Supporting information for: From Sphere to Multipod: Thermally Induced Transitions of CdSe Nanocrystals Studied by Molecular Dynamics Simulations

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Lattice parameters of ZB and WZ bulk CdSe at different temperatures

In order to investigate the lattice parameters of CdSe bulk materials at different temperatures, periodic systems of ZB CdSe (512 atoms) and WZ CdSe (432 atoms) were constructed based on the experimental lattice parameters.[1] The simulated atomic structures of WZ and ZB CdSe were obtained by molecular dynamics (MD) simulations in the Isobaric-Isothermal (NPT) ensemble. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 1 fs. At each temperature, a MD simulation of 0.5 ns was performed on the solids, out of which the first 0.1 ns was used for equilibration. The velocities were rescaled to the target temperatures during the equilibration. The temperatures and the pressure were controlled by the Nose-Hoover thermostat and barostat. The MD simulations were carried out under ambient pressure and the temperature was increased 50 K each step (0.5 ns) from 300 to 1000 K. The lattice parameters of WZ and ZB CdSe bulk as a function of temperature compared with experimental data are shown in Figure S1.

Surface energy calculations

To verify the capability of the Rabani potential[2] to describe the surface properties of CdSe, several CdSe surfaces with both the WZ and ZB structures were simulated by lattice statics simulation (LSS). The GULP code[3] was employed for surface simulations. In these simulations, 7 slab models with the WZ $(11\bar{2}0)$ $(10\bar{1}0)$, (0001) and $(000\bar{1})$ surfaces, and ZB (110), (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces were constructed with two dimensional periodic boundaryl conditions. The unit cells were split into two regions, and all the atoms in region 1 (surface region) were allowed to relax while all the atoms in region 2 (bulk region) were fixed. Then the surface energy can be calculated as follows:

$$E = \frac{E_{\text{surface}} - nE_{\text{bulk}}}{A}$$

where E_{surface} is the energy of all the atoms in the surface region, and n is the number of {CdSe} pairs in surface region, E_{bulk} is the energy per {CdSe} pair in the bulk and A is the surface area of the simulation cell. The slabs of the surface regions and bulk regions were at least 20 Åthick, while the surface areas ranged from 235 to 465 Å^2. To stabilize polar surfaces, "point" reconstructions[4] were applied for the polar surfaces. The surface energies of these CdSe low index surfaces compared with density functional theory (DFT) calculations[7] are shown in Table S1, and a reasonably good agreement was found.

A spherical WZ CdSe NC at 800 K

To compare with the spherical ZB CdSe NC, a spherical CdSe NC with the WZ structure was also constructed. This WZ CdSe nanosphere has the same radius (1.8 nm) and an approxiamatly same number of atoms (882 atoms) as the smallest ZB CdSe nanosphere ($Cd_{440}Se_{440}$). The setup of MD simulation for the WZ $Cd_{441}Se_{441}$ NC is the same as for the ZB NCs. Figure S2 shows the intial and final configurations of the WZ $Cd_{441}Se_{441}$ NC in a MD simulation of 30 ns at 800 K. During the simulation, the WZ $Cd_{441}Se_{441}$ NC changes from a sphere to hexagonal prism, accompanied by the migration of the surface atoms. A structural transition from the WZ structure to a body-centered-tetragonal structure (BCT) is observed.

Bond order parameters

Apart from analyzing the MD simulations by visualization, the transition in the NCs was also examined using a quantitative method. Local bond order parameters, or Steinhardt order paramteres,[8] q_l, were used to analyze the local structures inside NCs and are defined as:

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|q_{lm}(i)|^2}$$

whereby,

$$q_{lm}(i) = \frac{1}{N_{nn}(i)} \sum_{j=1}^{N_{nn}(i)} Y_{lm}(\mathbf{r}_{ij})$$

in which $N_{nn}(i)$ is the number of the nearest neighbors of atom i, and Y_{lm} are the spherical harmonics functions. In our calculations the number of the nearest neighbors is set to 12. The bond order parameters are sensitive to different symmetries depending on the choice of l, and the choice $l = 4, 6$ is commonly used to distinguish face-centered cubic and hexagonal close packed structures.[9–11]

Supporting movies

Supporting Movie M1

This movie shows the sphere-to-tetrapod transition of the 3.6 nm ZB CdSe NC at 800 K. The NC is shown in an (110) orientation. The blue and red spheres are Cd and Se atoms, respectively. The local structures are indicated by the brightness of colors: an atom with a lighter color indicates that it is at a local ZB site and an atom with a darker color indicates that it is at a local WZ site. However, the surface atoms are given a fixed brightness value . The local ZB-to-WZ transition can be found in two WZ legs in this projection: the longest WZ leg consisting of four bilayers (lower left) and another WZ leg consisting of three bilayers (lower right). The length of the movie corresponds to a simulation time of 30 ns.

Supporting Movie M2

Movie recorded during an in-situ heating experiment in the high-resolution transmission electron microscope (HRTEM), a FEI Titan operating at 300 kV while the specimen was kept at a temperature of 400 K. The movie is accelerated by a factor of 10 with respect to real time. The central domain with a triangular shape is the ZB core. At the top and at the right-hand side of the ZB core, WZ pods are attached, while the WZ pod at the bottom-left side has not developed. Strong atomic

mobility is clearly observable at the top atomic layers of the top WZ pod. More details are in the main text.

References

(1) Cohen, M. L.; Chelikowsky, J. R., *Electronic Structure and Optical Properties of Semiconductors;* Springer-Verlag: Berlin; 1988.

(2) Rabani, E., *J. Chem. Phys.,* **2002,** *116,* 258-262.

(3) Gale, J. D.; Rohl, A. L., *Mol. Simul.,* **2003,** *29,* 291-341.

(4) Hamad, S.; Cristol, S.; Catlow, C. R. A., *J. Phys. Chem. B* **2002,** *106,* 11002-11008.

(5) Iwanaga, H.; Kunishige, A.; Takeuchi, S., *J. Mater. Sci.,* **2000,** *35,* 2451-2454.

(6) Benkabou, F.; Aourag, H.; Certier, M., *Mater. Chem. Phys,* **2000,** *66,* 10-16.

(7) Manna, L.; Wang, L.; Cingolani, R.; Alivisatos, A. P., *J. Phys. Chem. B* **2005,** *109,* 6183-6192.

(8) Steinhardt, P.; Nelson, D. R.; Ronchetti, M., *Phys. Rev. B,* **1983,** *28,* 784.

(9) Moroni, D.; ten Wolde, P. R.; Bolhius, P. G., *Phys. Rev. Lett.,* **2005,** *94,* 235703.

(10) Coasne, B.; Jain, S. K.; Naamar, L.; Gubbins, K. E., *Phys. Rev. B,* **2007,** *76,* 085416.

(11) Auer, S.; Frenkel, D., *Adv. Poly. Sci.,* **2005,** *173,* 149.

Table S1: Comparison of the computer surface energies for low-index facets of CdSe, as calculated by lattice statics simulations and calculated by means of DFT.[7]

Structure	Suface	This work (J/m^2)	DFT results (J/m^2)
WZ	$(11\bar{2}0)$	0.43	0.59
	$(10\bar{1}0)$	0.42	0.69
	(0001)	0.65	0.62
	$(000\bar{1})$	0.69	0.78
ZB	(110)	0.44	
	(111)	0.67	
	$(\bar{1}\bar{1}\bar{1})$	0.70	

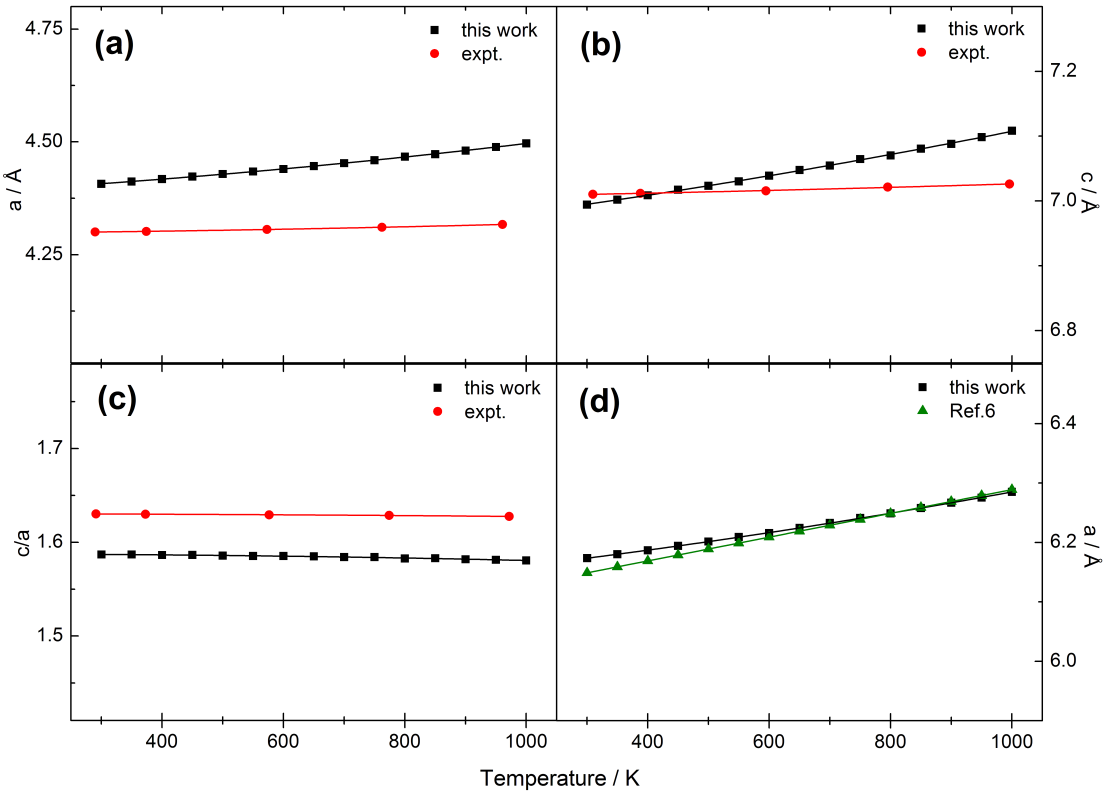

Figure S1: Lattice parameters *a* (a), *c* (b), and the ratio *c/a* (c) of WZ CdSe, and the lattice parameter of ZB CdSe (d) as a function of temperature. The red dots in (a), (b) and (c) are experimental data,[5] and the green dots in (d) are from previous molecular dynamics simulations of CdSe using a Tersoff potential.[6]

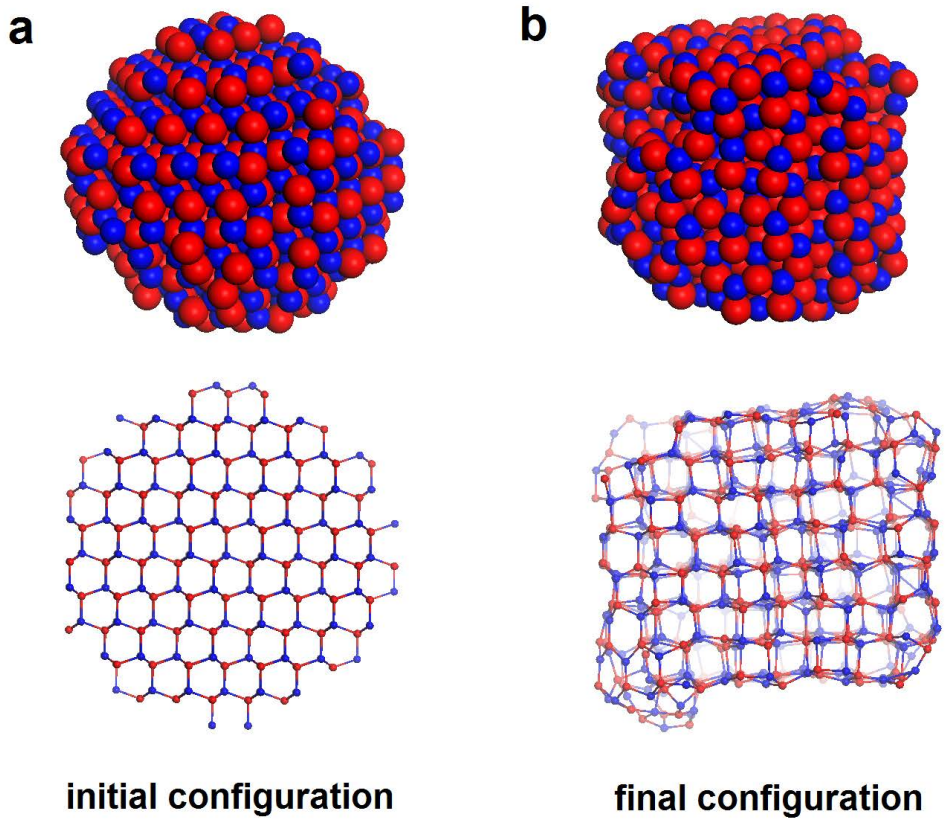

Figure S2: Initial and final configurations of a $Cd_{441}Se_{441}$ NC viewed along the WZ [11$\bar{2}$0] direction from a MD simulation of 30 ns at 800 K. This WZ CdSe nanosphere has the same radius (1.8 nm) as the smallest ZB CdSe nanosphere ($Cd_{440}Se_{440}$). The upper images show the morphological transition by an atomic representation and the lower images show the structural transition. The initially spherical morphology (a) changes to a final morphology (b) of a hexagonal prism while the initial WZ structure (a) transforms to a body-centered-tetragonal (BCT) structure (b). The blue and red spheres are Cd and Se atoms, respectively.