

Supporting Information

Spatial Separation of Dual-cocatalysts on One-dimensional Semiconductors for Photocatalytic Hydrogen Production

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Experimental

Chemicals

Bismuth (III)chloride Anhydrous (BiCl_3 , 98%), Cadmium oxide (CdO , 98%), (100 mesh, 99.5%), selenium powder (%), trioctylphosphine (TOP, 90%), tri-n-octyl phosphine oxide (TOPO, 99%), Stearic acid (98%) were purchased from Alfa Aesar. Acetone, Methanol, pyridine, Dichloroethane (DCE), Ethanol and toluene were purchased from Fisher. All chemicals were used as received.

Synthesis of CdSe NWs

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CdSe NWs were synthesized following a slightly modified method reported earlier.¹ Briefly, CdO (64 mg, 0.50 mmol) as Cd precursor was dissolved in a mixture of TOPO (3.00 g, 7.76 mmol) and stearic acid (0.41 g, 1.4 mmol) in three-necks round bottom flask which was subsequently heated and evacuated at 100 °C for one hour. After that, the flask was backed filled with argon and heated to 320 °C until it becomes an optically transparent solution. Once an optically clear solution obtained the temperature was lowered to 250 °C followed by the addition of an injection solution comprised of Se + TOP (24 mg, 0.30 mmol) in 1 ml of TOP and (300 μL) of 2 mM BiCl_3 in acetone. The reaction mixture was heated for two minutes at 250°C, before cooling to room temperature. 5 ml toluene was added at 70 °C to avoid TOPO coagulation. The samples were precipitated by centrifuging with methanol and consecutively washed with pyridine and toluene several times. For photocatalytic H_2 generation measurement the CdSe NWs samples stored in toluene were washed with ethanol several times.

Synthesis of Medium length CdSe nanorods by quenching

The preparation of CdSe nanorods was performed under the same conditions as the CdSe NWs except the quick quenching. Briefly, CdO (64 mg, 0.50 mmol) as Cd precursor was dissolved in a mixture of TOPO (3.00 g, 7.76 mmol) and stearic acid (0.41 g, 1.4 mmol) in three-necks round bottom flask which was successively heated and evacuated at 100 °C for one hour. After that the flask was backed filled with argon and heated to 320 °C until it becomes an optically transparent solution. Once an optically clear solution obtained the temperature was lowered to 250 °C followed by the addition of an injection solution comprised of Se + TOP (24 mg, 0.30 mmol) in 1 ml of TOP and 2 mM BiCl₃ in acetone (300 μL) and then the swift injection of 5 mL toluene into the solution to quench the growth after the mixture of Bi nanoparticles and TOP-Se solution had been injected. The samples were precipitated by centrifuging with methanol and subsequently washed with pyridine and toluene several times.

Synthesis of CdSe short Nanorods

CdSe Nanorods were prepared by following a reported methodology with slight modification.² Typically, (64 mg, 0.50 mmol) of CdO, (334 mg, 1.00 mmol) Octadecylphosphonic acid, (3.00 g, 7.76 mmol), tri-n-octylphosphine oxide were loaded into a reaction flask and heated to 350°C under argon atmosphere until the CdO reacted with Octadecylphosphonic acid to give a transparent solution. Once a transparent solution obtained then injected (1.0 mL) of tri-n-octylphosphine at 320°C followed by a swift injection of (24 mg, 0.30 mmol) Se in (1.0 mL) tri-n-octylphosphine. The mixed solution was stirred at 320 °C for 8 min, and the resulting CdSe NRs were purified by precipitation and centrifugation with an excess of ethanol and re-dispersed in n-hexane after repeated washing using ethanol twice.

Synthesis of CdSe Nanoparticles

CdSe nanoparticles were synthesized following a reported procedure with slight modification.³ Briefly, (25 mg, 0.2 mmol) CdO, (0.14 g, 0.4 mmol) Octadecylphosphonic acid and (3.00 g, 7.76 mmol) tri-n-octylphosphine oxide (TOPO) were added into a 50 ml three-neck round bottom flask and heated to 150 °C for 30 min under vacuum, then backfilled with Argon and increased the temperature up to 350°C and maintained at this temperature until the solution became transparent. After an optically clear solution, the temperature was decreased to 80°C where 10 μ L (0.13 mmol) of dichloroethane (DCE) was injected and the temperature was raised again. At 250°C, 0.42 mL (0.42 mmol) of a Se in TOP solution (1M) was injected before reducing the temperature to 240°C. After 4h, the reaction was quenched by injecting 3.5 mL of toluene. The resulting CdSe NPs were purified by three cycles of precipitation with methanol and toluene. Before photocatalytic H₂ generation measurements, suspensions in toluene were washed several times using ethanol.

Preparation of Pt/CdSe, CoO_x/CdSe and Pt-CoO_x/CdSe via in-situ photodeposition method.

Pt/CdSe: The deposition of Pt and CoO_x were loaded by *in situ* photo deposition as described.⁴ Typically, 0.1 g CdSe nanorods were dispersed in 100 ml aqueous solution of 0.1 M Na₂S-Na₂SO₃ by ultra-sonication for 15 min. after the addition of the required amount of H₂PtCl₆ solution (1.0 mg/L), the solution was degassed for 30 min under vacuum and irradiated with 300W Xe lamp for the whole H₂ evolution experiment. After the reaction, the solid samples were collected by centrifugation, washed several times with deionized water and dried in a vacuum oven at 60 °C for 12 hours.

CoO_x/CdSe: The CdSe nanorods powder (0.1 g), the required amount of Co (NO₃)₂ solution and NaIO₃ solution (0.02 M, 5 mL) were mixed in 100 mL deionized water, and the suspension was then irradiated by a 300 W xenon lamp ($\lambda > 420$ nm, 150 mW cm⁻²) under continuous stirring. After 3.5h photo-deposition, the precipitate was isolated using centrifugation, washed with ethanol more than 3 times, and finally dried at 60 °C overnight.

PdS/CdSe: The PdS nanoparticles were synthesized by in situ injecting a certain amount PdCl₂ solution into the 100 ml photocatalytic reaction suspension containing Na₂S-Na₂SO₃ solution prior to the addition of CdSe, sonicated and stirred vigorously for half an hour followed by the addition of CdSe. Then the solution was degassed after the addition of 0.1g CdSe catalyst for 30 min under vacuum then irradiated by a 300 W xenon lamp ($\lambda > 420$ nm, 150mW cm⁻²) under continuous stirring. After the reaction, the solid sample was collected by centrifugation, washed several times with deionized water and dried in a vacuum oven at 60 °C for 12 hours.

Pt-CoO_x/CdSe: The fabrication of dual cocatalysts on CdSe nanorods to synthesis Pt-CoO_x/CdSe was performed as follows. Briefly, 0.1 g calcinated sample of CoO_x/CdSe photocatalyst nanorods was dispersed in 100 ml aqueous solution of 0.1 M Na₂S-Na₂SO₃ by ultra-sonication for 15 min. After the addition of the required amount of H₂PtCl₆ solution (1.0 mg/L), the solution was degassed for 30 min under vacuum and then irradiated with 300W Xe lamp for the whole H₂ evolution experiment. After the reaction the solid sample was collected by centrifugation, washed three times with deionized water and dried in vacuum oven at 60 °C for 12 hours.

Pt-PdS/CdSe: Concisely, 0.1 g sample of Pt/CdSe photocatalyst nanorods were dispersed in 100 ml aqueous solution of 0.1 M Na₂S-Na₂SO₃ by ultra-sonication and for 30 min prior to the

addition of Pt/CdSe nanorods. After the addition of the required amount of PdCl₂ the solution was degassed for 30 min under vacuum and then irradiated with 300 W Xe lamp for the whole H₂ evolution experiment. After the reaction, the solid sample was collected by centrifugation, washed three times with deionized water and dried in a vacuum oven at 60 °C for 12 hours.

Synthesis of Pt/CdSe, PdS/CdSe, and Pt-PdS/CdSe by Impregnation Method

Typically, 0.1 g CdSe nanorods sample were added in to 100 ml DI water containing the required amount of cocatalysts Pt and PdS were added for the preparation of Pt-PdS/CdSe. The resulting solution was stirred for 2 h at room temperature. After centrifugation, the composite was washed with high purity water several times and dried at 60°C under a vacuum for 6 h.

Hydrogen Evolution experiment.

The photocatalytic hydrogen experiments were performed in 150 ml Pyrex glass having 38 cm² irradiation areas for the external incident light source, where a 300 W Xe-lamp equipped with a 420 nm cut-off filter was used to provide the visible light irradiation. The illumination intensity was adjusted to 100 mW cm⁻². During photocatalytic hydrogen production, 0.1 g powder sample was dispersed in 100 mL aqueous solution containing 0.1 M Na₂S and Na₂SO₃ was sonicated first for 15 min in order to well disperse the powder. Then the solution was degassed for 30 min to remove any trapped air inside. The evolved H₂ was measured through a gas chromatography connected with a thermal conductivity detector (TCD) detector

The apparent quantum yield (AQY) was measured under the same photocatalytic reaction conditions and illumination is provided by 300 W xenon lamp with a monochromator ($\lambda > 420$ nm). The focused intensity on the liquid level for the light source was measured AQY was calculated according to the following equations.

$$AQY[\%] = \frac{\text{Number of reacted electron}}{\text{Number incident photons}} \times 100$$

$$AQY[\%] = \frac{\text{Number of evolved } H_2 \times 2}{\text{Number incident photons}} \times 100$$

Characterization

The crystalline phase of the as synthesized CdSe and CdS nanorods samples were observed by X-ray diffraction (Rigaku; Mini Flex diffractometer with a Cu K α irradiation source). For the structural characterization TEM and HRTEM were used. The TEM images were obtained with Tecnai G2 Spirit (FEI Company) microscopy with the accelerating voltage of 120 kV. For the detail characterization HRTEM images obtained JEOL 2100. By using JASCO V-550 spectrophotometer an Ultraviolet-visible reflectance spectra (UV-vis DRS) were achieved, where XPS spectra were obtained by VG ESCALab220i-XL electron spectrometer with 300 W Mg K α radiation. The luminescence spectra were performed at room temperature by using FLS920 fluorescence spectrometer (Edinburgh Instruments)

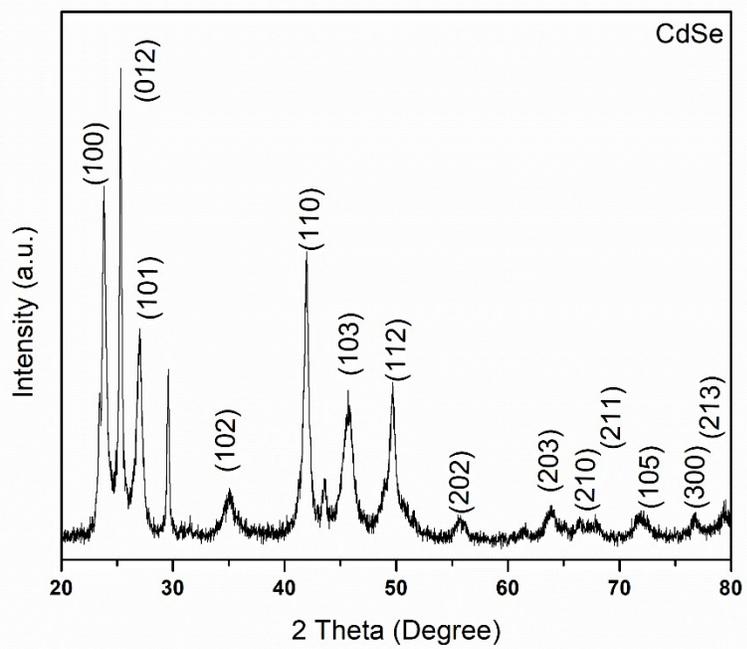


Figure S1. XRD patterns of as-prepared CdSe nanorods powder.

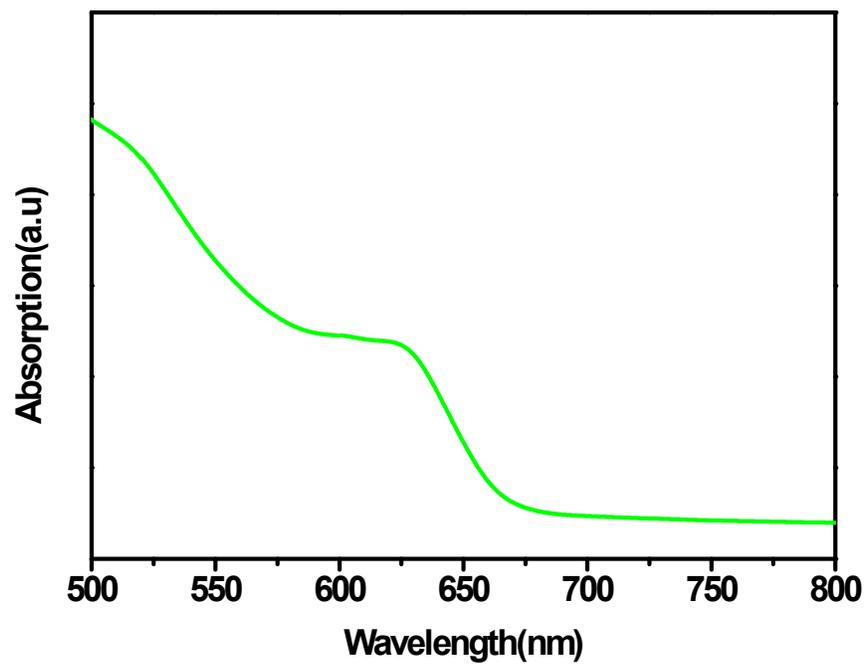


Figure S2. UV-vis absorption spectra of CdSe nanorods.

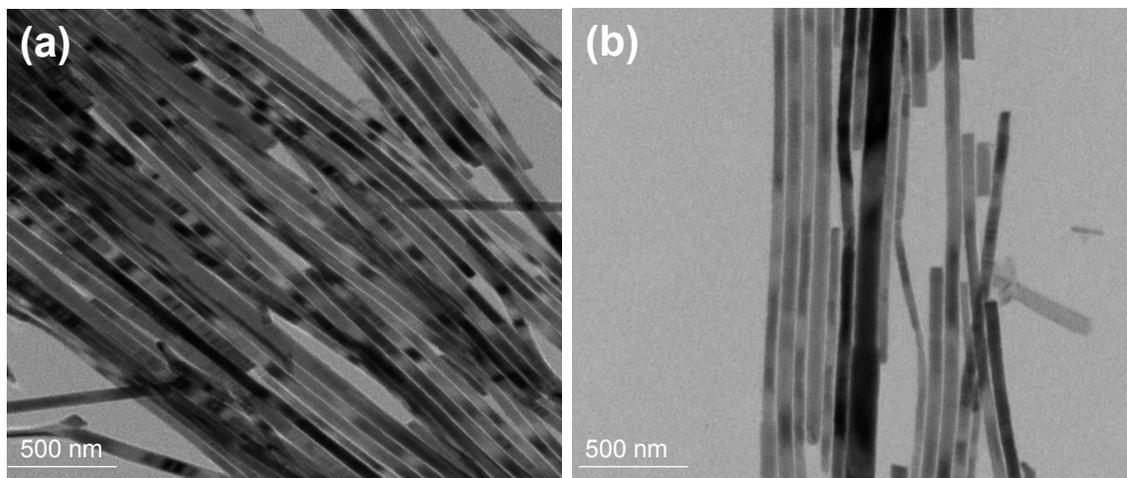


Figure S3. TEM images of CdSe nanorods.

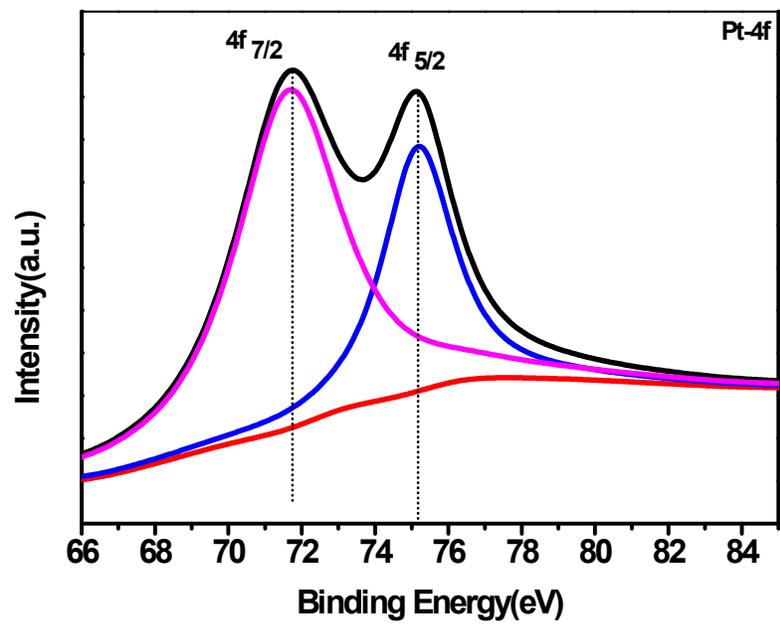


Figure S4. XPS spectra of Pt-4f for Pt /CdSe.

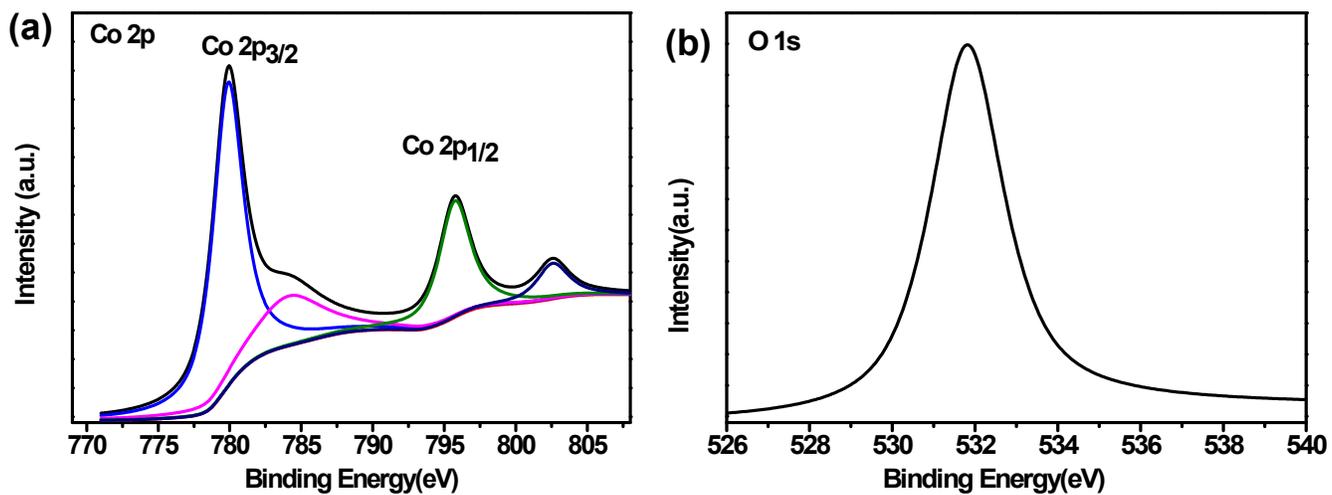


Figure S5. (a) XPS spectra for Co 2p (a) and (b) O 1s for CoO_x/CdSe.

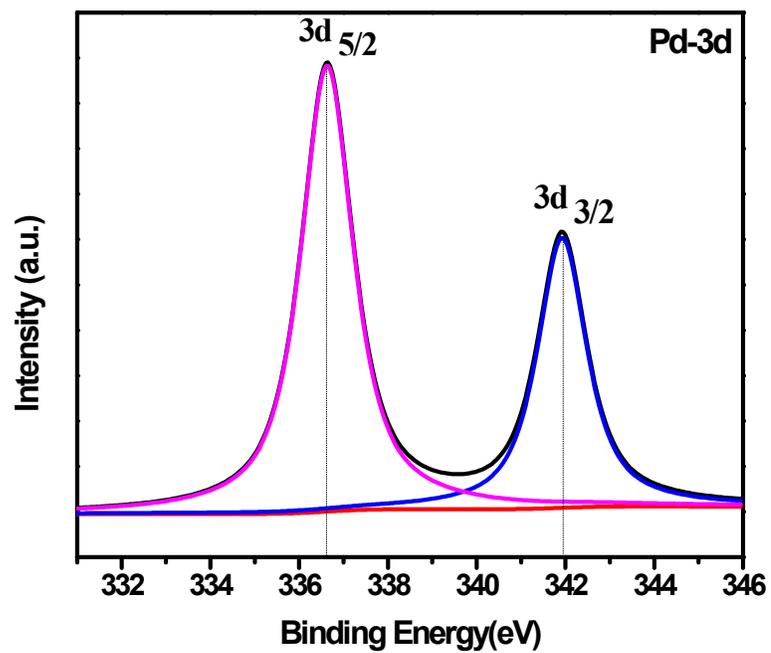


Figure S6. XPS spectra of Pd-3d for Pt-PdS/CdSe.

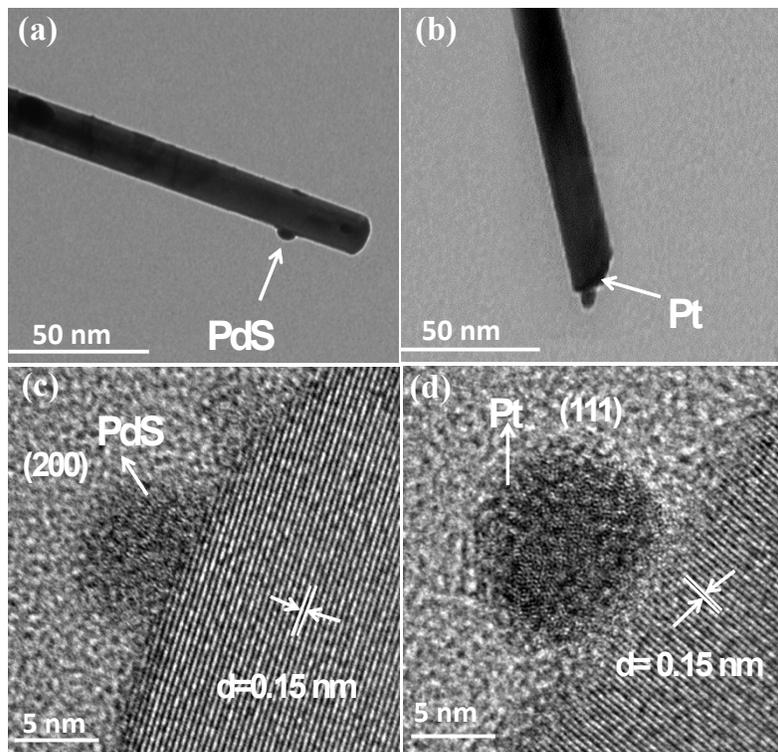


Figure S7. HRTEM images of selective deposition of different cocatalysts on the lateral facets and top of CdSe nanorods. (a, c) PdS; (b, d) Pt;

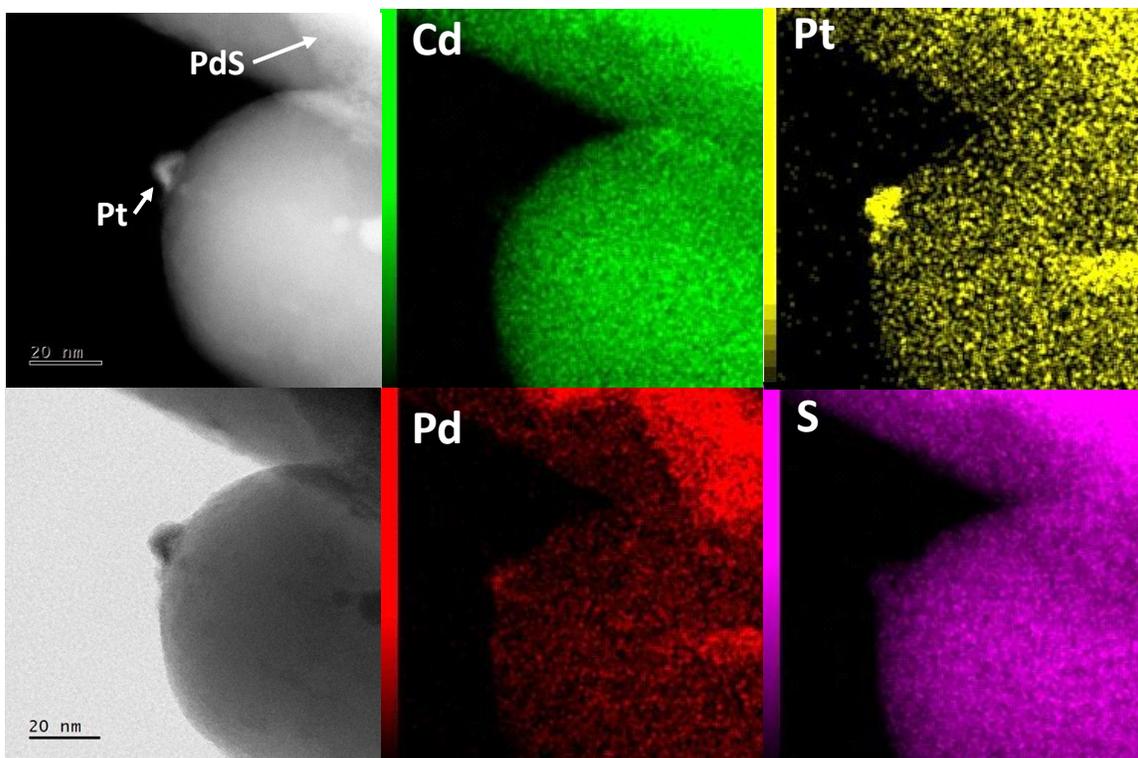


Figure S8. HRTEM and element mapping results of Pt-PdS/CdSe.

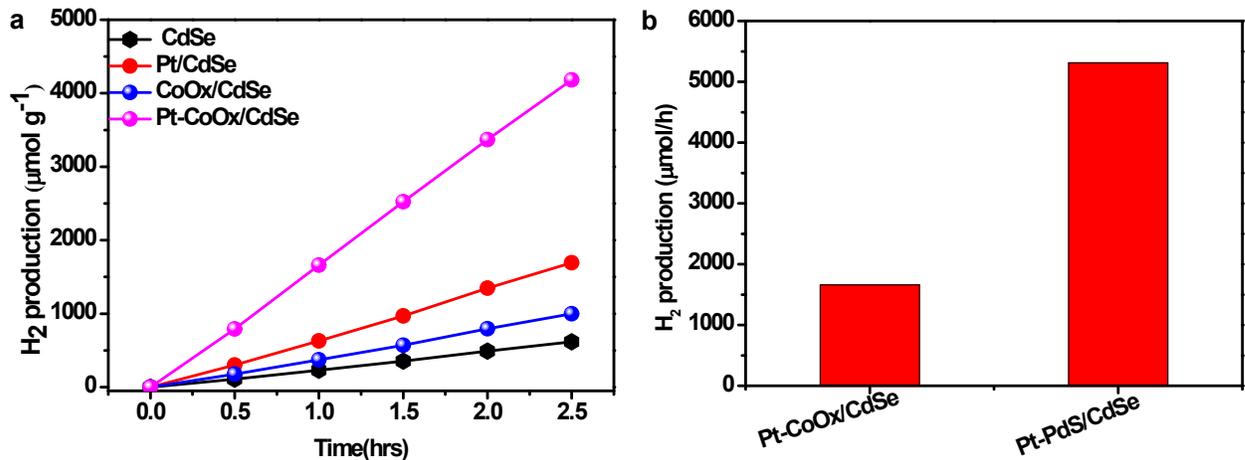


Figure S9. (a) Photocatalytic H₂ evolution under visible light irradiation over CdSe, Pt/CdSe, CoO_x/CdSe and Pt-CoO_x/CdSe, respectively; (b) Comparative H₂ evolution by CdSe Nanorods in the presence of different dual cocatalysts. Reaction condition: catalyst, 100 mg; 0.1 M Na₂S-Na₂SO₃ aqueous solution (100 mL); Light source: Xe lamp (300W) with an optical filter ($\lambda > 420$ nm); The amount of cocatalyst was fixed 0.5%.

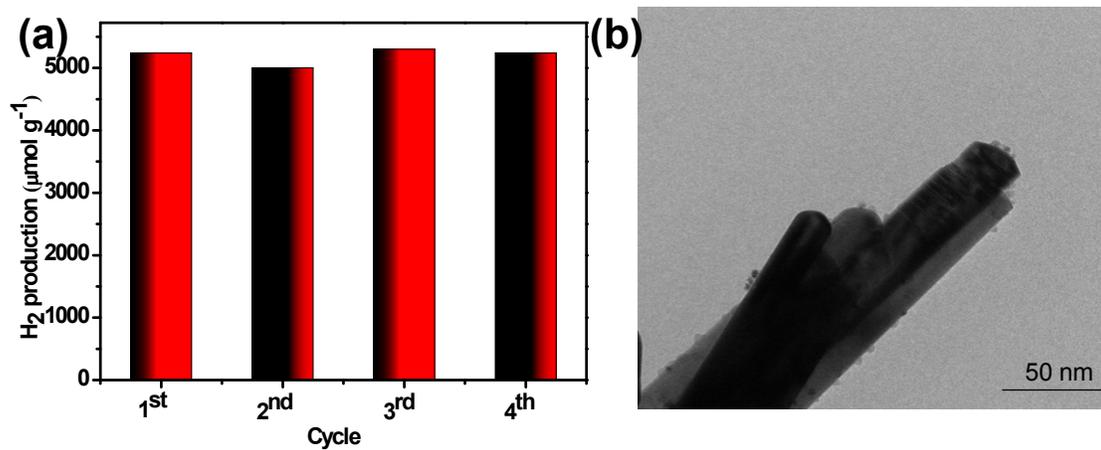


Figure S10. (a) H₂ generation rate in each 4 h reaction for consecutive four cycles (b) TEM image of CdSe nanorods after photocatalytic H₂ generation with dual cocatalysts.

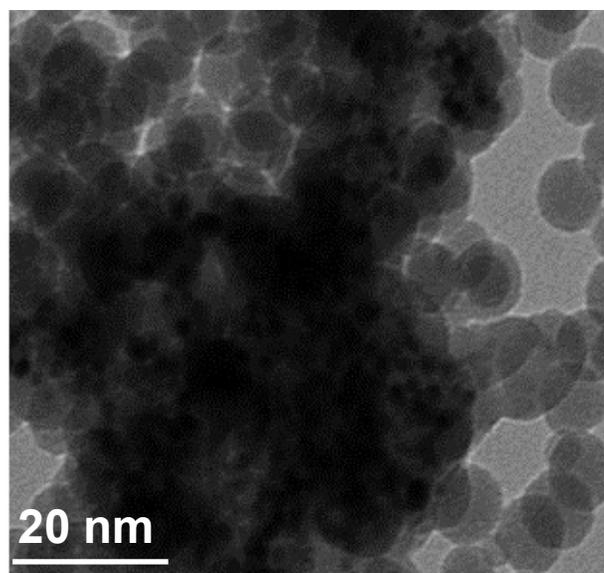


Figure S11. TEM image of CdSe nanoparticles in the presence of dual cocatalysts.

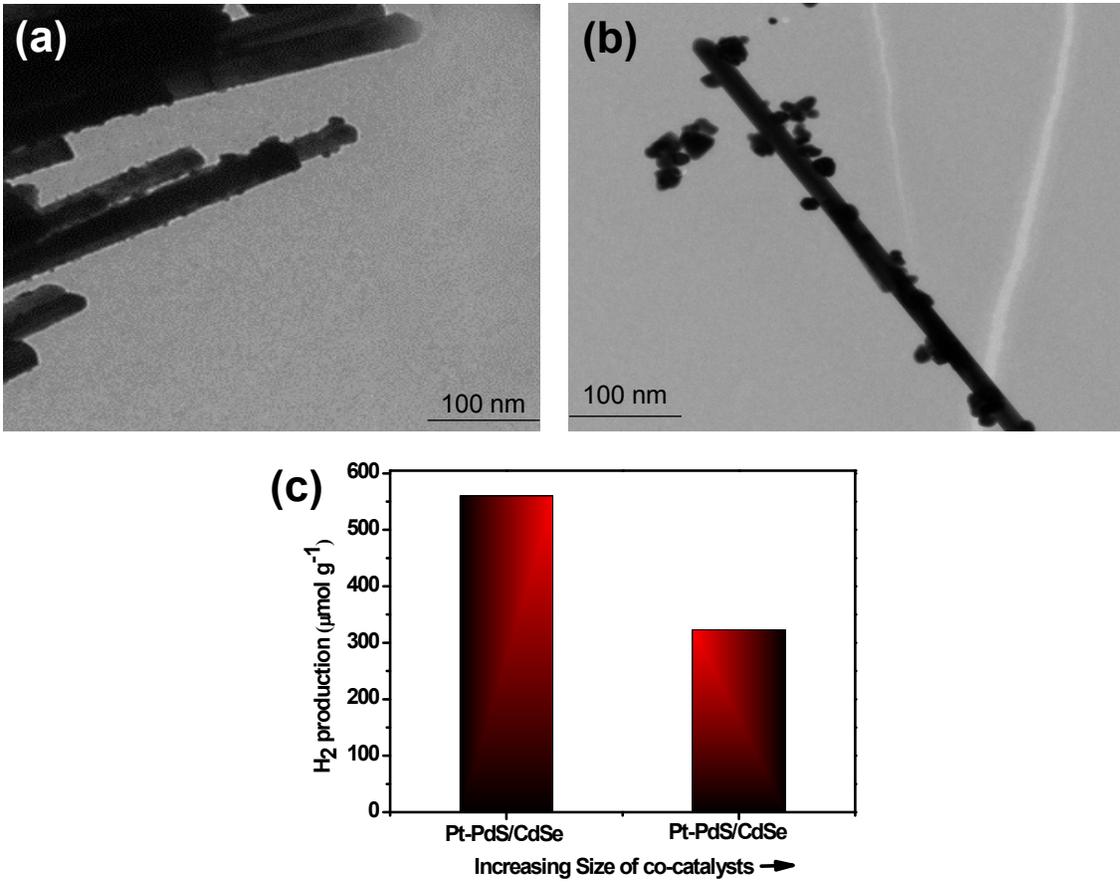


Figure S12. TEM images (a, b) and photocatalytic H₂ generation (c) of CdSe nanorods with dual cocatalysts of different sizes via impregnation method

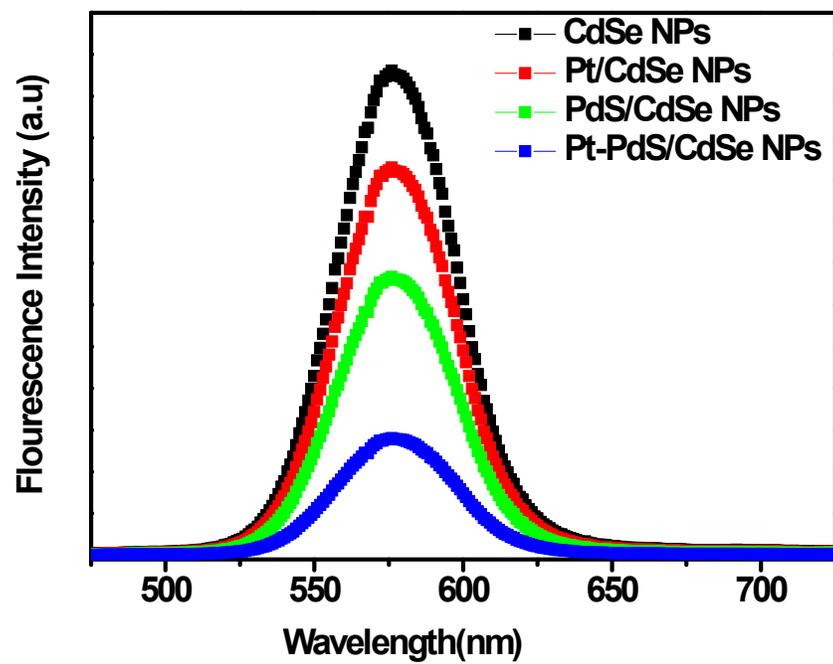


Figure S13. PL emission spectra of CdSe nanoparticles after depositing different cocatalysts.

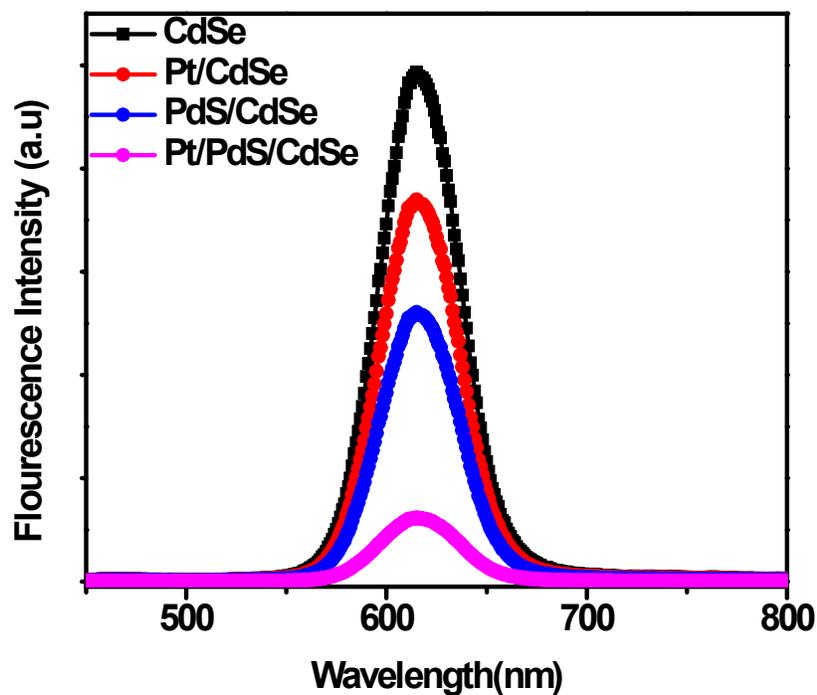


Figure S14. PL emission spectra of ~20 nm CdSe nanorods after depositing different cocatalysts.

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