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Electronic Supplementary Information

Hollow $CoSe_2$ nanocages derived from metal organic frameworks as an efficient non-precious co-catalyst for solar driven hydrogen production

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EXPERIMENTAL

Synthesis of CdS nanorods

Cadmium acetate dehydrate ((Cd($CH_3COO)_2 \cdot 2H_2O$) and thiourea (CH_4N_2S) with molar ratio of 1:3 were dissolved in 60 mL of ethylenediamine. The solution was transferred into 100 mL Teflon-autoclave and heated at 160 ℃ for 48 h. The autoclave was then cooled down to room temperature. The product was washed with distilled water and ethanol, which was dried at 60 ℃ for 12 h.

Synthesis of zeolitic imidazolate framework-67 (ZIF-67) nanocubes

In a typical procedure, 58 mg of $Co(NO_3)_2 \cdot 6H_2O$ and 1 mg of cetyltrimethylammonium bromide (CTAB) were dissolved in 2 ml of distilled water. The solution was rapidly injected into 14 ml of solution containing 908 mg of 2-methylimidazole and stirred vigorously for 30 min. Then, purple product was separated and washed with ethanol at least 5 times by centrifugation, which was dried in an oven at 60 ℃ to obtain the product.

Synthesis of $CoSe_2$ nanocages

To obtain the $CoSe_2$ nanocages, the above synthesized ZIF-67 and selenium powder with mass ratio of 1:2 were evenly mixed by grinding with a mortar and pestle. The blend was transferred into porcelain boat and heated at 350 ℃ for 2 h with ramping rate of 2 $℃ \cdot min^{-1}$ in Ar/H_2 (5 %) atmosphere.

Synthesis of CdS/$CoSe_2$ composites

$CoSe_2$ anchored on CdS was prepared by simple sonication method. The mass of as-synthesized $CoSe_2$ was controlled for making different wt.% composites. At first, targeted wt.% $CoSe_2$ was dispersed in DMF by sonication for 3 h and CdS was added, which was sonicated for additional 1 h. The sonicated solution was stirred overnight to form interfacial junction between $CoSe_2$ and

CdS. Finally the product was washed with distilled water and ethanol more than 3 times, which was dried at 60 °C.

Photo-deposition of Pt nanoparticles on CdS nanorods

The Pt-loaded hybrid particles were prepared using 150-W Xe-arc lamp by photo-deposition technique. In detail, 50 mg of synthesized CdS nanorods are suspended in 20 mL of mixed solvent of H_2O/lactic acid (80:20 v/v). Then, required stoichiometric amount of $H_2PtCl_6 \cdot 6H_2O$ (1, 2, 3, 4, and 5 wt.% of Pt) was added to the suspension. The solution was then thoroughly degassed and bubbled with Ar for 30 min to remove the air inside, which was irradiated by a 150-W Xe-arc lamp for 2 h. After irradiation, the filtered Pt-loaded CdS nanocomposites were washed with distilled water and ethanol to remove the unnecessary impurities, which were dried at 80 °C for 10 h to obtain the final products.

CHARACTERIZATIONS

The microstructure properties were measured using a JEOL JEM-2100F transmission electron microscope (TEM) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using a monochromated Al Kα X-ray source ($h\nu$ = 1486.6 eV) at an energy of 15 kV/150 W. The optical absorption measurements were performed using a Shimadzu UV-1800 double-beam spectrophotometer. Photoluminescence (PL) measurements were performed at room temperature using Hitachi F-7000 fluorescence spectrophotometer with an excitation wavelength of 380 nm. For time-resolved PL studies, nanocomposites were excited by the second harmonic (355 nm) of a cavity-dumped oscillator (Mira/Pulse Switch, Coherent, 1 MHz, 710 nm). Emission was collected using the lens, spectrally resolved using a monochromator, detected using a photomultiplier, and recorded using a time-correlated single photon counter (PicoHarp, PicoQuant).

Photocatalytic hydrogen production

The photocatalytic hydrogen evolution experiments were performed in a 150 ml quartz beaker at ambient temperature and atmospheric pressure. The flask was sealed with silicone rubber septum. A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp (Abet Technologies) was used as the light source. The output light intensity was adjusted to 1 sun (100 W/m^2) using 15151 low-cost calibrated Si reference cell (Abet Technologies). Before irradiation, the system was evacuation and bubbled with Ar for 30 min to remove the air inside. The hydrogen gas evolved was determined using an off-line gas chromatograph (Young Lin Autochro-3000, model 4900) equipped with thermal conductivity detector and a 5 Å molecular sieve column. The 100 μL of produced hydrogen gas in headspace of reactor was collected and injected into the gas chromatograph and calculated by a calibration plot to 5% standard gas of hydrogen.

The apparent quantum efficiency (QE) was measured according to the following equations.

$$QE = \left(\frac{nuber\ of\ reacted\ electrons}{number\ of\ incident\ photons}\right) \times 100\ (\%)$$

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

Here QE was measured under the same photocatalytic hydrogen evolution experimental conditions except the irradiation source, where 150 W Xe lamp with 425 nm band pass filter was used as light sources, instead of the solar simulator. The output light intensity was measured using Si reference cell. The liquid level is ~16 cm far from the window of lamp and the illuminated area is 21.24 cm^2.

Photo-electrochemical measurements

Photo-electrochemical measurements were performed using a standard three-electrode system of an electrochemical instrument (Bistat, Biologic Science Instruments). A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp was used as the irradiation source to produce monochromatic illuminating light. The output light intensity was adjusted to 1 sun (100 W/m^2) using Si reference cell. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and 0.5 M Na_2SO_4 aqueous solution served as the electrolyte. The measured pH value is 6.72. To prepare the working electrode, the as-synthesized 10 mg of CdS and $CdS/CoSe_2$ nanocomposites were first dispersed into mixtures of ethanol (450 μL) and Nafion (50 μL) using soft ultrasonic stirring to obtain a uniform suspension. The solution containing the catalyst (30 μL) was dropped onto the pretreated indium–tin oxide (ITO) conductor glass substrate, which was then dried in an oven at 80 °C for 3 h. Photo-responses were measured at 0.0 V during on-off cycling of the solar simulator. Electrochemical impedance spectroscopy (EIS) was carried out at open-circuit potential with an AC voltage magnitude of 5 mV.

SUPPORTING FIGURES AND TABLE

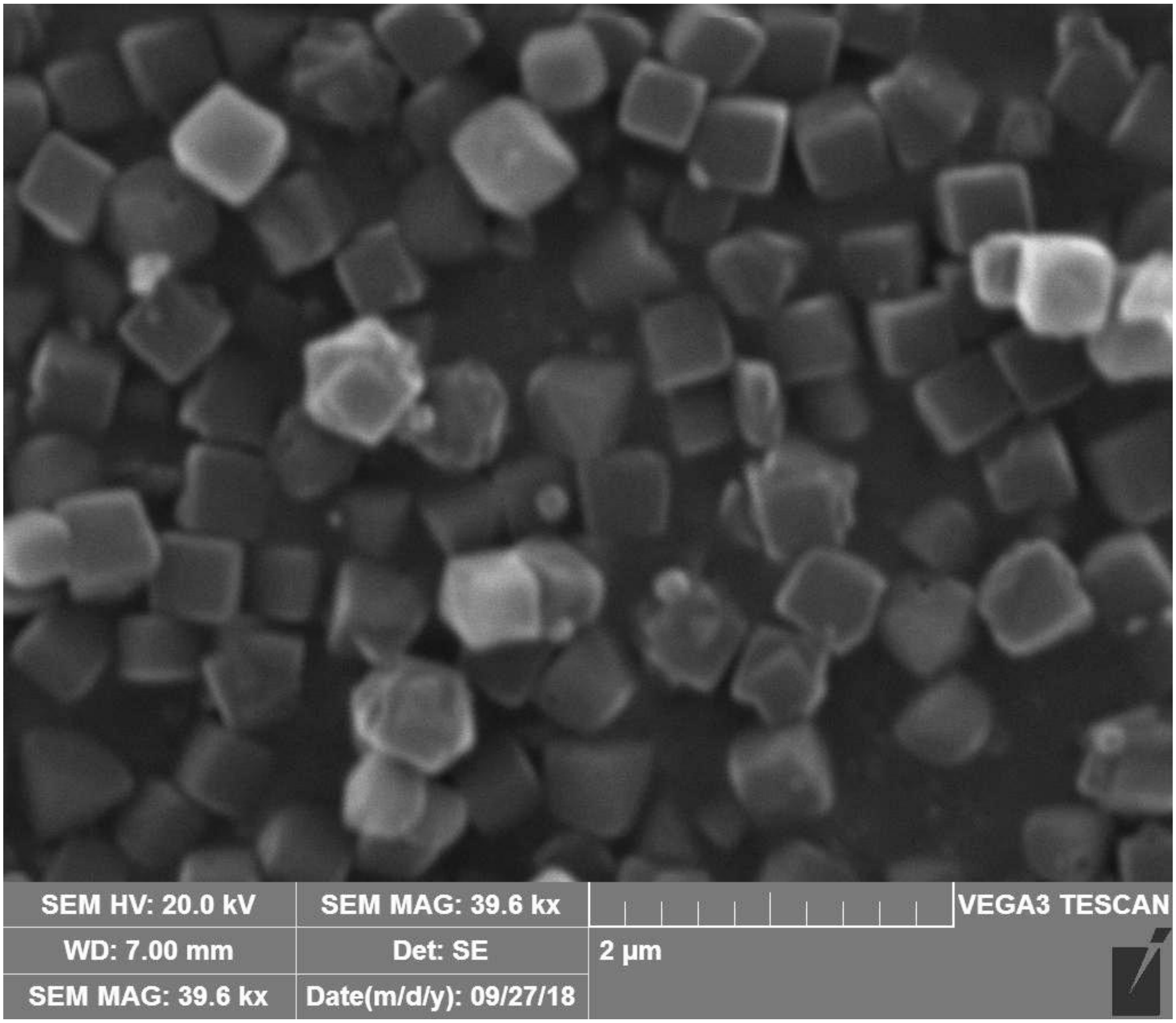

Figure S1. SEM image of the as-synthesized ZIF-67 nanocubes.

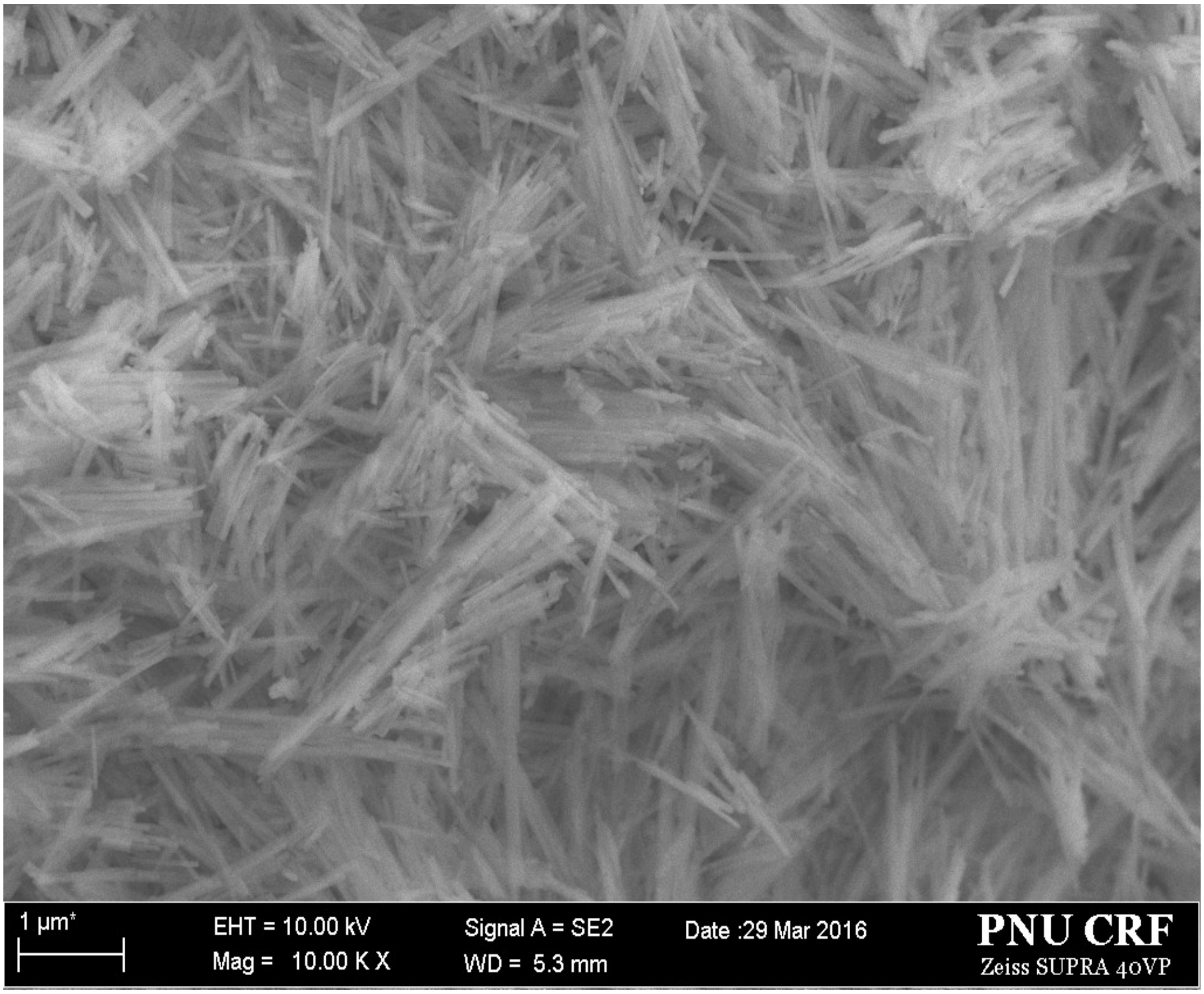

Figure S2. FESEM image of as-synthesized CdS nanostructures.

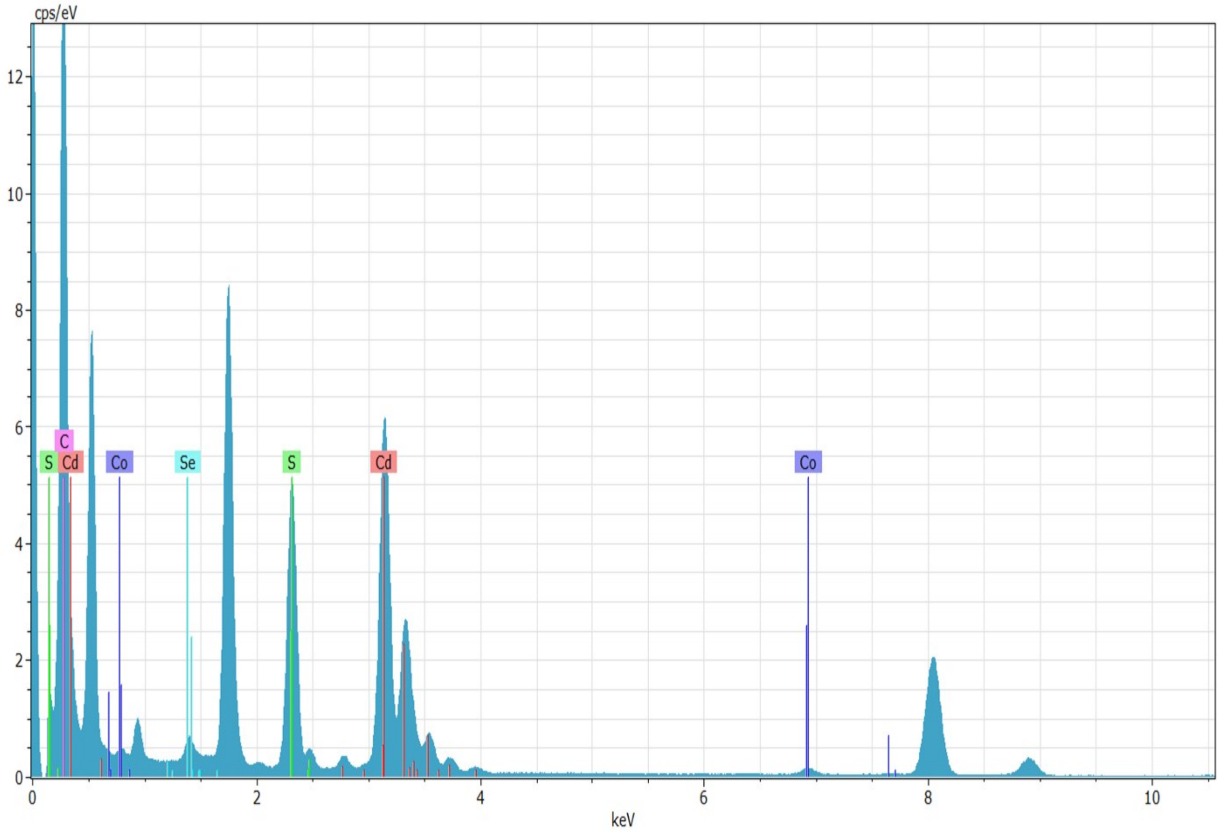

Figure S3. EDS Spectrum of CdS/$CoSe_2$ nanocomposite.

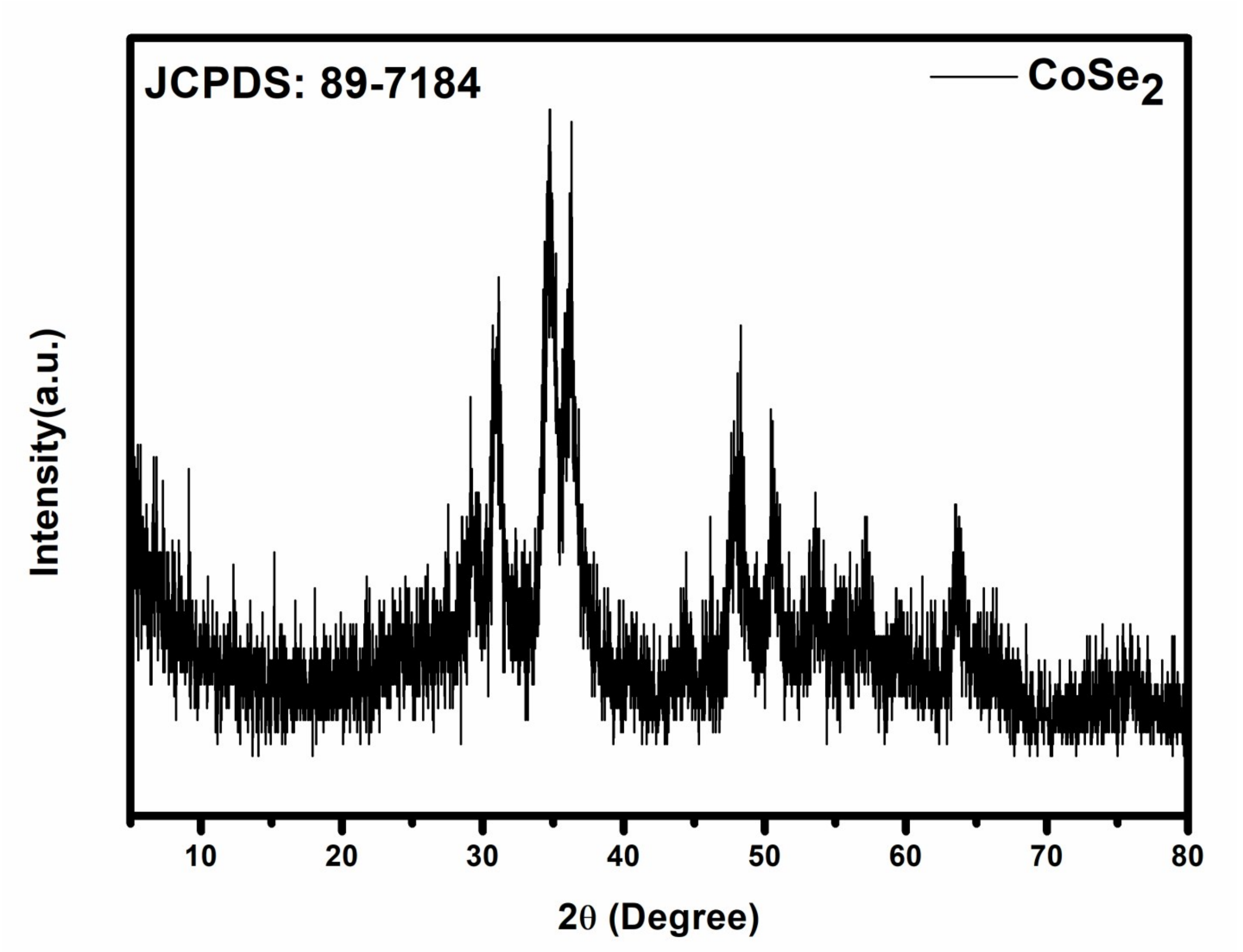

Figure S4. XRD Spectrum of $CoSe_2$ nanocages.

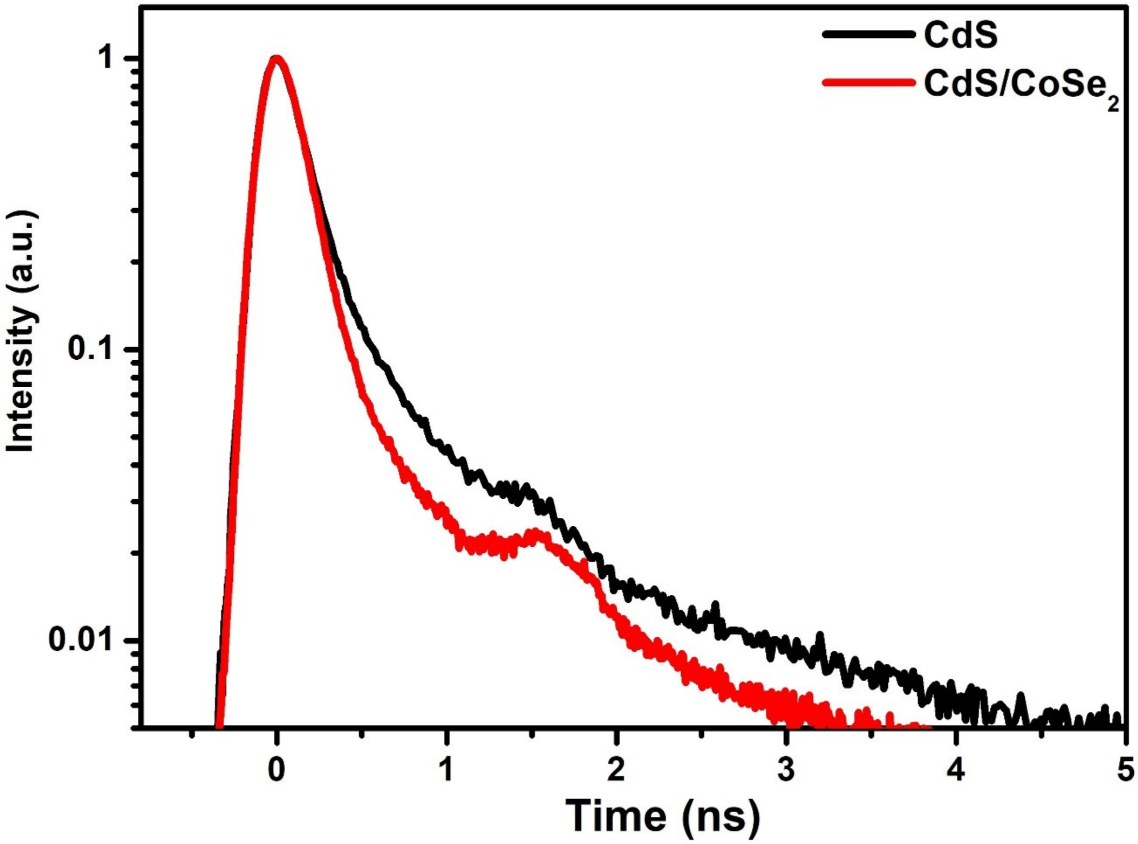

Figure S5. Time-resolved PL spectroscopic profiles of CdS and CdS/CoSe$_2$ nanocomposites.

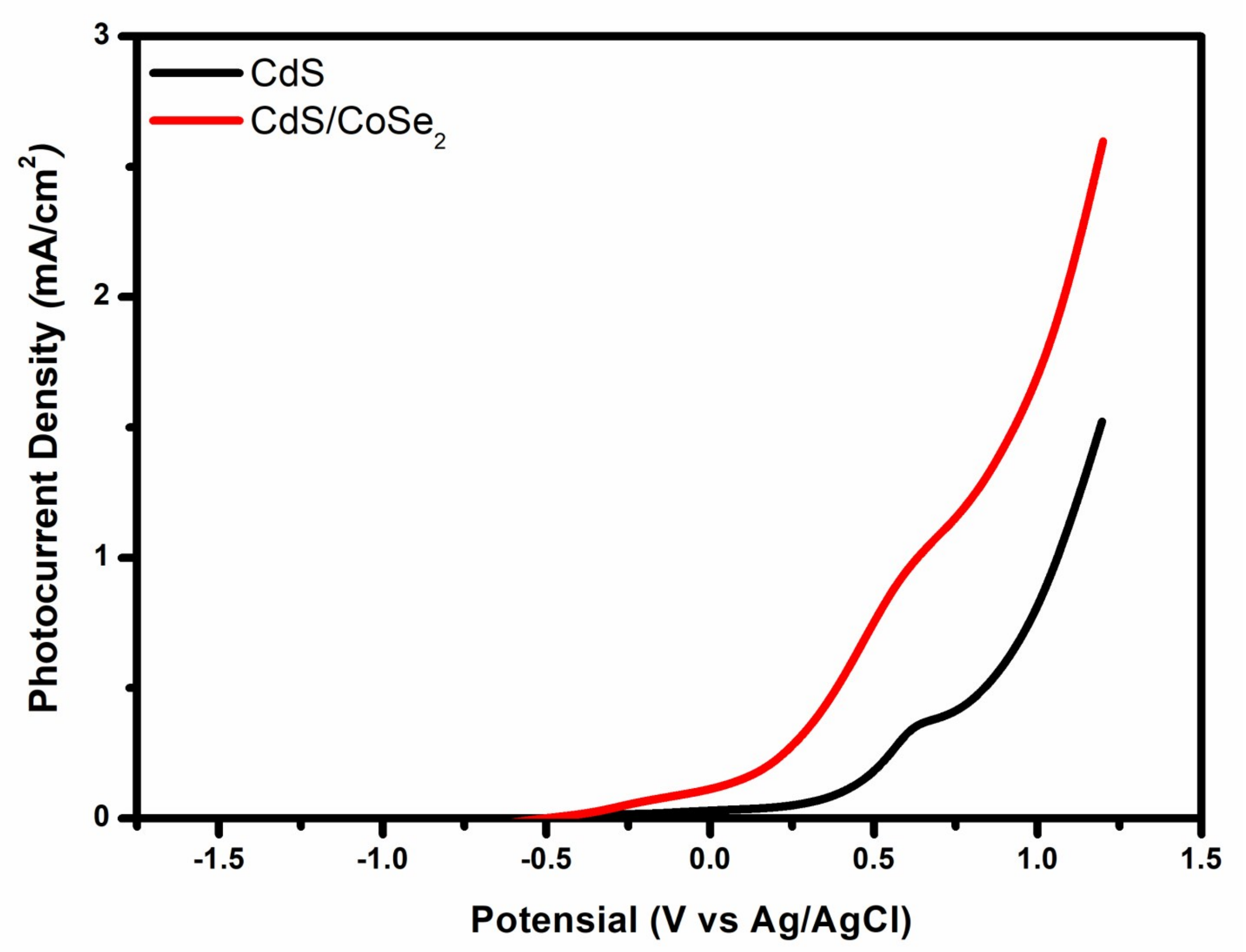

Figure S6. LSV spectra of CdS and CdS/CoSe$_2$ nanocomposites.

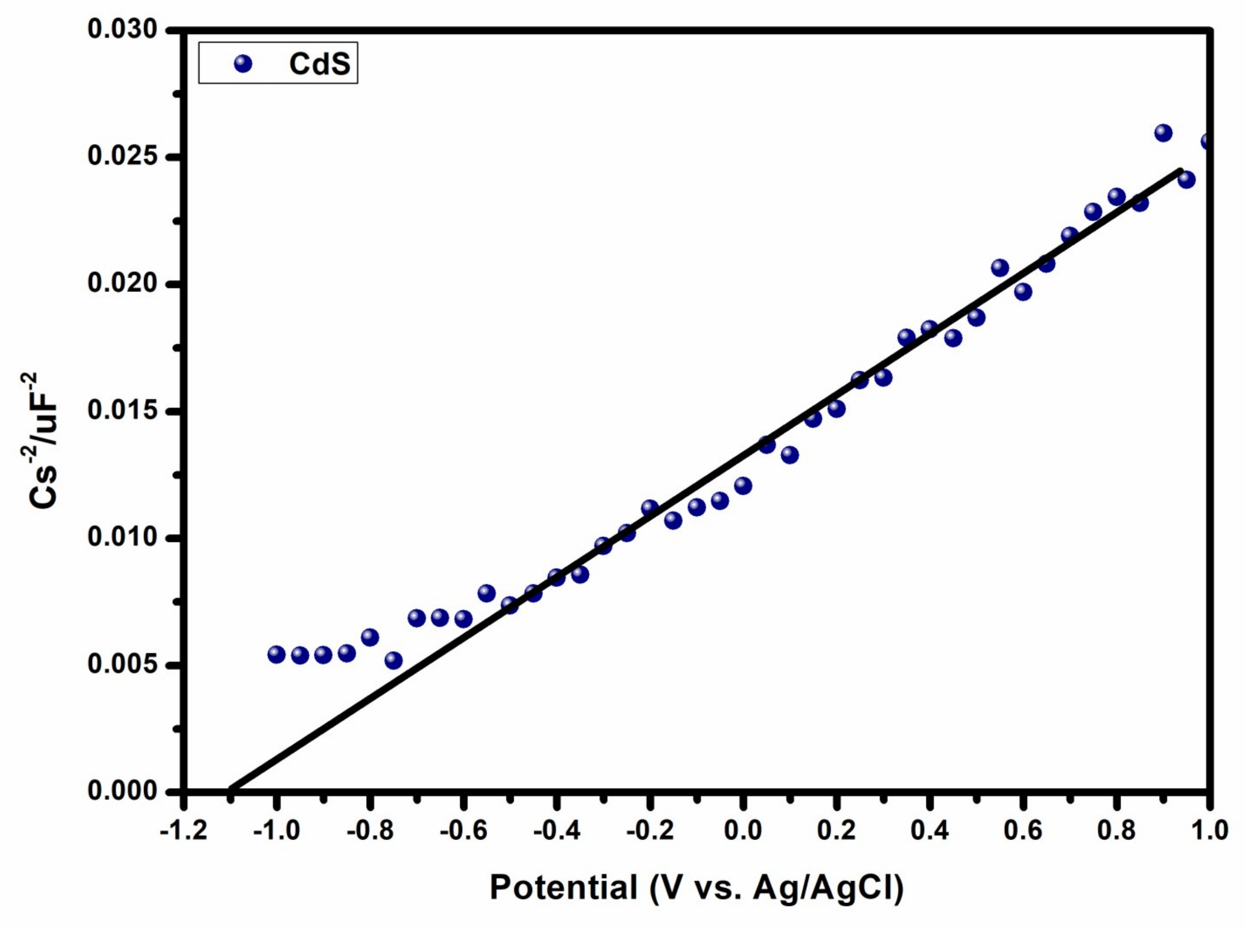

Figure S7. Mott-Schottky analysis of CdS nanorods.

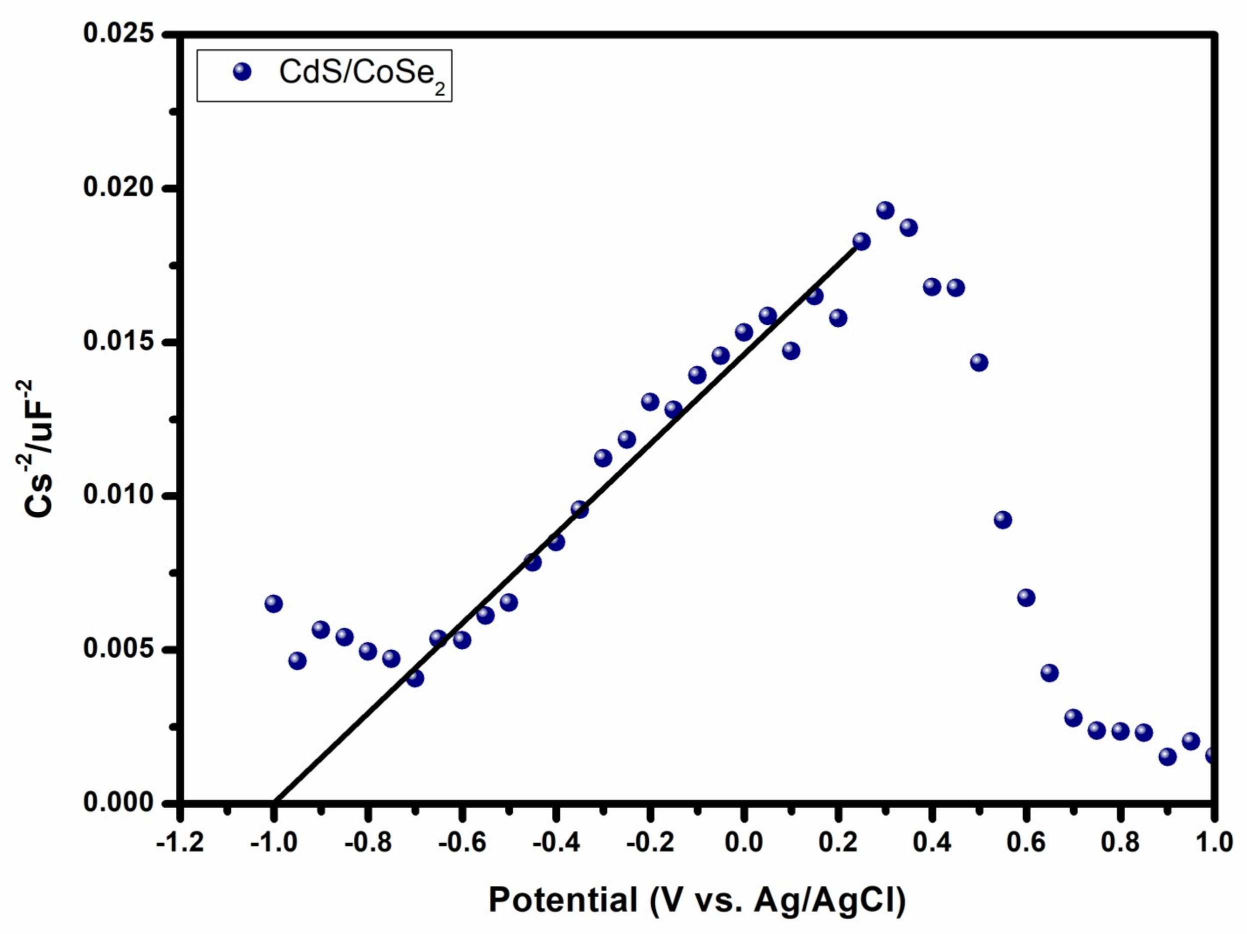

Figure S8. Mott-Schottky analysis of CdS/CoSe$_2$ nanocomposites.

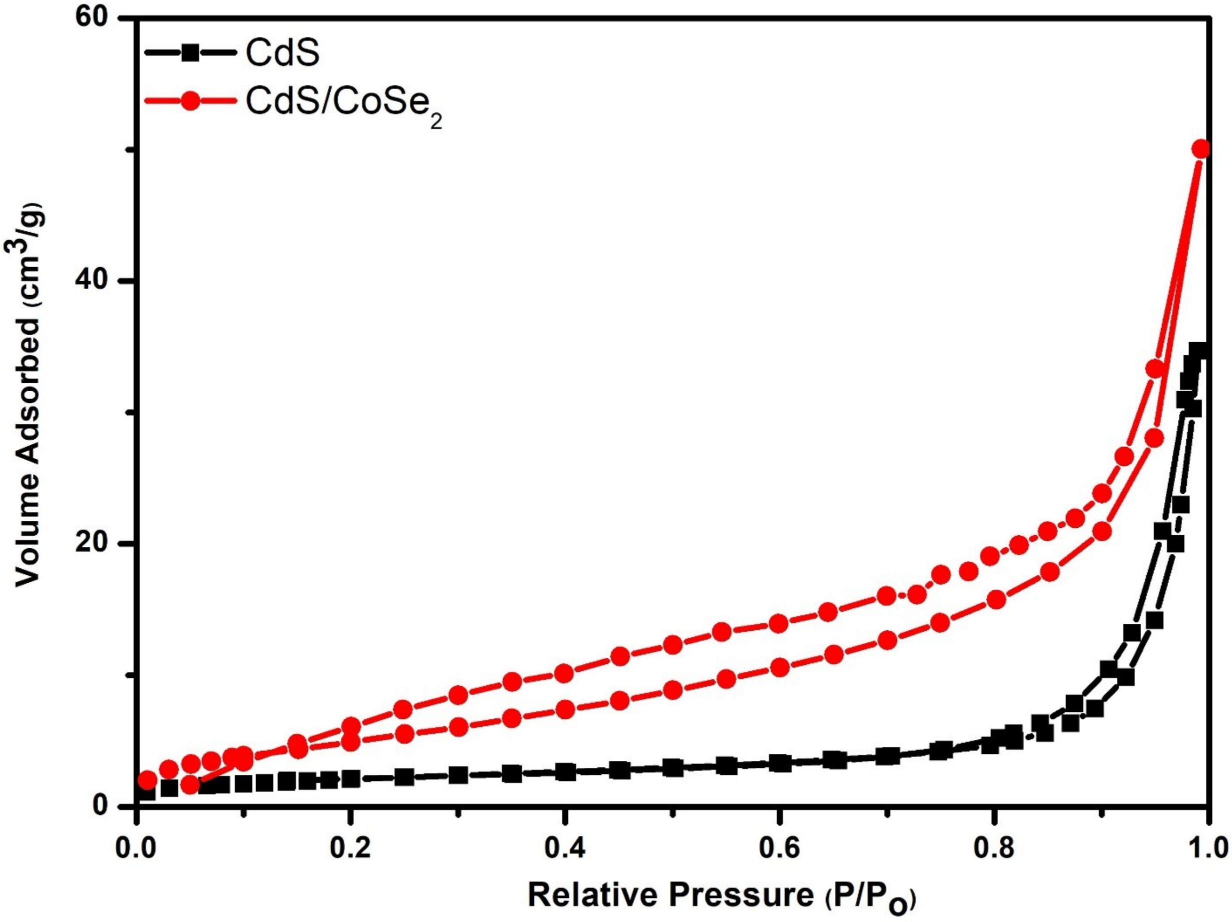

Figure S9. Nitrogen adsorption–desorption isotherms of CdS and CdS/CoSe$_2$ nanocomposites.

Table S1. Comparison of photocatalytic H_2 evolution rate reported in the literature using cobalt based nanostructures as a co-catalyst on CdS nanostructures with our present results

Photocatalyst	Catalyst dose (mg)	Scavenger	Light source	H_2 evolution rate (mmol·g^{-1}·h^{-1})	Ref.
$CdS/CoSe_2$	**1**	**Lactic acid**	**Simulated sunlight**	**82.5**	**This work**
$CdS/Co(OH)_2$	100	Ethanol	500 W Xe lamp	0.61	S1
$CdS/Co(OH)_2$ CdS/Co_3O_4 CdS/CoS CdS/CoO	50	Lactic acid	350 W Xe lamp (λ = 420 nm)	1.958 3.014 1.232 0.480	S2
$CdS/Co(OH)_2$	30	Lactic acid	350 W Xe lamp (λ > 420 nm)	14.43	S3
CdS/Co_3O_4	50	0.5 M Na_2S + Na_2SO_3	300 W Xe lamp (λ > 420 nm)	0.236	S4
CdS/Co_9S_8	20	Na_2S + Na_2SO_3	300 W Xe lamp (AM 1.5 G)	1.061	S5
CdS/Co-Pi	50	Lactic acid	300 W Xe lamp (λ > 420 nm)	13.3	S6
$CdS/Co\text{-}C@Co_9S_8$	1	Lactic acid	Simulated Sunlight	26.69	S7
CdS/Co_4S_3	1	Lactic acid	Simulated Sunlight	12.36	S8
CoS/CdS		Lactic acid	300 W Xe lamp (λ > 420 nm)	1.05	S9
CoO_x/ TiO_2/CdS		Lactic acid	300 W Xe lamp (λ > 420 nm)	0.66	S10
$CdS/NiTiO_3/CoS$	50	Lactic acid	300 W Xe lamp (λ > 420 nm)	6.236	S11
$CdS/C@CoS_2$	1	Lactic acid	Simulated sunlight	87.73	S12

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