Atomic structure of wurtzite CdSe (core) / CdS (giant shell) nanobullets related to epitaxy and growth

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SUPPORTING INFORMATION

Synthesis of CdSe dot in CdS bulk nanostructures

All synthesis were performed in a nitrogen atmosphere and stored in a glovebox and with pre-dried chemicals.

Chemicals. Cd(Ac)2 (Sigma-Aldrich, 99%), diethylzinc (Et2Zn, Sigma Aldrich, 1.0 M solution in hexane), Oleic acid (OA, Sigma-Aldrich, 90%), octadecene (ODE, Sigma-Aldrich, 90%), octadecene amine (ODA, Siga-Aldrich, 90%), selenium (Strem Chemicals, 99.99%), sulphur (Alfa Aesar, 99%), trioctylphosphine (TOP, Sigma-Aldrich, 90%), trioctylphosphine oxide (TOPO, Sigma-Aldrich, 99%), were used for the synthesis of nanoparticles (NPs).

Solvents. Acetone (Merck), cyclohexane (Sigma-Aldrich, anhydrous, 99%), hexane (Sigma-Aldrich, anhydrous, 99.8%), methanol (Sigma-Aldrich, anhydrous, 99.8%), toluene (Sigma-Aldrich, anhydrous, 99.8%)

Synthesis of CdSe nanocrystal seeds. In advance of the synthesis of the CdSe quantum dots 2 precursors were synthesized. Cd(OA)2-precursor: OA (3.68 g), ODE (25.92 g), and Cd(Ac)2 (0.64 g) were mixed, heated to 150°C, and kept under vacuum for 2 h to form Cd(OA)2. Se-precursor: selenium (4.25 g) was dissolved in TOP (22.5 g) at 50°C, followed by the addition of ODE (35.7 g).

CdSe nanocrystal seeds were synthesized in 50 ml three-neck flask using a Schlenk-line. TOPO (1.11 g), ODA (3.20 g), and Cd(OA)2-precursor (4.9 g) were mixed, heated to 300°C. When this temperature was reached the Se-precursor (5.2 g) was added rapidly. The size of the quantum dots can be tuned via changing the reaction time. This batch was grown/annealed for 10 minutes at 280°C.

The particles were diluted by adding 1 equivalent of hexane. The quantum dots were washed by adding 2 equivalents of methanol and collecting the upper hexane layer (coloured) and add 1 equivalent of acetone to precipitate the QDs. Finally, the nanocrystal seeds were re-dissolved in toluene and stored inside a glove box under nitrogen atmosphere.

Typical synthesis of CdSe/CdS/CdZnS/ZnS nanocrystal. In advance of the synthesis of the CdSe quantum dots the 3 precursors were prepared. The zinc precursor solution (0.1 M) was prepared by dissolving Zn(Et)2 (0.494 g) in oleic acid (5.05 mL) and ODE (19.8 mL) at 310 °C. The cadmium precursor solution (0.1 M) was prepared by dissolving Cd(Ac)2 (1.10 g) in oleic acid (10.83 g) and ODE (43.20 mL) at 120°C under vacuum for 2 hours. The sulphur precursor solution (0.1 M) was prepared by dissolving sulphur (0.032 g) in ODE (10 mL) at 180 °C. The Cd-, Zn-, and Cd/Zn-precursor solutions were kept at about 80 °C, while the sulphur injection solution was allowed to cool to room temperature. For each shell growth, a calculated amount of a given precursor solution was injected with a syringe using standard air-free procedures.

CdSe QDs (1•10-7M of 2.91 nm QDs), ODE (5.0 g) and ODA (1.5 g) were combined and heated up to 150 °C for 1 h to remove all toluene. The reaction temperature was increased to 240 °C and in steps with reaction periods of 30 minutes the precursors were added slowly to grow the cell layer by layer.

- 12 layers of CdS

- 2 layers of CdZnS

- 2 layers of ZnS

Afterwards the reaction mixture was cooled to room temperature and diluted by adding 1 equivalent of toluene. The quantum dots were washed by adding 2 equivalents of a methanol:buthanol (2:1) mixture to precipitate the QDs. Finally, the nanocrystal seeds were re-dissolved in cyclohexane and stored inside a glove box under nitrogen atmosphere.

Quantum yield

Quantum yield has been measured by reference to a dye, Lumogen red 305 (QY 95%), on nanocrystals dispersed in toluene. The measured quantum yield for the sample is 8%.

Figures

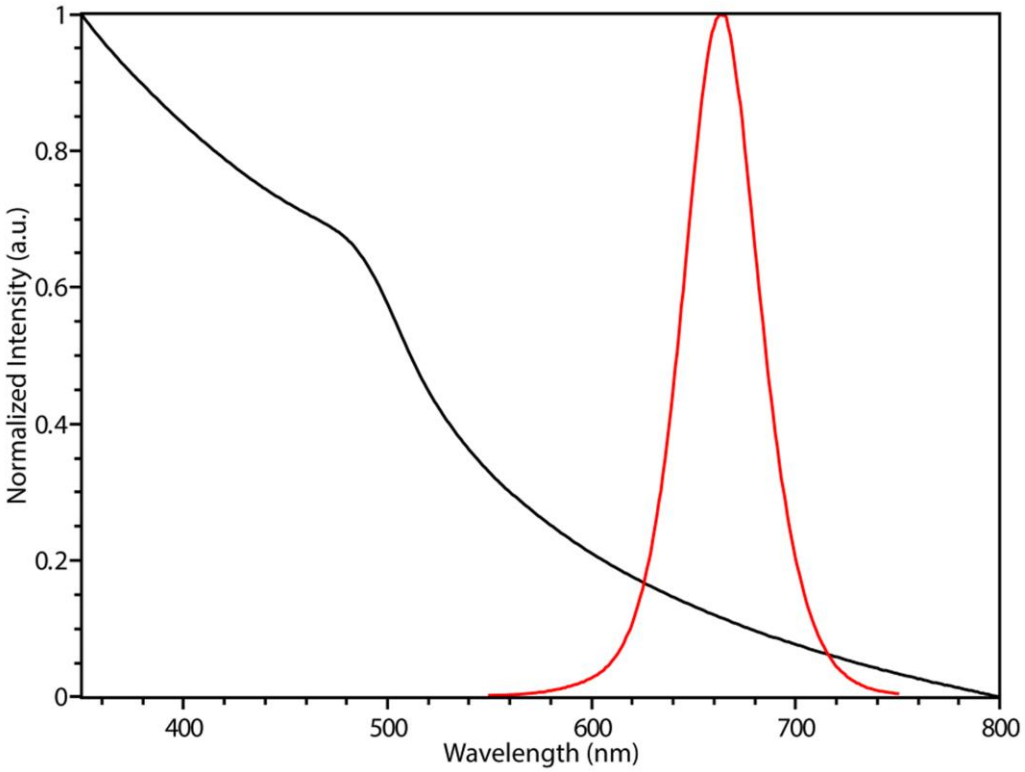

Figure S1. Absorption (black) and photoluminescence (PL) emission (red) spectra of the nanocrystals. The PL shows a maximum at 663 nm (with excitation at 400 nm).

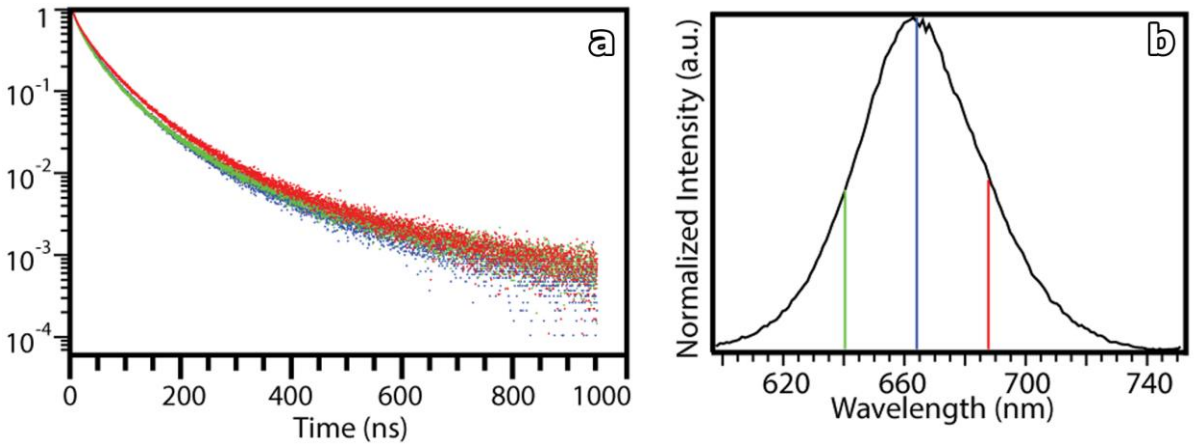

Figure S2. (a) PL decay curves of the nanocrystals acquired respectively at the maximum of the PL emission (blue – 663 nm), at 641 nm (green) and at 678 nm (red); (b) PL emission of the nanocrystals with the corresponding wavelengths at which the decay curves on the left were taken. The average lifetimes are 71.2 ns for the peak, 75.5 ns at the blue side and 78.4 ns at the red side of the peak.

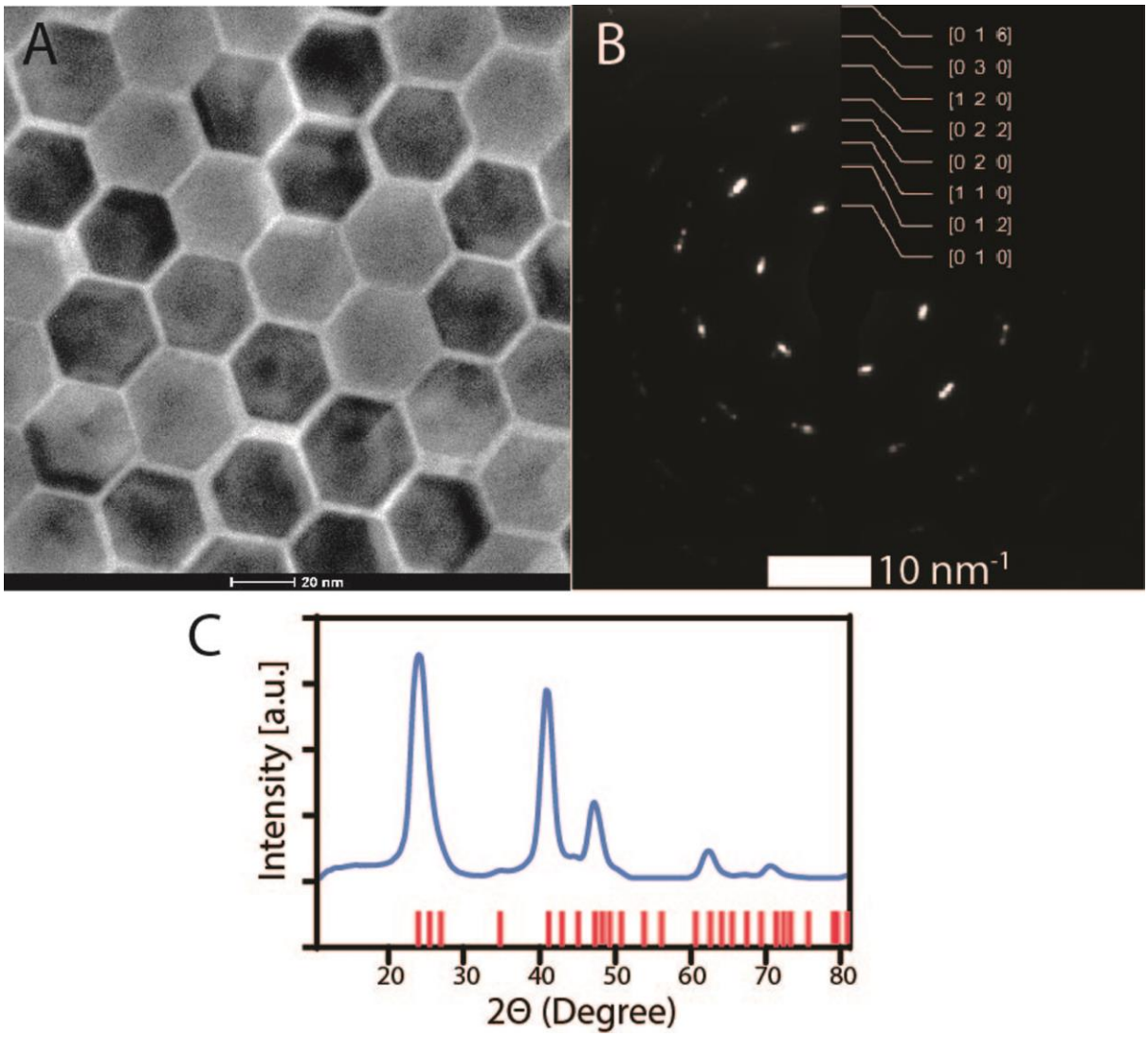

Figure S3. In (A) a self-assembled layer of bullet particles is shown and in (B) the corresponding small area electron diffraction pattern which shows the crystallographic alignment of these particles. In (C) an averaged electron diffraction image is displayed where the particles have a preferred orientation. In red the reference XRD spectra of wurtzite CdS (COD 1011054) is shown, proving the wurtzite crystal structure for these nanocrystals.

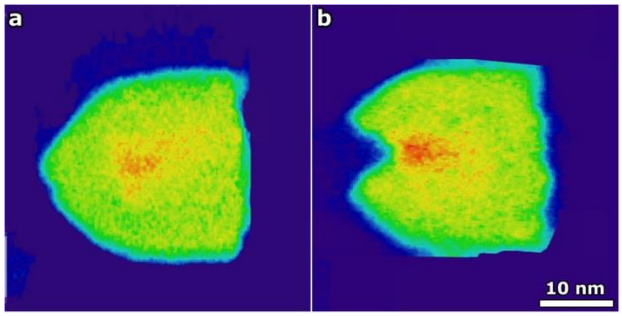

Figure S4. HAADF-STEM tomography on bullet-shaped CdSe/CdS hetero-nanocrystals to detect the position of the CdSe core. The orthoslices through the conventional SIRT reconstruction of the HNCs ending in a tip (a) and ending in a dip (b) provide a faint intensity contrast between the CdS shell and the CdSe core.

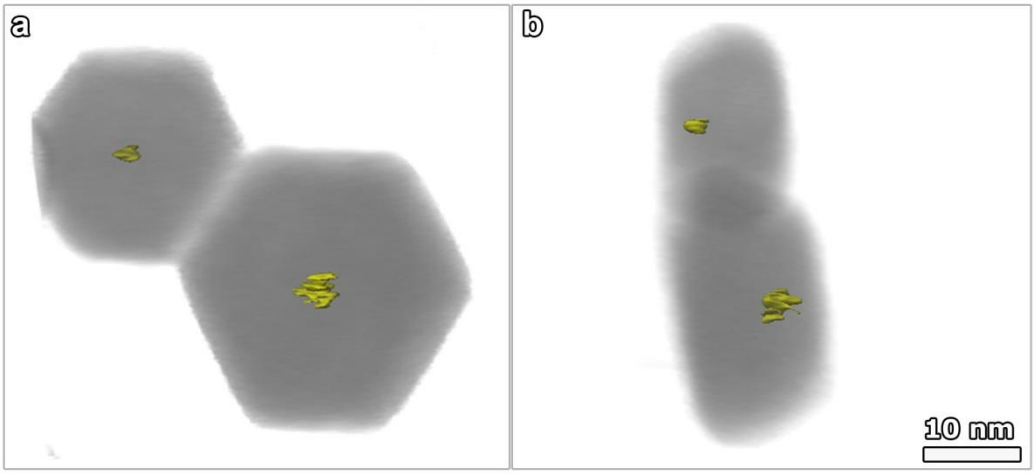

Figure S5. HAADF-STEM tomography on the first stage of the CdSe/CdS nanobullets with indication of the position of the CdSe core. The location of the CdSe core is shown in yellow in the 3D reconstructions (a,b), showing that the core is located closer to one of the basal facets.