

LETTERS

Threshold Size for Ambient Metastability of Rocksalt CdSe Nanocrystals

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We show that metastable rocksalt CdSe nanocrystals can persist at ambient pressure depending on the physical size of the particle. The size-dependence of the hysteresis loop was measured for the solid–solid transition in CdSe nanocrystals, between four- and six-coordinate structures. A systematic shift of the entire hysteresis loop to lower pressure results in a threshold size of ~ 11 nm for ambient metastability of the six-coordinate rocksalt structure. Smaller nanocrystals transform back to the four-coordinate structure as occurs in the CdSe bulk solid. Surface energy contributions are used to explain the shift. The results have important implications for the optimum synthesis of metastable nanocrystal solids under ambient conditions.

Many solids transform to denser structures under applied pressure, resulting in materials with novel properties without any change in the material composition. High-pressure phases can persist in a metastable state at ambient pressure if sufficiently large energetic barriers hinder transformation to the more energetically favorable structure. The best known example is diamond, which is a high-energy structure of carbon relative to graphite. Researchers have recently succeeded in trapping the high-pressure nonmolecular phase of nitrogen, a very dense material that could have practical use.¹ Metastable solids that are otherwise unavailable in the bulk solid have been engineered in nanoscale materials through complicated synthetic strategies. Some examples include the rocksalt phase of CdS for 100 nm particles synthesized in polymer films in the presence of certain surfactants and the rocksalt phase of CdSe trapped as thin layers electrodeposited on a gold substrate.^{2,3}

Despite interest in materials on the nanoscale, the influence of physical size on structural metastability is not well understood. In comparison, thermodynamic influences are well documented in the literature, such as for the case of synthesis of nanocrystalline alumina systems.⁴ The observation of variable

thermodynamic stability in alumina systems on particle size was explained by the notion that smaller crystallites preferentially favor polymorphs with surfaces of relatively low energy. The influence of physical size on thermodynamics is also known in melting studies on a wide variety of nanocrystal materials, for which a depression in melting temperature is observed with decreasing size.^{5,6} The liquid phase is stabilized relative to the solid in small sizes because surface energy contributions are minimized in liquids.

The influence of size on metastability is comparatively more complicated to understand because thermodynamic effects can be convoluted with kinetic effects in these systems. Theoretical estimates for lifetimes of metastable states can be off by many orders of magnitude because they must include largely unknown details of microscopic transition pathways.^{7,8} The existence of a threshold size for ambient structural metastability was previously predicted from a presumed increase of the transformation barrier with size⁹ or alternatively based on novel crystal shapes with desirable surface energies.¹⁰ A threshold size in the CdSe nanocrystal system is experimentally demonstrated here, showing that thermodynamic surface effects dominate the size-dependent behavior of the structural transformation.

The CdSe nanocrystal system has been used as a model for structural studies.^{11,12} The nanocrystals undergo the same

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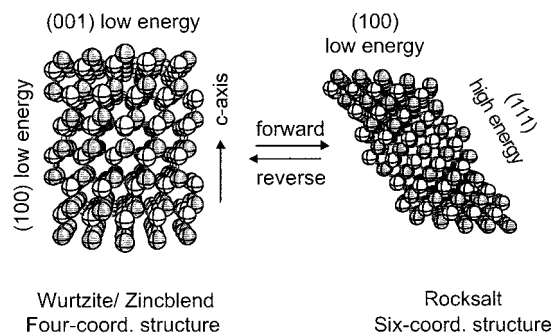


Figure 1. Schematic of the shape change in nanocrystals accompanying the CdSe solid–solid transformation, between four- and six-coordinate structures.²³ Crystallographic indexes of several exposed faces are labeled. The shape change exposes high-energy rocksalt faces, such as the (111) face, which would otherwise not be exposed in an annealed particle. The shape change takes place because the transition is a single-domain process and room temperature is too low for surface rearrangement to occur, as it is below the 575 K limit at which interparticle diffusion occurs and the crystals begin to aggregate.²⁴ The surface energies can be a significant contribution to the total free energy of the nanocrystal considering that over one-third of the atoms are on the surface in 3 nm particles.

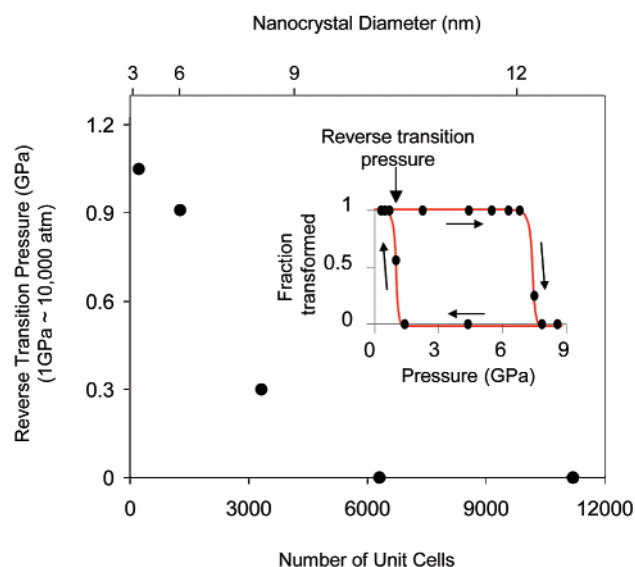


Figure 2. Reverse transition pressure versus size in CdSe nanocrystals at room temperature. The inset is a sample hysteresis loop for 3.5 nm diameter nanocrystals (see ref 12), from which the reverse transition pressure is taken as the point when 50% of the nanocrystals have converted back to the four-coordinate structure. The loop starts at low pressure and proceeds in the direction of the arrows, as the normalized ratio of sample transformed is monitored. Sizes with reverse transitions less than ambient pressure are trapped in the metastable rocksalt structure.

structural transition as in corresponding bulk but are synthesized as nearly monodisperse nearly defect-free crystals with controlled shape.¹³ The thermodynamic phase is a tetrahedrally bonded wurtzite/zinc blend structure at atmospheric pressure. The crystal transforms under pressure to a more densely packed six-coordinate rocksalt structure with an 18% reduction in volume (Figure 1). This transformation exhibits hysteretic behavior characterized by a large difference in pressure required to induce the forward compared to the reverse transition (Figure 2 inset). A previous study reported nearly constant hysteresis widths of ~ 6 GPa for CdSe nanocrystals 3–13 nm in diameter.¹¹ This massive hysteresis compared to the ~ 2 GPa width in CdSe bulk¹⁴ is attributed to the large barriers associated with the

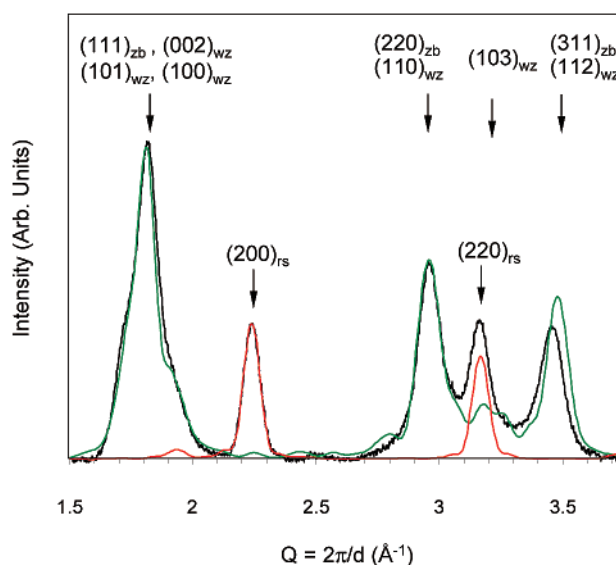


Figure 3. Powder X-ray diffraction (XRD) pattern of 11 nm CdSe nanocrystals after a transition cycle and the release of pressure. The crystallographic indexes are assigned to respective features. The figure shows the presence of metastable six-coordinate rocksalt (rs) nanocrystals, as well as recovered four-coordinate wurtzite (wz)/zinc blend (zb) nanocrystals. The (200) rocksalt peak is exclusive to the rocksalt structure, whereas the (220) peak overlaps with a potential (103) peak of the four-coordinate structure. The red line is the simulated contribution of the rocksalt structure, and the green line is for the four-coordinate structure. This pattern was collected at the Stanford Synchrotron Radiation Laboratory (SSRL), Menlo Park, California on Beamline 10–2 with photon energy of 17 KeV.

single-domain behavior of the transformation. In bulk CdSe, the four-coordinate structure recovers with the release of pressure.¹⁴

Nearly spherical nanocrystals between 3 and 13 nm in diameter with narrow size distribution ($\sigma = 5$ –10%) were synthesized using known methods.^{15,16} Sizes are the average diameter of the particles determined from low-resolution transmission electron micrograph (LRTEM) images. The nanocrystals were coated with an organic ligand (tri-octyl phosphine oxide) and dissolved in ethylcyclohexane, which acts as both a solvent and a pressure-transmitting medium. Pressures between 0 and 10 GPa were applied using a diamond anvil pressure cell (DAC) and measured with standard ruby fluorescence techniques.¹⁷ The transition was monitored through changes in the visible absorption of the sample because the four-coordinate structure is a direct band-gap semiconductor and has an electronic absorbance peak in the visible, whereas the six-coordinate structure is an indirect band gap semiconductor with a featureless absorption spectrum.¹²

The reverse transition pressure from the rocksalt to the four-coordinate structure is shown as a function of nanocrystal size in Figure 2. The transition pressure shifts to lower pressure with increasing size and crosses to a regime of metastability at ~ 10 nm, where the reverse transition pressure is less than 1 atm (~ 0 GPa on the scale). X-ray diffraction (XRD) measurements were collected for an 11 ± 1 nm sample. The sample was pressurized to 9 GPa to induce transformation to the rocksalt phase. The pressure was subsequently released to form air pockets (i.e., atmosphere) and reapplied to < 1 GPa to prevent sample leakage during data collection. Characteristic rocksalt peaks are present in the corresponding XRD pattern, in addition to peaks characteristic of the recovered tetrahedrally bonded phase (Figure 3). The metastable rocksalt phase comprises $\sim 20\%$ of the sample at ambient pressure, as calculated from structure

factors for the respective reflection planes. An additional pattern obtained on residual sample (remaining on a ruby chip placed for pressure calibration) after opening the DAC also contains the characteristic rocksalt peaks.

A threshold size of ~ 11 nm based on the XRD measurements is slightly higher than the 10 nm size indicated by the optical data. This can be attributed to the transformation kinetics because the optical data was collected in three-minute intervals, whereas the XRD patterns were collected over the course of days. Longer waiting times increase the probability that the reverse transformation takes place, resulting in larger threshold sizes. Nevertheless, the size-dependence of the reverse transition pressure is extremely strong, suggesting that the crossover size is "sharp" and particles above the threshold size should exhibit metastable lifetimes much longer than just days.

The primary reason for the mixture of recovered and metastable phases is likely due to the size distribution in the sample, such that the smaller particles in the sample recover while the larger particles remain metastable. The particle sizes in the 11 nm sample were calculated from the Debye–Scherrer broadening of the peaks in the XRD patterns. The diffraction peak widths indicate a structural coherence length in the 11 nm particles equivalent to an average of ~ 10 nm in diameter at ambient pressure. The peak widths for the recovered four-coordinate structure are equivalent to an average ~ 8 nm in diameter, and the metastable rocksalt domain is equivalent to an average ~ 7.7 nm in diameter. The 7.7 nm is consistent with an 18% volume reduction accompanying the structural transformation from the original 10 nm simulated diameter tetrahedrally bonded phase. The smaller 8 nm size for the recovered four-coordinate structure compared to the 10 nm simulated for the entire initial sample supports the explanation that the mixture of phases is largely due to the size distribution of the sample.

An alternative, but unlikely, explanation for the mixture is the coexistence of both phases within individual nanocrystals. Although multiple structures can be transiently present in a bulk solid, the interface is unstable and should grow quickly across a nanocrystal. Furthermore, if part of each nanocrystal were in the rocksalt phase, this would result in significant broadening of the XRD peaks to an estimated 0.4 fwhm in Figure 3. Instead, the experimental peak width corresponds to a domain size of ~ 7.7 nm in diameter, which is consistent with the notion that each nanocrystal must be in either one structure or the other. It is believed that like the 8 nm particles previously shown to be single-domain after a transformation cycle,¹¹ the metastable particles observed here are single domains of the rocksalt structure.

Figure 2 shows the empirical source of the threshold size is a systematic lowering of the reverse transition pressure with size. We emphasize that this trend is directly correlated to a relative shift of the entire hysteresis loop, because the hysteresis width is nearly size-insensitive over this size range.¹¹ A similar shift was previously observed for 2–4 nm particles and is now observed over a significantly extended size range.¹⁸ The shift reflects relative changes of the thermodynamic transition pressure with nanocrystal size, if it is assumed that the location of this pressure within the hysteresis loop does not significantly vary with size. The physical reasoning for the shift is that the surface energy contributions of the nanocrystal are different in the two structural phases. With decreasing crystal size, the thermodynamic transition pressure shifts to favor the structure with the lower surface energy. The rocksalt structure of CdSe nanocrystals should have higher surface energy than the tetrahedrally bonded phase because the shape change ac-

companying the transformation alters the crystallographic facets normally exposed in an annealed particle. The known shape change for the CdSe nanocrystals indicates these exposed faces in the rocksalt structure should be predominantly the (111) faces parallel to the crystallographic *c* axis (Figure 1), and geometrically, this is a particularly high-energy face. In the limit of a bulk solid, the rocksalt structure is not metastable despite minimal influence of the surface, because the hysteresis width is too narrow at room temperature. The threshold size is thus a tradeoff between the thermodynamics favoring larger systems and massive hysteresis occurring in the nanocrystal system. This work is further illustration that surface energy can play a dominant role in determining the relative stability of structural nanocrystalline phases and must be taken into consideration in studies of nanocrystal structural phase changes.

In contrast, the prediction for structural metastability in large nanocrystal sizes based on kinetic effects is unsuccessful for this system. This prediction was based on comparisons to magnetism in nanoparticles, used in everyday storage media.¹⁹ Magnetic and structural transitions are analogous in thermodynamics and statistical mechanics, and their behaviors in nanoparticles are often compared for general insight into transitions in small systems. Magnetic transitions between up and down magnetic moments produce a metastable state in which the material remains magnetized (remanent magnetization) after the removal of an applied magnetic field. The barrier to reversing the magnetization strongly increases with particle size in nanocrystals in the size range under study here, because magnetic reversal involves synchronized coordination of the entire nanocrystal solid.^{20,21} The result is a superparamagnetic limit, ~ 10 nm in Fe:Co alloys,²² which is the minimum threshold size for observable remanent magnetization. Kinetic barriers to the solid–solid transition were previously presumed to similarly increase with nanocrystal size, from which ambient structural metastability in CdSe nanocrystals would be produced as the hysteresis width broadened. However, nanocrystals 2–13 nm in diameter were recently found to transform between solids through nucleation mechanisms and the hysteresis width does not broaden with size.¹¹ As a consequence, the thermodynamics shift rather than a size-dependence of the kinetics is responsible for the structural metastability. Although production of metastable phases in both these nanocrystalline transitions depends on the physical size of the particle, the engineering approaches for producing metastability are now known to be quite different in the two cases.

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