# Electronic Supplementary Information

# β-NiS modified CdS nanowires for photocatalytic $H_2$ evolution with exceptionally high efficiency

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**Shundong Guan, et al., *Chemical Science*, Figure S1**

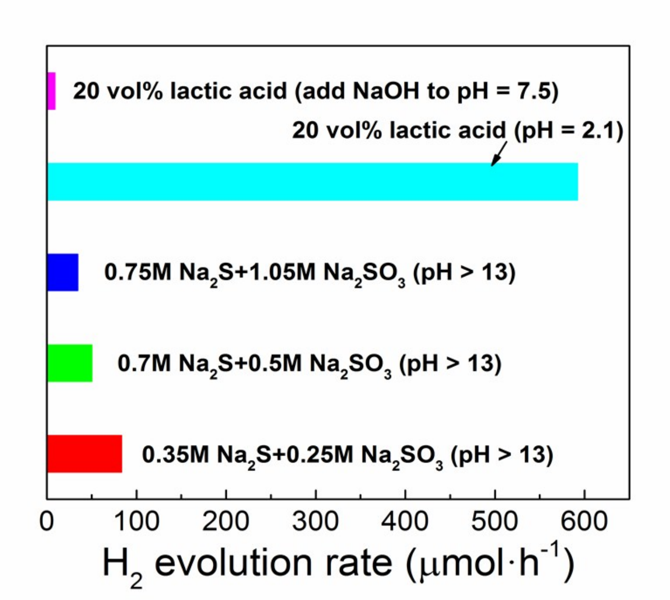


**Figure S1** The $H_2$ evolution rate under different sacrificial agent solutions over the optimal NiS/CdS NWs prepared at the Ni/Cd feed molar ratio of 0.8. The data were calculated based on the $H_2$ amount generated in the first 4 h reaction. Reaction conditions: 5 mg of the catalyst; 100 mL of aqueous solution; 7 °C; and visible light irradiation (λ ≥ 420 nm) provided by a 300 W Xe lamp with an UV cut-off filter. This figure reveals that the acidic conditions provided by 20 vol.% of lactic acid aqueous solution is beneficial for the photocatalytic $H_2$ evolution over the present NiS/CdS NWs.

**Shundong Guan, et al., *Chemical Science*, Figure S2**

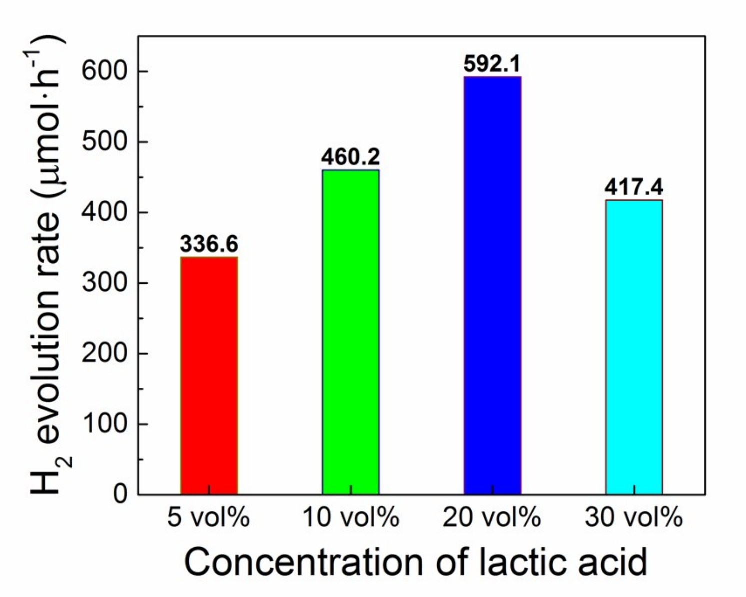


**Figure S2** The rate of photocatalytic $H_2$ evolution in different concentrations of lactic acid aqueous solution over the β-NiS modified CdS nanowires (NiS/CdS NWs) prepared at a Ni/Cd feed molar ratio of 0.8 in the synthesis reaction. The data were calculated based on the $H_2$ amount generated in the first 4 h of reaction. Reaction conditions: 5 mg of the photocatalyst; 100 mL of aqueous solution; 7 ºC; and visible light irradiation (λ ≥ 420 nm) provided by a 300 W Xe lamp with an UV cut-off filter. This figure reveals that the optimum concentration of lactic acid for the photocatalytic $H_2$ evolution over the as-prepared NiS/CdS NWs is 20 vol.%.

**Shundong Guan, et al., *Chemical Science*, Figure S3**

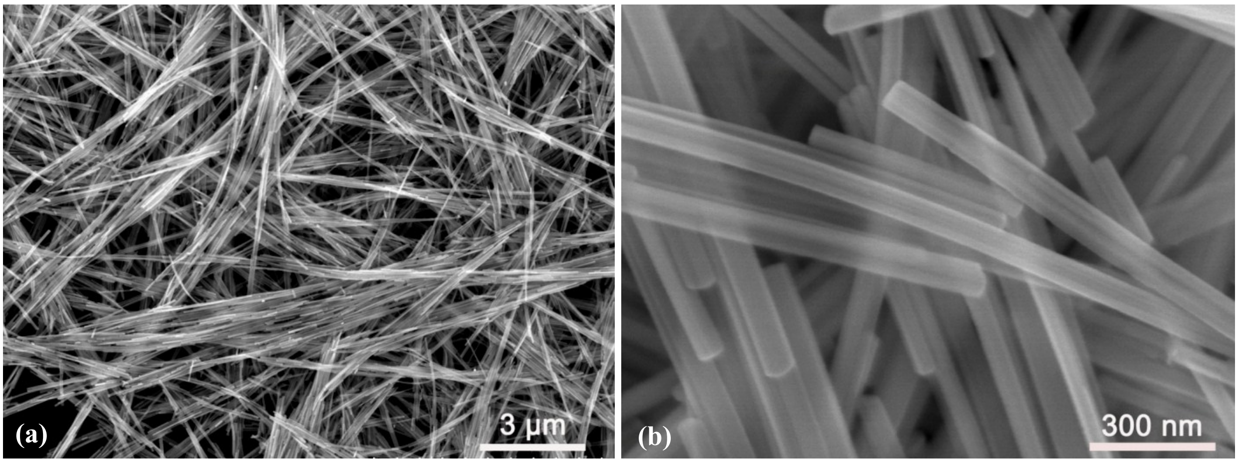


**Figure S3** Typical SEM images of the synthesized pure CdS NWs at low (a) and high (b) magnifications. The CdS NWs have an average diameter of about 30 nm and a length of 5-10 μm.

**Shundong Guan, et al., *Chemical Science*, Figure S4**

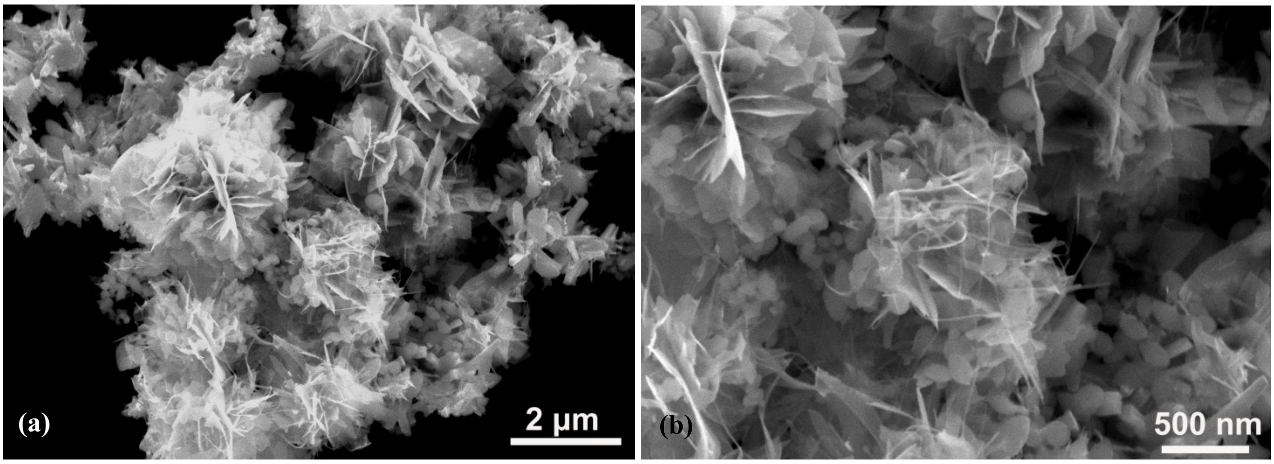


**Figure S4** Typical SEM images of the synthesized pure NiS sample at low (a) and high (b) magnifications, indicating that it consists of flower-like nanosheets and nanoparticles.

**Shundong Guan, et al., *Chemical Science*, Figure S5**

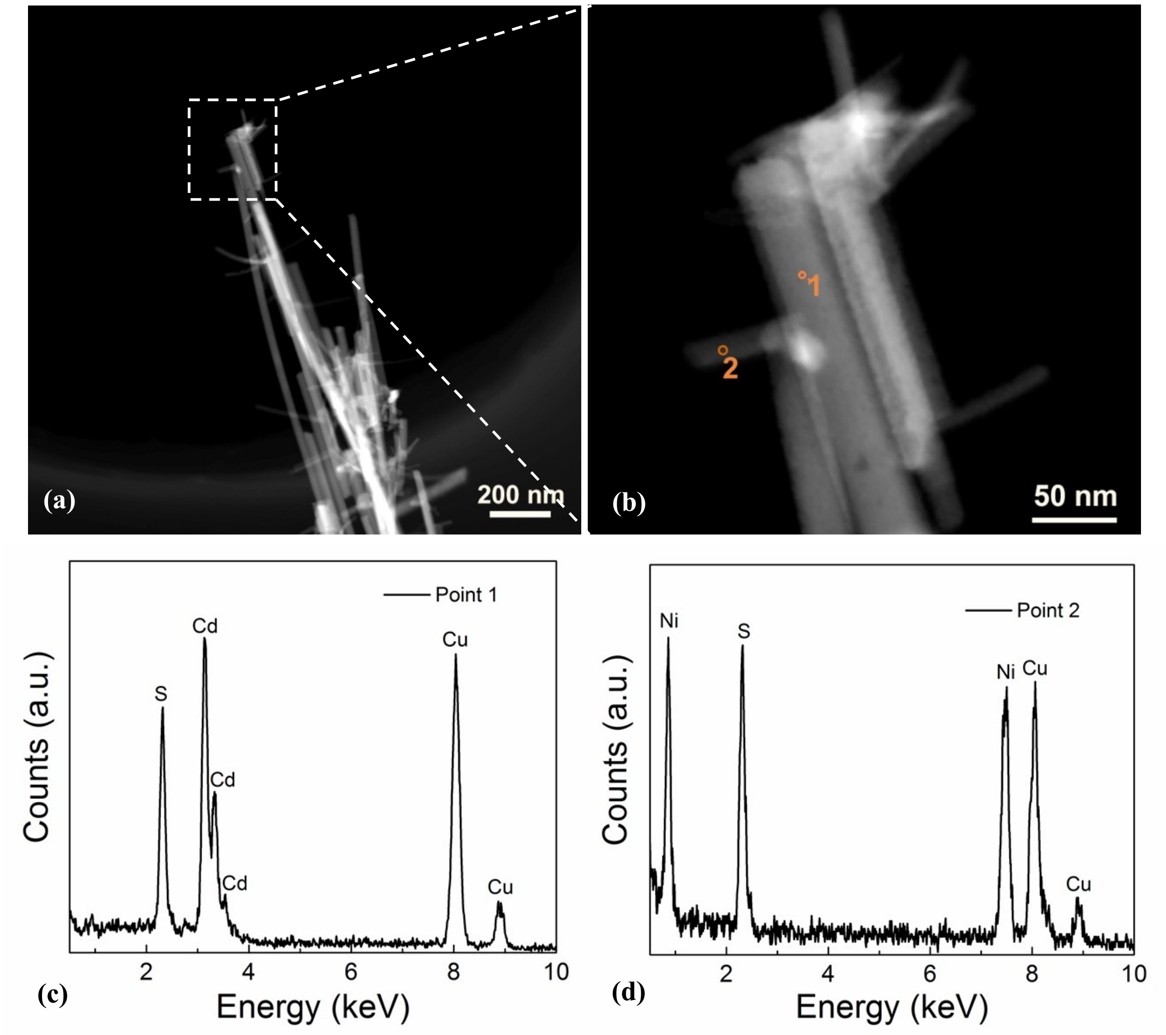


**Figure S5** (a) low and (b) high magnification STEM images of the optimal NiS/CdS NWs prepared at the Ni/Cd feed molar ratio of 0.8. (c) and (d) EDX spectra of the point 1 and 2 as shown in (b), respectively. This figure indicates the successful loading of NiS nanoflakes onto CdS NWs.

**Shundong Guan, et al., *Chemical Science*, Figure S6**

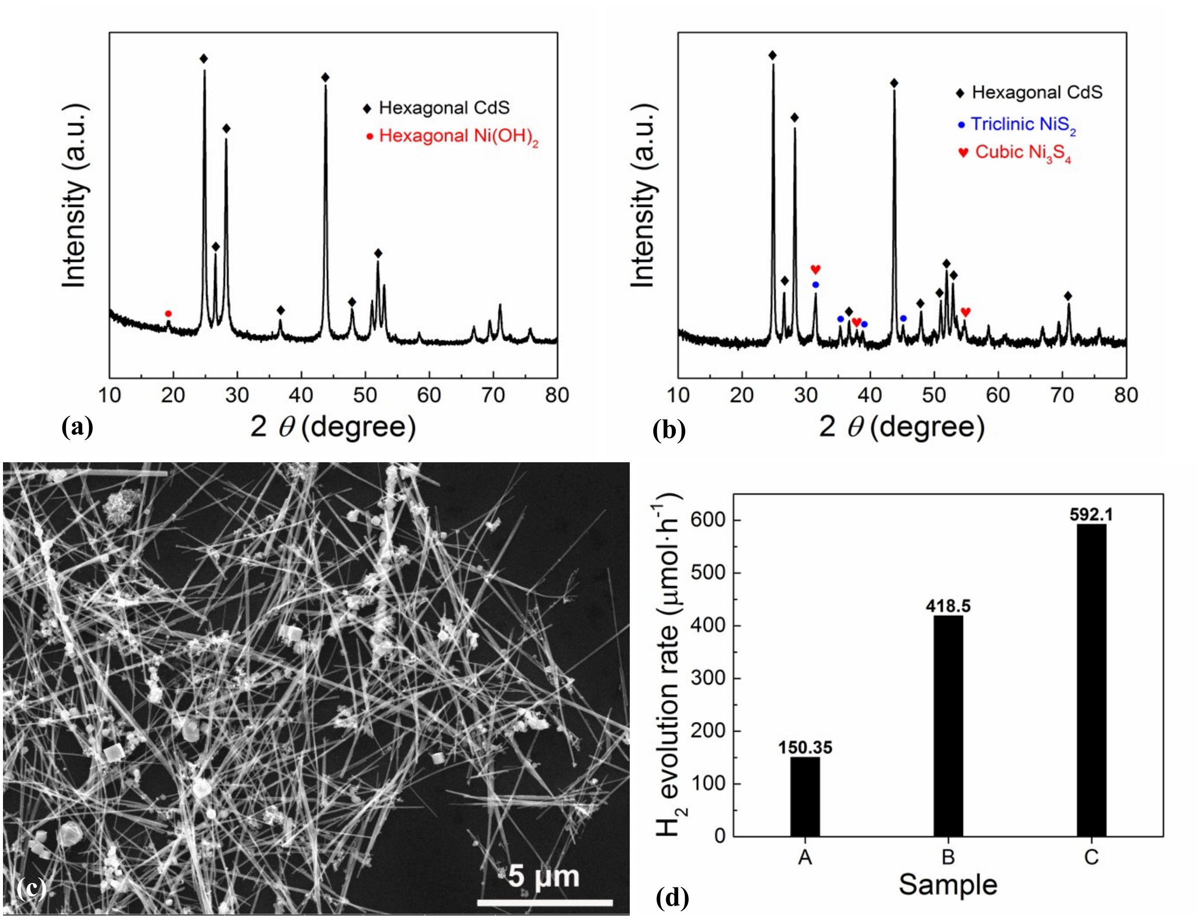


**Figure S6** XRD patterns of the products prepared at a Ni/Cd feed molar ratio of 0.8 without $NaH_2PO_2{\cdot}H_2O$ while the Ni/S molar ratio was 1:4 (a) and 1:20 (b), respectively. (c) Typical SEM image of the product prepared at a Ni/Cd feed molar ratio of 0.8 and Ni/S feed molar ratio of 1:20 without $NaH_2PO_2{\cdot}H_2O$. (d) The $H_2$ evolution rate over the products prepared under different conditions. Among them, Samples A and B were prepared at a Ni/Cd feed molar ratio of 0.8 without $NaH_2PO_2{\cdot}H_2O$ while the Ni/S molar ratio was 1:4 and 1:20, respectively; and Sample C was prepared at a Ni/Cd feed molar ratio of 0.8 with 0.6 mmol of $NaH_2PO_2{\cdot}H_2O$ while the Ni/S feed molar ratio was 1:4. The data were calculated based on the $H_2$ amount generated in the first 4 h reaction. Reaction conditions: 5 mg of the catalysts; 100 mL of aqueous solution containing 20 vol.% lactic acid; 7 °C; and visible light irradiation ($\lambda \geq 420$ nm) provided by a 300 W Xe lamp with a cut-off filter. This figure reveals that $NaH_2PO_2{\cdot}H_2O$ is crucial for the successful loading of β-NiS onto CdS NWs to prepare a high-performance photocatalyst.

**Shundong Guan, et al., *Chemical Science*, Figure S7**

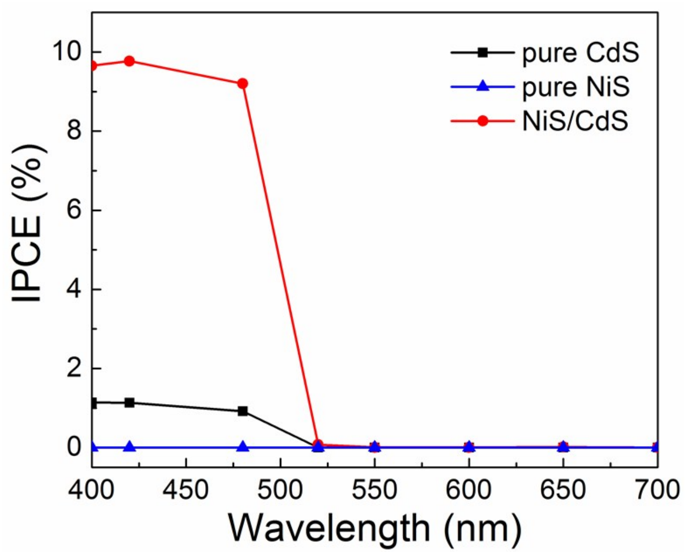


**Figure S7** Incident photon-to-electron conversion efficiencies (IPCE) of the pure CdS NWs, pure NiS nanostructures and optimal NiS/CdS NWs prepared at the Ni/Cd feed molar ratio of 0.8.

All the IPCE data were calculated by,[S1]

$$IPCE = \frac{1240 \times J}{\lambda \times I_{light}} \times 100\% \quad (1)$$

where $J$ is the measured photocurrent, and $I_{light}$ is the light intensity at the wavelength $\lambda$ of 400±5, 420±5, 480±5, 520±5, 550±5, 600±5, 650±5 and 700±5 nm, respectively, which is measured by an irradiatometer (FZ-A, Photoelectric Instrument Factory of Beijing Normal University, Beijing, China).

As is seen from this figure, under light irradiation in the range of 400-520 nm, pure β-NiS nanostructures almost have no ability to photo-to-electron conversion, while pure CdS NWs presented a small photon-to-electron conversion efficiency. However, after the loading of β-NiS onto CdS NWs, the photon-to-electron conversion efficiency was dramatically enhanced through the present NiS/CdS NWs hybrid structures. Meanwhile, under light irradiation after 520 nm, all the three samples (pure CdS, pure NiS and NiS/CdS hybrid structure) have very low photon-to-electron conversion efficiency. These results reveal that in the present NiS/CdS NWs hybrids, NiS is not a photocatalyst but only serves as a co-catalyst for CdS NWs to effectively promote the separation of photo-generated electron-hole pairs.

**Shundong Guan, et al., *Chemical Science*, Table S1**

**Table S1** Practical molar ratios of NiS in the photocatalysts prepared at various Ni/Cd feed molar ratios measured by SEM-EDX analysis

| | | | | | | |
|---|---|---|---|---|---|---|
| **Designed Ni/Cd feed molar ratio** | 0:1 (pure CdS) | 0.2:1 | 0.3:1 | 0.4:1 | 0.5:1 | 0.6:1 |
| **Practical molar percentage of NiS** | 0% | 0.53% | 0.96% | 2.39% | 4.87% | 7.01% |
| **Designed Ni/Cd feed molar ratio** | 0.7:1 | 0.8:1 | 0.9:1 | 1:1 | 1.2:1 | 1:0 |
| **Practical molar percentage of NiS** | 9.89% | 11.75 % | 13.8% | 15.2% | 18.6% | 100% (pure NiS) |

**Table S2** Review on CdS-based noble metal-free photocatalysts for $H_2$ evolution

| Photocatalyst | Co-catalyst | Light source[a] | Aqueous[b] | T[c] | $H_2$ evolution | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | | Rate (μmol·h$^{-1}$·g$^{-1}$) | AQY (%) | F[d] | |
| CdS nanowires | NiS | 300 W Xe (λ ≥ 420 nm) | 20 vol% Lactic acid | 7 ˚C | 118420 | 57.8 (420 nm) | 204 | This work |
| | | | | 25 ˚C | 158720 | 74.1 (420 nm) | 250 | |
| CdS nanorods | 0.5 wt% $Ni_2P$ | 300 W Xe (λ ≥ 420 nm) | 1.05 M $Na_2SO_3$ + 0.75 M $Na_2S$ | RT | 1200000 | 41 (450 nm) | 22 | [3] |
| CdS nanorods | Ni | LED (447 nm) | Ethanol | RT | 63000 | 53 (447 nm) | | [5] |
| CdS | MoP | 300 W Xe (λ ≥ 420 nm) | 20 vol% Lactic acid | 20 ˚C | 73333 | 45 (460 nm) | | [11] |
| CdS | 15 wt% $MoS_2$ | 300 W Xe (λ ≥ 420 nm) | 0.02 M $Na_2SO_3$ + 0.1 M $Na_2S$ | RT | 4470 | | 10 | [12] |
| CdS | 0.2 wt% $MoS_2$ | 300 W Xe (λ ≥ 420 nm) | 10 vol% Lactic acid | RT | 5400 | | 36 | [13] |
| CdS nanorods | 16.7 wt% MoP | 300 W Xe (λ ≥ 420 nm) | 10 vol% Lactic acid | RT | 163200 | 5.8 (450 nm) | 20 | [14] |
| CdS | 11 mol% $WS_2$ | 300 W Xe (λ ≥ 420 nm) | 10 vol% Lactic acid | RT | 1984 | | 16 | [15] |
| CdS | 10 wt% WC | 500 W Xe (λ ≥ 420 nm) | 0.02 M $Na_2SO_3$ + 0.1 M $Na_2S$ | RT | 1400 | | 23 | [16] |
| CdS | 1 wt% $WS_2$ | 300 W Xe (λ ≥ 420 nm) | 10 vol% Lactic acid | 10±5 ˚C | 4200 | 5 (420 nm) | 28 | [17] |
| CdS nanorods | 6 wt% $Co_2P$ | 300 W Xe | 10 vol% Lactic acid | RT | 10800 | | 16 | [18] |
| CdS nanowires | 6.5 mol% $Co(OH)_2$ | 300 W Xe (λ ≥ 420 nm) | 30 vol% TEOA | RT | 14430 | | 206 | [19] |
| CdS nanorods | 6.8 mol% $Co(OH)_2$ | 500 W Xe | 25 vol% Ethanol | RT | 61 | | 41 | [20] |
| CdS nanorods | 3 mol% $Co_3O_4$ | 300 W Xe (λ ≥ 420 nm) | 0.5 M $Na_2SO_3$ + 0.5 M $Na_2S$ | RT | 236 | | 33 | [21] |
| CdS nanorods | 4.86 wt% $Ni_3N$ | 300 W Xe (λ ≥ 420 nm) | 0.35 M $Na_2SO_3$ + 0.25 M $Na_2S$ | RT | 88000 | ~13 (420 nm) | 10 | [22] |
| CdS | 13.2 mol% $Ni_2O_3$ | 300 W Xe (λ ≥ 400 nm) | 30 vol% Methanol | RT | 4456 | | 4.1 | [23] |
| CdS | 1 mol% $NiO_x$ | 300 W Xe (λ ≥ 400 nm) | 30 vol% Methanol | RT | 5908 | 8.6 (400 nm) | 117 | [24] |
| CdS | 32 mol% NiO | 500 W Phoenix tungsten halogen lamp | 0.25 M $Na_2SO_3$ + 0.35 M $Na_2S$ | RT | 745 | 6.02 | | [25] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| CdS nanorods | 23 mol% $Ni(OH)_2$ | 300 W Xe (λ ≥ 420 nm) | 25 vol% TEOA | RT | 5084 | 28 (420 nm) | 145 | [26] |
| CdS | 1.2 mol% NiS | 300 W Xe (λ ≥ 420 nm) | 30 vol% Lactic acid | RT | 7267 | 51.3 (420 nm) | 34 | [27] |
| CdS nanorods | 5 mol% NiS | 300 W Xe (λ ≥ 420 nm) | 0.25 M $Na_2SO_3$ + 0.35 M $Na_2S$ | RT | 1131 | 6.1 (420 nm) | 21 | [28] |
| CdS | NiS | 300 W Xe (λ ≥ 420 nm) | 30 vol% Lactic acid | 35 ˚C | 28600 | 60.4 (420 nm) | ~30 | [29] |
| CdS nanorods | 3 mol% CuS | 500 W Xe | 0.25 M $Na_2SO_3$ + 0.35 M $Na_2S$ | RT | 332 | | 3.5 | [31] |
| CdS nanorods | 0.44 wt% $Cu_3P$ | 300 W Xe (λ ≥ 420 nm) | 1.75 M $Na_2SO_3$ + 1.25 M $Na_2S$ | RT | 200000 | 25 (420 nm) | 6.6 | [32] |
| CdS nanorods | 4 wt% Ni | 300 W Xe (λ ≥ 420 nm) | 1 M $(NH_4)_2SO_3$ | RT | 25848 | 26.8 (420 nm) | | [S2] |
| CdS nanorods | 5 wt% Ni | 300 W Xe (λ ≥ 400 nm) | 50 vol% Lactic acid | RT | 30048 | | | [S3] |
| CdS | Ni | 300 W Xe (λ ≥ 395 nm) | 4.6 M $Na_2SO_3$ + 3.3 M $Na_2S$ | RT | 2.5 | | 10 | [S4] |
| CdS | 0.4 wt% RGO +2 wt% $MoS_2$ | 500 W UV-vis lamp | 10 vol% Lactic acid | RT | 6857 | | 71 | [S5] |
| CdS nanorods | 30 wt% $Fe_2P$ | 300 W Xe (λ ≥ 420 nm) | 0.5 M Ascorbic acid | RT | 186000 | 15 (450 nm) | 31 | [S6] |
| CdS | 2 wt% $Ni_2P$ | simulated solar radiation | 20 vol% Lactic acid | RT | 33480 | | 62 | [S7] |
| CdS nanorods | 6 wt% $WS_2$-$MoS_2$ | 150 W Xe (AM 1.5G) | 20 vol% Lactic acid | RT | 209790 | 51.4 (425 nm) | 83 | [S8] |
| CdS nanowires | $MoS_2$ | 300 W Xe (λ ≥ 400 nm) | 50 vol% Lactic acid | 5 ˚C | 10850 | 22 (475 nm) | 28 | [S9] |
| CdS | $MoS_2$ | 300 W Xe (λ ≥ 420 nm) | 20 vol% Lactic acid | RT | 3875 | 14.7 (420 nm) | 65 | [S10] |
| CdS nanorods | 5.0 wt% $Cu_2MoS_4$ | 150 W Xe | 20 vol% Lactic acid | RT | 15560 | | 4.2 | [S11] |
| CdS | $Ti_3C_2$ | 300 W Xe (λ ≥ 420 nm) | 22 vol% Lactic acid | RT | 14342 | 40.1 (420 nm) | 136 | [S12] |
| CdS nanorods | 6 wt% $MoS_2$ | natural solar radiation | 20 vol% Lactic acid | RT | 174000 | 38.7 (425 nm) | 14.5 | [S13] |

a) Xe: xenon lamp; Hg: mercury lamp

b) TEOA: triethanolamine

c) T: reaction temperature; RT: room temperature

d) F: enhancement factor (vs. pure CdS)

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