

Supporting Information

New Co(OH)₂/CdS Nanowires for Efficient Visible Light Photocatalytic Hydrogen Production

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Experiment details

Chemicals and Materials. All chemicals are of analytical grade and were used without further purification. The CdS nanowires were prepared by an ethylenediamine assisted solvothermal method as reported previously.¹

Preparation of CdS NWs. In a typical synthesis, CdO (256.8 mg, 2 mmol), L-cysteine (242.3 mg, 2 mmol) and sulfur powder (64.1 mg, 2 mmol) were dissolved in 80 ml hydrous ethylenediamine under magnetic stirring at room temperature for 30 min to form a uniform solution. The resulting mixture was then transferred into a 100 ml Teflon-lined autoclave and maintained at 180 °C for 12 h. After the mixture was cooled to room temperature, the yellow precipitates were collected by centrifugation and rinsed for seven times with distilled water and ethanol. The final production was dried at 80 °C for 12 h.

Preparation of C0, C0.5, C4.8, C6.5 and C9.1. The Co(OH)₂/CdS NWs were fabricated by facile precipitation method. In a typical procedure, 0.16 g of CdS NWs obtained above were dispersed in 40 ml of 0.125 M NaOH aqueous solution, and then a certain volume of 0.05 M Co(NO₃)₂ aqueous solution was added dropwise to the solution under magnetic stirring. The resulting mixture was stirred for 10 h at room temperature. After that, the precipitate was collected by centrifugation, and rinsed with distilled water and alcohol thoroughly. The final product was fast dried in a vacuum oven at 80 °C for 30–40 min to remove the residual alcohol. The nominal molar ratios of Co(OH)₂ to (Co(OH)₂+CdS) were 0, 0.5, 4.8, 6.5 and 9.1 mol%, and the resulting samples were labeled as C0, C0.5, C4.8, C6.5, and C9.1, respectively.

Preparation of Pt/CdS and C100. For comparison, the pure Co(OH)₂ sample was prepared under the same experimental conditions, and the resulting Co(OH)₂ sample was labeled as C100. In addition, 1 wt% Pt modified CdS NWs (Pt/CdS) was prepared by literature method¹⁻³ as benchmark in photocatalytic activity H₂ production.

Preparation of Co(NO₃)₂/CdS Nanowires. In this experiment, the nominal molar ratios of Co(NO₃)₂ to CdS were 0, 1.6, 7.5, 10, 12.5 and 20 mol%, and the resulting samples were labeled as N0, N1.6, N7.5, N10, N12.5 and N20, respectively. To avoid the formation of Co(OH)₂, a 10 vol% lactic acid aqueous solution was added as sacrificial agent to replace the 30 vol% tri(2-hydroxyethyl) amine aqueous solution. And the hydrogen production procedure is as same as the Co(OH)₂/CdS NWs samples.

Material characterization. The XRD patterns, performed on a D/Max-RB X-ray diffractometer (Rigaku, Japan) using Cu-Kα irradiation ($\lambda = 1.54056 \text{ \AA}$) at a scan rate of 0.05° 2θ s⁻¹, were used to determine the crystal structure of prepared samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) observations were conducted on a JEM-2100F electron microscope (JEOL, Japan) using a 200 kV accelerating voltage. X-ray photoelectron spectroscopy measurements (XPS) were done on a VG ESCALAB MKII XPS system with Mg Kα source and a charge neutralizer. The samples were excited using Mg Kα (1253.6 eV) radiation (operated at 200 W) of a twin anode in the constant analyzer energy mode with a pass energy of 30 eV. The XPS data were calibrated using the binding energy of C1s (285.00 eV) from adventitious carbon as reflectance standard. The ultraviolet–visible (UV-Vis) diffused reflectance spectra of the samples were obtained for the dry-pressed disk samples by a UV-Vis spectrometer (UV2550, Shimadzu, Japan) with BaSO₄ as nitrogen adsorption apparatus (USA). All powdered samples were degassed in a vacuum environment at 150 °C used as a reflectance standard. The chemical compositions of the prepared samples were measured by inductively coupled plasma atomic emission spectrometry (ICP–AES) using an Optima 4300 DV spectrometer (Perkin-Elmer). The Brunauer–Emmett–Teller (BET) specific surface area (SBET) of the powders was analyzed by nitrogen adsorption using a Micromeritics ASAP 2020 prior to nitrogen adsorption measurements. The BET surface area was calculated by a multipoint BET method using adsorption data in the relative pressure (P/P₀) range of 0.05–0.3. Adsorption isotherm was used to determine the pore size distribution via the Barret–Joyner–Halender (BJH) method, assuming a cylindrical pore model. The volume of the adsorbed nitrogen at the relative pressure (P/P₀) of 0.99 was used to determine the pore volume and the average pore size.

Photocatalytic Hydrogen Production. According to the standard procedure reported previously,⁴⁻⁷ the photocatalytic hydrogen production experiments were performed in a 100 ml Pyrex flask at room temperature and atmospheric pressure, and the openings of the flask were sealed with a silicone rubber septum. A 300 W Xenon arc lamp through a UV-cutoff filter ($\lambda \geq 420 \text{ nm}$), which was positioned 20 cm away from the reactor, was used as a visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was ca. 150 mW cm⁻², which was measured by a FZ-A visible light radiometer (made in the photoelectric instrument factory of Beijing Normal University, China) with the wavelength range of 400–1000 nm. In a typical photocatalytic experiment, 50 mg of

Co(OH)₂ modified CdS NWs was dispersed under a constant stirring in an 80 ml 30 vol% triethanolamine aqueous solution (20 ml triethanolamine and 60 ml water). Before irradiation, the system was bubbled with nitrogen for 40 min to remove air and ensure an aerobic condition in the reaction system. Then 0.4 ml of gas was intermittently sampled through the septum, and hydrogen was analyzed by gas chromatograph (GC-14C, Shimadzu, Japan, TCD with nitrogen as a carrier gas and 5 Å molecular sieve column). All glassware was carefully rinsed with distilled water prior to the experiment. The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction conditions. Four low-power 420 nm-LEDs (3 W) (Shenzhen LAMPLIC Science Co. Ltd. China), which were positioned 1 cm away from the reactor in four different directions, were used as light sources to trigger the photocatalytic reaction. The focused intensity and areas on the flask for each 420 nm-LED were ca. 6.0 mW cm⁻² and 1 cm², respectively. The QE was calculated according to the following equation:

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

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

BET Surface Areas and Pore Size Distributions. Figure S1 shows the nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves (inset) of the samples C0 and C6.5. The two samples have isotherms of type IV according to the Brunauer–Deming–Deming–Teller (BDDT) classification⁸ and the hysteresis loops of type H3 outspread at a relative pressure range of 0.8–1, indicating the presence of mesopores (2–50 nm). Moreover, the observed hysteresis loops approach P/P₀ = 1, indicating the presence of macropores (> 50 nm).⁹ The pore size distributions (inset in Figure S1) further demonstrated a wide distribution range from 2 to 150 nm for C0. As to the SEM images shown in Figure S2, the CdS nanowires cross and overlap each other to form a network structure, resulting in numerous meso- and microporous, which are beneficial for enhancing the transportation of reactants and products. Table S1 lists the BET surface areas and pore volumes of the samples as-prepared. Both BET surface areas and pore volumes progressively decrease with the increasing amount of Co(OH)₂. This can be explained that the accumulated Co(OH)₂ clusters may continually deposit on the surface of CdS nanowires or partly embedded in the pores, thus reducing the specific surface area and pore volume.

QE of the samples

Figure S3 shows the QE of the samples C6.5 and C0 at 420 nm. The corresponding QE of C6.5 and C0 reaches 6.09 % and 0.08 %. The low value of QE might due to the H₂ production rate of this system partly depending on light intensity.

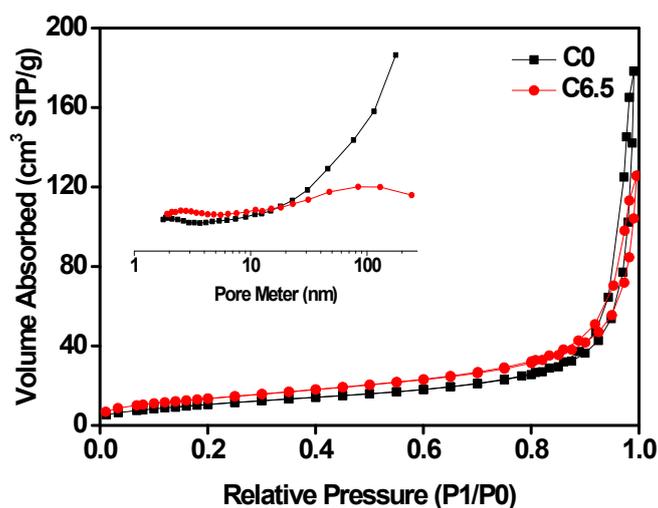


Figure S1. Nitrogen adsorption–desorption isotherms and corresponding pore-size distribution curves (inset) of C0 and C6.5 samples.

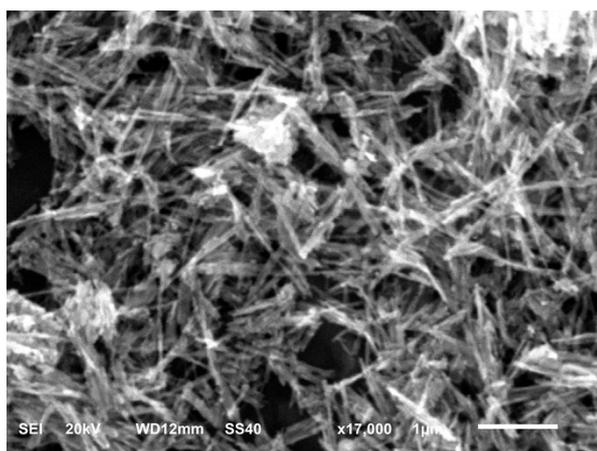


Figure S2. SEM image of sample C6.5.

Table S1. Effects of R on the physicochemical properties and activity of Co(OH)₂/CdS nanowires.

Samples	R	Co(OH) ₂ mol % (ICP-IES)	S _{BET} (cm ² g ⁻¹)	PV ^a (cm ³ g ⁻¹)	APS ^b (nm)	HPR mmol ⁻¹ g ⁻¹	QE%
C0	0	0	40	0.12	11.8	0.070	0.08
C0.5	0.5	0.13	41	0.11	10.9	1.86	
C4.8	4.8	2.22	38	0.11	11.2	9.19	
C6.5	6.5	3.06	50	0.11	8.86	14.43	6.09
C9.1	9.1	7.52	129	0.25	7.59	3.65	
C100	100	100	79	0.36	18.0	0	
Pt-CdS	--	--	44	0.13	11.4	4.68	2.29

PV: pore volume, APS: average crystallite size.

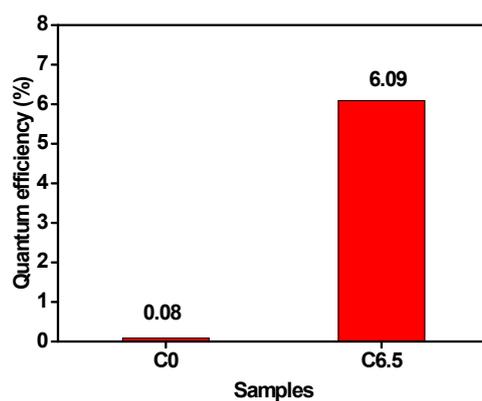


Figure S3. Quantum efficiency of samples C0, C6.5 under 420 nm irradiation from 3W LED lamp at room temperature.

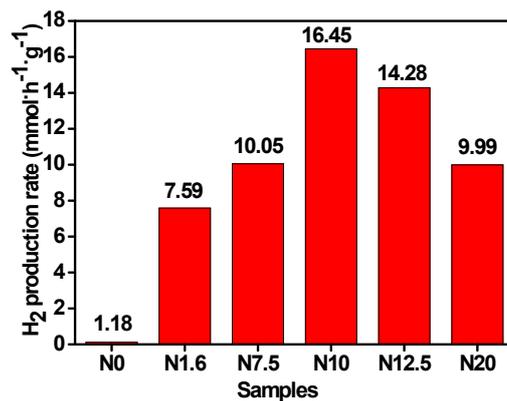


Figure S4. HPR of N0, N1.6, N7.5, N10, N12.5 and N20 in 10 % lactic acid aqueous solution under visible light irradiation ($\lambda \geq 420$ nm).

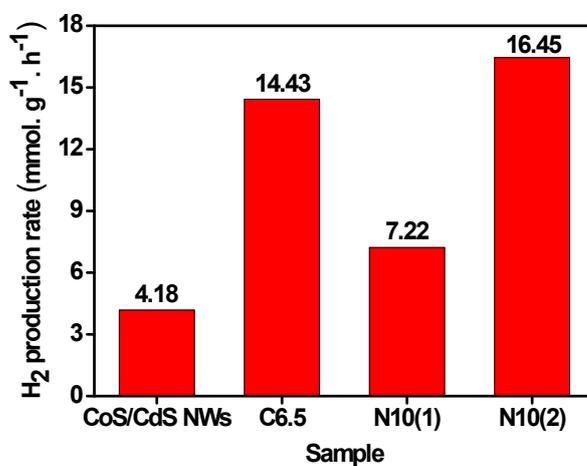


Figure S5. HPRs of CoS/CdS NWs (the nominal molar ratios of CoS to (CdS+CoS) is 6.5 mol%), C6.5, N10 (1) in 30 vol% tri(2-hydroxyethyl) amine aqueous solution, and N10 (2) in 10 vol% lactic acid aqueous solution.

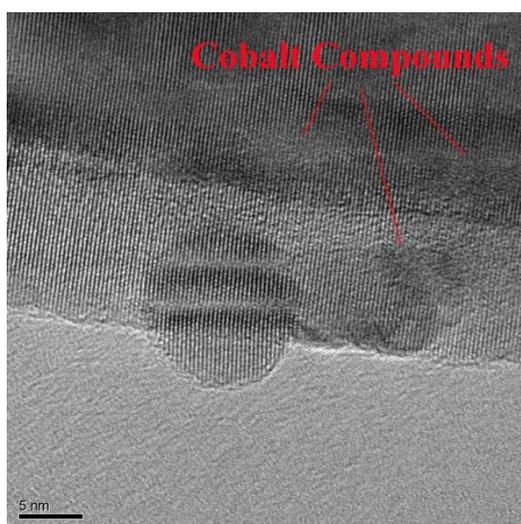


Figure S6. HR TEM image of the N10 after photocatalytic hydrogen production.

References

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