# Supplementary Information

## Double heterojunction nanowire photocatalysts for hydrogen generation

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### Materials

Cadmium oxide (CdO, 98%), selenium powder (100 mesh, 99.5%), tri-n-octylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 90%), sodium sulfide ($Na_2S$), sodium sulfite ($Na_2SO_3 \geq 98\%$), oleic acid (90%), and pyridine (99%) were purchased from Aldrich. Oleylamine (80-90%), diphenyl ether (99%), 1,2 dichlorobenzene (99%), anhydrous bismuth (III) chloride ($BiCl_3$, 98%), and platinum (II) acetylacetonate (98%) were purchased from Acros. Dimethylcadmium ($CdMe_2$, 99.998%), and sulfur powder (99%) were purchased from Strem Chemicals. Squalane (99%) was purchased from Fluka. Stearic acid (98%) was purchased from Alfa Aesar. Methanol, acetone, and toluene were purchased from Fisher Scientific and VWR. Unless otherwise noted, all chemicals were used as received. 1 M TOPSe was prepared under nitrogen in a glovebox by mixing Se powder (0.39 g, 5 mmol) with TOP (5 mL, 11.2 mmol). The solution was then left to stir overnight to complete the reaction. Bi catalyst was freshly prepared prior to each NW synthesis by adding 12.6 mg (0.04 mmol) of $BiCl_3$ to 20 mL of acetone.

### *CdSe NW synthesis*

CdSe NWs were synthesized through Solution-Liquid–Solid (SLS) growth, using a procedure adopted from Puthussery et al.[1] A 3-neck flask containing TOPO (2.5 g, 6.47 mmol), stearic acid (0.17 g, 0.598 mmol) and CdO (25 mg, 0.19 mmol) and connected to a Schlenk line was heated and degased at 110 °C for 1 hour. The reaction mixture was then backfilled with $N_2$ and was heated to 350 °C until the solution turned clear. The temperature was then lowered to 250 °C whereupon an injection solution consisting of 1 M TOPSe (50 μL, $5 \times 10^{-2}$ mmol) and 2 mM $BiCl_3$ in acetone (100 μL, $2 \times 10^{-4}$ mmol) was introduced. The reaction was left at this temperature for two minutes whereupon the initially clear solution became dark brown, indicating NW growth. The mixture was then cooled to 70-60 °C and was diluted with 5 mL of toluene to prevent TOPO from solidifying. CdSe NWs were precipitated from the resulting suspension by adding 3 mL of methanol followed by centrifugation. The supernatant was discarded and the recovered wires were dispersed in 5 mL of pyridine to remove any excess stearic acid. The NWs were subsequently washed three times in toluene and were ultimately stored in toluene.

*CdS NW synthesis*

CdS NWs were synthesized using a slightly modified procedure from Puthussery et al.[1] A 3-neck flask containing TOPO (1.0 g, 2.59 mmol), octadecene (3mL, 9.38 mmol), oleic acid (0.40 mL, 1.26 mmol) and CdO (64.2 mg, 0.49 mmol) and connected to a Schlenk line was dried and degased at 110 °C for 30 minutes. The reaction mixture was then backfilled with $N_2$ and was heated to 315 °C until it became clear. After this, an injection solution consisting of 1 M TOPS (80 μL, $8 \times 10^{-2}$ mmol) and 2 mM $BiCl_3$ in acetone (50 μL, $1 \times 10^{-4}$ mmol) was introduced. Upon injection, the color of reaction mixture immediately became bright yellow and then proceeded to orange. The reaction was left at this temperature for 2 minutes. It was then cooled to 70-60 °C and was diluted with 5 mL of toluene to prevent TOPO from solidifying. The obtained CdS NWs were precipitated by adding 3 mL of methanol followed by centrifugation.

Recovered wires were washed with toluene three times and were stored as a suspension in toluene.

*CdSe/CdS core/shell NW synthesis*

The surfaces of CdSe NWs used to prepare core/shell wires were first “stripped” using pyridine.[2] Briefly, CdSe NWs in toluene were precipitated by centrifuging the suspension. The supernatant was discarded and the recovered NWs were redispersed in pyridine. The resulting suspension was then heated at 60 °C for 15 minutes while being gently stirred. Once complete, the NWs were precipitated by adding hexane followed by centrifugation. Recovered wires were then resuspended in fresh pyridine. This heating/precipitation sequence was repeated two additional times. Resulting NWs were stored in toluene as a stock solution for subsequent CdS overcoating (described below).

CdSe/CdS core/shell NWs were synthesized using a procedure adopted from a previous study.[3] A 3-neck flask containing pyridine-stripped CdSe NWs in toluene (1 mL, $1.66 \times 10^{-13}$ mol), sulfur powder (0.05 g, 1.56 mmol) and TOPO (3 g, 7.8 mmol) was dried and degassed on a Schlenk line for 40 minutes at 100 °C. Once complete, the vessel was backfilled with $N_2$ and the temperature was raised to 120 °C. At this temperature, an injection solution consisting of $CdMe_2$ (8.0 μL, 0.11 mmol) and squalane (5 mL, 9.58 mmol) was introduced into the three-neck flask at a controlled rate of 10 mL/h using a syringe pump. On introduction, the color of the reaction mixture changed from dark brown to orange-brown. Following addition, the mixture was cooled to 70 °C and the coated NWs were extracted by centrifuging the suspension with an excess of toluene. Recovered wires were cleaned by centrifuging them out of fresh toluene suspensions three additional times. All final precipitates were resuspended and stored in toluene.

*Transmission electron microscopy*

Transmission Electron Microscopy (TEM) was used to characterize all synthesized materials. Low and high magnification TEM micrographs were taken with a Titan 80-300 (FEI) and a JEOL JEM2011 TEM operating at 300 kV and 200 kV, respectively. Ensemble absorption spectra of NW samples were acquired with a Cary 50 Bio spectrometer.

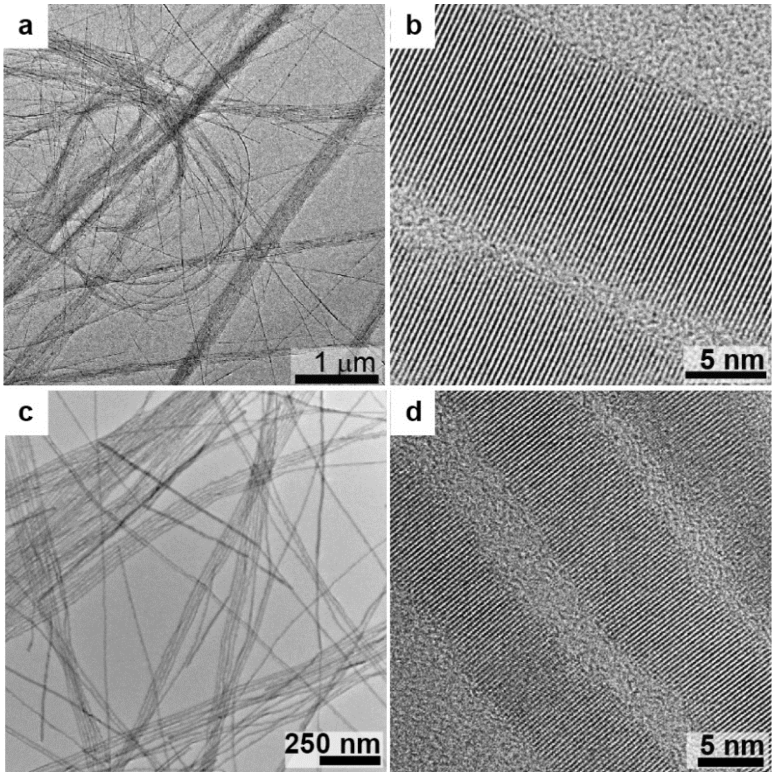

**Fig. S1** Low and high magnification of TEM images of (a-b) CdSe and (c-d) CdS NWs.

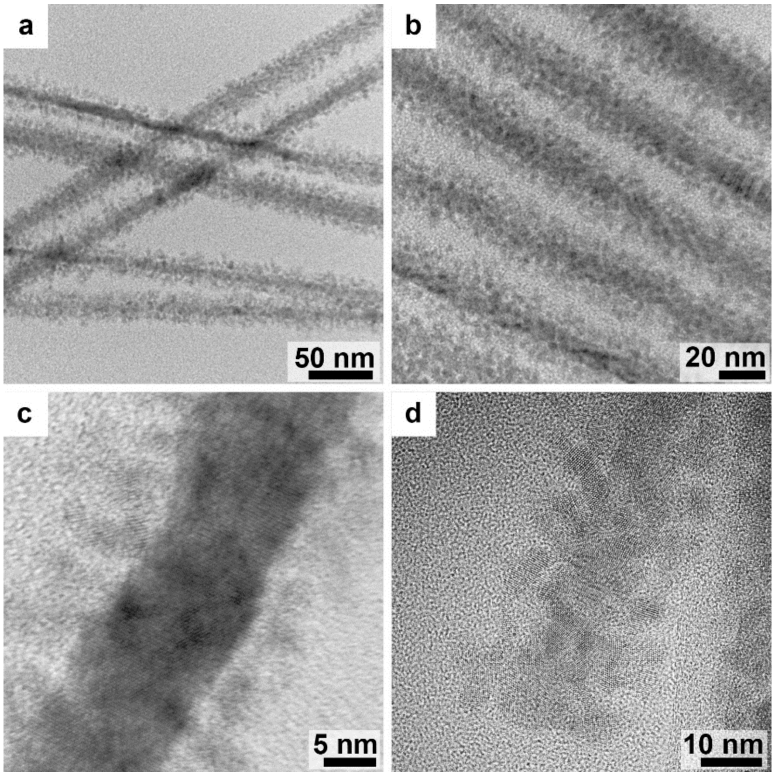

**Fig. S2** (a-b) Low and (c-d) high magnification TEM images of CdSe /CdS core/shell NWs.

*Estimate of NW concentrations for Pt NP decoration*

NW concentrations were estimated using the following expression for single nanowire absorption cross sections:[4,5]

$$\sigma(cm)^2 = \left(\frac{\omega}{n_m c}\right)(\pi a^2 l)(1 + \left|\frac{2\varepsilon_m}{\varepsilon_m + \varepsilon_s}\right|^2)(n_s k_s) \tag{S1}$$

where $\omega$ is the incident light angular frequency (rad/s), $n_m$ is the refractive index of the surrounding medium, $c$ is the speed of light, $a$ is the NW radius, $l$ is its length, and $n_s$ ($k_s$) is the real (imaginary) part of the NW refractive index, $\varepsilon_m$ and $\varepsilon_s$ are the complex dielectric constants of the surrounding medium and semiconductor, respectively.

Obtained absorption cross sections were then used to find the associated molar extinction coefficient ($\varepsilon$) through

$$\sigma(cm^2) = \frac{2.303(1000)\varepsilon}{N_A} \tag{S2}$$

whereupon Beer's Law was used to determine the sample's molar concentration.

### *Example: CdSe NWs*

CdSe NW concentrations were estimated using a mean NW diameter of 14 nm and a 10 μm length. The following parameters were used in Equation S1:

$\varepsilon_s = 7.96 + i1.52$ (at 1.91 eV)

$n_s = 2.83$ (at 1.91 eV)

$k_s = 0.27$ (at 1.91 eV)

$\varepsilon_m = 2.2$ (toluene)

$n_m = 1.5$ (toluene)

$\omega = 2.90 \times 10^{15} rad\ s^{-1}$ (at 650 nm)

$a = 7\ nm$

$l = 10\ \mu m$

The estimated absorption cross section at 650 nm is therefore $\sigma_{650\ \mathrm{nm}} = 8.97 \times 10^{-11}$ cm$^2$. The corresponding molar extinction coefficient is $\varepsilon_{650\ \mathrm{nm}} = 2.34 \times 10^{10}$ M$^{-1}$ cm$^{-1}$. Given an absorption of 0.07, at 650 nm from 80 μL stock diluted with 2.5 mL toluene, the corresponding CdSe NW stock solution concentration is $9.62 \times 10^{-11}$ M.

### *Example: CdS NWs*

CdS NW concentrations were estimated using a mean NW diameter of 12 nm and a 10 μm length. The following parameters were used in Equation S1.

$\varepsilon_s = 7.77 + i2.02$ (at 2.58 eV)

$n_s = 2.81$ (at 2.58 eV)

$k_s = 0.36$ (at 2.58 eV)

$\varepsilon_m = 2.2$ (toluene)

$n_m = 1.5$ (toluene)

$\omega = 3.93 \times 10^{15} rad\ s^{-1}$ (at 480 nm)

$a = 6\ nm$

$l = 10\ \mu m$

The estimated absorption cross section at 480 nm is therefore $\sigma_{480\ nm} = 1.19 \times 10^{-10}\ cm^2$. The corresponding molar extinction coefficient is $\varepsilon_{480\ nm} = 3.10 \times 10^{10} M^{-1} cm^{-1}$. Given an absorbance at 480 nm of 0.4 from 100 µL stock diluted in 2.5 mL toluene, the estimated CdS NW stock concentration is $3.35 \times 10^{-10}$ M.

*Decorating NWs with Pt NPs*

CdS, CdSe and CdSe/CdS core/shell NWs were decorated with Pt NPs using a thermal deposition approach adapted from Weller et al.[6] Briefly, a mixture of diphenyl ether (10 mL, 63 mmol), oleylamine (0.2 mL, $6.08 \times 10^{-4}$ mol) and oleic acid (0.2 mL, $6.33 \times 10^{-4}$ mol) was degassed at 100 °C for 30 minutes. The reaction vessel was then backfilled with $N_2$, whereupon the temperature was raised to 200 °C. Following this, a NW solution (~$1.44 \times 10^{-10}$ M in dichlorobenzene) exposed overnight to $Pt(acac)_2$ (10 mg, 0.025 mmol) was injected into the reaction mixture. After several seconds, a black precipitate appeared, indicating Pt NP growth. The resulting Pt NP size was controlled by varying the time the solution was kept at 200 °C. A typical reaction time of 7 minutes produced Pt NPs in the 3-5 nm diameter range.

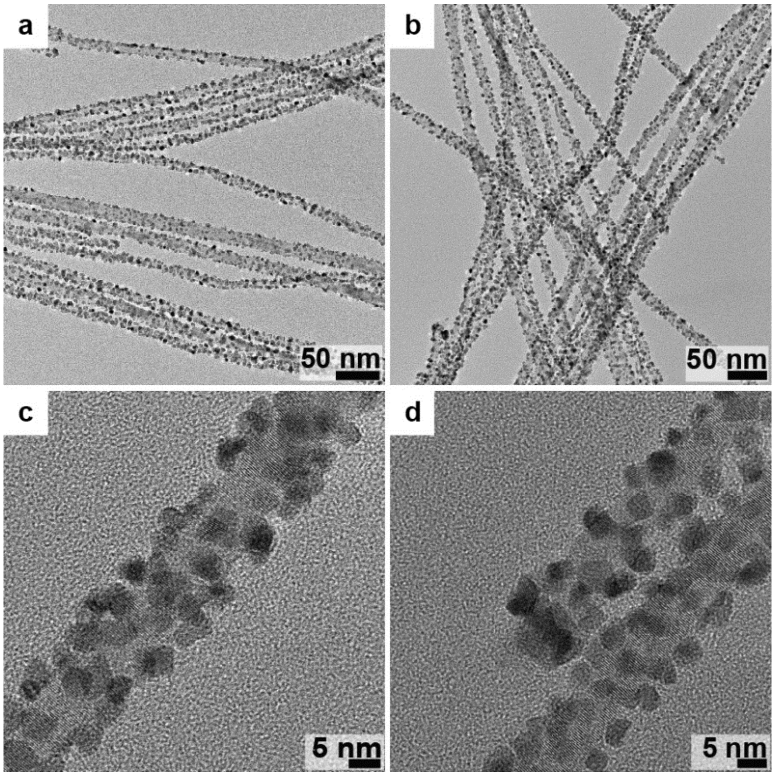

**Fig. S3** (a-b) Low and (c-d) high magnification TEM images of CdSe/Pt NP NWs

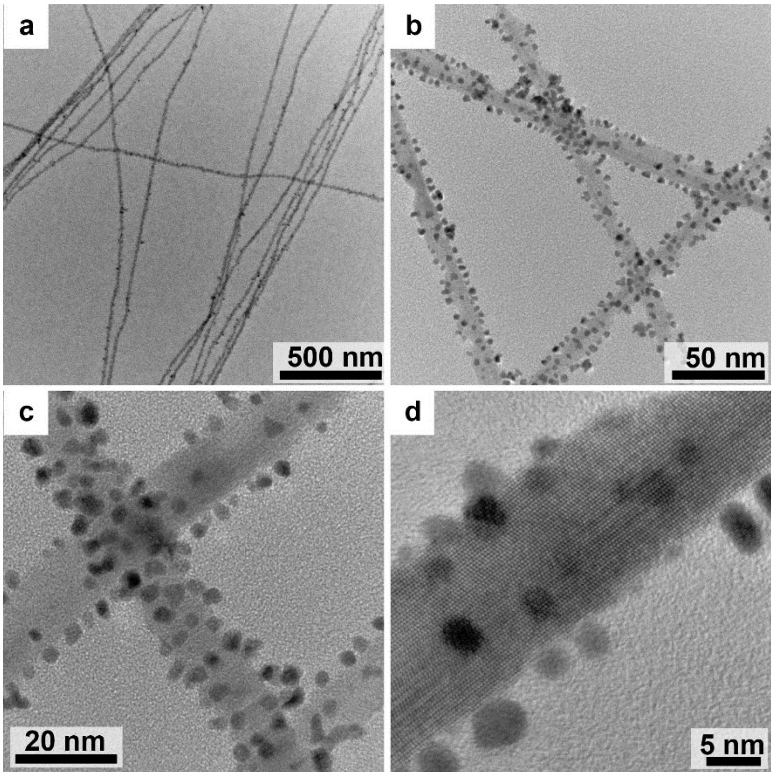

**Fig. S4** (a-b) Low and (c-d) high magnification TEM images of CdS/Pt NP NWs.

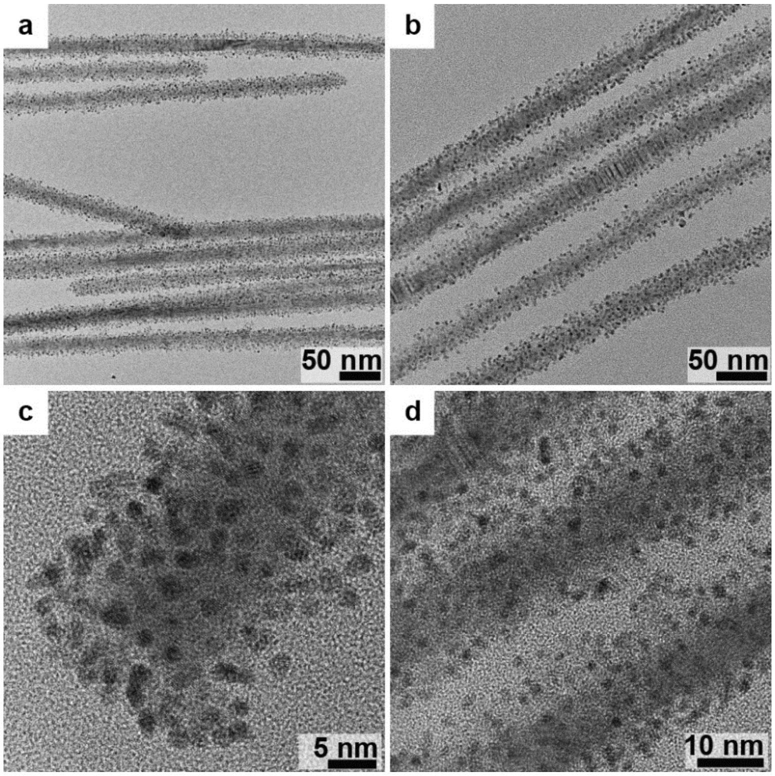

**Fig. S5** (a-b) Low and (c-d) high magnification TEM images of CdSe/CdS/Pt NP NWs.

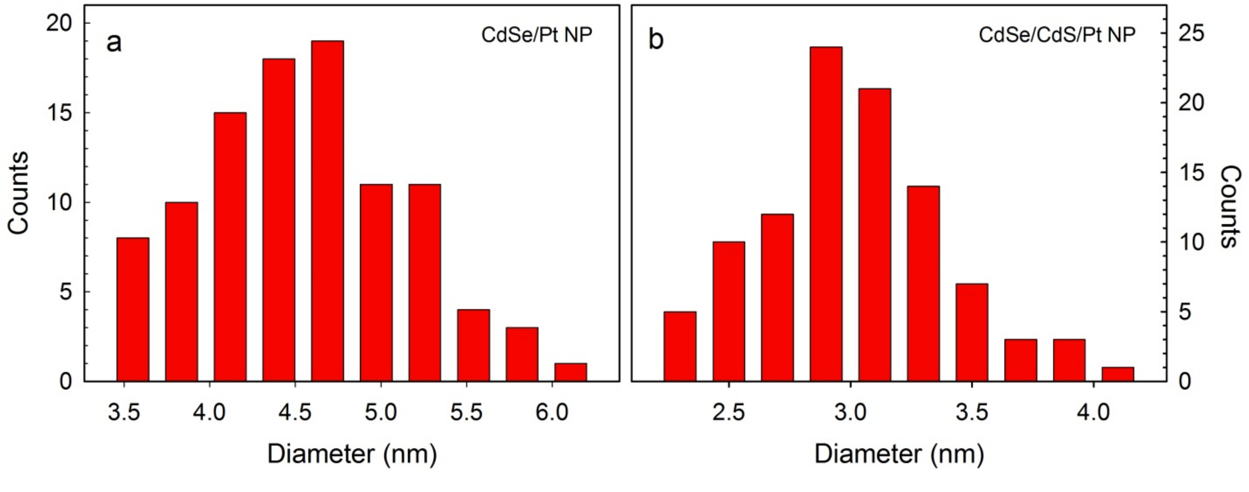

**Fig. S6** Size distribution of Pt NP diameters (nm) for (a) CdSe/Pt NP and (b) CdSe/CdS/Pt NP NWs.

Pt loading was determined based on EDS spectra recorded in the JEOL 7500-F FE-SEM at low resolution (magnification × 500). Such low magnification allows to obtain an average elemental composition of the sample.

Atomic ratio in CdSe/CdS/Pt:

| **Atomic %** | | | |
|---|---|---|---|
| Cd | S | Se | Pt |
| 40.7 | 36.1 | 8.9 | 14.3 |

Atomic ratio in CdSe/Pt:

| **Atomic %** | | |
|---|---|---|
| Cd | Se | Pt |
| 38.9 | 35.3 | 25.8 |

Atomic ratio in CdS/Pt:

| **Atomic %** | | |
|---|---|---|
| Cd | S | Pt |
| 39.7 | 38.0 | 22.3 |

Catalytic activity of nanosized metal catalyst usually correlates with the surface area of the metal (amount of exposed metal atoms and types of catalytic sites). Since CdSe/Pt and CdSe/CdS/Pt had different size distribution of Pt nanoparticles (**Fig. S6**) we adjusted Pt loading so that the surface area of Pt co-catalyst exposed to the reacting mixture is approximately same for these two samples. Thus in CdSe/Pt sample mean diameter of Pt NP was d=4.56±0.59 nm and Pt loading was 25.8 at % (41.28 wt %), that corresponded to ~912 cm$^2$ of total Pt surface area; in CdSe/CdS/Pt sample Pt diameter was d=3.00±0.39 nm, Pt loading – 14.3 at % (30.24

wt%) and total Pt surface area was calculated to be ~846 cm$^2$. We assumed that ratio of exposed Pt atoms to the Pt atoms at metal/semiconductor interface was same for all samples. By our estimation the amount of exposed Pt atoms in the two samples that we compared varied within ±8%. This accuracy is acceptable considering complexity of the multistep synthesis of heterojunction nanowires.

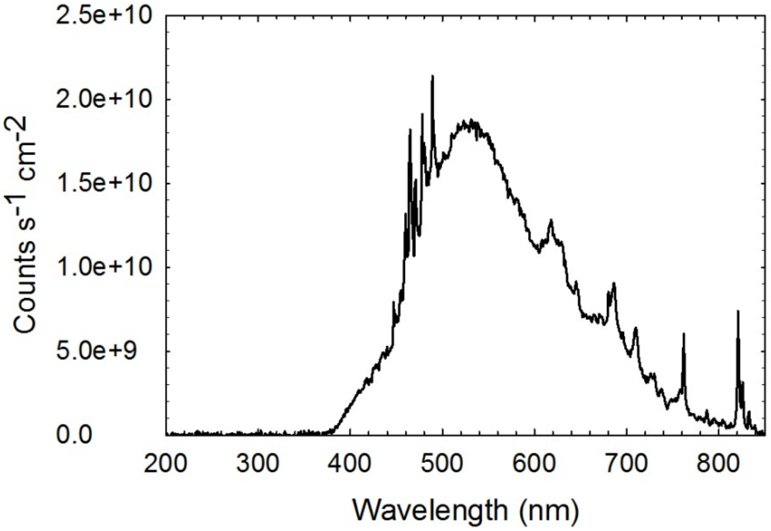

**Fig. S7** Raw spectral profile of the Xe arc lamp used for photocatalytic $H_2$ generation experiments. Spectrum acquired after a $CuSO_4$ filter.

*Photocatalytic $H_2$ generation measurements*

For photocatalytic $H_2$ generation measurements, CdS, CdS/Pt NP, CdSe, CdSe/Pt NP, CdSe/CdS and CdSe/CdS/Pt NP NW suspensions in toluene were washed 3-4 times using ethanol. The wires were then resuspended in 4 mL of an aqueous solution containing both 0.1 M $Na_2S$ and 0.1 M $Na_2SO_3$ (1:1 ratio). The solution was then placed in a quartz cell whereupon it was degassed using several freeze pump thaw cycles. Afterwards, the solution was irradiated with a 450 Watt Xe arc lamp for 15 hours. A 0.01 M $CuSO_4$ filter was used to eliminate wavelengths in the ultraviolet and infrared. The spectral profile of the Xe arc lamp used in the study is shown in **Fig. S7**. Photocatalytic $H_2$ generation experiments were also carried out using 200 mW of 520 nm excitation. This wavelength selectively excited CdSe. Evolved gases were analyzed using a Shimadzu GC-17A gas chromatograph.

*Estimated photon absorption rate*

A broadband photon absorption rate was estimated using the lamp spectral profile shown in **Fig. S7**. The photon flux at all wavelengths was obtained from the data point at 450 nm, which was independently calibrated to a flux of $6.174 \times 10^{16}$ photons/s using actinometry [Reinecke's salt ($KCr(NH_3)_2(NCS)_4$ as a chemical actinometry][7]. NW cross sections in toluene were simultaneously calculated across all lamp wavelengths (1 nm increments) using Equation S1. The total number of photons absorbed by the NW was then estimated by summing the product of the cross section at a given wavelength with the associated lamp photon flux at that wavelength. In this manner, we obtained a broadband photon flux of $5.48 \times 10^{8}$ $\text{cm}^2\ \mu\text{m}^{-1}\ \text{s}^{-1}$.

In the case of 520 nm LED excitation with $P_{520}$=200 mW measured with a power meter (Thorlabs PM100) incident on the cuvette, the corresponding photon flux is $5.25 \times 10^{17}$ $\text{s}^{-1}$ [$\phi_{520} = P_{520}/(h\nu_{520})$]. The product of flux with the absorption cross section at 520 nm ($\sigma_{520\ \text{nm}}=1.85 \times 10^{-11}$ $\text{cm}^2\ \mu\text{m}^{-1}$, employed parameters: $n_s = 2.719$, $k_s = 0.455$, $n_m = 1.5$, $\varepsilon_m = 2.2$, $\varepsilon_s = 7.16 + 2.64i$, $\omega = 3.63 \times 10^{15}$ rad $\text{s}^{-1}$) gives a net photon absorption rate of $9.71 \times 10^{6}$ $\text{cm}^2\ \mu\text{m}^{-1}\ \text{s}^{-1}$.

*Transient differential absorption measurements*

NW samples for transient differential absorption (TDA) measurements were suspended in toluene and were placed in a two millimeter pathlength cuvette. Optical densities (OD) were ~0.3 at either of two excitation wavelengths ($\lambda_{\text{exc}}$ = 387 nm and $\lambda_{\text{exc}}$ = 560 nm).

Ultrafast TDA experiments were performed with a Clark MXR CPA 2010 laser system employing a fiber-based spectrometer. TDA experiments were conducted by exciting CdS, CdSe, CdSe/CdS core/shell NWs and their Pt NP decorated counterparts at 387 nm (3.20 eV) and 560 nm (2.21 eV) with ~150 fs pulses (pump fluence 20 μJ/cm$^2$). $\lambda_{exc}$ = 387 nm excitation was generated using the second harmonic of the fundamental while $\lambda_{exc}$ = 560 nm was obtained using an Optical Parametric Amplifier (OPA, TOPAS). Transient absorption spectra were subsequently acquired with a delayed, low-intensity white light continuum with wavelengths between 425 and 750 nm (2.92-1.65 eV). White light was generated by passing a fraction of the fundamental through a sapphire crystal. Bleach kinetics at 450 nm (2.76 eV), 495 nm (2.51 eV) and 683 nm (1.82 eV) were monitored, corresponding to the band edges of the CdS shell in core/shell wires, CdS NWs, and CdSe NWs.

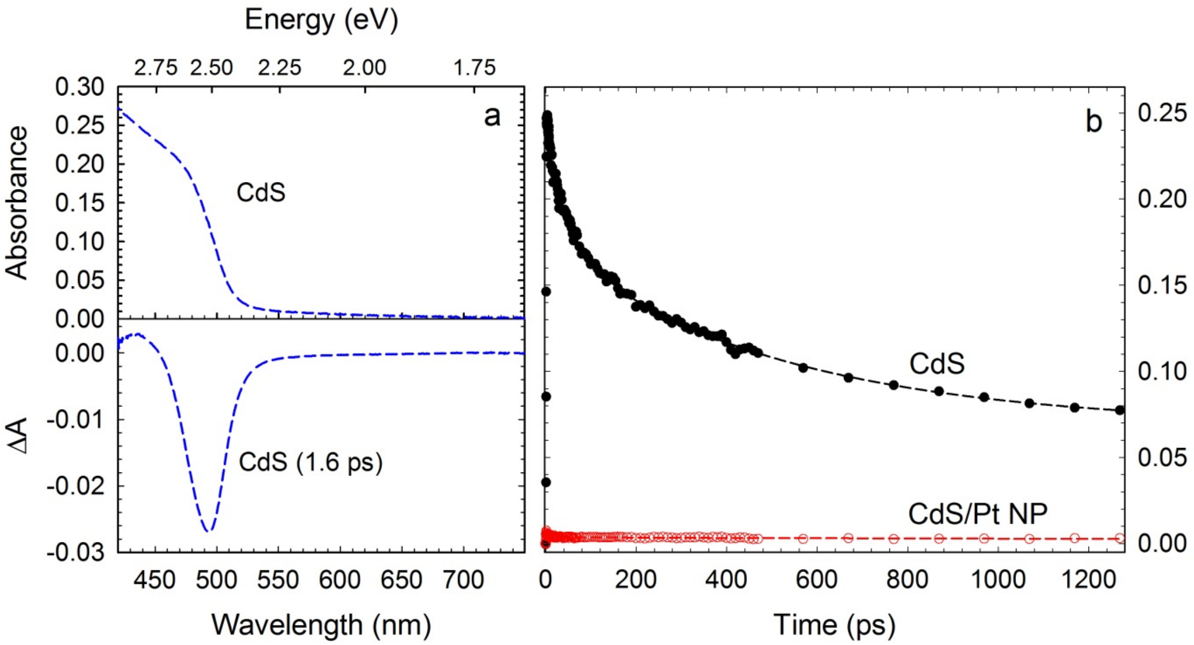

**Fig. S8** (a) Linear absorption (top) and corresponding TDA spectrum (bottom) of CdS NWs. (b) Comparison of CdS and CdS/Pt NP NW band edge bleach kinetics when excited at $\lambda_{exc}$ = 387 nm.

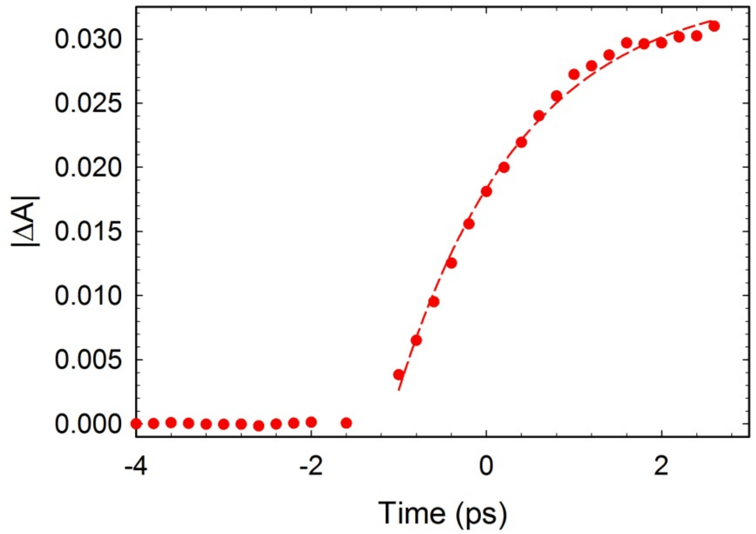

**Fig. S9** Growth of the CdSe NW band edge bleach following excitation at $\lambda_{exc}$ = 387 nm.

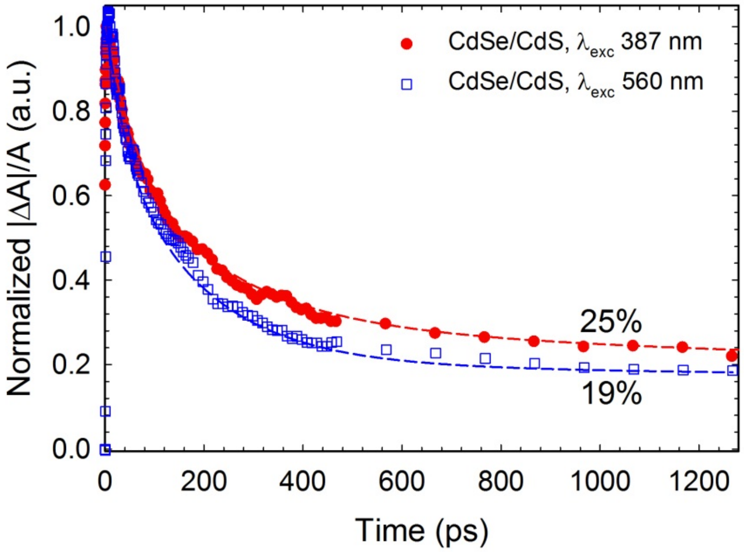

**Fig. S10** Comparison of CdSe band edge bleach kinetics in CdSe/CdS core/shell NWs when excited at $\lambda_{exc}$ = 387 nm and $\lambda_{exc}$ = 560 nm**.**

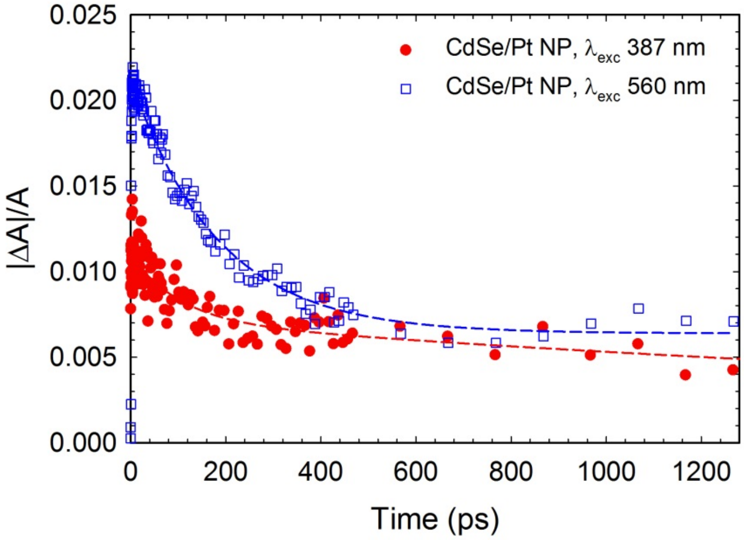

**Fig. S11** Comparison of CdSe band edge bleach kinetics in CdSe/Pt NP NWs when excited at $\lambda_{exc}$ = 387 nm and $\lambda_{exc}$ = 560 nm**.**

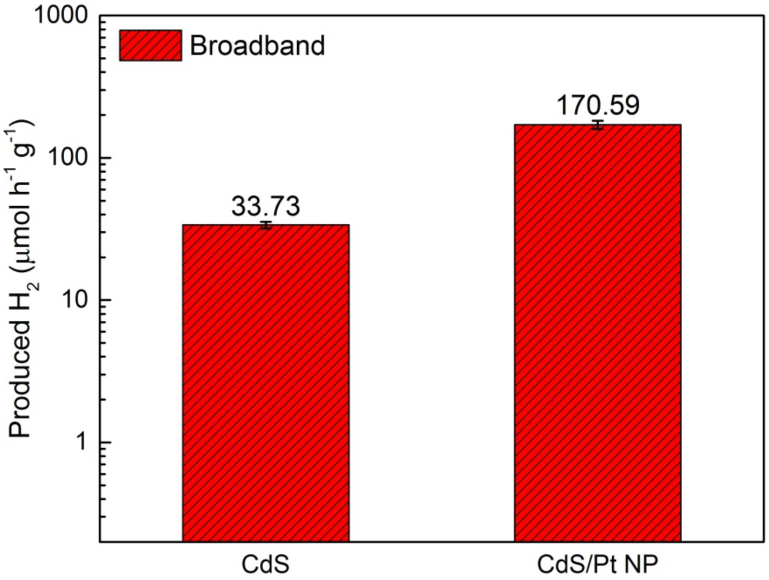

**Fig. S12** Broadband photocatalytic $H_2$ generation rates of CdS NWs and their Pt NP decorated counterparts in aqueous solutions of sodium sulfide and sodium sulfite.

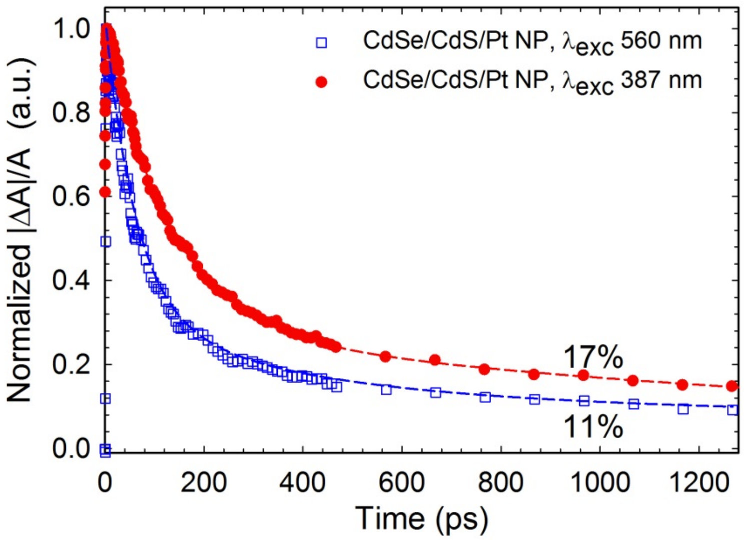

**Fig. S13** Comparison of CdSe band edge bleach kinetics in CdSe/CdS/Pt NP NWs when excited at $\lambda_{exc}$ = 387 nm and $\lambda_{exc}$ = 560 nm**.**

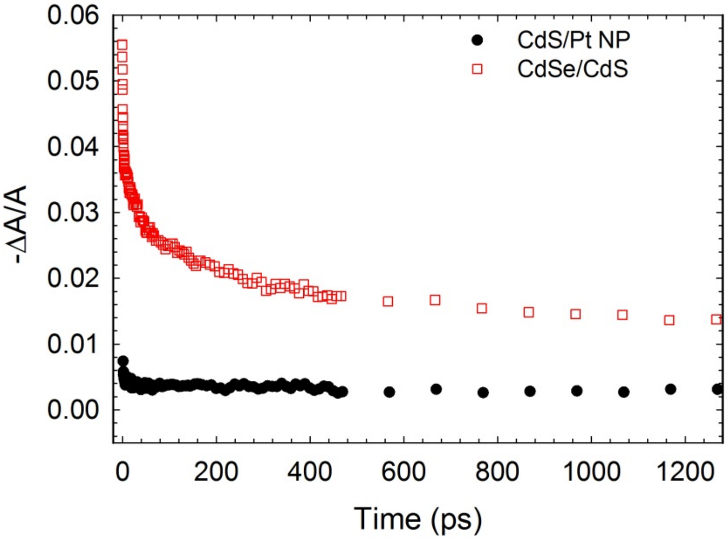

**Fig. S14** Comparison of CdS band edge bleach kinetics in CdS/Pt NP and CdSe/CdS core/shell NWs when excited at $\lambda_{exc}$ = 387 nm**.**

## References

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