Electronic Supplementary Information of

Oligomerization of Cadmium Chalcogenide Nanocrystals into CdTe-Containing Superlattice Chains

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Table of Contents

1. Experimental procedure

2. Diameter distributions of seeded nanocrystals and grown oligomers (Figure S1)

3. Length control of oligomers (Figure S2)

4. A selected area electron diffraction pattern of CdSe-CdTe oligomers (Figure S3)

5. XRD patterns of seed NCs and oligomers (Figure S4)

1. Experimental.

All chemicals were used as received. Cadmium oxide (CdO, 99%), 1-headecylamine (HDA, technical grade, 90%), 1-octadecene (ODE, technical grade, 90%), trioctylphophine oxide (TOPO), and tributylphosphine (TBP, 97%) were purchased from Aldrich. Oleic acid (OA), stearic acid (SA), selenium powder, and toluene (spectrum grade) were supplied from Wako chemical. Tellurium powders (99.7%) were obtained from Kishida chemical. CdS and CdSe seed nanocrystals were synthesized by following literatures.^[Ref. A,B]

Synthesis of CdS-CdTe nanowires: For a typical synthesis of CdS-CdTe nanowires 2.5×10^{-5} mmol of OA-capped CdS nanocrystals (3.5 nm in diameter) in toluene and 6.0 g of ODE/HDA (1/1) mixture solvent were loaded in a 20 mL two-neck flask. The mixture was subjected under vacuum at 100 °C to degas and evaporate toluene for 30 minutes, and then heated to 180 °C under N2 atmosphere. 1.0×10^{-2} mmol of Cd-OA and Te-TBP in ODE (0.02 M) were injected twice into the flask, and the reaction temperature was kept at 180 °C for 60 minutes under vigorous stirring. Then the reactant was subjected to annealing at 240 °C for 10 min. Note that prolonged annealing at 240 °C led to alloying of the constituent materials. The mixture was cooled to 70 °C, followed by precipitation using ethanol for purification. The precipitates were well-dispersed in low-polar solvents, typically toluene. For further size-selective purification, the nanocrystals were precipitated using toluene/ethanol (1/1) solvent, followed by centrifugation (10,000 rpm, 10 min) and re-dispersion in toluene.

Synthesis of CdSe-CdTe nanowires: CdSe-CdTe nanowires were synthesized following the almost same procedure for CdS-CdTe nanowires, except for using 2.0×10^{-5} mmol of HDA/SA/TOPO-capped CdSe nanocrystal seeds.

Instrumentation: BF-TEM, high angle annular dark field scanning TEM (HAADF-STEM), and EDS were conducted by JEOL JEM-3100FEF. Hot sample solutions (~ 60 °C) were drop-cast on carbon-coated Cu microgrids (high resolution carbon substrate, STEM100Cu grids, Ohkenshoji Co., Ltd.) for BF-TEM and HAADF-STEM. For cryo-TEM studies, the sample solution was cast on Cu microgrids without coating (CU 200MESH, JEOL), the cast grid was then quickly dipped in liquid ethane, and finally transferred to a sample chamber in TEM at 77 K.

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^B J. J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson, X. Peng, *J. Am. Chem. Soc.* 2003, **125**, 12567-12575

2. Diameter distributions of seeded nanocrystals and grown oligomers



Figure S1. Diameter distribution histograms of CdS nanocrystals (blue, 3.5 ± 0.6 nm) and CdS-CdTe nanowires (red, 3.7 ± 0.6 nm) in Figure 2, and CdSe nanocrystals (green, 3.6 ± 0.6 nm) and CdSe-CdTe nanowires (red, 3.3 ± 0.8 nm) in Figure S2a, respectively. A resolution of the histograms is 0.3 nm, and the diameters were calculated by Gaussian curve fitting.

3. Length control of oligomers



Figure S2. CdSe-CdTe oligomers synthesized from (a) 3.6 nm-, and (b) 5.0 nm-CdSe nanocrystals. Nanowire length is a crucial factor to design their structure, such as networks and composite materials. Therefore length must be optimized. We found that the oligomer length might rely on size of seed nanocrystals. Concentration of both seed nanocrystals and precursors could also affect the length of oligomers, where lower concentration condition leads to the formation of shorter oligomers.

4. A selected area electron diffraction pattern of CdSe-CdTe oligomers



Figure S3. Slected area electron diffraction patterns of CdSe NCs and CdSe-CdTe oligomers.

5. XRD patterns of seed NCs and oligomers



Figure S4. X-ray diffraction patterns of (a) CdS NCs and (b) CdS NC-CdTe oligomers. Blue, green, and red bars: zinc-blende CdS, wurtzite CdS, and partially-alloyed zinc-blende $CdS_{0.2}Te_{0.8}$, respectively. Asterisks are diffraction patters attributed to wurtzite TeO₂. TeO₂ impurity observed in XRD might be due to partial oxidization of the oligomers, but STEM data showed no TeO₂ nanoparticles which should indicate Te signals and no Cd signal. There might be TeO₂ as an impurity encapsulated in the nanowire networks.