Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Spontaneous Shape and Phase Control of Colloidal ZnSe nanocrystal by tailoring Se precursor reactivity

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1. Experimental Section

1.1 Chemicals.

$Zn(NO_3)_2$•$6H_2O$ (99%), 1-octadecene (ODE, 90%), selenium powder (Se, 99%), lithium trithyborohydride ($LiBH(CH_2CH_3)_3$, super hydride, SHR,) solution in THF (1 M), chloroform (99% anhydrous), and ethanol (99.8% anhydrous) were purchased from Sigma-Aldrich. Oleylamine (OLA, 90%) was purchased from FujiFilm Wako Pure Chemicals Corporation. All chemicals were used as received without further purification.

1.2 Synthesis of ZnSe nanoparticles.

All experiments were carried out using standard Schlenk-line techniques under dry nitrogen. Aliquots were taken using an injector with needle through the rubber plug on the three-neck flask.

Preparation of Se stock solution.

A 0.1 M Se stock solution was prepared by dissolve 3 mmol (237 mg) Se powder in 30 ml oleylamine in a three-neck flask. The mixture was degassed and refilled with N2 three times at room temperature and then heated to 110 °C and kept at this temperature for 0.5 h to remove air and water. Then the solution was heated to 220°C and kept at this temperature for 2 h. After cooling down to room temperature, a brown Se stock solution was obtained and then transferred into a glovebox for further use.

Preparation of Se precursor by reducing Se-oleylamine using superhydride.

Superhydride solution and Se oleylamine solution were kept in a glove box. Then a certain volume of superhydride was injected it into the Se stock solution in a 10-mL vial in the glove box. Color change of the Se-oleylamine solution was observed immediately

after the superhydride was added. The mixture kept in a vial with a septum was removed from the glove box and injected into the flask for the particle growth.

Synthesis of ZnSe Nanodots.

In a typical synthesis, 0.2 mmol (59.5 mg) $Zn(NO_3)_2 \bullet 6H_2O$, 5 mL 1-octadecene and 1 ml oleylamine were mixed in a three-neck flask. The mixture was degassed and refilled with N_2 three times at room temperature and then heated to 110 °C and kept for 0.5 h. At 160 °C, a mixture of 3 mL of Se stock solution and 0.4 ml superhydride solution was injected into the flask. After the injection, the solution was heated up to 200°C and kept for 10 mins, then was further heated up to 260°C and kept at this temperature for 10-120 mins to obtain nanodots.

Synthesis of ZnSe Nanorods.

In a typical synthesis, 0.2 mmol (59.5 mg) $Zn(NO_3)_2 \bullet 6H_2O$, 5 mL 1-octadecene and 1 ml oleylamine were mixed in a three-neck flask. The mixture was degassed and refilled with N_2 three times at room temperature and then heated to110 °C and kept at this temperature for 0.5 h. At 160 °C, a mixture of 3 mL (0.3mmol) of Se stock solution and 0.1 ml (0.1 mmol) super hydride solution was injected into the flask. After the injection, the solution was heated up to 200°C and kept at this temperature for 10 mins. The reaction solution was further heated up to 260°C and kept at this temperature for 10-120 mins to obtain nanorods with varied diameter.

Synthesis of ZnSe Nanorods from magic small ZnSe dots.

The magic small ZnSe dots were synthesized at 200°C and kept at this temperature for 10 mins as described above, then the reaction was terminated by removing the heating mantle. The magic small ZnSe dots was cleaned out from the remaining precursor by

addition of ethanol and centrifugation for 5 mins at 5000 rpm. The cleaned magic small ZnSe dots were dissolved in the mixture of 5ml ODE and 1 ml oleylamine again followed by degas and refill with N_2 at 110℃, then heated up to 260℃ for 120 mins to obtain ZnSe nanorods.

1.3 Sample Characterization.

UV-Vis Absorption Spectroscopy.

UV−vis absorption spectroscopy was performed on an Agilent Cary 4000 spectrometer using 1 cm quartz cuvettes. Purified samples were dispersed in chloroform and transferred to a cuvette, a blank of chloroform solution was used to calibrate the baseline.

Powder X-ray diffraction (XRD).

Powder X-ray diffraction (XRD) patterns were obtained using Cu Kα photons from a Bruker AXS D8 Advance operated at 40 kV and 30 mA. Each sample was dispersed in chloroform to get a condensed solution and then deposited as a thin layer on a low background-scattering silicon substrate. The scanning range was 20-70°.

Transmission Electron Microscopy (TEM).

TEM grids were prepared by depositing one drop of the solution of purified nanoparticles onto a standard carbon-coated copper grid. TEM and High-resolution TEM (HRTEM) was performed using a FEI Talos Fs200x G2 FEG transmission electron microscope with a tungsten filament running at an accelerating voltage of 200 kV.

2. Ab Initio Calculations

High-level calculations using double-hybrid density functional theory were performed to probe the reactivity of the Zn^{2+} cation with the possible selenium dianions present in solution (Se^{2-}, Se_2^{2-}, and Se_3^{2-}). Double-hybrid density functional theory (DHDFT) includes non-local correlation from second-order Møller–Plesset (MP2) perturbation theory in addition to the regular ingredients of hybrid DFT[1]. In conjunction with sufficiently large basis sets, [2] DHDFT methods have been found to give structural parameters and reaction energies that are more accurate than those obtained from DFT and MP2 calculations.[1, 3-7] Here we use the spin-component-scaled DSD-PBEP86 DHDFT method of Kozuch and Martin[6, 7] in conjunction with the quadruple-zeta Def2-QZVPP basis set of Weigend and Ahlrichs. [8] Bulk solvent effects were included using the charge-density-based SMD continuum solvation model of Marenich et al. [9] The Gaussian16 suite of programs was used for all the DHDFT calculations[10].

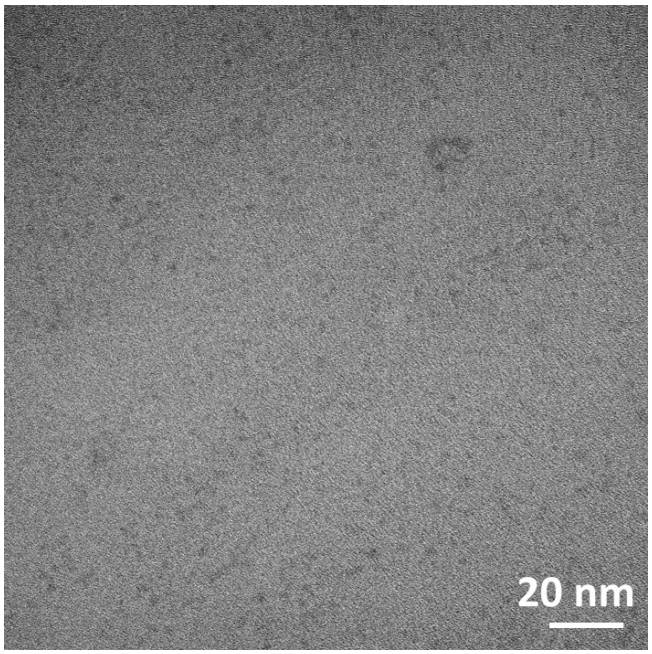

Fig.S1 TEM image of sample 1 in Fig.4

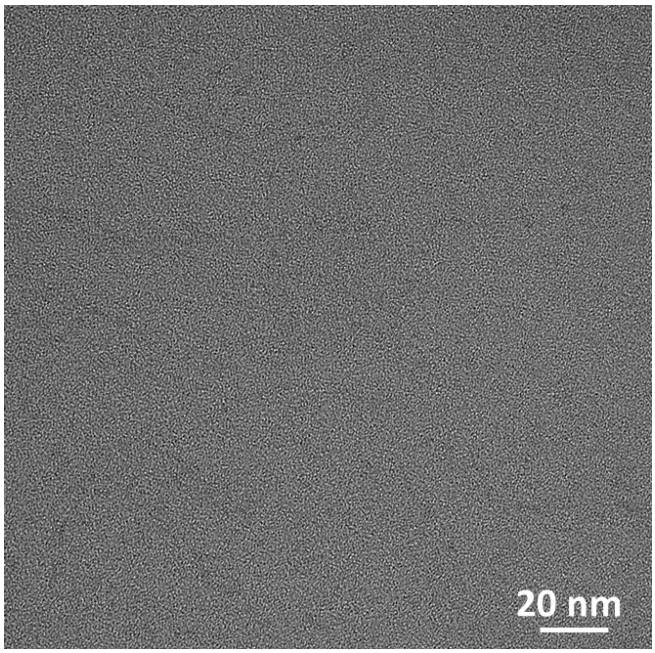

Fig. S2 TEM image of sample 1 in Fig.5

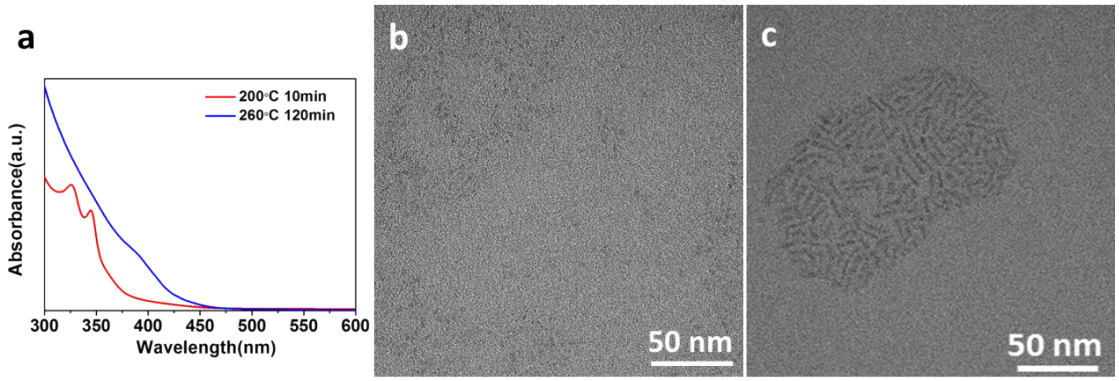

Fig. S3 ZnSe nanorods synthesized from magic-size small ZnSe nanodots based on the oriented attachment mechanism. (a) Absorption spectra. (b-c) TEM images of ZnSe nanoparticles. (b) Magic size nanoclusters. (c) Nanorods.

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