Supporting Information

Significant enhancement in photocatalytic water splitting enabled by elimination of surface traps in Pt-tipped CdSe nanorods

Kowsalya Devi Rasamani,[a,†] Zheng Li,[b,†] and Yugang Sun[a,*]

[a] *Department of Chemistry, Temple University, 1901 North 13th Street, Philadelphia, Pennsylvania, 19122, USA*

[b] *Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA*

* *E-mail: ygsun@temple.edu*

Methods

Preparation of CdSe nanorods. 0.710 g tetradecylphosphonic acid (TDPA, 2.6 mmol), 0.160 g hexylphosphonic acid (HPA), 0.20 g cadmium oxide (CdO, 1.6 mmol) were mixed with 3.0 g trioctylphosphine oxide (TOPO) in a three-neck flask, followed by N_2 bubbling at room temperature for 10 minutes and at 120 °C for additional 10 minutes. The solution was then heated to 300 °C under N_2 atmosphere, followed by injection of 1.8 ml trioctylphosphine (TOP) into the flask, prior to the addition of selenium precursor. In a separate vial with septum, 0.073 g Se (0.92 mmol) was dissolved in 0.50 ml TOP with assistance of gentle sonication. The selenium precursor was then quickly injected into the flask after the temperature stabilized at 300 °C. The temperature was maintained at 300 °C for 5 minutes to complete the reaction. The heating mantle was then removed. 3 ml toluene was added to the reaction flask when the reaction solution was cooled down to 70 °C to prevent the reaction solution from solidification.

Decoration of the CdSe nanorod ends with Pt nanocrystals. 0.25 ml of the as-prepared solution of CdSe nanorods was mixed with 17.5 ml toluene and 7.5 ml isopropanol, followed by centrifugation at 8500 rpm for 5 minutes. After the supernatant was decanted, the precipitate was dispersed in 17.5 ml toluene and 7.5 ml isopropanol. Centrifuging at 8500 rpm for 5 minutes and decanting the supernatant removed unreacted precursors. The precipitate of CdSe nanords was re-dispersed together with 10 mg of platinum(II) acetylacetonate ($Pt(acac)_2$) in 2 ml of 1,2-dichlorobenzene under sonication. In a separate three-neck flask, 86 mg 1,2-hexadecanediol, 0.4 ml oleic acid, 0.4 ml oleylamine, and 20 ml diphenyl ether were mixed together under vigorous magnetic stirring. After bubbling at room temperature with nitrogen for 10 minutes, the reaction flask was pumped down with vacuum at 80 °C for additional 30 minutes, then the reactants were heated to 200 °C. The dispersion of the purified CdSe nanorods and $Pt(acac)_2$ in 1,2-dichlorobenzene was injected to the inert solvent at 200 °C, and the reaction at this temperature lasted 4 minutes to deposit Pt tips at both ends of individual CdSe nanorods.

Overgrowth of CdS shell on CdSe nanorods with Pt tips. Half portion (~11 ml) of the as-prepared CdSe nanorods with Pt tips was purified and the other half portion was kept as the control. Around 11 ml of the as-prepared CdSe nanorods with Pt tips was mixed with an equal volume of toluene. Centrifuging the dispersion at 6000 rpm for 5 minutes and decanting the supernatant left the precipitate in the centrifuge tube. The precipitate was dispersed in 11 ml toluene and 11 ml ethanol followed by centrifugation at 3000 rpm for 5 minutes. Decanting the supernatant resulted in clean Pt-tipped CdSe nanorods collected at the bottom of the centrifuge tube. The washed precipitate was then mixed with 0.012 g sulfur and 1.8 ml TOP, and kept aside. In a three-neck flask, 0.009 g CdO, 0.008 g HPA, 0.029 g octadecylphosphonic acid (ODPA) and 3 g TOPO were mixed under N_2 bubbling at room temperature. The N_2 bubbling continued for 10 minutes at room temperature and at 120 °C for additional 10 minutes. The temperature of this solution was then ramped to an appropriate temperature (e.g., 270-300 ^{o}C) under nitrogen blanket. In a typical synthesis shown in Figure 1, the temperature was increased to and stabilized at 285 °C followed by a quickly injection of 1.8 ml TOP. The purified Pt-tipped CdSe nanorods with sulfur in TOP were then injected to the hot solution. The reaction solution was maintained at 285 °C for additional 6 minutes. Taking the heating mantle away from the flask cooled down the reaction solution. 3 ml toluene was added to the reaction solution to prevent the reaction solution from solidification when the temperature reached 70 ^{o}C.

Transferring the nanords to aqueous solutions. For evaluation of the nanords in photocatalytic hydrogen production, the same batch of Pt-tipped CdSe nanorods with/without CdS shell were transferred to water phase in parallel. The nanords were washed with equal volume of toluene and ethanol for three times through sequentially centrifugation, decanting of supernatant, and re-dispersing of precipitates. The precipitates were then mixed with 10 mg of 11-mercaptoundecanoic acid (MUA, 95%, Aldrich) and 1 ml of $CHCl_3$. After gentle shaking, the solution was stored in dark overnight. Adding 4 mL KOH aqueous solution (5 mg/mL) and 0.2 ml $CHCl_3$ to the organic dispersion led to the successful phase transfer of the nanorods from the organic phase to the aqueous phase. After careful removal of the bottom $CHCl_3$ layer with syringe, 10 ml methanol were added followed by centrifugation at 6000 rpm for 10 minutes to wash the nanorods. The precipitated nanorods were then re-dispersed in 0.5 ml 0.35 M Na_2SO_3/0.25 M Na_2S aqueous solution.

Photocatalytic hydrogen generation. The aqueous solution of 0.35 M Na_2SO_3/0.25 M Na_2S containing nanorods (serving as photocatalyst) was added to an airtight septum vial and purged with nitrogen for at least 20 minutes to get rid of air. And a 200 W Xenon lamp with light intensity of 100 mW/cm^2 (white light, > 400 nm) was used to irradiate the solution. For every 15-minute interval, the gas above the solution in the vial was sampled with a syringe, and was immediately injected into Agilent 5975C GC to quantitatively analyze the concentration of hydrogen.

Characterization. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Varian Cary 50 spectrophotometer, using a quartz cuvette with a 10 mm optical path length. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired on a JEOL 2010F(s) microscope operated at 200 kV accelerating voltage. TRPL (time resolved photoluminescence) were measured on Horiba Jobin-Yvon Nanolog Spectrofluorometer.

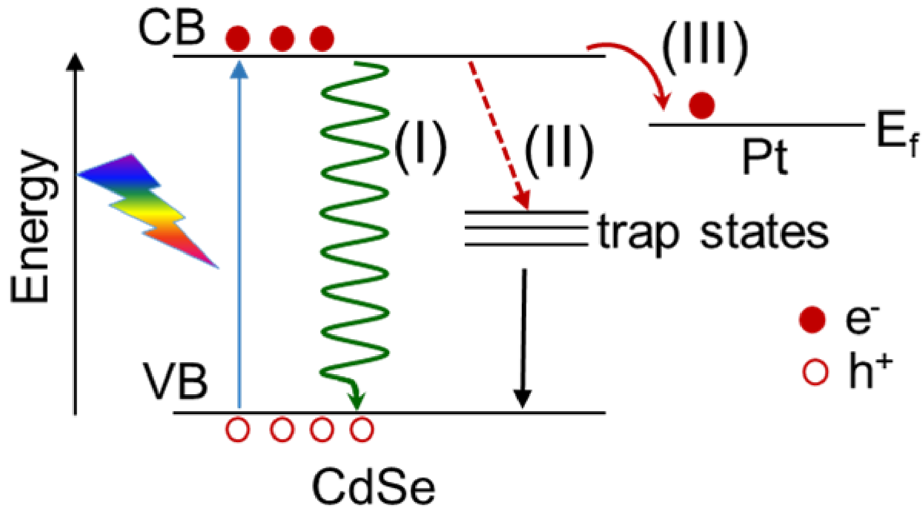

Fig. S1. Schematic depiction of the three major pathways responsible for exciton relaxation. The first channel (**I**) represents the recombination of excitons in the semiconductor through photoluminescence. Channel (**II**) corresponds to the trapping of electrons in surface defects followed by the release of excess energy as phonons. The third channel (**III**) highlights the migration of the energetic electrons from semiconductor (CdSe) to metal (Pt), which can drive chemical reactions.

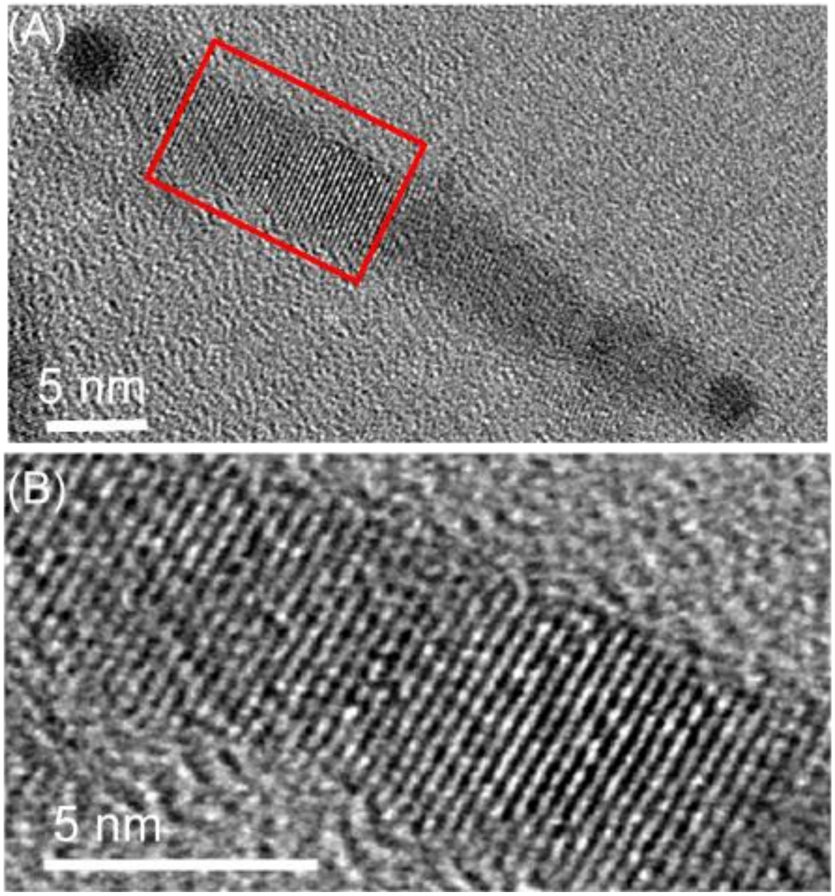

Fig. S2. (A) HRTEM image of an individual Pt-tipped CdSe@CdS core-shell nanorod. (B) Blowup of the portion in the red box in (A). The absence of discontinuity in lattice fringes indicates the epitaxial relationship between the CdSe nanorod and the CdS shell.

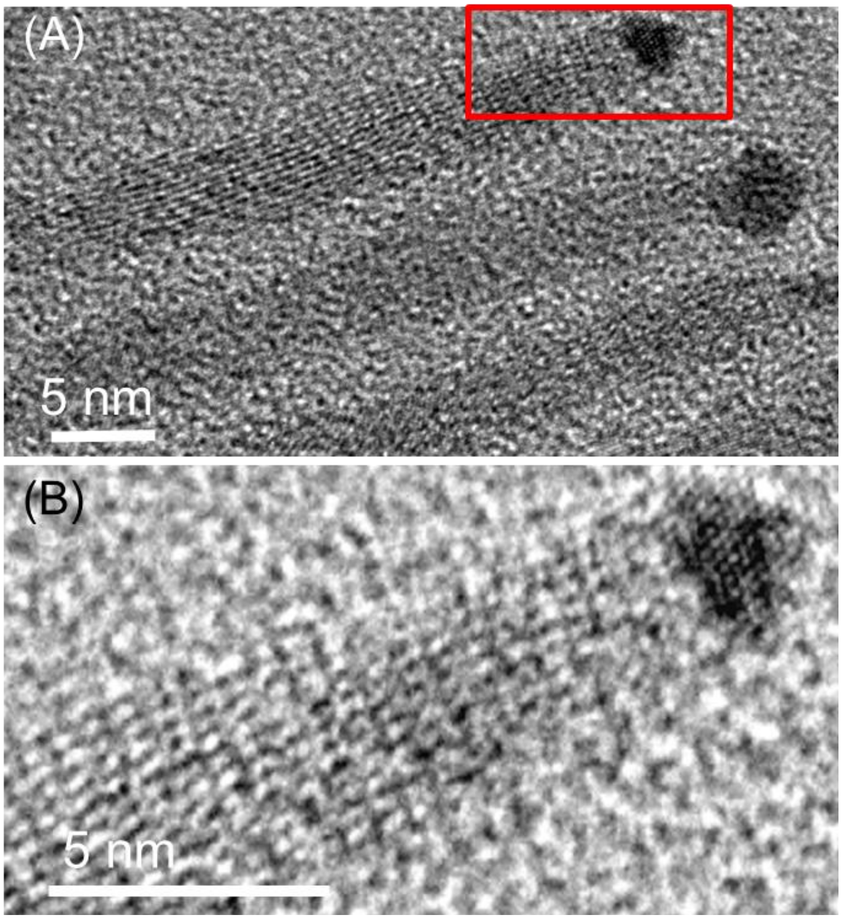

Fig. S3. (A) HRTEM image of individual Pt-tipped CdSe@CdS core-shell nanorods. (B) Blowup image of the Pt tip in the area of the red box highlighted in (A).

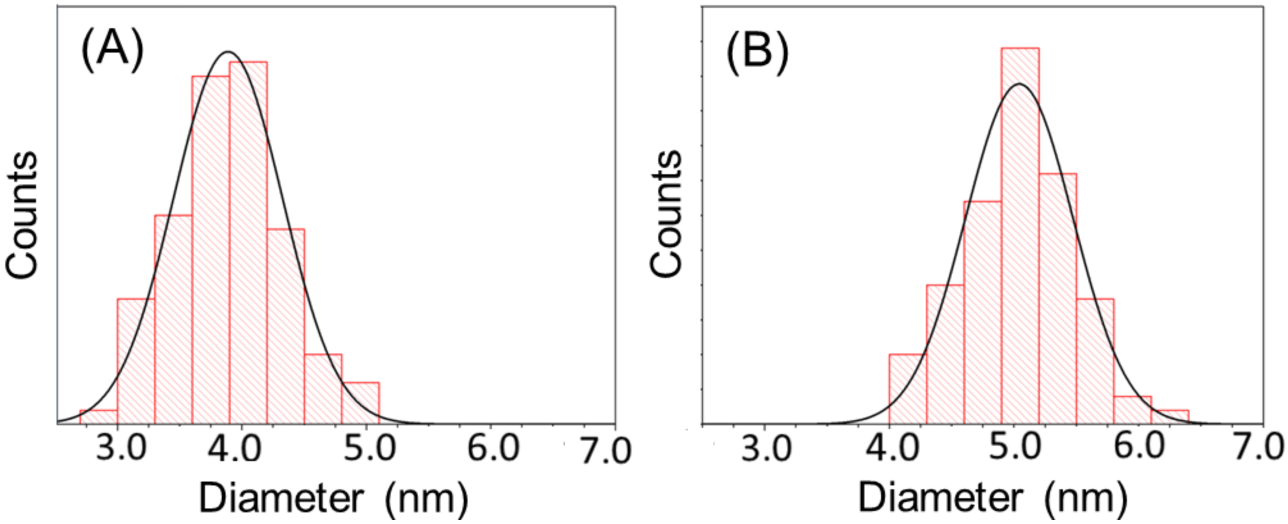

Fig. S4. Distribution of diameters of the Pt-tipped CdSe nanorods before (A) and after (B) coating of CdS shell through reaction at 285 °C for 6 minutes. The diameters were determined from more than 100 nanorods in the TEM images.

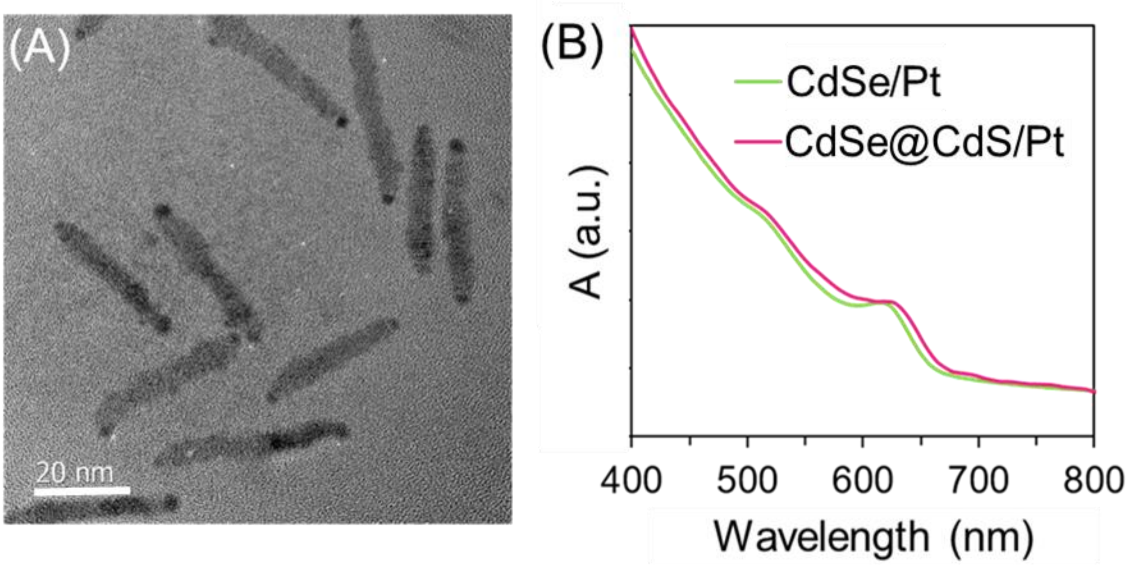

Fig. S5. (A) TEM image of the Pt-tipped CdSe nanorods after the growth of CdS shell at 270 °C for 6 minutes. (B) UV-vis absorption spectra of the Pt-tipped CdSe nanorods before and after the growth of CdS shell, showing a red shift of absorption edge by 6 nm.

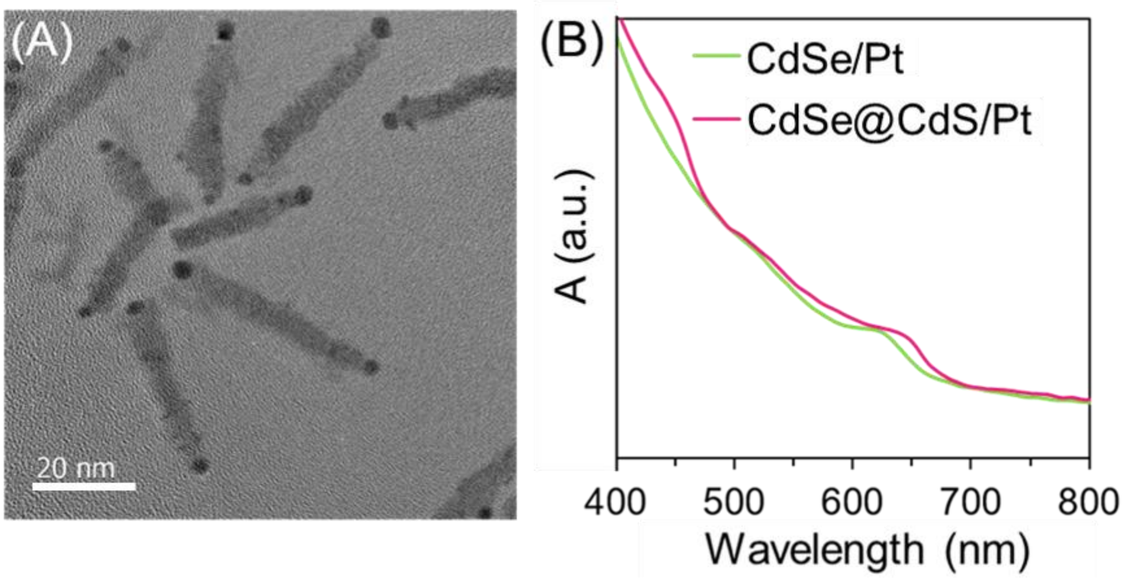

Fig. S6. (A) TEM image of the Pt-tipped CdSe nanorods after the growth of CdS shell at 300 ^{o}C for 6 minutes. (B) UV-vis absorption spectra of the Pt-tipped CdSe nanorods before and after the growth of CdS shell, showing a red shift of absorption edge by 26 nm.

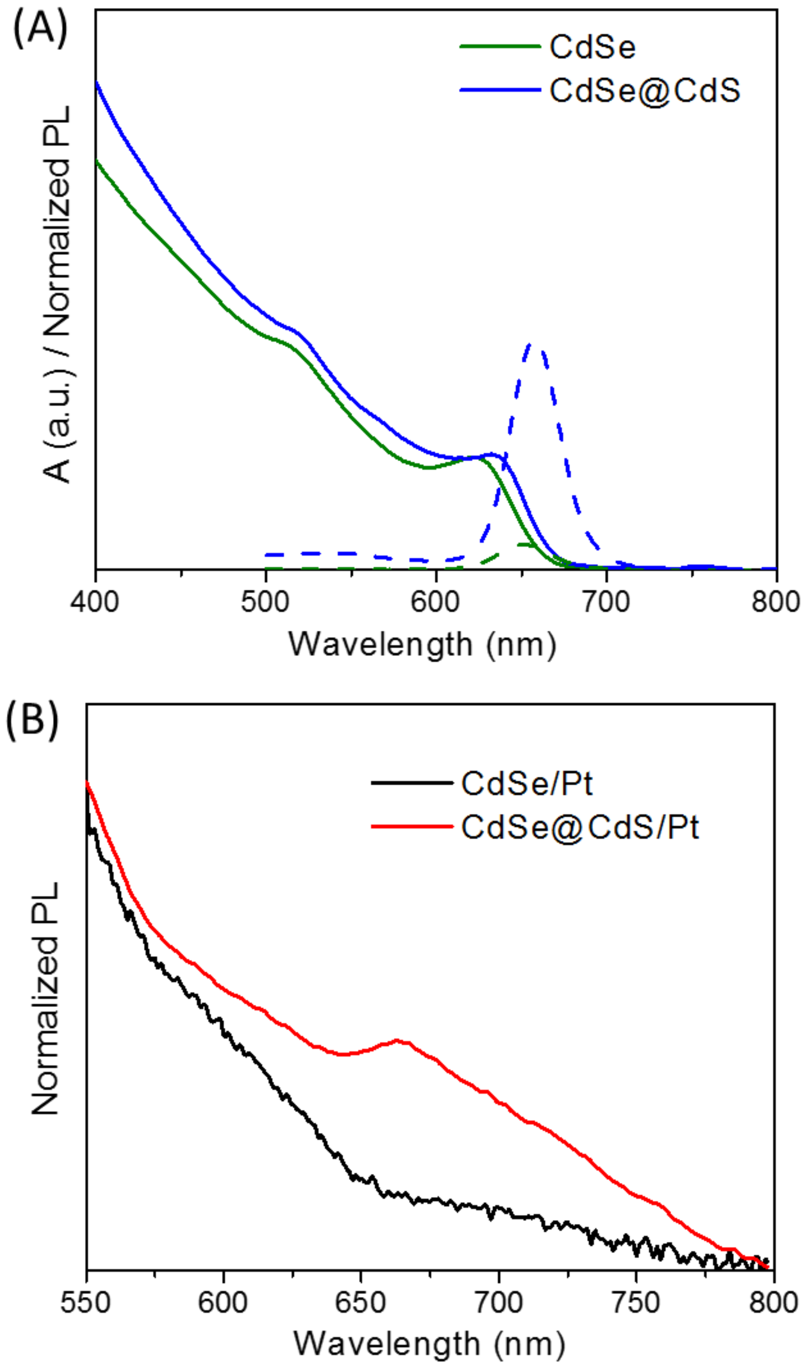

Fig. S7. (A) UV-Vis absorption and photoluminescence spectra of CdSe nanorods and the corresponding CdSe@CdS core-shell nanorods. (B) Photoluminescence spectra of Pt-tipped CdSe nanorods and Pt-tipped CdSe@CdS core-shell nanorods. Their corresponding absorption spectra are presented in Fig. S9. Both comparisons show an increase of photoluminescence when CdSe nanorods are coated with CdS shell, which can eliminate surface trap states.

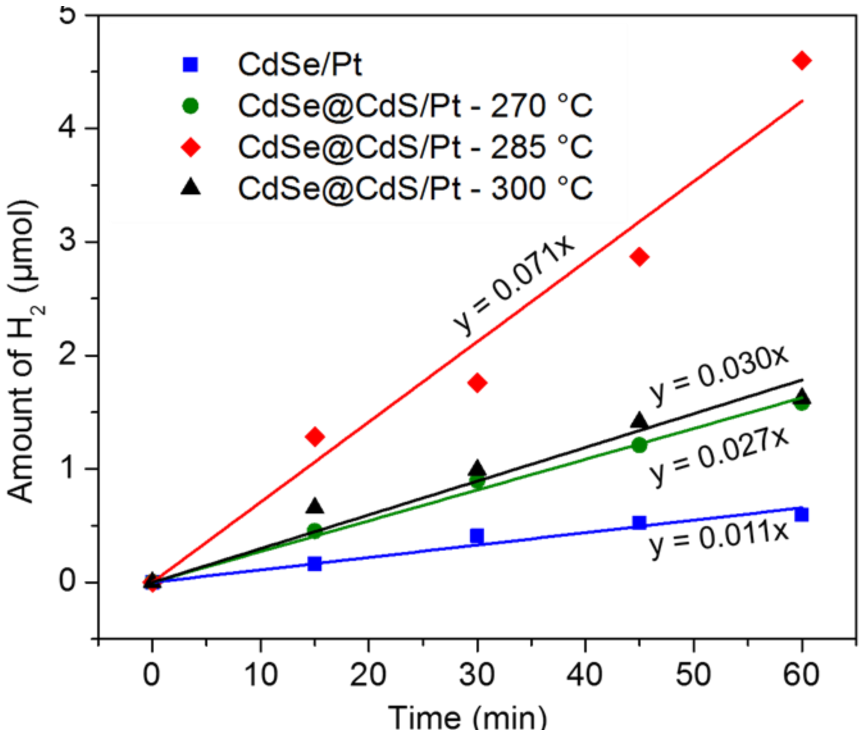

Fig. S8. Photocatalytic hydrogen evolution displayed by the photocatalysts Pt-tipped CdSe nanorods (CdSe/Pt, blue squares) and Pt-tipped CdSe nanorods coated with CdS shells grown at different temperatures: 270 ºC (green circles), 285 ºC (red diamonds), and 300 ºC (black triangles) for 6 minutes. Thickness of the CdS shell increases with temperature, i.e., 0.8 nm, 1.1 nm, and 1.5 nm for 270 ºC, 285 ºC, and 300 ºC, respectively.

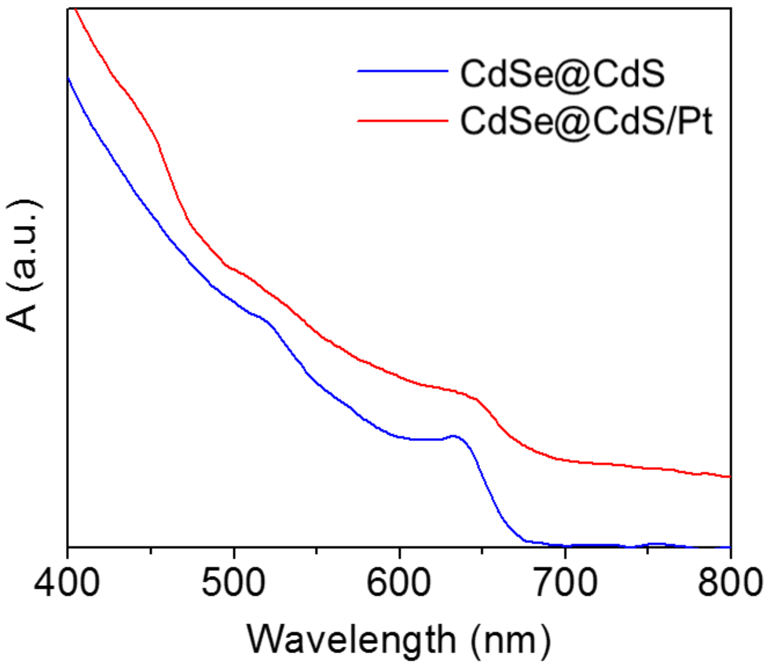

Fig. S9. UV-Vis absorption spectra of the CdSe@CdS core-shell nanorods with and without Pt tips, showing the higher absorption in the Pt-tipped nanorods. The higher absorbance of Pt-tipped CdSe@CdS than the CdSe@CdS nanorods is ascribed to the broadband absorption of Pt tips and the influence of Pt tips on electronic structure of the CdSe@CdS nanorods. The higher absorbance of the Pt-tipped CdSe@CdS nanorods is not due to a background variation.

Table S1. TRPL decay parameters (solvent: toluene)

Nanorods	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)
CdSe	3.57E+06	4.44	36.57	15.37	4.44
CdSe@CdS	5030.44	7.83	4.49	27.84	7.89
CdSe@CdS/Pt	1.98	0.048	0.19	0.54	0.31

Note:

Recombination rate constants (k_r) for CdSe nanorods with and without CdS shell: The exciton recombination rate constants of CdSe and CdSe@CdS nanorods are calculated from the average lifetime of photoluminescence dacay (τ_{avg}) of the respective nanorods using $k_r = 1 / \tau_{avg}$. The k_r calculated for CdSe nanorods and CdSe@CdS nanorods are 0.225×10^9 s^{-1} and 0.126×10^9 s^{-1}, respectively.

Percentage of charge carriers recovered from CdS passivation: The recovered percentage can be calculated by

Recovered charge carriers, % = $[(k_{r(CdSe)} - k_{r(CdSe@CdS)}) / k_{r(CdSe)}] \times 100$.

Using the above rate constants of both CdSe and CdSe@CdS nanorods, the percentage of charge carriers recovered from CdS passivation is 44 %.

Electron transfer rate from CdSe@CdS to Pt in CdSe@CdS/Pt nanorods: The electron transfer rates for CdSe@CdS/Pt structures can be calculated employing $K_{ET} = k_{r(CdSe@CdS/Pt)} - k_{r(CdSe@CdS)}$. The calculated electron transfer rate is 3.10×10^9 s^{-1}.