Supporting Information

Formation and Stepwise Self-Assembly of Cadmium Chalcogenide Nanocrystals to Colloidal Supra-Quantum Dots and the Superlattices

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Materials. Tri *n*-octylphosphine oxide (TOPO) (90% and 99%), cadmium acetate dihydrate ($Cd(Ac)_2 \cdot 2H_2O$, 98 %), stearic acid (SA) (95%), tri *n*-octylphosphine (TOP, 90%), selenium pellet (99.999+%, ca. 2 mm), tellurium shot (99.999%, 1-2 mm), sulfur powder (99.98 %, trace metal basis), 3-mercaptopropionic acid (3-MPA, >99%), cadmium chloride hemi-pentahydrate ($CdCl_2 \cdot 2.5H_2O$, >98%), anhydrous chlorobenzene (99.8%) cadmium oxide (CdO) (99.5%), and pyridine (99+%) were purchased from Aldrich. 1-octylphosphonic acid (OPA) (99%), n-octadecylphosphonic acid (ODPA) (97%), n-hexylphosphonic acid (HPA), 1-tetradecylphosphonic acid (TDPA) (98%) were purchased from Alfa Aesar. Acetone and iso-propanol were purchased from J. T. Baker. Methanol was purchased from Mallinckrodt Chemicals.

Synthesis of CdS, CdSe, CdTe, CdTeSe supra quantum dots (SQDs). All manipulations were performed using standard air-free techniques with Schlenk line. For typical CdSe SQD synthesis, cadmium acetate dihydrate (2 mmol), stearic acid (0.25 mmol) and TOPO 6 g was degassed at 110 °C for 2 h in a 25-mL three-neck round-bottomed flask, then heated to 270 °C under N_2 gas flow. For CdSe [CdS] SQD synthesis, 0.5 mmol of selenium pellets in 1 mL of TOP solution (0.5 M TOPSe 1 mL) [0.5 mmol of sulfur powder in 1 mL TOP solution] was injected rapidly to three-neck round bottle flask with vigorous stirring. For CdTe SQDs, 0.5 mmol of tellurium shot dissolved in 1 mL of TOP was used. The 0.25 mmol of selenium precursor and 0.25 mmol tellurium precursor injected together when CdTeSe alloy SQDs were synthesized. All solutions were kept at 270 °C for 5 min after injection, then the heating mantle was turned off. The reaction mixture was cooled to room temperature, then diluted using hexanes. To remove excess organics, the SQD crude product was precipitated by addition of excess ethanol, collected by centrifugation, and re-dispersed in small amount of hexanes.

To control the size of CdSe SQDs, cadmium precursor solution was prepared to follow the typical method to synthesize of Cd:SA=4:1. The cadmium precursor was degassed at 110 °C for 2 h in a 25-mL three-neck round-bottomed flask, then heated to 270 °C under N_2 gas flow. The size of CdSe SQDs was controlled by adjusting the concentration and volume of prepared selenium precursor, and the volume of sequentially-injected TOP. The detailed injection condition for selenium precursor was as follows: 0.5 M TOPSe 1 mL for 46-nm SQDs, 1 M TOPSe 0.5 mL with successive injection of TOP 0.5 mL for 55-nm SQDs, 1 M TOPSe 0.5 mL for 64-nm SQDs, 2 M TOPSe 0.25 mL with successive injection of TOP 0.75 mL for 72-nm SQDs, 2 M TOPSe 0.25 mL with successive injection of TOP 0.25 mL for 94-nm SQDs, and 2 M TOPSe 0.25 mL solutions for 105-nm SQDs.

Selenium precursor was injected rapidly to the three-neck round-bottomed flask with vigorous stirring. Reaction solutions were held maintained at 270 °C for 5 min after injection, then the heating mantle was off. The reaction mixture was cooled to room temperature, then diluted by hexanes.

CdSe and CdTe SQD synthesis with different ratios of Cd/SA. For the synthesis protocol in this manuscript, the Cd:SA ratio was varied from 1:1 to 16:1 with the same absolute amount of cadmium, and the other parameters were maintained as in the typical synthesis of CdSe and CdTe SQDs.

Synthesis of SQDs with different amounts of TOP and technical grade TOPO. All syntheses procedures were conducted under air-free condition. To control the amount of TOP, 0, 1, 2.6, 5, or 10 mmol of TOP (Cd:TOP=1:0.5, 1, 1.3, 2.5, 5, respectively) was injected just after the injection of 0.5 mL 1 M TOP-Se solution. Other conditions followed the typical synthesis protocol for CdSe SQD. To investigate the effect of TOPO, TOPO 90%: (1) 3 g of TOPO 90% degassed for 1 h, (2) 12 g of TOPO 90 % degassed for 4 h, (3) 18 g of TOPO 90% degassed for 6 h was used as solvent instead of 6 g of TOPO 90 %. (1/2 times, 2 times, and 3 times TOPO 90 % was used compared to typical synthesis condition.) Other conditions were maintained the same as in the typical condition to synthesize CdSe SQD.

Synthesis of SQDs without technical grade TOPO. In typical synthesis of CdSe SQD, 6 g of technical grade TOPO (90% purity TOPO, TOPO 90%) was used as coordinating solvent. Instead of TOPO 90%: (1) the same amount of 99% purity TOPO, TOPO 99%, or (2) 15 mmol of ODE was used as solvent. Other conditions were the same as typical synthesis condition of CdSe SQD.

Preparation of ultramicrotomed SQD film. Dilute SQDs hexane solution was dropped on a NaCl disk, then evaporated at room temperature. The disk was floated off the substrate onto the surface of a water pool. An epoxy block was used to catch the film such that the sample was on top of the block. The epoxy along with the sample were cured at 60 °C for at least 4 h to ensure good contact between epoxy and the nanocomposite thin film. Thin sections, ~100 nm in thickness, were microtomed using a rotary ultramicrotome and picked up on copper TEM grids.

Ligand exchange. The purified CdSe SQDs were dissolved in 3 mL of toluene (Optical density 1.5 at 400 nm, 0.01 μmol) and stirred for 24 h at room temperature with 0.01 mmol of 3-MPA. Upon completion of the surface ligand exchange, 3-MPA capped SQDs were transferred to a water layer of pH 13. The pH was adjusted by titration using a 2 N NaOH aqueous solution. Water-soluble CdSe SQDs were stable for more than one year. To modify the surface of CdSe SQDs with various organic ligands [oleic acid, octylamine], the purified 1 nmol CdSe SQDs were dissolved in 1 mL of toluene and stirred for 24 h at room temperature with 1 mmol of the ligands. The CdSe SQDs maintained their colloidal stability more than one year.

Size-selective precipitation of SQD. A 1-mL sample of the crude SQD solution was diluted with the same volume of hexane. The diluted SQD solution was held in a glass vial for 1 day without disturbance; relatively large SQDs settled to the bottom of the vial. The supernant solution was carefully extracted without settled SQDs. The extracted solution was centrifuged at 2000 x g for 10 min without any other modification. The supernant solution, which included relatively small SQDs, was discarded and black precipitates on the bottom was washed gently with methanol. The precipitates were collected and dispersed in hexane to induce formation of SQD superlattice.

Sample characterization. A UV-Vis spectrophotometer (Agilent Technology 8453) with quartz cuvettes of 1-cm path length were used for absorption measurements. TEM was performed using a JEOL JEM-1011 operated at 100 kV. The precipitated samples were re-dissolved in hexane and deposited from dilute solution onto a film 3-4 nm thick of amorphous carbon supported by 400-mesh copper grids (purchased from Ted Pella, Redding, California, USA). HR-TEM was performed using JEOL JEM-2200FS operated at 200 kV. SEM was performed using JEOL JSM-7401F. XRD measurements were performed using a Rigaku Max-2500V, which was equipped with a Cu Kα X-ray source, and analyzed samples were prepared on a glass substrate.

Supporting Figures

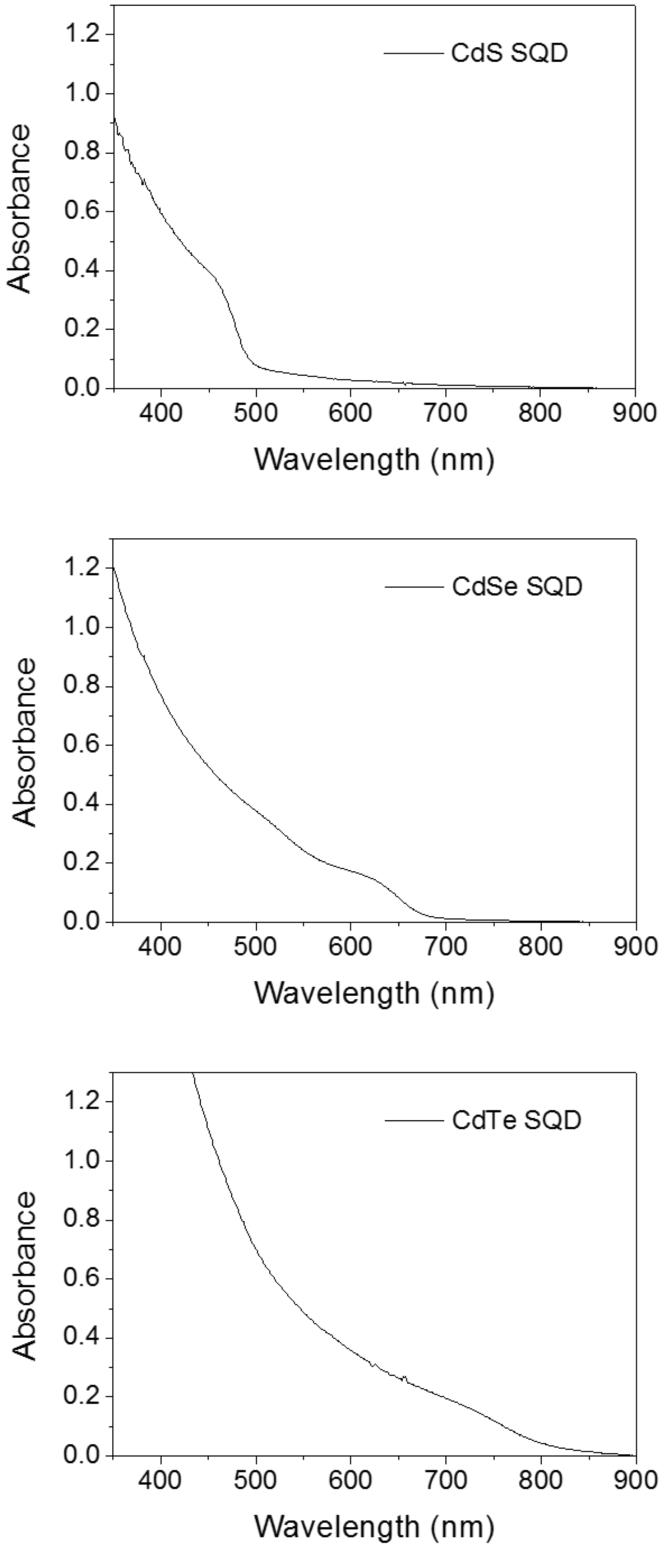

Figure S1. Enlarged absorption spectra of CdSe, CdS, and CdS SQDs.

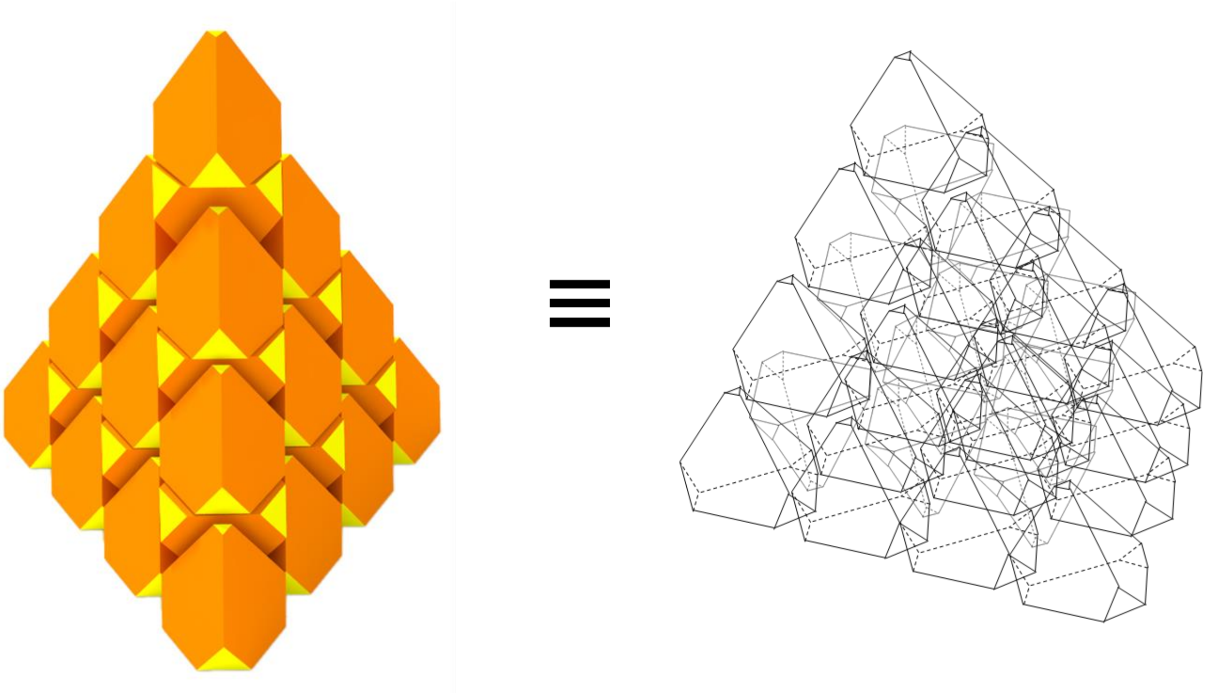

Figure S2. Schematic illustration of internal stacking order of a SS by 30 PSs. A SS with four PSs along each edge consists of twenty upward PSs and ten downward PSs.

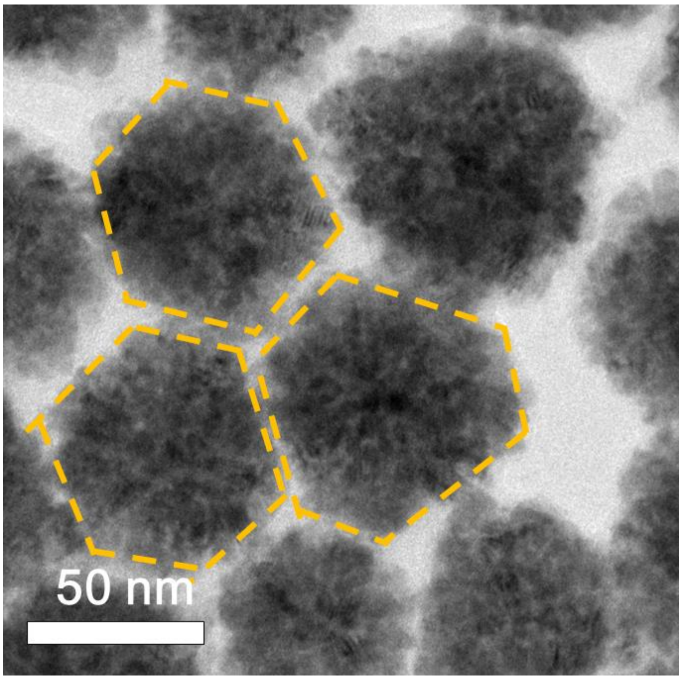

Figure S3. TEM image during Stage (3) of CdSe SQD synthesis. The intermediate structures between TS and SQD were highlighted with yellow dotted polygons.

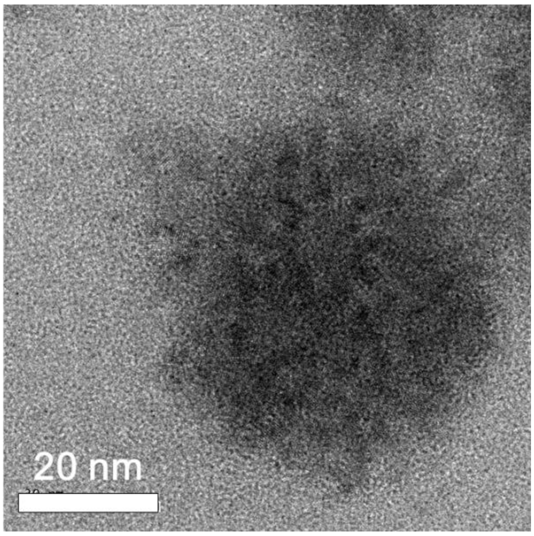

Figure S4. TEM images of a TS attached by a a SS during the transition state from TS to SQD.

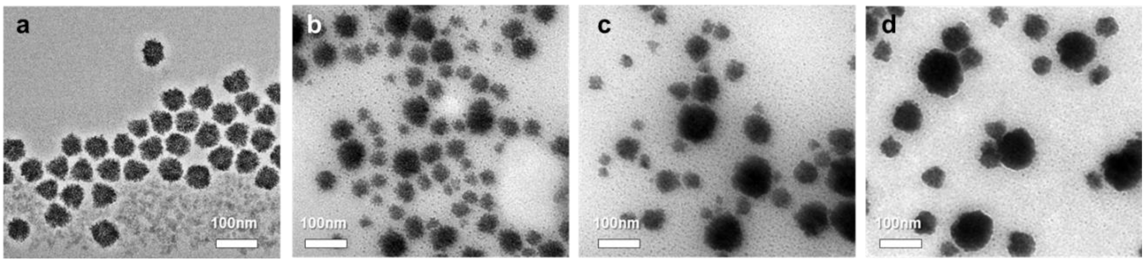

Figure S5. TEM images of CdSe SQDs synthesized with (a) stearic acids, (b) hexadecylic acids, (c) myristic acids, and (d) oleic acids in the ratio of Cd : acid = 8 : 1.

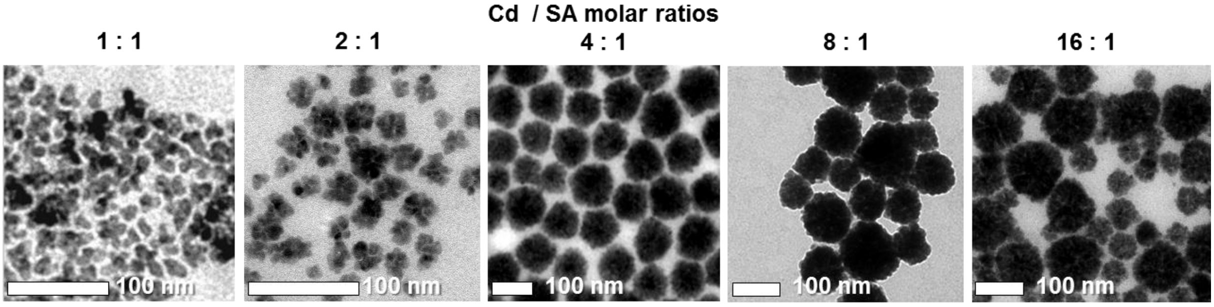

Figure S6. TEM images of CdTe samples when the Cd/SA molar ratio was varied from Cd:SA = 1 : 1 to 16 : 1.