

# Aqueous Phase Reactions on Hollow Silica Encapsulated Semiconductor Nanoheterostructures

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## **Experimental Details**

### **1. Chemicals**

Cadmium oxide (CdO, 99.5%), dodecylamine (DDA, 98%), potassium gold(III) chloride (KAuCl<sub>4</sub>, 99.9%), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O), palladium(II) nitrate dehydrate (Pd(NO<sub>3</sub>)<sub>2</sub>•2H<sub>2</sub>O), silver nitrate (AgNO<sub>3</sub>), 1-octadecene (ODE, 90%), sulfur (S, reagent grade), selenium powder (Se, 99.99%), myristic acid, oleic acid (OA, 90%), oleylamine (technical grade, 70%), 11-mercaptoundecanoic acid (MUA), tetraethyl orthosilicate (TEOS), ammonium hydroxide solution (NH<sub>4</sub>OH) and Igepal CO-520 were purchased from Sigma Aldrich. Trioctylphosphine (TOP, 90%) was purchased from Alfa Aesar. Trioctylphosphine oxide (TOPO, 99%), n-Octadecylphosphonic acid (ODPA, 97%) and n-hexylphosphonic acid (HPA, 97%) were purchased from Strem. Hydrofluoric acid solution (HF, 49% wt) was purchased from Honeywell. All the chemicals were used as received without further purification. Unless stated otherwise, all the reactions were conducted in oven-dried glassware under nitrogen atmosphere using standard Schlenk techniques.

### **2. Synthesis of spherical Zinc Blende CdSe seeds**

Nearly monodispersed zb-CdSe nanocrystals (NCs) were synthesized via a previously reported method [1]. In a 50 mL three-neck round bottom flask 0.3 mmol CdO, 0.6 mmol myristic acid and 5 mL of ODE were degassed at 90 °C for about 1hr. The solution was then heated to 250 °C for ~10-15 min to yield a clear solution, followed by the addition of 12 mL of ODE before cooling to 90 °C to degas for another 1 hr. Upon cooling to room temperature, 0.012 g (0.15 mmol) of 100 mesh Se powder (99.999%) was added to the reaction mixture and degassed at 50 °C for ~20 minutes. Upon heating under N<sub>2</sub>, a colour change from colourless to yellow at ~150 °C and then to orange-red colour upon reaching 240 °C were observed, signifying the formation of zb-CdSe. A degassed mixture of 0.5 mL oleic acid and 0.5 mL oleylamine in 2 mL of 1-ODE was subsequently added dropwise to the reaction mixture. As a guideline, the growth time for a ~ 4 nm diameter NC was approximately 2 hr.

As-synthesized zb-CdSe NCs were precipitated out from the growth solution by adding acetone, and were subsequently allowed to undergo two more cycles of re-dispersion and precipitation in toluene and methanol respectively.

### **3. Preparation of stock solution of CdSe seeds**

Processed zb-CdSe NCs were dispersed in a minimum amount of toluene and their concentration was determined by measuring their absorbance at 350 nm, whose molar absorptivity is known.[2] The toluene was then removed under vacuum and TOP was added to make up a zb-CdSe NC concentration of 100  $\mu$ M. This mixture will subsequently be referred to as the zb-CdSe stock solution.

### **4. Synthesis of CdSe seeded CdS tetrapod heterostructures:**

Tetrapod-like CdSe seeded CdS heterostructures were synthesized, with slight modifications, via the seeded growth approach [3]. Briefly, 2.65g TOPO (99%), 0.05175 g CdO, and a mixture of ligands (HPA 67mg and OA 0.5mL) were degassed at 150 °C for about 1.5 h in a 50 mL three-neck round bottom flask. The reaction mixture was then heated to 350°C under N<sub>2</sub>, whereupon the solution turned from reddish brown to colourless. Separately, a mixture of S, TOP and CdSe seeds was derived by first dissolving 0.0065g of S in 0.6 mL of TOP at 50°C before adding 25  $\mu$ L of CdSe stock solution. Upon reaching the desired injection temperature 350 °C, 0.9 mL TOP was added and the temperature was allowed to recover to 350 °C before the mixture of S, TOP and CdSe was swiftly injected. The temperature was again allowed to recover to 350 °C for the growth of CdS arms at this temperature for 10 minutes. The heating mantle was then removed and the solution was allowed to cool to 80 °C. As-synthesized CdSe seeded CdS heterostructures were then processed by repeated cycles of precipitation in methanol and re-dispersion in cyclohexane. See Figure S1A.

### **5. Silica encapsulation of CdSe seeded CdS tetrapod with hollow interior heterostructures**

#### **Synthesis of silica-coated CdSe/CdS tetrapods**

The synthesis procedures for the coating of semiconductor nanoparticles with SiO<sub>2</sub> were adapted from a previous report with several modifications [4]. Briefly, 0.2mL Igepal CO-520 was added to 1.5mL of cyclohexane, followed by the sequential addition of 5  $\mu$ M of CdSe/CdS tetrapods (in 8  $\mu$ L cyclohexane), 30  $\mu$ L of aqueous ammonia (30%), 30  $\mu$ L of DI water and 5 $\mu$ L of TEOS. Between each addition step, the reaction mixture was allowed to stir for ~20 min. The final mixture was then stirred continuously for 24 hr. The resulting nanoparticles were recovered by the addition of ethanol followed by centrifugation at 13000 rpm for 10 min. The recovered silica coated CdSe/CdS tetrapods (Figure S1B) were repeatedly rinsed with ethanol and finally dispersed in water.

#### **Partial etching of silica shell to form a hollow interior**

Processed silica coated CdSe/CdS tetrapods were dispersed in 1mL DI water, followed by the addition of 0.1 mL diluted HF solution (0.5% wt). The mixture was stirred at 60 °C for ~30 min, and the particles were isolated by

centrifugation at 13000 rpm for 10 min. The final product (Figure 1(C) main text) was then redispersed in water.

\*It should be noted that dilute HF solution should be handled with extreme care, beyond that accorded to other acids. Due to the ability of HF to penetrate tissue, poisoning can occur when exposed of skin or eyes, and inhaled or swallowed.

## **6. Ligand exchange of CdSe/CdS tetrapod to facilitate transfer from organic to aqueous phase.**

The procedure for the transfer of CdSe/CdS tetrapods from the organic to aqueous phase via the use of MUA was adapted from a previous report with several modifications [5]. Briefly, 400 pmol of CdSe/CdS tetrapods were dissolved in 2 mL chloroform followed by the sequential addition of 50 mg of MUA. The whole solution was stirred until MUA was totally dissolved. 1 mL of 0.1M NaOH solution was then added to the tetrapod-MUA mixture, followed by vigorous stirring until a light yellow emulsion was formed. Separation of the aqueous and organic phase was subsequently achieved by centrifuging, and excess MUA was removed by repeated cycles of precipitation in methanol and re-dispersion in DI water.

## **7. Synthesis of Pt decorated silica coated CdSe/CdS tetrapod and control experiments**

For the preparation of the Pt stock solution, 13 mg of  $\text{H}_2\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$  was dissolved in 5 mL of water, yielding a light yellow solution. Silica encapsulated CdSe/CdS tetrapods with a hollow interior were first dispersed in 1mL water, followed by the addition of 0.2 - 1mL of the Pt stock solution. The mixture was then heated to 60 °C and stirred for ~2 hours. The solution color changed from light yellow to dark yellow. In order to separate the Pt-deposited tetrapods from possible free Pt nanoparticles, the solution was centrifuged at 13000 rpm and the supernatant was removed. The residue was re-dispersed in water and then centrifuged again for a few more cycles before TEM characterization, as illustrated in Figure 2 and Figure S2.

### Control (1): Using bare CdSe/CdS tetrapods

In this control experiment, CdSe/CdS tetrapods were transferred from the organic to the aqueous phase via ligand exchange with MUA. This was followed by the addition of 1mL of the 5 mM Pt stock solution. The mixture was then heated to 60 °C and stirred for ~2 hours. Characterization via TEM of the final product revealed the occurrence of severe aggregation, as seen in Figure S4(A).

### Control (2): Using silica coated CdSe/CdS tetrapods

In this control experiment, silica coated CdSe seeded CdS tetrapods that were not exposed to a HF etching process (therefore no hollow interior) were used while all other conditions were kept the same. No Pt deposition was observed, as evident in Figure S4(B).

### Control(3): Pt precursor heating

In this control experiment, the precursor  $\text{H}_2\text{PtCl}_6$  was simply heated in distilled water in the absence of light. The solution turned from light yellow to a slight brown color. TEM analysis revealed the presence of Pt nanoparticles, as shown in Figure S4(C)

## 8. Etching process for preparation of hollow PtS and Pt-derivatized PtS tetrapods.

Hollow silica-encapsulated CdSe seeded CdS tetrapods exposed to a relatively low and high amount of Pt precursors were processed and dispersed in 1 mL of water, followed by the addition of 0.1mL of diluted HF (0.5%wt) and 0.5mL of 0.1M HCl. The mixture was then heated to 60 °C and stirred for ~1 hour. The resulting particles were then processed and re-dispersed in water.

## 9. Synthesis of Pt-Ag<sub>2</sub>S and Pt-PdS hybrid nanoparticles and control experiments

**Pt-Ag<sub>2</sub>S synthesis:** Processed Pt nanoparticle-decorated CdSe/CdS tetrapods (achieved by using a high amount Pt precursor) encapsulated within a hollow silica shell were first dispersed in 1 mL water, followed by the addition of 60 μL of a 20 mM aqueous AgNO<sub>3</sub> solution with stirring at room temperature for ~ 1 hr. The resulting solution was centrifuged at 13,000 rpm and the supernatant removed. The residual particles (Figure S5(A)) were re-dispersed in water for subsequent analysis.

**Control (1):** Using bare CdSe/CdS tetrapods

CdSe/CdS tetrapods were transferred from the organic to aqueous phase via ligand exchange with MUA, followed by the addition of AgNO<sub>3</sub>. After cation exchange between Cd<sup>2+</sup> and Ag<sup>+</sup>, 1mL of a 5mM Pt stock solution was added with stirring at 60°C for ~2 hours. The resulting tetrapods were generally agglomerated but showed no evidence of Pt deposition, as may be seen from Figures S5(B) and S5(C).

**Control (2):** Using silica coated CdSe/CdS tetrapods

Adding AgNO<sub>3</sub> solution to silica coated CdSe/CdS tetrapods, we successfully obtained silica encapsulated Ag<sub>2</sub>S based tetrapods. However even with the addition of relatively high concentrations of Pt precursors, no evidence of Pt deposition on the Ag<sub>2</sub>S arms was observed, as shown in Figure S5(D).

**Pt-PdS tetrapod synthesis:** The processed Pt nanoparticle-decorated CdSe/CdS tetrapods (achieved by using a high amount of Pt precursor) encapsulated within a hollow silica shell was first dispersed in water, followed by the addition of 50 μL of a 50mM Pd(NO<sub>3</sub>)<sub>2</sub> solution with stirring for 1hr at 60 °C. The resulting solution was centrifuged at 13,000 rpm and the supernatant removed. The residual particles (Figure S6(A)) were re-dispersed in water for subsequent analysis.

**Control (1):** Using bare CdSe/CdS tetrapods

CdSe/CdS tetrapods were transferred from the organic to aqueous phase via ligand exchange with MUA, followed by the addition of Pd(NO<sub>3</sub>)<sub>2</sub>. The mixture was heated to 60 °C and stirred for ~1 hr, after which a brown precipitate was found at the bottom of the reaction vessel. TEM characterization indicated serious aggregation with palladium-containing particles present but there was no sign of cation exchange between Cd<sup>2+</sup> and Pd<sup>2+</sup> to give PdS tetrapods, in agreement with a previous report [6]. Figures S6(B) and S6(C) summarize these results.

Control (2): Using silica coated CdSe/CdS tetrapods

Upon the addition of Pd(NO<sub>3</sub>)<sub>2</sub> to silica coated CdSe/CdS tetrapods, we successfully obtained PdS based tetrapods encapsulated within a silica shell. Upon addition of the Pt precursor, however, no sign of Pt deposition was evident, as exemplified in Figures S6(D) and S6(E).

#### **10. Synthesis of PtS hollow tetrapod with SiO<sub>2</sub> shell cation exchange with Ag and Pd precursors**

The processed Pt nanoparticle-decorated CdSe/CdS tetrapods (achieved by using a high amount of Pt precursor) encapsulated within a hollow silica shell was first dispersed in water, followed by the addition of 1 mL of 0.1M HCl with stirring for 2 hrs at 60 °C. The resulting solution was centrifuged at 13,000 rpm and the supernatant removed. The residual particles were re-dispersed in water for the subsequent addition of AgNO<sub>3</sub> and Pd(NO<sub>3</sub>)<sub>2</sub> at RT and 60 °C, respectively. Quantified EDX results showed that the Pt to S ratio is still 1 : 1, which suggested that PtS did not undergo cation exchange with Ag and Pd to form Ag<sub>2</sub>S and PdS. See Figure S7.

#### **11. Synthesis of Au decorated silica coated CdSe/CdS tetrapod and cation exchange to Au-Ag<sub>2</sub>S**

For the preparation of the Au precursor solution, 60 mg of KAuCl<sub>4</sub> (0.16 mmol) was dissolved in 5 mL of water, yielding a homogenous clear solution. This will subsequently be referred to as the Au stock solution. The transfer of KAuCl<sub>4</sub> (aqueous solution) from water to toluene was performed following a procedure previously reported by Yang et. al. [7]. In a 10 mL open top vial, 1 mL of the Au stock solution (which was appropriately diluted when lower Au precursor concentrations was desired) was mixed with 1 mL of a mixture comprising of 280 mg of DDA dissolved in 10 mL ethanol, and allowed to stir for 3 min. To this reaction mixture, 1 mL of a mixture comprising of 5 μM hollow silica coated CdSe/CdS tetrapods and 6 mg of ODPA in toluene was added and the reaction was allowed to continue for a fixed amount of time, typically 1.5 hr and then quenched with MeOH. This resulted in Au-decorated CdSe/CdS tetrapods encapsulated within a hollow shell of silica, as shown in Figure S8(A).

The processed silica encapsulated Au decorated CdSe/CdS tetrapods were dispersed in water, followed by the addition of 60 μL of a 20mM AgNO<sub>3</sub> solution with stirring for 1hr at room temperature. The resulting solution was centrifuged at 13,000 rpm and the supernatant removed. The residual particles were re-dispersed in water for characterization, as illustrated in Figures S8(B) and S8(C).

### **Details of Instrument Characterization**

#### **1. TEM characterization:**

JEOL JEM-1220 and 2010 (with accelerating voltages of 100 kV and 200 kV respectively) microscopes were used to obtain bright-field TEM images of the nanoparticles. For TEM sample preparation, a drop of the nanoparticle solution was placed onto a 300 mesh size TEM grid. Excess solution was removed by an adsorbent paper and the sample was dried at room temperature. The High-Resolution TEM images, High-Angle Annular Dark Field Scanning-TEM (HAADF-STEM) studies and detailed elemental composition analysis were carried out on a

FEI Titan 80-300 electron microscope operated at 200 kV, which was equipped with an electron beam monochromator and energy dispersive X-ray spectroscopy (EDX). The probing electron beam size for the EDX measurement was around 0.3 nm. The dwell time for each EDX spectrum was around 10 seconds.

## **2. Optical characterization:**

UV-visible absorption spectra were obtained with an Agilent 8453 UV-Visible spectrophotometer. Care was taken to ensure that the concentrations of the various nanostructures were sufficiently dilute to avoid contributions from re-absorption or energy transfer.

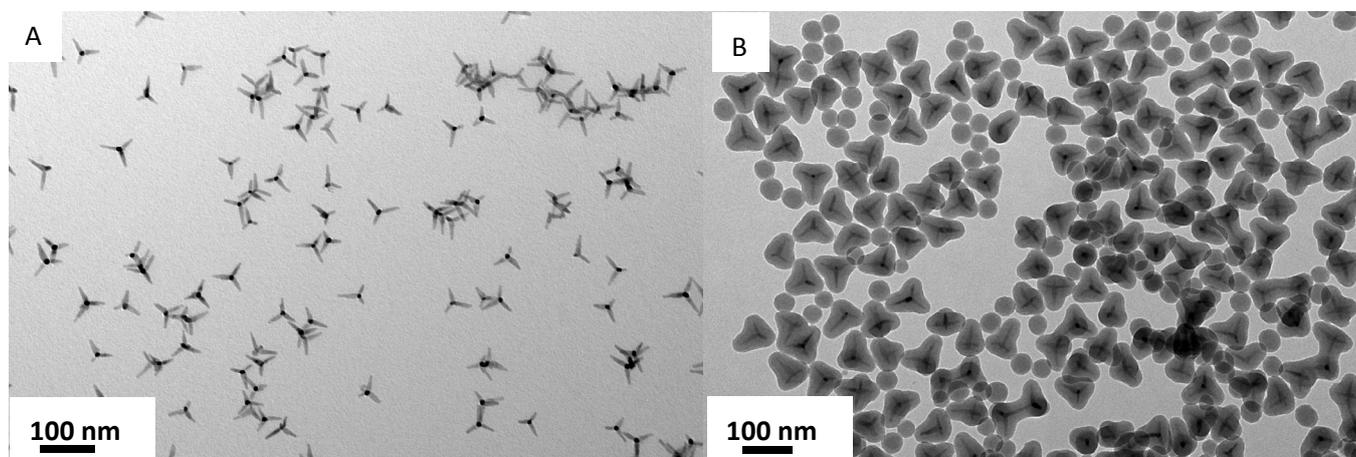
## **3. XRD Characterization:**

X-ray Diffraction (XRD) data was obtained with a diffractometer (Bruker AXS, GADDS) using Cu-K $\alpha$  radiation ( $\lambda=1.540598\text{\AA}$ ) in the range of 20° to 80°. Samples were prepared on a clean silicon wafer by placing drops of concentrated nanoparticles in toluene on the silicon surface and dried at 80°C in the oven. This was repeated several times until a thin layer of solid was formed on the silicon substrate.

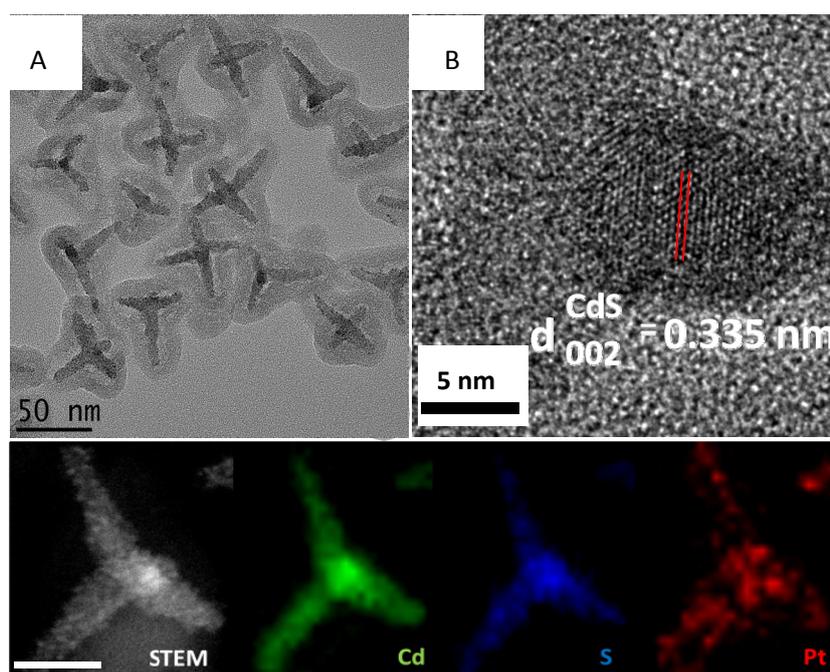
## **4. XPS Characterization:**

XPS measurements were performed using the Thermo Scientific Theta Probe XPS. Monochromatic Al-K $\alpha$  X-ray ( $h\nu=1486.6\text{eV}$ ) was employed for analysis with an incident angle of 30° with respect to the surface normal. Photoelectrons were collected at a take-off angle of 50° with respect to the surface normal. The analysis area was approximately 400 $\mu\text{m}$  in diameter while the maximum analysis depth fell within the range of 4 – 10 nm.

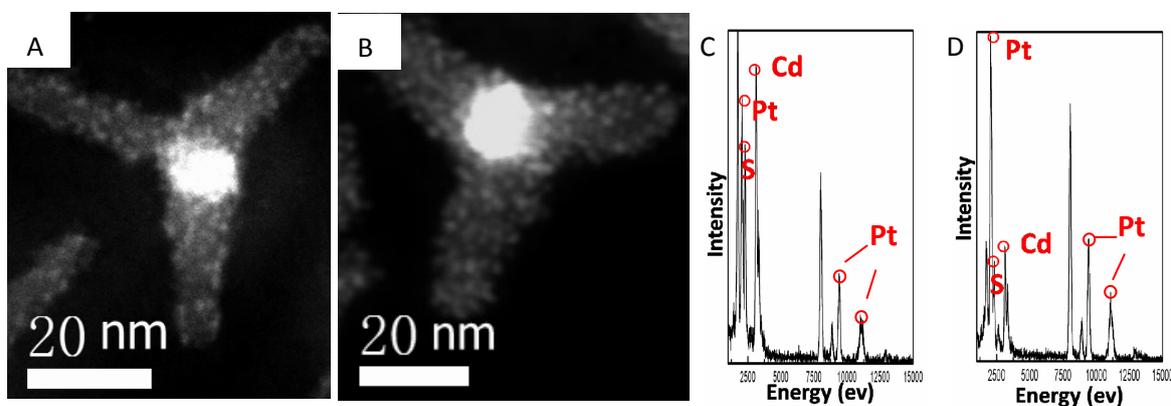
## Supporting Figures



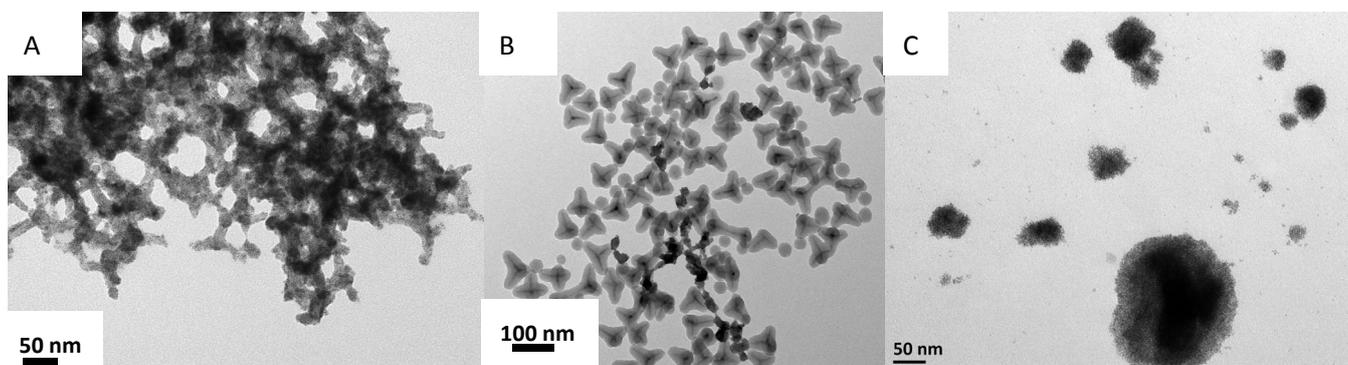
**Figure S1:** Low magnification TEM images of relatively monodispersed (A) CdSe seeded CdS tetrapods and (B) silica coated CdSe/CdS tetrapods. The spherical particles are silica structures which did not encapsulate any semiconductor tetrapods.



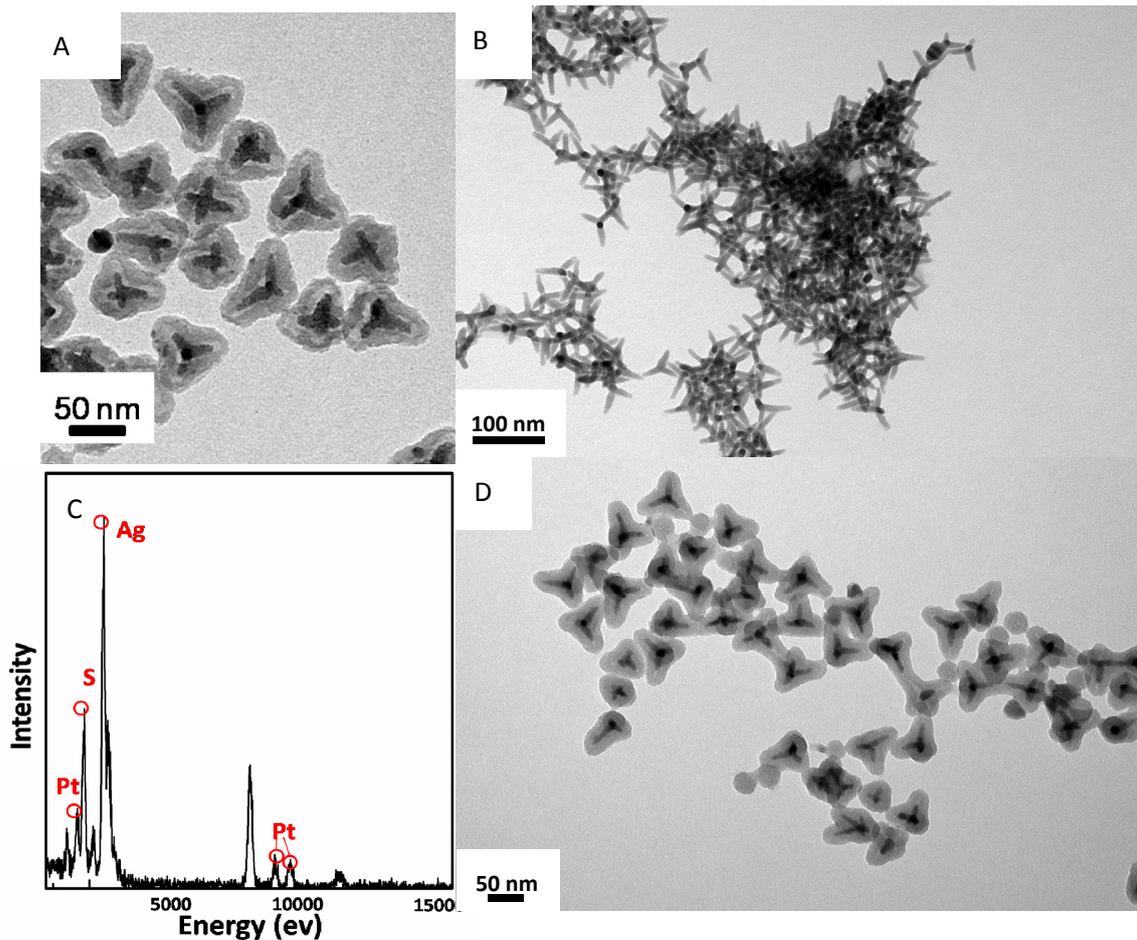
**Figure S2:** TEM images of small Pt clusters deposition on CdSe/CdS tetrapods with hollow silica shell, low magnification (A) and high magnification (B). (C) Chemical mapping of elements Cd, S, and Pt of low amount of Pt deposition. From left to right: HAADF-STEM image, corresponding Cd map, S map and Pt map. Scale bar = 20 nm.



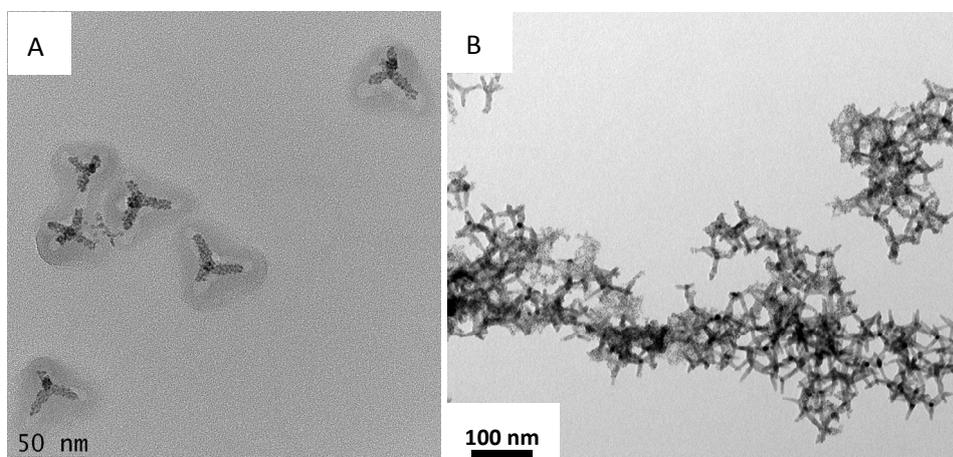
**Figure S3:** HAADF-STEM images of Pt-decorated CdSe/CdS tetrapods with (A) small Pt cluster deposition and (B) large Pt NP deposition. Their corresponding EDX measurements showing Cd, S and Pt signals are given in (C) and (D) respectively. The quantified EDX results indicate atomic percentages of Cd, S, and Pt at 38.56%, 40.42% and 21.01% respectively for the tetrapods in (A) and 23.84%, 25.93% and 50.21% respectively for the tetrapods in (B).

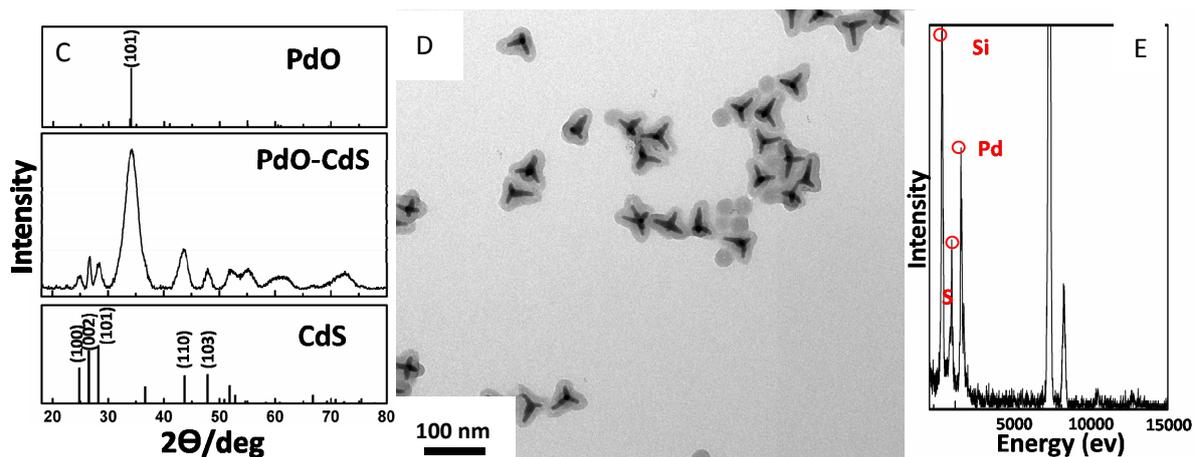


**Figure S4:** TEM images of the control experiments for Pt deposition on CdSe/CdS tetrapods: (A) without a silica shell, showing serious aggregation; and (B) with a non-hollow silica shell showing no obvious indication of Pt deposition despite high amounts of Pt precursor added such that the homogeneous nucleation and growth of Pt may be seen. (C) Pt nanoparticles were formed via the heating of  $\text{H}_2\text{PtCl}_6$  in distilled water in the absence of light.

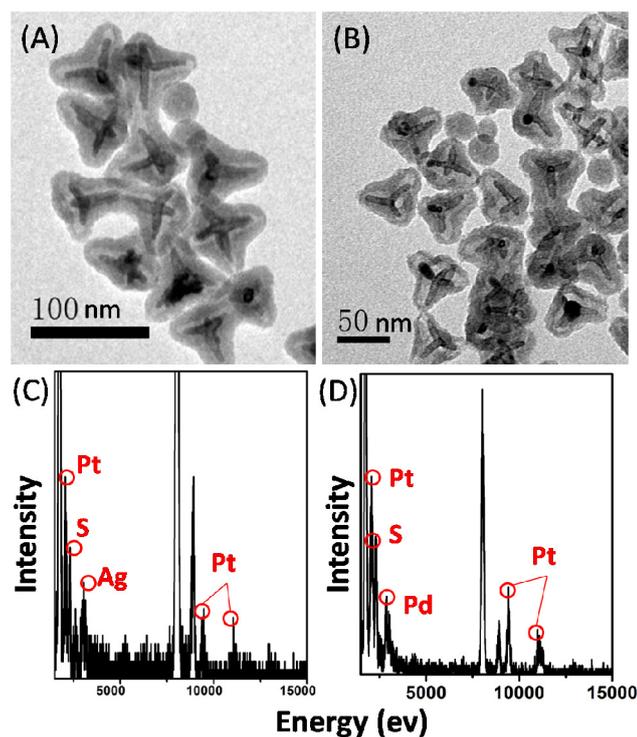


**Figure S5:** (A) Low magnification TEM image of hollow SiO<sub>2</sub> coated Pt decorated Ag<sub>2</sub>S tetrapods. Control experiments for synthesis of Pt decorated on Ag<sub>2</sub>S tetrapods: (B) without the silica shell, showing no obvious sign of Pt deposition and severe aggregation. The corresponding EDX image in (C) showed mainly Ag and S signals as well as a weak Pt signal; (D) with a non-hollow silica shell, no sign of Pt deposition was observed.

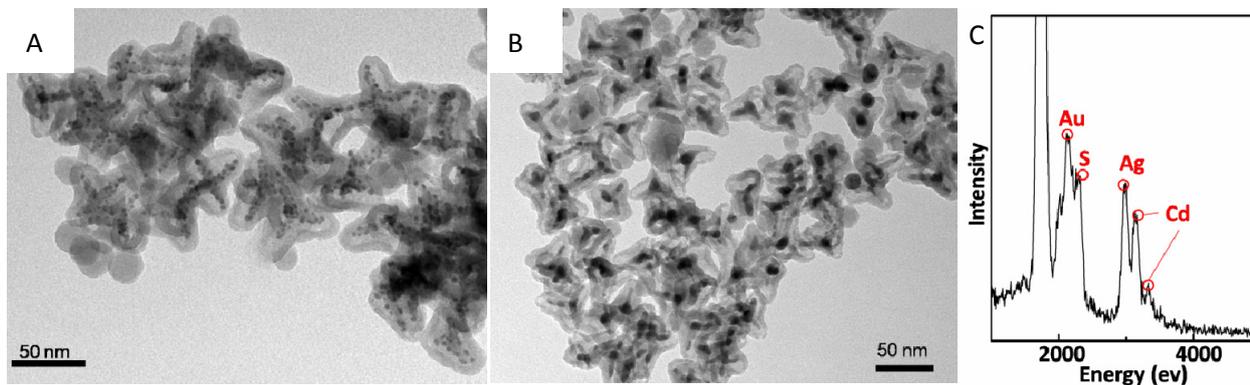




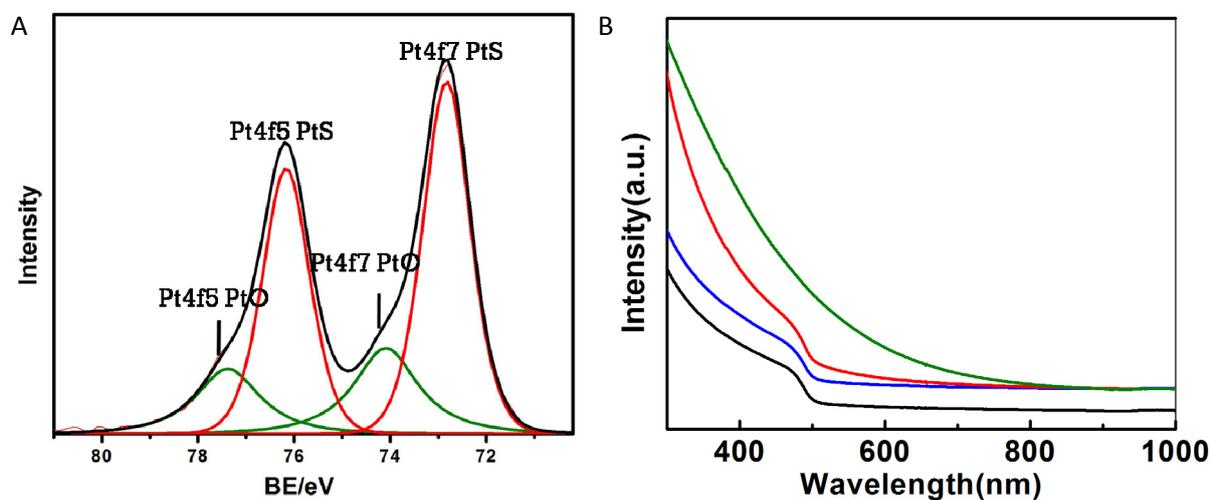
**Figure S6:** (A) TEM image of Pt nanoparticle decorated PdS tetrapods encapsulated within a hollow SiO<sub>2</sub> shell. (B-E) Control experiments for synthesis of Pt decorated on PdS tetrapods with hollow silica shell. (B) Without the silica shell, no cation exchange seen except for the formation of a Pd-containing product, which was characterized via XRD, as shown in (C). (D) With the non-hollow silica shell, CdSe/CdS tetrapods were transformed into PdS based tetrapods, however the corresponding EDX image (E) showed only Pd and S signals but not Pt.



**Figure S7:** TEM image of PtS hollow tetrapods encapsulated within SiO<sub>2</sub> after undergoing exposure to (A) Ag<sup>+</sup> and (B) Pd<sup>2+</sup> respectively. Their corresponding area EDX data yielded atomic percentages of Pt, S as (C) 50.72% and 49.27%, and (D) 47.57% and 52.42% respectively, suggesting cation exchange did not occur. The presence of Ag and Pd may be attributed to deposition of very small amounts of these metals onto the PtS surface.



**Figure S8:** TEM images of (A) Au deposition on hollow silica coated CdSe/CdS tetrapods. (B) cation exchange to  $\text{Ag}_2\text{S}$  by adding  $\text{AgNO}_3$  precursor, which showed the partial removal of gold NPs and some degradation of original tetrapod shape. (C) EDX measurements showed a persistent Cd signal which suggested that with gold deposition on the surface of the CdS arms, it was not possible to undergo complete cationic exchange to  $\text{Ag}_2\text{S}$  tetrapods.



**Figure S9.** (A) XPS in Pt 4f spectral region of the ultra thin semiconductor nanostructures. The experimental data (black) were fitted to PtS (red) and PtO (green). (B) UV-vis spectra of silica coated CdSe/CdS tetrapods (black), silica coated CdSe/CdS tetrapods with hollow interior (blue), small Pt clusters deposition on silica coated CdSe/CdS tetrapods with hollow interior (red), and large Pt particles deposition silica coated CdSe/CdS tetrapods with hollow interior (green).

## References:

- [1] Yang, Y. A.; Wu, H.; Williams, K. R.; Cao, Y. C. *Angew. Chem.* **2005**, *117*, 6870-6873; *Angew. Chem. Int. Ed.* **2005**, *44*, 6712-6715.
- [2] Leatherdale, C. A.; Woo, W. K.; Mikulec, F. V.; Bawendi, M. G. *J. Phys. Chem. B* **2002**, *106*, 7619-7622.
- [3] Fiore, A.; Mastria, R.; Lupo, M. G.; Lanzani, G.; Giannini, C.; Carlino, E.; Morello, G.; Giorgi, M. D.; Li, Y.; Cingolani, R.; Manna, L. *J. Am. Chem. Soc.* **2009**, *131*, 2274
- [4] Selvan, S.T.; Tan, T. T.; Ying, J. Y. *Adv. Mater.* **2005**, *17*, 1620.
- [5] Salant, A.; Amitay-Sadovsky, E.; Banin, U. *J. Am. Chem. Soc.* **2006**, *128*, 10006.
- [6] Shemesh, Y.; Macdonald, J. E.; Menagen, G.; Banin, U. *Angew. Chem. Int. Ed.* **2011**, *50*, 1185.
- [7] Yang, J.; Levina, L.; Sargent, E. H.; Kelley, S. O. *J. Mater. Chem.* **2006**, *16*, 4025-4028.