Electronic Supplementary Information for

Transformation of Zinc Blende Nanoparticles into Wurtzile Microrods by a Dissolution-Regrowth Process: Intergrowth-Homojunction with Enhanced Photocatalytic Activity

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Experimental Section

Chemicals and materials. Cadmium acetate ($Cd(Ac)_2 \cdot 2H_2O$), thioacetamide (TAA), thiourea, sodium sulfide ($Na_2S \cdot 9H_2O$), sodium sulfite (Na_2SO_3), sodium hydroxide (NaOH), and ethanediamine (EN) were obtained from Sinopharm Chemical Reagent Co., Ltd. All the materials were analytical grade and used without further purification. The water used in all syntheses was deionized water with a resistivity of 18.25 MΩ·cm.

Syntheses. CdS photocatalysts were prepared *via* a one-pot solvothermal synthesis. In a standard synthesis, 50 mL of NaOH solution (12 M) was mixed with 10 mL of EN that contains 2 mmol of $Cd(Ac)_2 \cdot 2H_2O$. Afterwards, 2.5 mmol of TAA was added into the obtained mixture. The entire process was carried out under magnetic stirring to form a homogeneous suspension. The suspension was then sealed in a 100 ml-capacity Teflon-lined autoclave, and heated to 180 ºC. The reaction was allowed to proceed for 24 h. After cooling, the product was separated by centrifugation, washed several times with deionized water and ethanol, and dried at 80 °C for 5 h in a vacuum oven. For the synthesis of CdS microrods with smooth surface, 60 mL of EN containing 16.2 mmol of $Cd(NO_3)_2 \cdot 4H_2O$ and 48.6 mmol of thiourea were sealed in a 100 mL-capacity teflon-lined stainless steel autoclave, followed by heat treatment at 180 ºC for 24 h. After cooling, the product was also separated by centrifugation, washed several times with deionized water and ethanol, and dried at 80 °C for 5 h in a vacuum oven.

Photocatalytic reaction. Photocatalytic reactions of hydrogen production from water were conducted in a gas-closed system with a side irradiation Pyrex cell. 100 mg of photocatalyst powder was dispersed into solution (220 mL) containing 0.35 mol/L Na_2S and 0.25 mol/L Na_2SO_3 by a magnetic stirrer. After being evacuated by N_2 gas, The suspension was irradiated by visible light irradiation from a 300 W Xe lamp coupled with a 420 nm cutoff filter. The amount of H_2 gas was determined using a gas chromatography of Bruker GC-450. Each test was conducted at least 3 times to confirm the reproducibility, which also gave the mean activity of the photocatalyst. For rapid comparison of the photocatalytic activities of different photocatalysts, each test was conducted for 5 h. Mass and specific activities were thus the mean values obtained from the initial 5-h test.

*Characterization*s. The X-ray diffraction (XRD) patterns were obtained from a PANalytical X'pert MPD Pro diffractometer operated at 40 kV and 40 mA using Ni-filtered Cu *K*α irradiation (Wavelength 1.5406 Å). Ultraviolet-visible absorption spectra (UV-vis) were measured on a HITACHI U4100 instrument equipped with labsphere diffuse reflectance accessory using $BaSO_4$ as the reference. A JSM-7800F instrument (JEOL) was used to perform field emission scanning electron microscopy (FESEM). The transmission electron microscopy (TEM) images and scanning transmission electron microscopy (STEM) images were obtained from a FEI Tecnai G2 F30 S-Twin transmission electron microscope at an accelerating voltage of 300 kV. An OXFORDMAX-80 energy-dispersive X-ray detector (EDX) which was mounted in the above TEM was used to conduct elemental analysis. N_2 adsorption–desorption isotherms were conducted at 77 K using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020, Micromeritics) after degassing the samples at 150 °C for 2 h. Surface area was determined using the Brunauer–Emmett–Teller (BET) methods. The core and valence band levels were obtained by X-ray photoelectron spectroscopy (XPS, Axis Ultra^{DLD}, Kratos) with mono Aluminum *K*α radiation after an argon gun etching for 60 s with a 4 keV high voltage so as to clean the surface. The charge calibration was done by correcting C 1s line of adventitious carbon setting to 284.8 eV to compensate the charge effect.

Table S1. Temporal phase composition of the as-prepared CdS photocatalyst during a standard synthesis calculated from the time-course XRD patterns.

Reaction time (h)	1	2	3	6	12	24
ZB (%)	80	70	50	25	12	6
WZ (%)	20	30	50	75	88	94

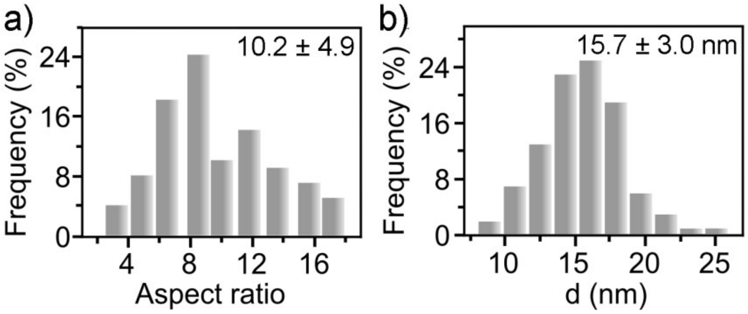

Fig. S1 a) Distributions of aspect ratio calculated for the as-prepared nanoparticle-decorated CdS microrods, and b) the diameter calculated for the surface nanoparticles. All the calculations were performed by measuring 100 rods/particles shown in a low-resolution SEM image (*n* = 100).

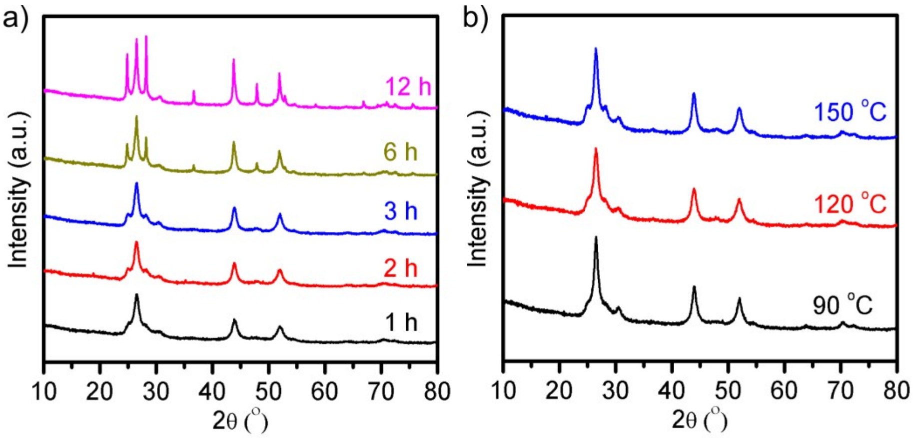

Fig. S2 XRD patterns of CdS samples synthesized using a standard process except that a) different reaction times, and b) different reaction temperatures were employed.

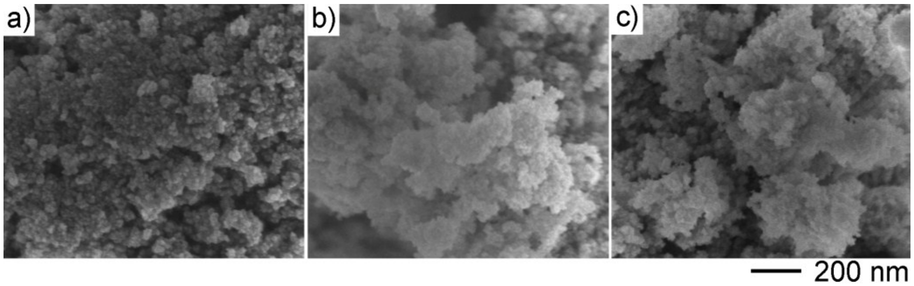

Fig. S3 SEM images of CdS photocatalysts synthesized using a standard process except that the reaction temperatures were tuned to a) 90 ^{o}C, b) 120 ^{o}C, and c) 150 ^{o}C, respectively.

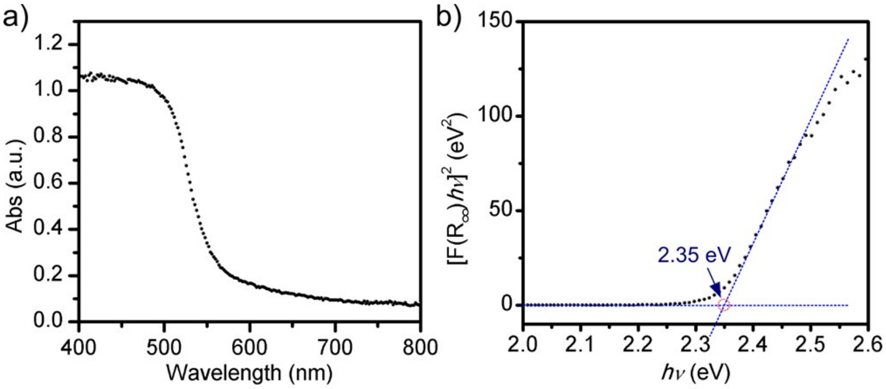

Fig. S4 (a) UV-vis spectra of the as-prepared CdS photocatalyst using a standard synthesis except the temperature was set to 150 ^{o}C, and (b) the corresponding K-M plot showing its band-gap energy.

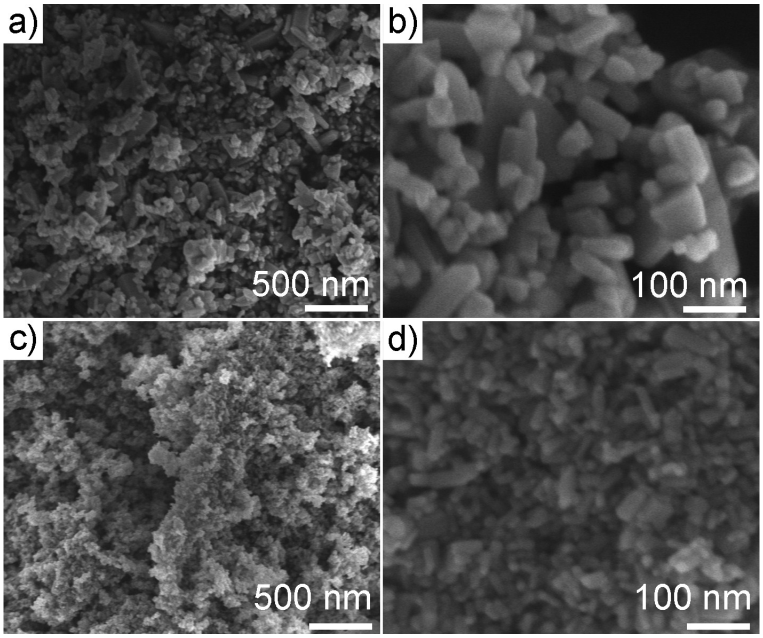

Fig. S5 SEM images of CdS samples synthesized using a standard process except that the reactions were proceeded in the absence of a, b) EN, and c, d) NaOH. b) and d) are corresponding magnified images.

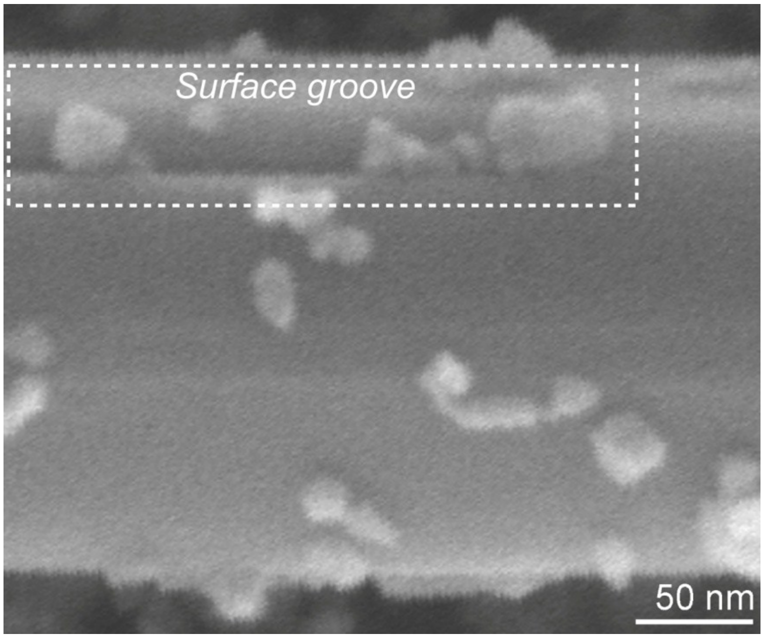

Fig. S6 Magnified SEM images of a single CdS microrod synthesized using a standard process except the reaction was allowed for 18 h. The image shows a clear surface groove structure for the following regrowth of CdS monomers.

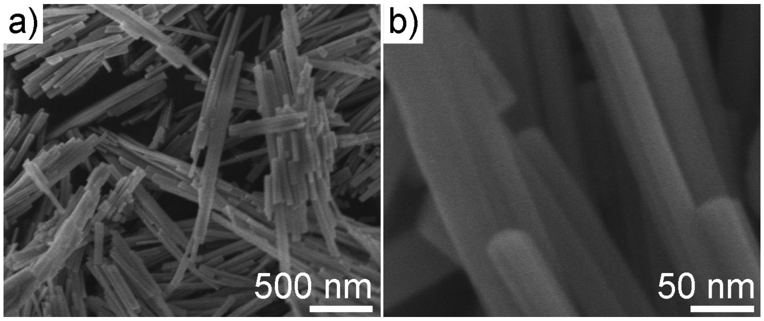

Fig. S7 The SEM images of CdS microrods synthesized in pure EN solution.

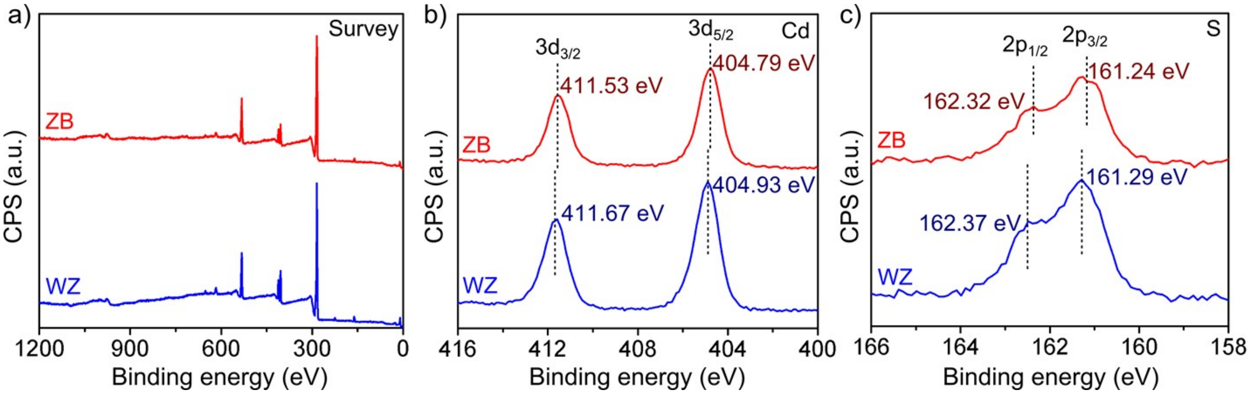

Fig. S8 XPS spectra of ZB CdS nanoparticles (obtained using a standard synthesis except the temperature was set to 150 ^{o}C) and WZ CdS microrods (obtained in pure EN). a) survery spectra, and b, c) the corresponding high-resolution elemental scans of Cd 3d, and S 2p, respectively.

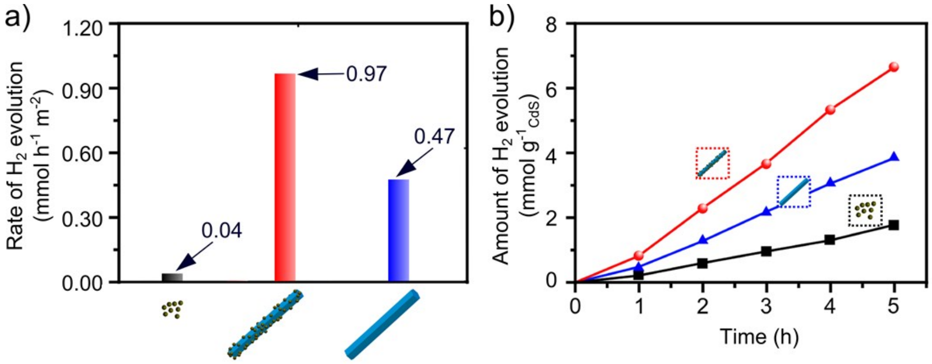

Fig. S9 Visible-light-driven H_2 evolution from an aqueous solution containing 0.35 M of Na_2S, 0.25 M of Na_2SO_3, and 100 mg of CdS photocatalyst. a) Specific activities of the as-prepared CdS nanoparticles, nanoparticle-decorated microrods, and pure microrods, by normalizing the initial average hydrogen evolution rates with respect to their BET specific areas, and b) the corresponding time courses of photocatalytic hydrogen production.