Structure Direction of II-VI Semiconductor Quantum Dot Binary Nanoparticle Superlattices by Tuning Radius Ratio

Supporting Information

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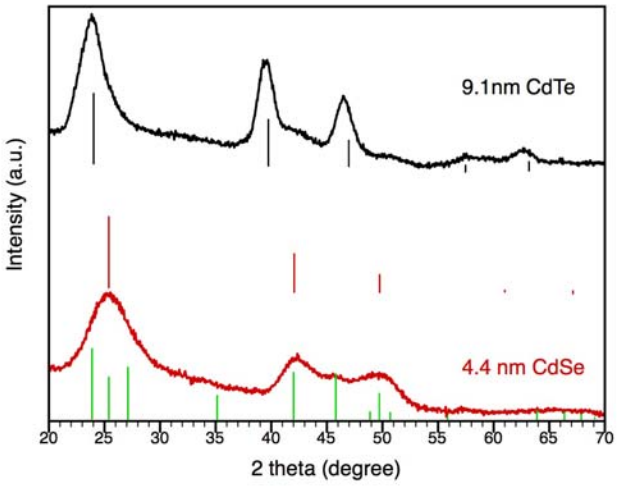
CdTe nanoparticle synthesis procedure: First, the TOP-Te solution was made by dissolving 0.035g Te in 0.313g TOP at 250 °C under nitrogen ambience and rapid stirring for at least 3 hours until a light yellow transparent solution was obtained. This TOP-Te solution was then transferred into a glove box for storage. Then, the Cadmium phosphonate solution was prepared by dissolving 0.035g CdO in the mixture of 0.275g ODPA and 3.725g TOPO in a 25 mL flask at 280 °C under Nitrogen and rapid stirring until colorless transparent. Then this Cadmium phosphonate solution was degassed under vacuum at 110 °C for at least 3 hrs to ensure removal of the water generated by the reaction of CdO with ODPA. After degassing the system was refilled with nitrogen and the temperature of the solution was brought up to an injection temperature point (under nitrogen flow). The injection temperature used for the synthesis of 9.1 nm, 8.1 nm and 7.0 nm diameter CdTe NPs is 325 °C and for the 5.9 nm CdTe is 280 °C. Then the TOP-Te solution was taken out from the glove box and rapidly injected into the solution at the injection temperature under rapid stirring. The reaction mixture was cooled to ~ 315 °C (for 325 °C injection) or ~ 270 °C (for 280°C injection) and this temperature was maintained for further nanoparticle growth. The growth time for the 9.1 nm, 8.1 nm, 7.0 nm and 5.9 nm CdTe nanoparticles was 9, 6, 2 and 1 minute, respectively. Size selection process (by centrifugation and precipitation with controlled amount of non-solvent) was needed for the 9.1 nm, 8.1 nm and 5.9 nm batches. No size selection was necessary for the 7.0 nm batch. Attempts to synthesize CdTe NPs larger than 9.1 nm was made by 325 °C injection for a growth time of 15 minutes and 335 °C injections for a growth time of both 9 and 15 minutes. These attempts produced in average larger (> 9.1 nm) CdTe NPs but with a much larger size distribution (standard deviation > 10 %) even after size selection attempts and some particles with elongated shapes. The reaction was stopped by quickly lowering the temperature to below 100 °C and ~ 10 mL of anhydrous

Toluene of room temperature (RT) was injected when the temperature of the reaction was around 60 °C. After cooling to RT, the CdTe nanoparticles were then precipitated from the crude solution by adding anhydrous ethanol (non-solvent). Precipitated nanoparticles was then redispersed into toluene or TCE. Additional wash (by adding ethanol and centrifugation) was needed for three to four more times to remove extra unreacted organics.

CdSe nanoparticle synthesis procedure: Typically, 1.0 M TOP-Se solution was made by dissolving Se shots into TOP solution around 80 °C under nitrogen and rapid stirring until a colorless transparent solution was obtained. This TOP-Se solution was then kept in a glove box. In a 50 mL reaction flask, 0.0514g of CdO was dissolved in 0.455g SA under nitrogen and rapid stirring at 280 °C until colorless transparent. After cooling to RT, 16 mL of ODE, 2g of TOPO, and 2g of ODA were added. The system was then degassed under vacuum at 110 °C for 3 hrs to ensure removal of the water generated by the reaction of CdO with SA. After degassing, the system was refilled with Nitrogen and heated to 300 °C under stirring. 2mL of 1.0 M TOP-Se was then quickly injected into the solution. The temperature of the system was decreased to 280 °C for the growth of nanoparticles. The size of the CdSe NPs stabilizes at ~ 4.4 nm after 10 minutes of growth time and we used a growth time of 15 minutes. No size selection was needed for these CdSe NPs. The reaction was stopped by quickly lowering the temperature to RT. The precipitation and washing procedure are the same as in the case of CdTe nanoparticles.

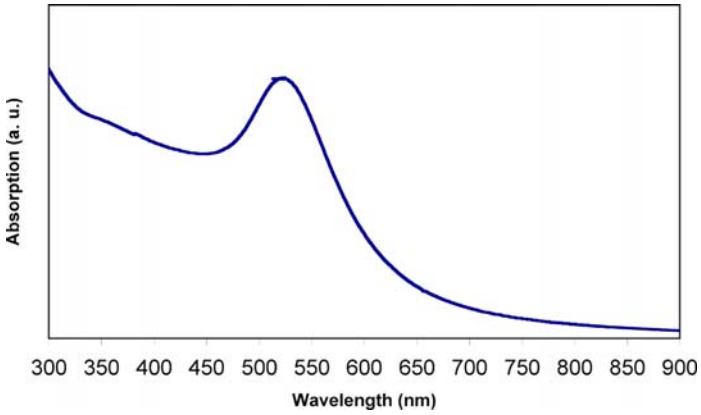
Powder XRD spetra of representative CdTe and CdSe samples:



Supporting figure S1. Powder XRD spetra of CdTe nanocrystals of average diameter 9.1 nm (dark curve) and CdSe nanocrystals of average diameter 4.4 nm (red curve). The dark, red, and green line spectra give the bulk reflections of CdTe (zincblende, JCPDS 75-2086), bulk CdSe (zinc blende, JCPDS 19-0191) and bulk CdSe (wurzite, JCPDS 77-2307), respectively.

Au nanoparticle Synthesis: Typically, 34 mg of gold chloride, 92.5 mg of didodecyldimethylammonium bromide and 10 mL toluene was mixed by sonication. The solution was stirred vigorously, into which 40 μL of 9.4 M $NaBH_4$ in water solution was injected. After 15 minutes, 800 μL 1-dodecanethiol was added followed by another 5 minute of stirring. The product was purified by ethanol/toluene solvent pair and finally dispersed in a 10 mL toluene and 800 μL 1-dodecanethiol mixtures. The solution was refluxed for 30 minutes. The final product was purified twice with ethanol/toluene solvent pair by centrifugation and precipitation and finally dispersed in toluene or TCE solution. For the preparation of BNSLs, single component Au NP solution were prepared by dissolving Au NPs in a TCE solution with 0.006 volume fraction additive of 1-dodecanethiol and a particle concentration ~ 1.72×10^{15} /mL.

UV-Vis absorption of 5.5 nm Au NPs in toluene:



Supporting figure S2. UV-Vis absorption of 5.5 nm Au NPs in toluene.