

Supplementary Information

Metal tips on pyramid-shaped PbSe/CdSe/CdS heterostructure nanocrystal photocatalysts: study of ripening and core/shell formation

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Experimental procedures

1. Preparation of MUA-capped PbSe/CdSe/CdS core/shell/shell nanocrystals

0.65 g of PbO, 2.7 ml of oleic acid and 4 ml of phenyl ether were loaded in a round-bottom flask and heated to 150 °C under Ar. The mixture turned colorless and this clear solution was further heated to 170 °C, at which 2 M of trioctylphosphine (TOP)-Se solution (0.316 g of Se powder dissolved in 2 ml of TOP) was injected. After 30 s, we quenched the reaction by immersing the flask into an iced water bath, and washed the product by collecting precipitates after adding methanol. The washing procedure was repeated one more time to ensure that residual oleic acid and TOP were removed.

0.5 g of CdO, 3 ml of oleic acid, and 8 ml of phenyl ether were mixed in a flask and heated to 250 °C under Ar until the mixture became optically clear and colorless. After cooling it to 75 °C, we transferred the solution to a separate flask that contained 3 mL of PbSe nanocrystal solution in toluene (10 mg/mL). The solution was kept at 70 °C for 3 days. The resulting PbSe/CdSe core/shell nanocrystals were then isolated by precipitation with methanol and collected by centrifugation.

We synthesized PbSe/CdSe/CdS core/shell/shell heterostructure nanocrystals (HNCs) via previously reported synthetic procedures.^{1,2} 61.5 mg of CdO, 1.2 mL of oleic acid, and 10.8 mL of 1-octadecene (ODE) were mixed in a three-neck round-bottom flask and heated to 250 °C under Ar. In a separate flask, 12.8 mg of S and 10 mL of ODE were mixed and heated to 200 °C under Ar. The Cd-oleate solution was cooled to 70 °C and the S-ODE solution was cooled to room temperature. In another flask was PbSe/CdSe core/shell nanocrystal solution, into which Cd-oleate (0.49 mL) and S-ODE (0.45 mL) were injected dropwise in 9 alternating cycles of Cd and S injections. Then, the reaction product was collected through anti-solvent precipitation: adding 30 mL of ethanol and centrifuging the mixture. The washing step was repeated one more time by adding ethanol to the hexane solution of the solid product and centrifuging the mixture. The final product was redispersed in hexane.

The PbSe/CdSe/CdS HNCs capped with oleic acid were mixed with excess amount of mercaptoundecanoic acid (MUA) to form a stable suspension in aqueous solution. More specifically, 2 mg of PbSe/CdSe/CdS HNCs, 100 mg of MUA, and 10 mL of methanol were mixed in a 20 mL vial and the pH of the solution was adjusted to pH 12 by adding tetramethyl ammonium hydroxide pentahydrate. The mixture was sonicated for a few seconds until it becomes optically clear. The MUA-capped HNCs were precipitated by adding 30 mL of toluene and dispersed in methanol.

2. Metal-tip growth via chemical reduction

1.7 nm-sized Au tips growth - 1.8 mg of AuCl₃ dissolved in 20 mL of water was added to the MUA-capped NC solution (2 mg/25 mL of water) under stirring. The Au-tipped HNCs were collected after 30 min and dissolved in 3 mL of methanol. We added tetramethyl ammonium hydroxide pentahydrate until pH of the whole mixture became 7.

Ag tips growth - 0.3 mg of AgNO₃ dissolved in 3 mL of water was added to the MUA-capped HNCs solution (2 mg/17 mL of water) and stirred for 5 min. The Ag-tipped HNCs were collected by centrifugation and dissolved in 3 mL of methanol.

3. Photoreduction of Au or Ag salts on Au-HNCs

Ag growth- 2 mg of pyramid NCs (Au-tipped pyramid NCs), 0.3 mg of AgNO₃ 1.3 mg of DDA, 18 mg of triethylamine, and 6 mL of toluene were stirred under 530 nm light.

Au growth- 2 mg of pyramid NCs (Au-tipped pyramid NCs), 4 mg of HAuCl₄ 5.2 mg of DDA, 72 mg of triethylamine, and 6 mL of toluene were stirred under 530 nm light.

4. Au tip growth on a Cu wire

A Cu wire (1 mm diameter x 10 cm length) was soaked briefly in the 1 mg/mL hexane solution of pyramid HNCs, and then removed from the solution. The coated Cu wire was dried and then subsequently immersed in aqueous AuCl₃ solution (1 mg/mL) for further Au-tip growth under stirring.

5. Characterizations

Morphology and atomic compositions were analyzed by transmission electron microscopy (TEM, Philips Tecnai F20) and energy dispersive X-ray spectroscopy (EDS). The optical property of HNCs was probed with UV-vis spectroscopy (Shimadzu UV3600).

We examined photocatalytic activities for the reduction of methylene blue (MB). A 785 nm laser (power: 25 W) was used as a light source for the photocatalytic reduction. Photocatalysts of varying shapes and forms of metal tips were tested: PbSe/CdSe/CdS HNCs without metal tips, Au-tipped, rAu-tipped, Ag-tipped, and Au/Ag core/shell-tipped HNCs. In

a typical experiment, 2 mg of MUA-capped HNCs and 6 μM of MB were dissolved in 0.5 mL of methanol as a sacrificial agent and 2 ml of water. We set the solution to pH 7 and kept it dark for 30 min to reach equilibrium for adsorption/desorption of the reactants. During the 4 hr irradiation of 785 nm, absorption spectra of co-suspended photocatalysts and MB in the solution were monitored.

Estimation of the ratio of Au:HNCs

We estimated the composition of HNCs, which are composed of PbSe core (diameter = 3.3 nm), spherical CdSe shell (shell thickness = 1 nm) and pyramid CdS shell (length of one side = 11.4 nm) from the spectroscopy data and TEM images in Fig. S4 and Fig. S5, respectively. For example, the volume of each components was calculated based on the geometric information (e.g., diameter, shell thickness, and length of one side in pyramid). We then estimated the numbers of Pb, Cd, Se and S atoms in a single HNC using the following equation.

$$\text{A number of each atoms in a single HNC} = \frac{\text{Volume}}{\text{Unit Cell Volume}} \times \text{atom number in unit cell}$$

$$\text{A numbers of Pb and Se in PbSe core} = \frac{18.81 \text{ nm}^3}{0.230 \text{ nm}^3} \times 4$$

$$\text{A numbers of Cd and Se in CdSe shell} = \frac{88.67 \text{ nm}^3}{0.225 \text{ nm}^3} \times 4$$

$$\text{A numbers of Cd and S in CdS shell} = \frac{67.10 \text{ nm}^3}{0.086 \text{ nm}^3} \times 2$$

The calculation reveals that a single HNC is composed of 328 atoms of Pb, 1,728 atoms of Cd, 1,428 atoms of Se and 628 atoms of S and the weight of 1 mole of HNCs (6.02×10^{23} particles) is 39.52 kg. In the experiment, when metal tips are loaded, 2 mg of HNCs were

introduced. We presumed that the organic ligand takes up to 20 % of total weight of a single HNC while inorganic components 80 %.³ Taking the organic part into account, for the 2 mg, the number of HNCs is 5.1 nmol. Since 6 μ mol of the Au precursor introduced in a typical experiment, the ratio of the number of Au *atoms* to HNC *particles* was estimated to be ~1200:1.

Figures

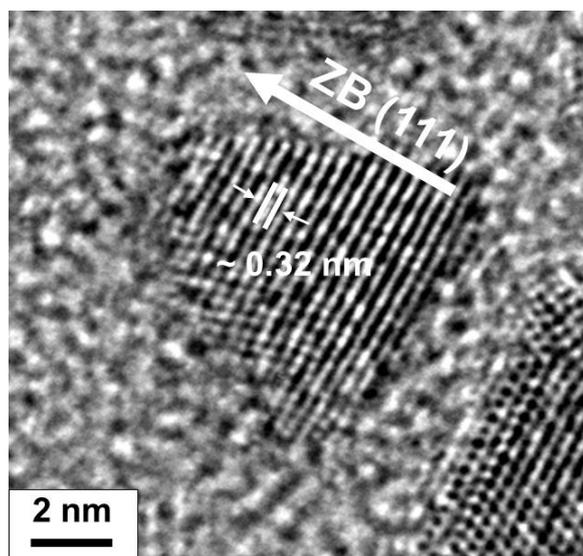


Fig. S1 High resolution TEM image of pyramidal PbSe/CdSe/CdS HNCs.

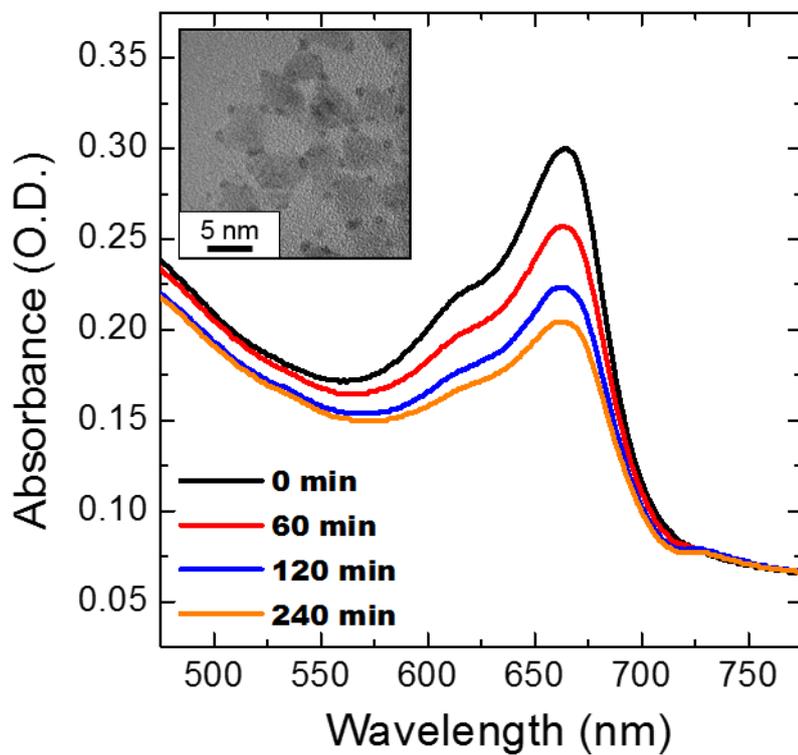


Fig. S2 Absorption spectra of MB after exposure to 785 nm light with Au-tipped pyramidal PbSe/CdSe/CdS HNCs as a function of reaction time. The absorption peak of MB is clearly shown and diminishes as the MB reduces to MBH. (inset) TEM image of Au-tipped nanopyramids prepared in aqueous solution.

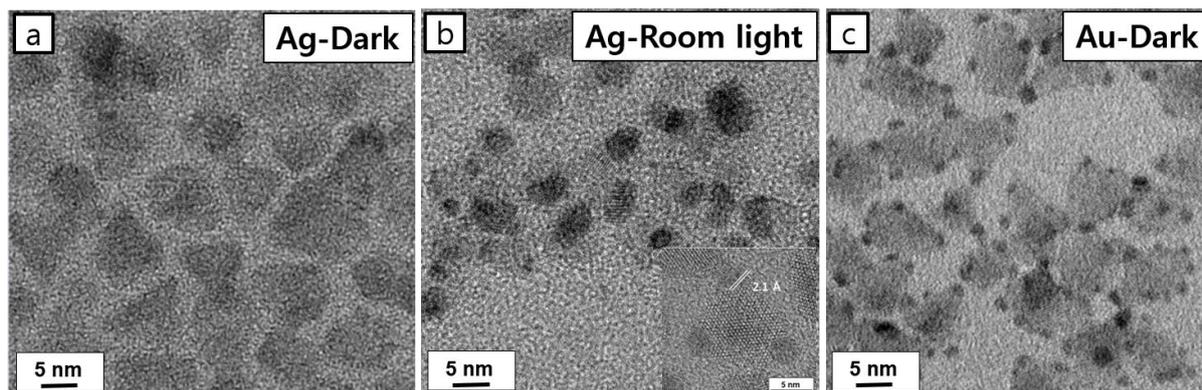


Fig. S3 Photocatalytic Ag growth on PbSe/CdSe/CdS pyramid nanocrystals in (a) dark and (b) room light, and (c) photocatalytic Au growth on PbSe/CdSe/CdS pyramid nanocrystals in dark.

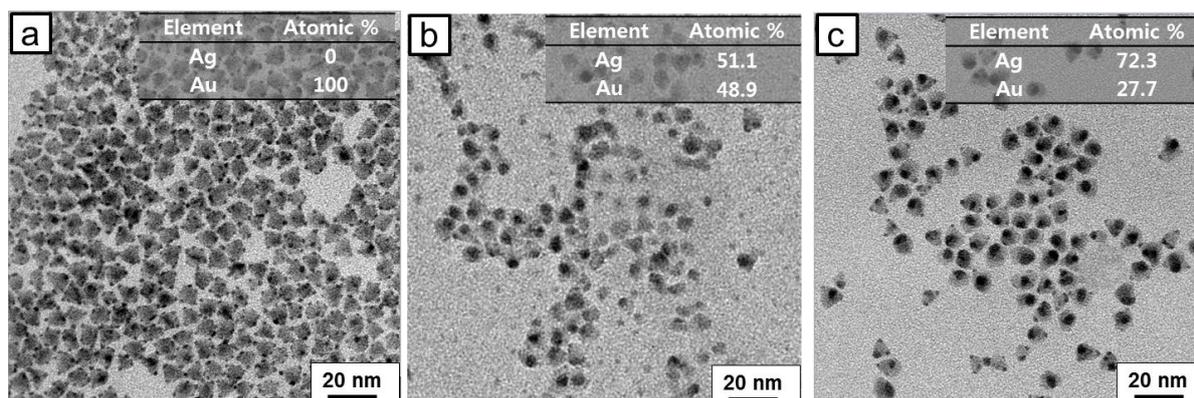


Fig. S4 TEM images and (Inset) elemental analysis data of metal-HNCs (a) before and after (b) 5 min and (c) 30 min of Ag growth on Au-HNCs.

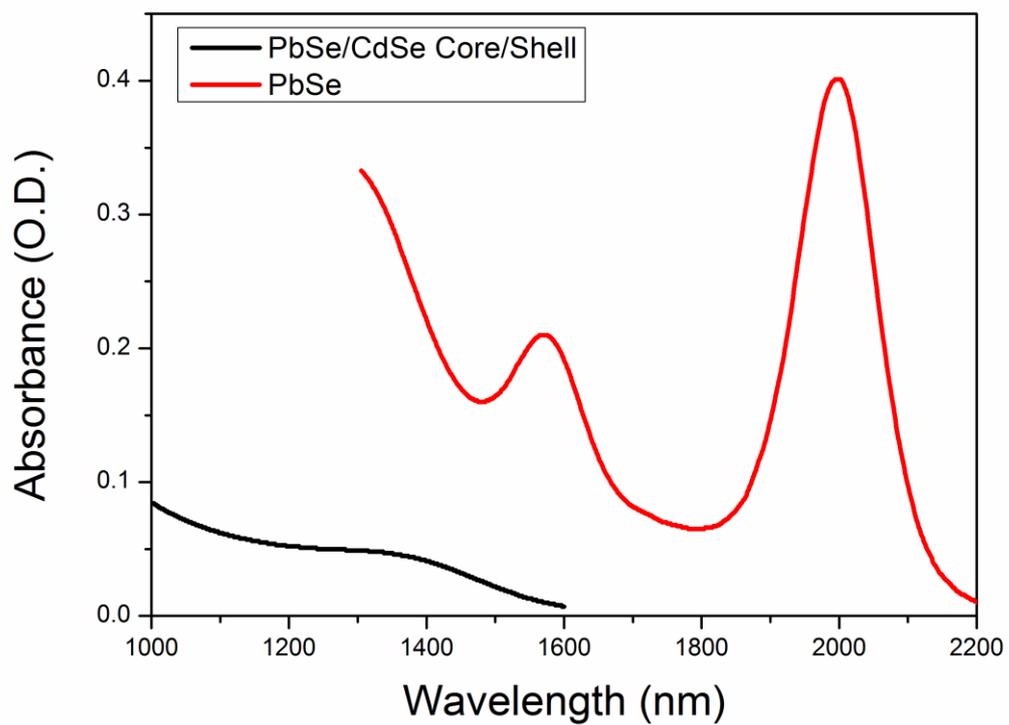


Fig. S5 Absorption spectra of PbSe (black) and PbSe/CdSe core/shell (red) nanocrystals before and after cation exchange process, respectively.

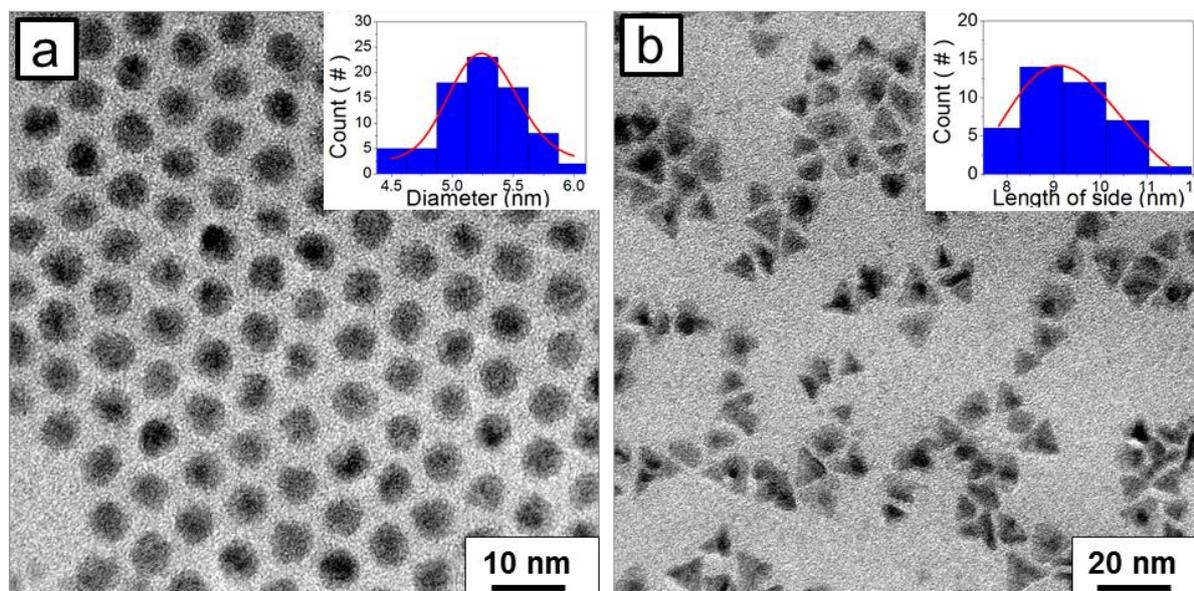


Fig. S6 TEM images of (a) PbSe/CdSe core/shell nanocrystals and (b) PbSe/CdSe/CdS core/shell/shell pyramid HNCs after CdS deposition via the successive ionic layer adsorption and reaction (SILAR) method. (Inset) Histogram of nanocrystal size from the corresponding TEM image.

References

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