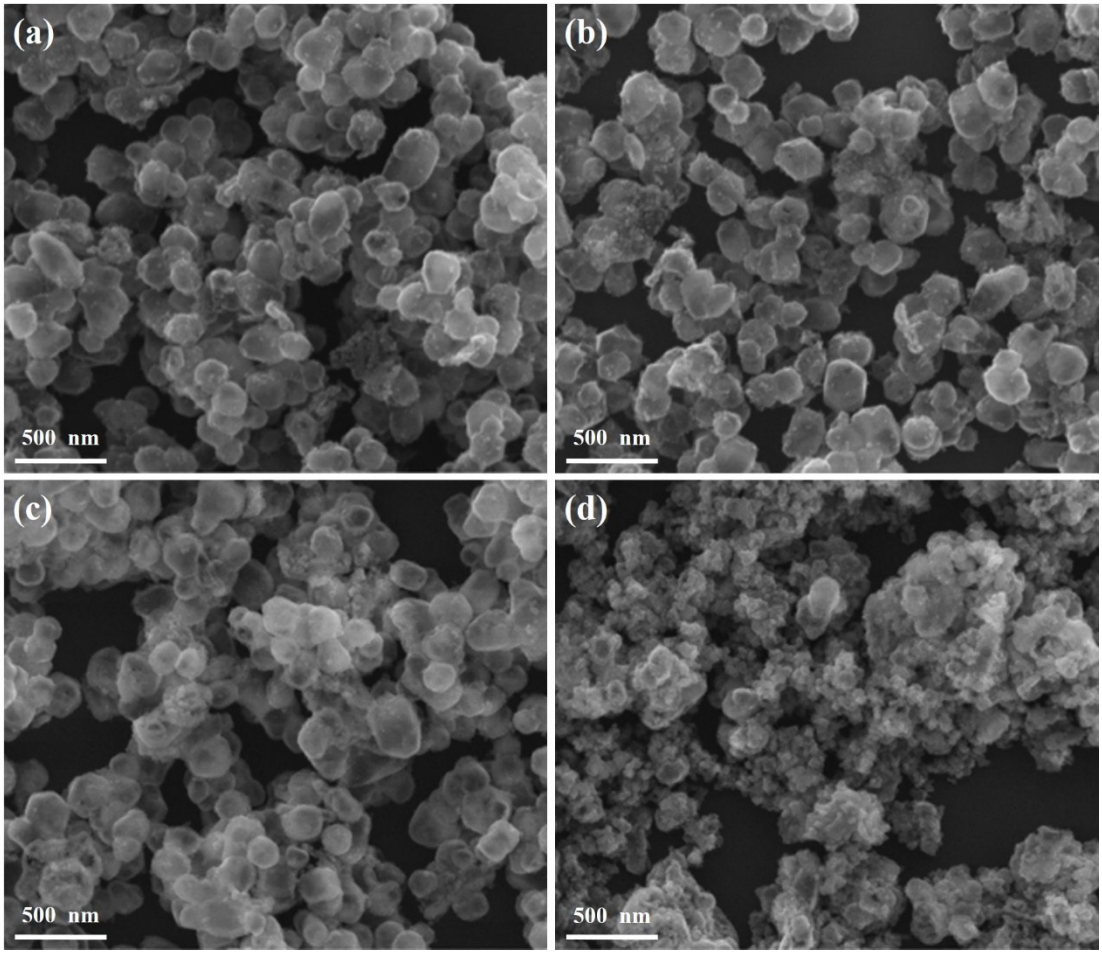


**Fig. S4.** SEM images of CdS (a), $CdSe_{30}S$ (b), $CdCu_2S$ (c), $CdSe_{30}Cu_2S$ (d).

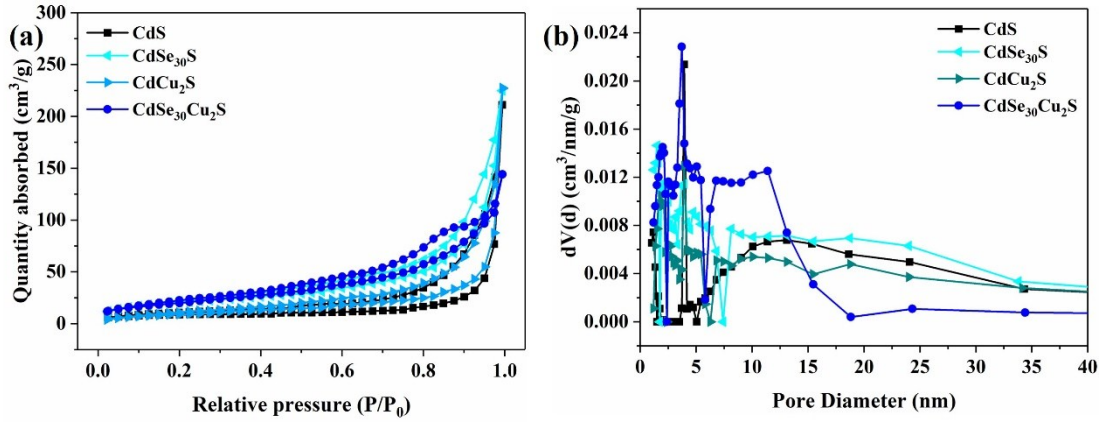


**Fig. S5.** $N_2$ adsorption-desorption isotherms (a) and pore size distribution curves (b) of the as-synthesized samples.

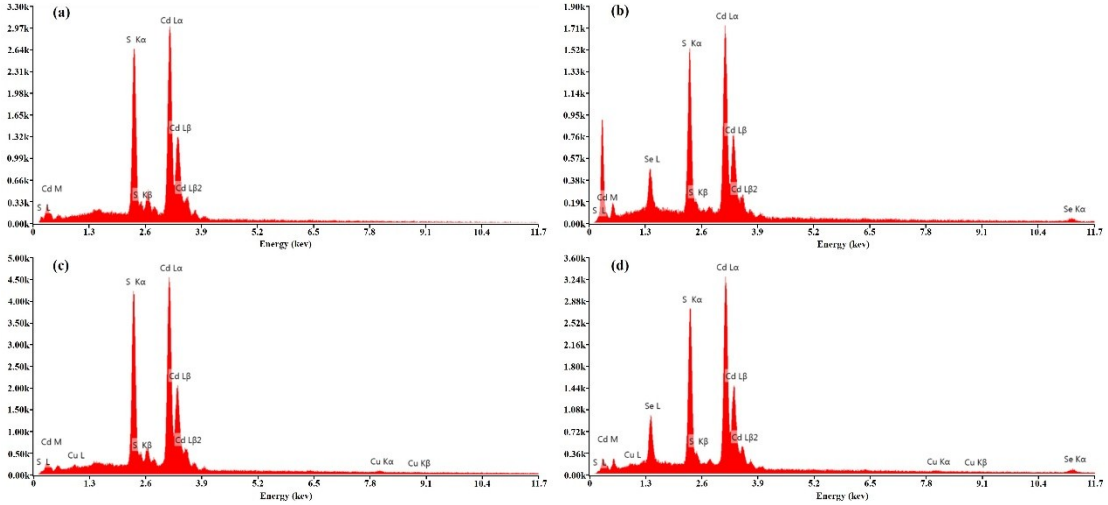


**Fig. S6.** EDX spectra of CdS (a), $CdSe_{30}S$ (b), $CdCu_2S$ (c), $CdSe_{30}Cu_2S$ (d).

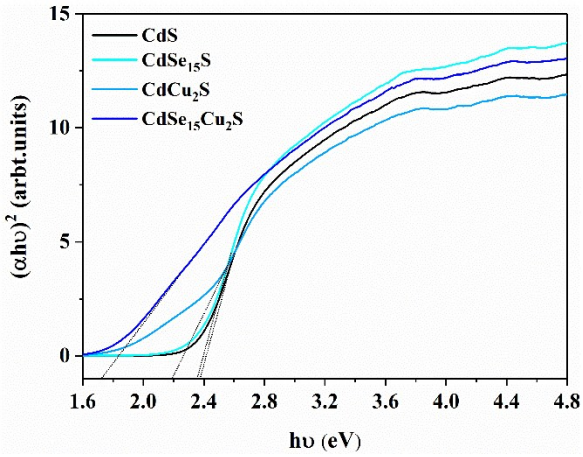


**Fig. S7.** Tauc plots of the as-synthesized samples.

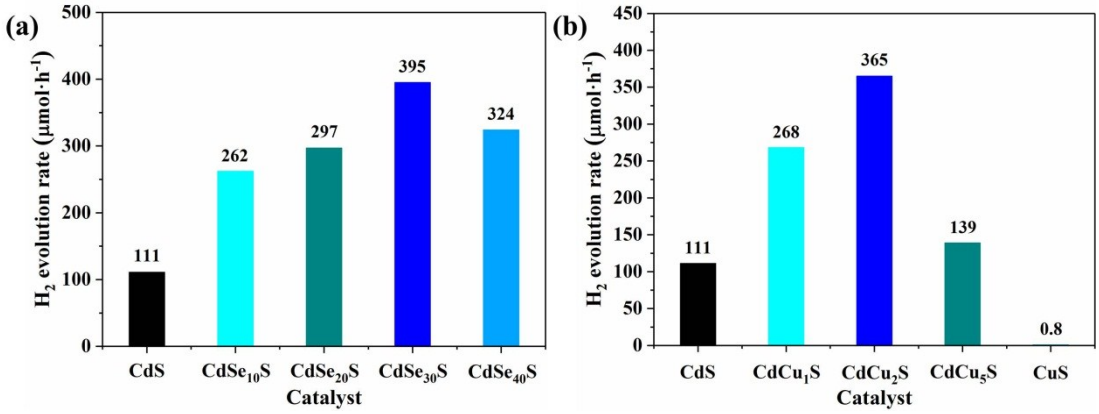


**Fig. S8.** The average photocatalytic $H_2$ evolution rates of CdS/CdSe HNPs (a), CdS/CuS HNPs (b).

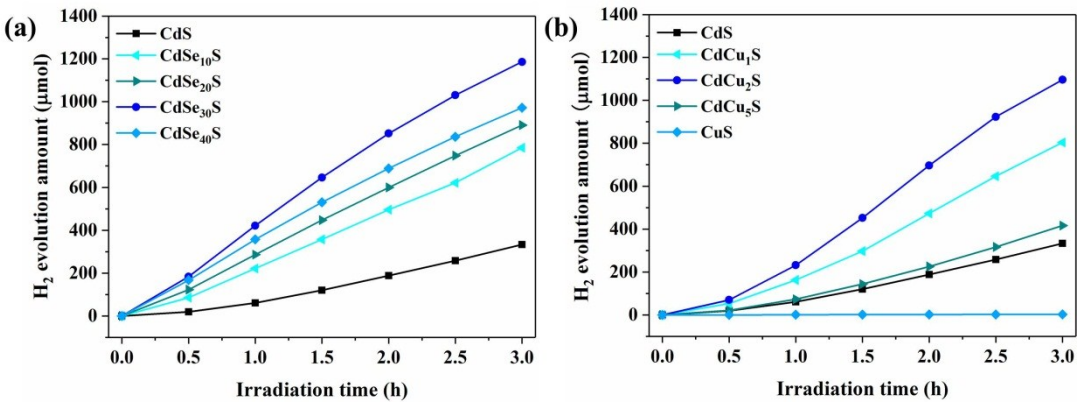


**Fig. S9.** Time courses of $H_2$ evolution over CdS/CdSe HNPs (a), CdS/CuS HNPs (b).

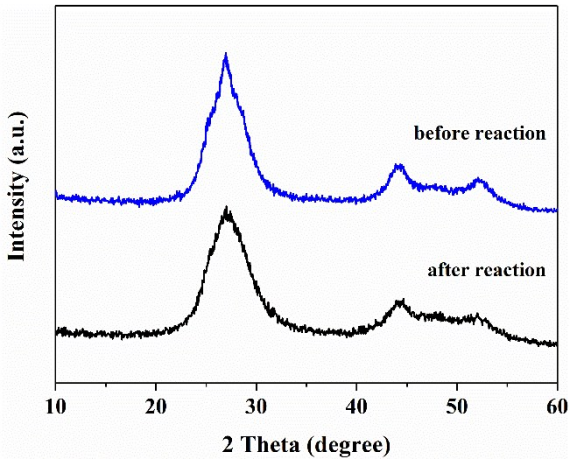


**Fig. S10.** XRD patterns of the $CdSe_{30}Cu_2S$ sample before and after cycling tests.

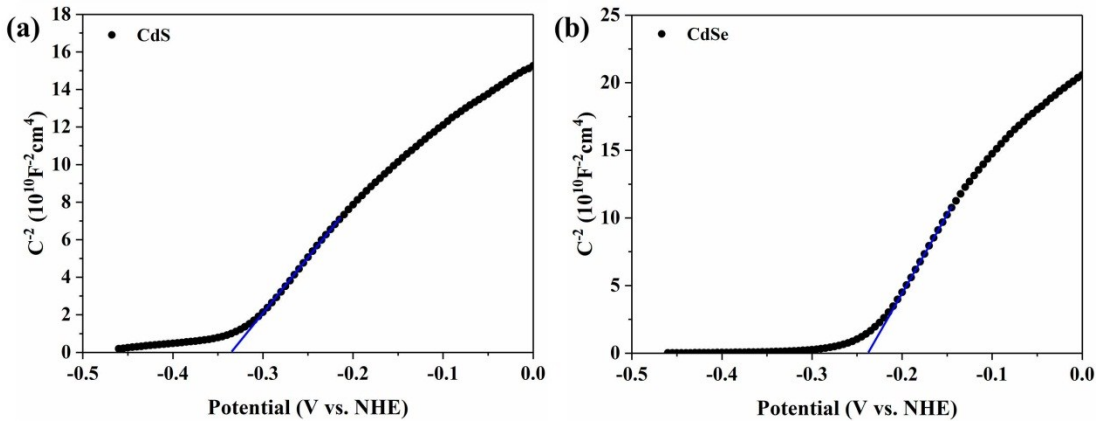


**Fig. S11.** Mott-Schottky plots of CdS with $E_{fb}$ of about -0.34 eV (a), CdSe with $E_{fb}$ of about -0.24 eV (b) versus NHE.

## 4. Tables

**Table S1** The specific surface areas ($S_{BET}$) of the as-prepared samples.

| **Sample** | CdS | $CdSe_{30}S$ | $CdCu_2S$ | $CdSe_{30}Cu_2S$ |
|---|---|---|---|---|
| **$S_{BET}$ ($m^2/g$)** | 29.41 | 73.38 | 34.05 | 74.80 |

**Table S2** The percentages of Cd, S, Se and Cu in the as-synthesized samples measured by the EDX.

| **Sample** | CdS | $CdSe_{30}S$ | $CdCu_2S$ | $CdSe_{30}Cu_2S$ |
|---|---|---|---|---|
| Cd L (at. %) | 47.57 | 41.23 | 45.94 | 40.96 |
| S K (at. %) | 52.43 | 46.87 | 52.64 | 46.21 |
| Se K (at. %) | - | 11.91 | - | 11.65 |
| Cu K (at. %) | - | - | 1.42 | 1.18 |

**Table S3** The band gap values of the as-prepared samples.

| **Sample** | CdS | $CdSe_{30}S$ | $CdCu_2S$ | $CdSe_{30}Cu_2S$ |
|---|---|---|---|---|
| **Band gap (eV)** | 2.41 | 2.39 | 2.26 | 1.84 |

**Table S4** Comparison of the photocatalytic $H_2$ evolution rates over different CdS-based photocatalysts.

| Catalyst | R($H_2$) (mmol/g/h) | Sacrificial agents | Reference |
|---|---|---|---|
| CdS HNPs | 11.1 | 0.35 M $Na_2S$ and 0.25 M $Na_2SO_3$ | This work |
| $CdSe_{30}Cu_2S$ | 72.3 | 0.35 M $Na_2S$ and 0.25 M $Na_2SO_3$ | This work |
| Au/CdS/PdS | 16.35 | 0.35 M $Na_2S$ and 0.25 M $Na_2SO_3$ | [1] |
| CdS/NiS | 1.4445 | 0.25 M $Na_2S$ and 0.35 M $Na_2SO_3$ | [2] |
| CdSe/CdS/$TiO_2$/Pt | 9.8 | 0.25 M $Na_2S$ and 0.25 M $Na_2SO_3$ | [3] |
| ZnO/CdS/ZnS | 44.7 | 0.35 M $Na_2S$ and 0.25 M $Na_2SO_3$ | [4] |
| $CdS_{0.9}Se_{0.1}$ | 29.12 | 0.35 M $Na_2S$ and 0.25 M $Na_2SO_3$ | [5] |
| CdS/NiS | 1.131 | 0.35 M $Na_2S$ and 0.25 M $Na_2SO_3$ | [6] |
| Pt-PdS/CdS | 29.23 | 0.5 M $Na_2S$ and 0.5 M $Na_2SO_3$ | [7] |
| CdS/$MoS_2$ | 4.65 | 0.45 M $Na_2S$ and 0.55 M $Na_2SO_3$ | [8] |
| CdS/$Ni_2P$ | 85.0 | 0.25 M $Na_2S$ and 0.35 M $Na_2SO_3$ | [9] |
| Pd/CdS/PdS | 89.2 | 0.1 M $Na_2S$ and 0.1 M $Na_2SO_3$ | [10] |

**Table S5** AQE over the $CdSe_{30}Cu_2S$ sample at different wavelengths.

| **λ (nm)** | 365 | 380 | 420 | 500 |
|---|---|---|---|---|
| **AQE (%)** | 13.35 | 9.03 | 2.07 | 1.00 |

**Table S6** Apparent quantum yield values of CdS-based photocatalysts for hydrogen evolution.

| Catalyst/weight | Light source | Wavelength | Sacrificial agent | AQE | Reference |
|---|---|---|---|---|---|
| $CdSe_{30}Cu_2S$/20 mg | 225 W lamp | 365 nm | $Na_2S$ and $Na_2SO_3$ | 13.35 % | This work |
| $CdSe_{30}Cu_2S$/20 mg | 225 W lamp | 420 nm | $Na_2S$ and $Na_2SO_3$ | 2.07 % | This work |
| CdS/$Nb_2O_5$/N-graphene/25 mg | 150 W lamp | 400 nm | $Na_2S$ and $Na_2SO_3$ | 1.5 % | [11] |
| $CdS_{0.9}Se_{0.1}$/50 mg | 300 W lamp | 400 nm | $Na_2S$ and $Na_2SO_3$ | 4.2 % | [5] |
| CdS/Pt/20 mg | 300 W lamp | 435 nm | $Na_2S$ and $Na_2SO_3$ | 10.4 % | [12] |
| CdS/NiO/200 mg | 500 W lamp | 420 nm | $Na_2S$ and $Na_2SO_3$ | 6.02 % | [13] |
| CdS/SrS/Pt/200 mg | 350W lamp | 420 nm | $Na_2S$ and $Na_2SO_3$ | 2.85 % | [14] |

## References


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