

## Supporting Information

### A Flexible CdS Nanorods-Carbon Nanotubes/Stainless Steel Mesh photoanode for Boosted Photoelectrocatalytic Hydrogen Evolution

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#### Chemicals

Cadmium nitrate tetrahydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), ethylenediamine and L-cysteine were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd, China. Thiourea was purchased from Shanghai Macklin Biochemical Co., Ltd, China. Carbon nanotubes (CNTs) were purchased from Shenzhen Nanotech Port Co., Ltd, China. All chemicals are analytical grade and used as received without further purification. Deionized water (DIW) was used throughout the experiments.

#### Synthesis of photoanodes

Synthesis of CdS-NRs/CNTs composites:

The catalysts were synthesized using microwave method. Firstly, 0.308 g  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.0195 g CNTs were dissolved in 40 mL ethylenediamine. After ultrasonication for 10 min, 0.485 g L-cysteine was dissolved in the above solution for another 10 min ultrasonication. The mixture was moved to the quartz tube with a Teflon lid and heated at 200 °C for 90 min under a heating rate of 18 °C  $\text{min}^{-1}$  and an initial pressure of 20 bar by nitrogen in a single chamber microwave digestion system (Ethos TC. Milestone), and then cooled down to room temperature by circulation condensate. The reaction chamber was fitted with a temperature probe and a pressure probe to track the real time reaction situation. The desired time, temperature and pressure were programmed by using Milestone's Easy Control Software. After reaction, the resulting powder was washed by distilled water and ethanol for 3 times and dried at 60 °C overnight under vacuum. The samples of CdS-NRs/CNTs with various concentration of carbon were denoted as CT1, CT1.5, CT2 and CT3, where the number represented the molar ratio of carbon/Cd (1:1, 1.5:1, 2:1, 3:1).

Synthesis of CdS-NPs/CNTs composites:

The CdS nanoparticles and CNTs composites were synthesized using the microwave method as above. 0.308 g  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 0.0195 g CNTs and 0.304 g thiourea were dissolved in 50 mL  $\text{H}_2\text{O}$ . Then the solution was ultrasonically dispersed and stirred for 5min. The resulted mixture was moved to the quartz tube with a Teflon lid and heated at 200 °C for 30 min under a heating rate of 18 °C  $\text{min}^{-1}$  and an initial pressure of 20 bar by nitrogen in a single chamber microwave digestion system (Ethos TC. Milestone), and then cooled down to room temperature by circulation condensate. After reaction, the resulting powder was washed by distilled water and ethanol for 3 times and dried at 60 °C overnight under vacuum.

Preparation of CdS-NRs/CNTs flexible electrode:

2.0 cm\*3.5 cm stainless steel mesh were cleaned ultrasonically with distilled water and ethanol, and dried in an oven at 80 °C. 20 mg CdS-NRs/CNTs were dispersed in 10 mL distilled water with ultrasonication for 5 min. A certain amount of the above solution was transferred to the surface of clean stainless steel mesh used by Micro

sampler with Filtration method to get the preliminary electrode. After suction filtration, the electrode was dried at 80 °C. Finally, the preliminary electrode was calcined at 200 °C for 2 h.

### Characterization

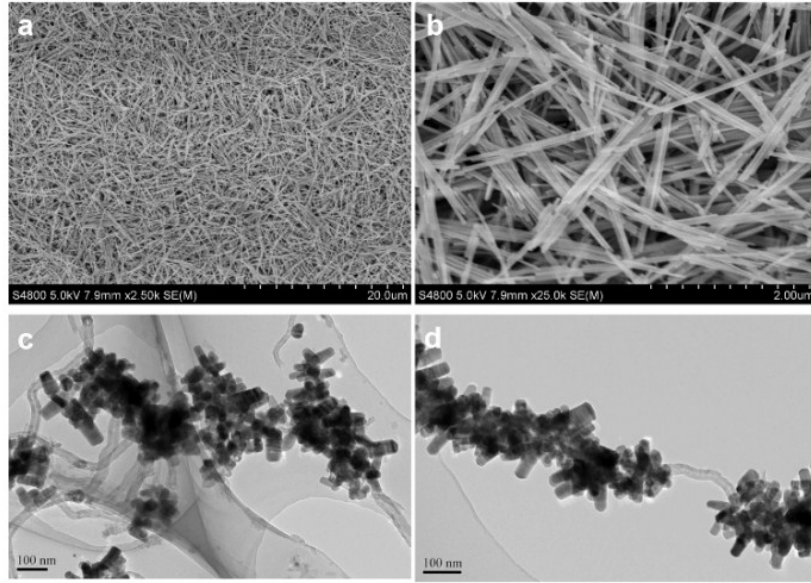
The crystal phase was determined by X-ray diffraction instrument (XRD, Rigacu Dmax-3C Cu-Ka). The N<sub>2</sub> adsorption-desorption isotherms were recorded at 77 K by a Micromeritics TriStar II 3020 instrument. The specific surface area (SBET) and pore volume (VP) were calculated through Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models on desorption branches. The UV-Vis diffuse reflectance spectra (DRS) were obtained on a UV-Vis spectrophotometer (UV-Vis DRS, Shimadzu UV-2450). Sample size and morphology were determined on a transmission electron microscopy (TEM, JEOL-2010F, 200 kV) and a field scanning electron microscopy (FESEM, HITACHI, S-4800). The photoluminescence spectra (PL) were examined on a fluorescence spectrophotometer (HITACHI F-4600). Photoelectrochemical measurements were carried out in a conventional three-electrode, double-compartment quartz cell on an electrochemical station (CHI 660E). The sample with an active area of *ca.* 4.0 cm<sup>2</sup> on stainless steel mesh was served as the working electrode. A platinum foil (*ca.* 4.0 cm<sup>2</sup>) and a Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively.

### Photoelectrocatalytic (PEC) Hydrogen generation test

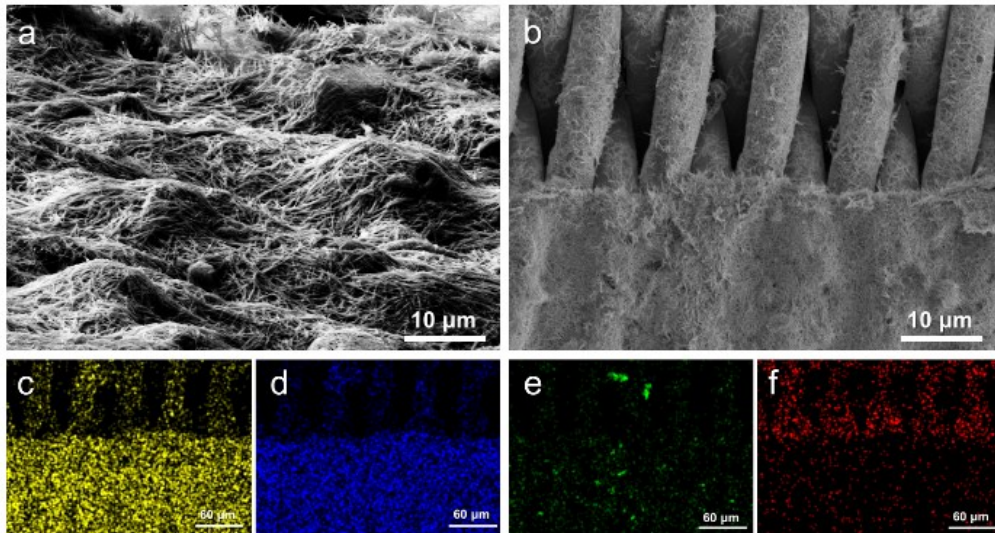
All PEC measurements were performed in a 3-electrode cell with a Pt counter electrode and an Ag/AgCl reference electrode at ambient temperature and atmospheric pressure. The PEC hydrogen production experiments were performed in a 100 mL double-compartment quartz cell at ambient temperature and atmospheric pressure. A 420 nm LED lamp (CEAULIGHT CEL-LED100) was used as the light source to trigger the photoelectrocatalytic reaction. It was positioned 10 cm away from the reactor. The photoelectrode was immersed in 65 mL of mixed solution containing 15 mL of methanol and 50 mL of NaOH solution (1.0 M), respectively. The active area of photoanode is 4 cm<sup>2</sup>, where 2.4 mg CdS-NRs/CNTs catalyst were loaded. Prior to irradiation, the reactor was bubbled with nitrogen for 10 min to completely remove the dissolved oxygen and hydrogen. After reacting for 1 h, 0.5 mL gas was intermittently sampled through the septum and then analyzed by gas chromatography (GC 9800N, Kechuang, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column).

### Photoelectrochemical measurement

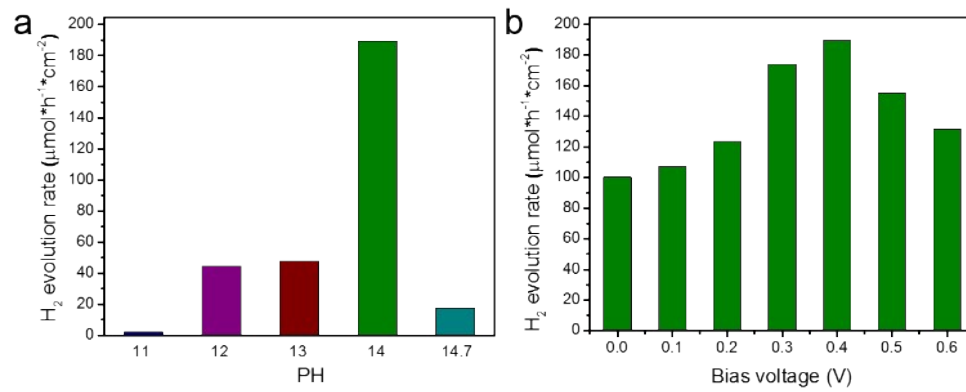
The photocurrents and electrochemical impedance spectroscopy (EIS) measurements were carried out in a conventional three-electrode, double-compartment quartz cell on an electrochemical station (CHI 660E). Samples with an active area of *ca.* 4.0 cm<sup>2</sup> on the stainless steel mesh served as the working electrode. A platinum foil and Ag/AgCl were used as the counter and reference electrodes respectively. A bias voltage of 0.4 V was utilized for driving the photogenerated electrons transferring. A 90 W 420 nm LED light (CEAULIGHT CEL-LED100) placed at 10 cm away from the photoelectrochemical cell was used as the light source. NaOH aqueous solution (1 M) was used as the electrolyte. The EIS tests were carried out at the bias of the 0.4 V and obtained over the 10<sup>-1</sup> to 10<sup>5</sup> Hz frequency. Incident photon to current efficiency (IPCE) was measured on an optical bench (CIMPS-pcs) equipped with a LED light source (TLS03), including the monochromator, and a single-compartment quartz cell. A 2.0 × 2.0 cm<sup>2</sup> platinum foil was used as the counter electrode. Both the cathode and anode were immersed in a 1.0 M NaOH electrolyte solution and connected through an external circuit to a digital multi-meter (Tektronix DMM4040). The measurement of Mott-schottky plots is same like the EIS test with 10000 Hz from 0 V to -1.0 V.

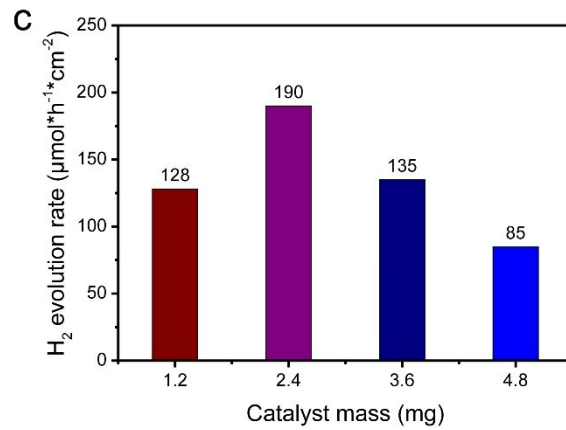


**Figure S1.** FESEM images of pure CdS-NRs (a, b) and TEM images of CdS-NPs/CNTs (c, d).

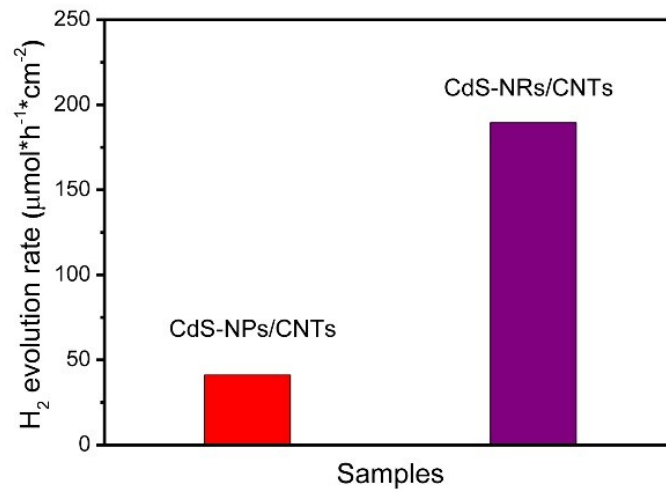


**Figure S2.** (a) Cross-sectional FESEM image of a CdS-NRs/CNT photoelectrode, (b) FESEM image and EDX elemental mapping with areal distributions of (c) cadmium, (d) sulfur, (e) carbon and (f) iron, respectively.

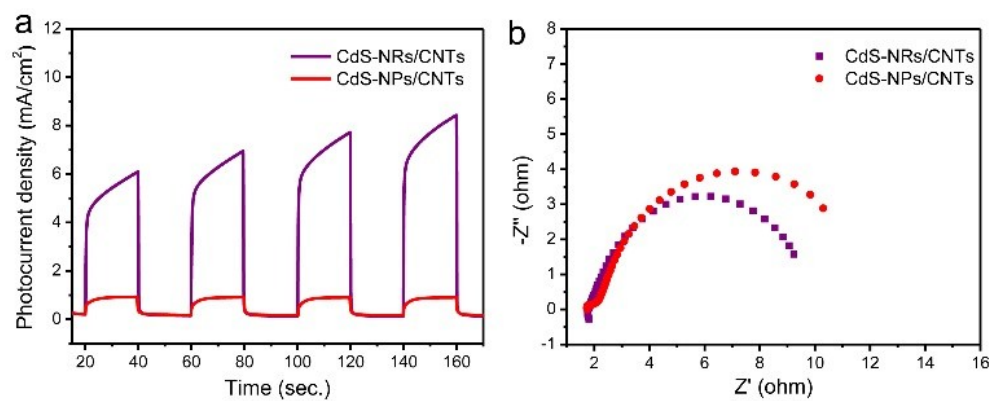




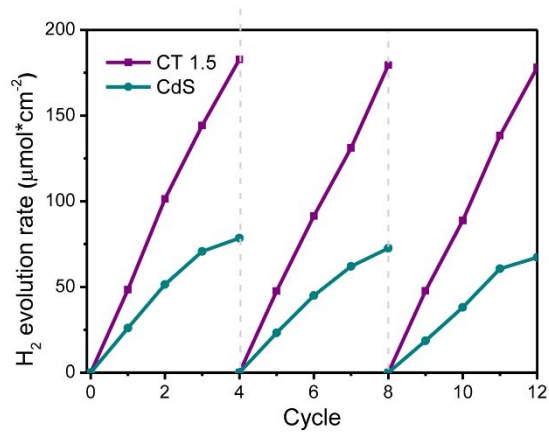
**Figure S3.** Performances of photoelectrocatalytic H<sub>2</sub>-evolution of CT1.5 photoanode in aqueous solution with (a) various pH value at a bias voltage of 0.4 V, (b) different bias voltage with a pH value of 14, and (c) loaded with various amount (1.2, 2.4, 3.6, and 4.8 mg).



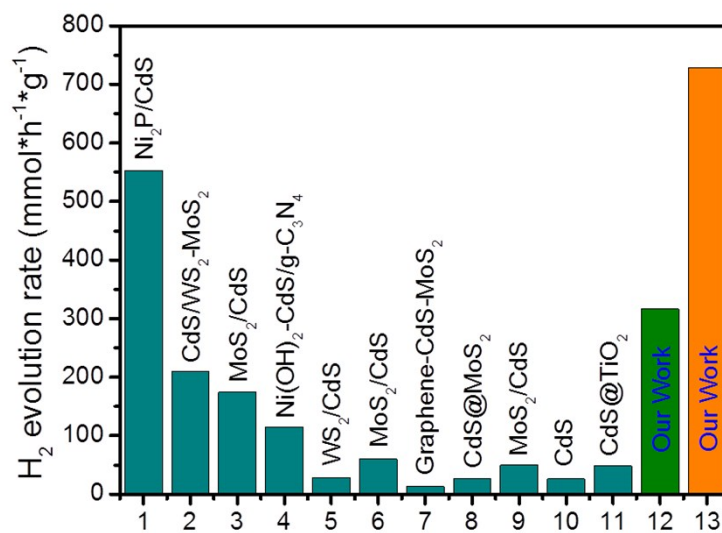
**Figure S4.** The comparison of the photoelectrocatalytic H<sub>2</sub> evolution performance of both CdS-NRs/CNTs and CdS NPs/CNTs photoanodes.



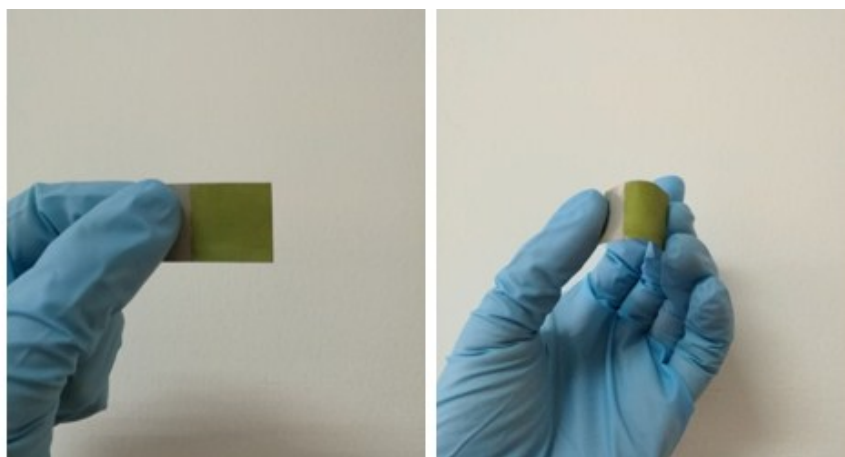
**Figure S5.** Photocurrent responses (a) and EIS (b) of the CdS-NRs/CNTs and CdS NPs/CNTs photoelectrodes.



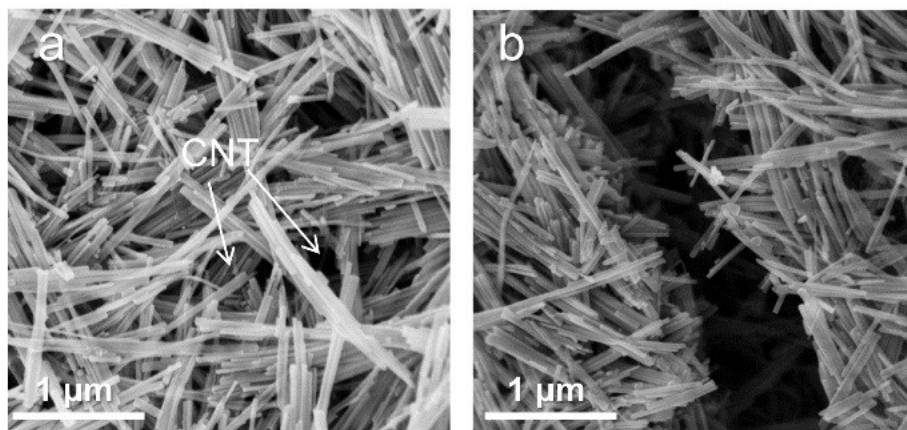
**Figure S6.** Stability test of H<sub>2</sub> production performance of CT1.5 and CdS-NRs photoanodes.



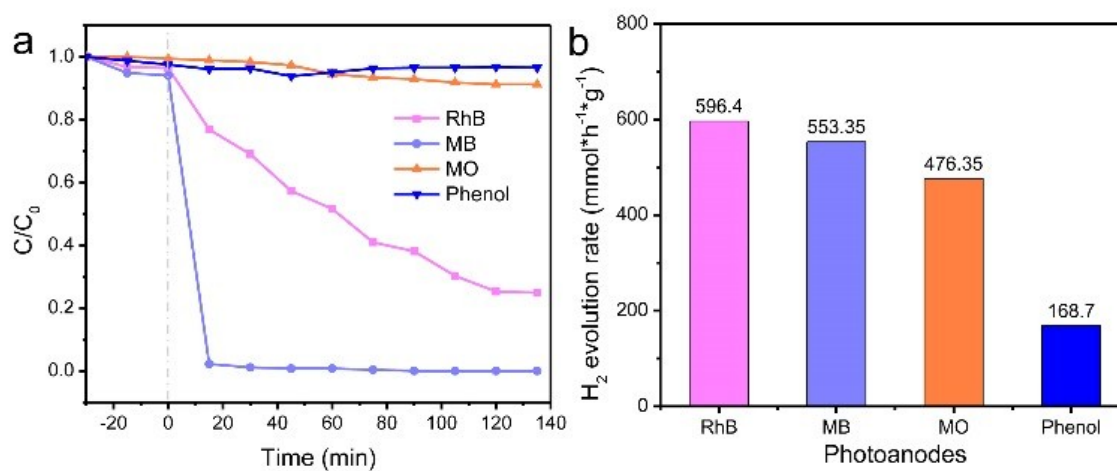
**Figure S7.** Comparison of the photocatalytic hydrogen evolution performance of CT1.5 under visible-light irradiation (with 420 nm LED; 300 W Xe lamp) and reported CdS-based photoactive materials.



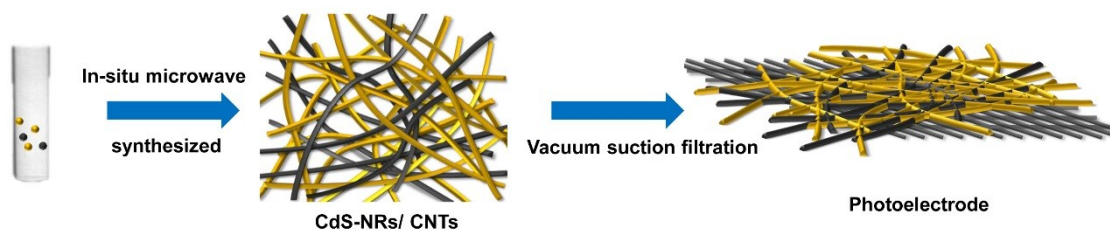
**Figure S8.** Digital images of the flexible photoanode with the CT1.5 photoanode.



**Figure S9.** (a, b) SEM images of CT1.5 and CdS-NRs photoelectrode after bending 5000 cycles.



**Figure S10.** Performance of photoelectrocatalytic simultaneous (a) degradation of organic pollutants and (b) hydrogen evolution on CT1.5 photoanode at bias voltage of 0.4 V in aqueous solution with a pH = 14.



**Scheme S1.** The fabrication process of the CdS-NRs-CNTs/Stainless steel mesh photoelectrode.

**Table S1.** Comparison of Hydrogen Evolution Data of CdS-based Composites Compared with Few of the Literature Reports.

Catalyst	Catalyst amount (mg)	Light source	Scavenger	Hydrogen production (mmol/h/g)	Ref.
Ni <sub>2</sub> P/CdS	1	300 W Xe lamp (λ ≥ 400 nm)	Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>3</sub>	553	[1]
CdS/WS <sub>2</sub> -MoS <sub>2</sub>	1	150 W Xe lamp AM 1.5	Lactic acid	210	[2]
MoS <sub>2</sub> /CdS	1	150 W Xe lamp AM 1.5	Lactic acid	174	[3]
Ni(OH) <sub>2</sub> -CdS/g-C <sub>3</sub> N <sub>4</sub>	1	300 W Xe lamp (λ ≥ 420 nm)	Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>3</sub>	115	[4]
WS <sub>2</sub> /CdS	200	300 W Xe lamp (λ ≥ 400 nm)	Lactic acid	28	[5]
MoS <sub>2</sub> /CdS	200	300 W Xe lamp (λ ≥ 400 nm)	Lactic acid	60	[6]
Graphene-CdS-MoS <sub>2</sub>	40	300 W Xe lamp (λ > 420 nm)	Lactic acid	13	[7]
CdS@MoS <sub>2</sub>	20	300 W Xe lamp (λ > 41 nm)	Lactic acid	26	[8]
MoS <sub>2</sub> /CdS	200	300 W Xe lamp (λ > 420 nm)	Lactic acid	50	[9]
CdS	20	300 W Xe lamp (λ > 420 nm)	Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>3</sub>	26	[10]
CdS@TiO <sub>2</sub>	-	150 W Xe lamp AM 1.5	Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>3</sub>	48	[11]
CdS NF/R-TiO <sub>2</sub> NR	-	solar simulator	Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>3</sub>	0. 336	[12]
CdS-Cu <sub>2</sub> O	-	300 W Xe lamp (λ ≥ 400 nm)	Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>3</sub>	0. 161	[13]
<b>CdS NRs/CNTs</b>	2.4	100 W LED 420 nm	CH <sub>3</sub> OH	<b>316</b>	<b>This work</b>
<b>CdS NRs/CNTs</b>	2.4	300 W Xe lamp (λ > 420 nm)	CH <sub>3</sub> OH	<b>728</b>	<b>This work</b>

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