Selective Growth of Metal Sulfide Tips onto Cd-Chalcogenide Nanostructures

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Supporting Information:

Experimental Section:

Chemicals. All chemicals and solvents were used as received. Sulfur (99.98%), trioctylphosphine (TOP, 90%), 1-dodecanethiol (98%), sodium diethyldithiocarbamate (99%), silver nitrate (99%), 1-octadecene (ODE,90%), cetyltrimethylammonium bromide (CTAB, 95%) and oleic acid (90%) were purchased from Sigma Aldrich. Cadmium oxide (99.99%), selenium (99.99%), tellurium (99.999%), trioctylphosphine oxide (TOPO,99%), tetradecylphosphonic acid (TDPA,97%), octadecylphosphonic acid (ODPA,97%), lead acetate trihydrate (99.999%) and copper nitrate trihydrate (99.5%), were purchased from Strem Chemicals. Synthesis of CdS rods. Nanorods of CdS were prepared following a previous report.¹⁷ For the synthesis of CdS nanorods, the cadmium precursor was prepared by degassing a mixture of 0.0563g CdO (0.438mmol), 0.2100g TDPA (0.75 mmol) and 1.7495g TOPO in a 50ml flask under nitrogen flow at 65°C for one hour. The mixture was then heated to 300°C for 15 minutes until the colour of the solution changed from dark red to colourless indicating the formation of the Cd-TDPA complex. The solution was then heated to the desired injection temperature of 320°C. The chalcogen precursor was prepared by dissolving 0.04g sulfur powder (0.5mmol) in 4 ml of TOP and heating to 50° C for 30 minutes. Nanorods were synthesized by injecting 0.5ml of the chalcogen precursor every 2 minutes until all 4ml was consumed. After the injections, the solution was maintained at 300^{0} C for 45 minutes until colour of the solution changed from colourless to yellow, then the reaction was stopped by removing the heating mantle and allowing the solution to cool to 60°C. The nanorods were purified by addition of 5ml toluene and 3ml methanol followed by centrifugation for 15 minutes.

Synthesis of CdSe rods. CdSe nanorods were prepared according to a previously published report with a few change.¹⁷ Briefly, 0.1097g CdO, 80mg HPA, 305mg TDPA and 1.5g TOPO were degassed under nitrogen flow and then heated to 300°C until the solution was clear. After the solution turns colourless 0.55ml of TOP was injected in the reaction mixture. The solution was then heated to the growth temperature of 320°C. At this temperature, 0.46ml of 0.0873gr of Se powder in 1ml of TOP was injected quickly to the solution. After the injection the reaction mixture was cooled to 300°C for five minutes and then it was further cooled to 60°C with a water bath. The nanorods were precipitated with methanol for cleaning and re-dissolved in toluene for further experiments.

Synthesis of CdSe cubes. Cubes of CdSe were prepared following a previous report.²⁶ For the synthesis of CdSe cubes, the Se precursor was prepared by dissolving 0.0125gr selenium powder in 0.125gr TOP. The mixture was heated with stirring until the Se powder was dissolved completely and this solution was cooled to room temperature. 0.102g CdO, 0.7971gODPA and 3.2g TOPO were degassed under N_2 flow at 120^oC for 20 minutes, and then the mixture was heated to 300^oC until the solution was clear. Next, 1.5g of TOP was added

and then the temperature was increased to 320° C. After that the Se:TOP precursor solution was injected quickly. The temperature dropped to 315° C and was maintained for 6 minutes. Then, the reaction was stopped and cooled to room temperature by removing the heating mantle. The Cubes were precipitated by addition of methanol and centrifugation.

Synthesis of CdSe terapods. CdSe tetrapods were prepared according to a previously published report.²⁷ 0.1299g CdO, 1.7734g oleic acid and 20ml of 1-octadecene were degassed under nitrogen flow at room temperature for 20 minutes, and then the solution was heated to 250°C until the solution was clear. After cooling the solution to 190°C, TOP:Se solution (0.03948g Se powder in 1.5ml TOP with 0.02g CTAB in 3ml toluene) was injected quickly. The temperature dropped to 160°C for and maintained 60 minutes. After that the reaction was stopped by removing the heating mantle. When the solution reached to room temperature 1ml toluene was added. The particles were precipitated with 20ml acetone and 2ml methanol and centrifuged at 5000rpm. Synthesis of metal-diethyldithiocarbamates.

The diethyldithiocarbamate salts of copper or lead or silver were prepared according to previously published methods.²² The chosen water soluble metal salt ($Cu(NO_3)_2 \cdot 3H_2O$, 6.5mmol; $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, 6.5mmol; $Ag(NO_3)$, 17.5mmol) was dissolved in 50ml of deionized water. Sodium diethyldithiocarbamate (3g, 17.5mmol) was dissolved separately in 50 ml of deionized water and then added to the metal solution. The precipitate was allowed to form and was then filtered, dried, and recrystallized in hot chloroform.

Selective growth of PbS, Ag, Cu₂-xS on CdS or CdSe nanorods. The selective growth of PbS , Ag, Cu_{2-x}S on CdS was achieved by mixing a known amount of CdS nanorods (OD= 1.00 at the first excitonic transition, 459 nm) with (Ag or Pb or Cu)- bisdiethyldithiocarbamate: 1mg Ag[S₂CNEt₂] (4×10⁻³mmol) or 5mg Pb[S₂CNEt₂]₂ (1×10⁻²mmol) or 10mg Cu[S₂CNEt₂]₂

 $(3 \times 10^{-2} \text{mmol})$ in 2.5 ml TOP. The mixture was heated to the decomposition temperature (250°C for Pb[S₂CNEt₂]₂ and Ag[S₂CNEt₂, and 290°C for Cu[S₂CNEt₂]₂) for 5 minutes. The reaction was then stopped by removing the heating mantle and allowing the solution to cool to room temperature. The particles were cleaned two times by addition of 3ml toluene and 3ml methanol followed by centrifugation for 15 minutes. Selective growth of Ag₂S on CdS, CdSe nanorods in dodecanethiol:

The selective growth of Ag_2S on CdS, CdSe was achieved by mixing a known amount of CdS, CdSe nanorods (optical density = 1 at the first excitonic transition 459nm, 519nm respectively) and Ag-

bisdiethyldithiocarbamate: $1 \text{mg Ag}[S_2\text{CNEt}_2] (4 \times 10^{-3} \text{mmol})$ in 2.5ml dodecanethiol. The mixture was then heated to the decomposition temperature of $\text{Ag}[S_2\text{CNEt}_2]$ at 218°C for 3 minutes. The reaction was then stopped by removing the heating mantle and allowing the solution to cool to room temperature. The particles were cleaned by addition of 3 ml toluene, 3 ml acetone and 2 ml methanol followed by centrifugation for 15 minutes. Selective growth of PbS on CdSe cubes or tetrapods. The selective growth of PbS on CdSe was achieved by mixing a known amount of CdSe cubes (optical density = 0.4 at the first excitonic transition, 660nm) with 3mg Pb-bisdiethyldithiocarbamate in 4ml TOP. The mixture was heated to decomposition temperature of Pbbisdiethyldithiocarbamate at 250°C for 4 minutes. The reaction was then stopped by removing the heating mantle and allowing the solution to cool to room temperature. The particles were cleaned by addition of 3 ml toluene and 3ml methanol and 3ml acetone followed by centrifugation for 15 minutes.

^{1.} L.Manna, D. J. Milliron, A. Meisel, E. C. Scher, A. P. Alivisatos, Nature Materials, 2003, 2, 382.

^{2.} W.Y. L. Ko, H. G. Bagaria, S. Asokan, K. J. Lina , M. S. Wong, J. Mater. Chem, 2010, 20, 2474.



S1. (A) CdS rods (~42 nm) templates before the growth of PbS (Fig. 1A), (B) CdS rods (~60 nm) templates before the growth of Ag₂S (Fig. 1B), (C) CdS rods (~35 nm) templates before the growth of $Cu_{2-x}S$ (Fig. 1B).



S2. (A) CdSe rods (~62 nm) templates before the growth of PbS and Ag_2S (Fig. 1D, E), (B) CdSe rods (~26 nm) templates before the growth of $Cu_{2x}S$ (Fig. 1F).



S3. (A) TEM image CdS-Ag, (B) Absorption spectra of CdS nanorods (black line), CdS-Ag (red line), (c) High resolution TEM image of CdS-Ag, show that Ag metal growth on the tip of CdS hexagonal, (D) XRD for CdS-Ag (the peak that sign by star is belong to silicon).



S4: TEM image of CdSe Cubes with higher concentration of PbS.



S5. EDX for CdS-PbS (red), CdS-Ag_S (green) and CdS-Cu_{2-X} S (blue).