

From Nearly Monodispersed toward Truly Monosized Nanocrystals: Chemical Potential Well during Growth of Nanocrystals

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ABSTRACT: An approach toward truly monosized nanocrystals based on a mechanism of the chemical potential well during crystal growth is presented. Nanocrystals are first grown to sizes corresponding to stable crystallographic configurations in a lower energy state, for example, the magic closed-shell structure. Second, the nanocrystals are treated by a quenching process to suspend the crystal growth, which can place the nanocrystals in the chemical potential well generated by the stable magic closed-shell structure. The last isothermal annealing provides a thermodynamic regime for the nanocrystals to adjust their sizes and morphology to the magic closed-shell structure, which finally narrows the size distribution. By this approach, size deviation of CdSe nanocrystals with 3.6 nm diameter is reduced about 45%. The final size deviation is limited by random temperature fluctuations from a heating source.

Colloidal nanocrystals (NCs) have drawn significant interest from scientists in the past decade because of their unique properties such as the quantum confinement effect that can result in a size-tunable electronic band structure.^{1–4} In the case of the II–VI semiconductors, the emission wavelength strongly relates to the average size of the NCs; for instance, 2.4-nm CdSe NCs have a band-edge emission at 530 nm ($E_g = 2.34$ eV), while 2.9-nm NCs red-shift to 553 nm ($E_g = 2.24$ eV).⁵ The NCs show potential applications in various areas such as biolabeling, lighting, and display devices.^{6–8} However, as-synthesized NCs usually show about 30 nm in full width at half maximum (FWHM) of photoluminescence (PL) peaks, which corresponds to a size deviation of more than ± 0.3 nm for 2.9-nm NCs. This size deviation may result in an inaccuracy in some electrical or optical measurements, or an overlap in size if mean sizes of two NC samples are very close.

Although a post treatment such as size sorting can be used to separate a specific size within a narrow size distribution, the treatment is time-consuming and requires considerable effort. Also, quantity of nanocrystals from the size sorting is limited by the original amount and the initial size distribution of products.¹ Consequently, control of size dispersion is an essential issue for advanced applications of NCs. Precise control over average size and size distribution relies on the understanding of the kinetics of nucleation and growth of the NCs, the methodology of which has been proposed previously.^{9,10} But to achieve a very narrow size distribution remains a challenge, owing to the inconsistent growth rate of each NC that causes size diversity. In an ideal situation toward monosized NCs, all stable nuclei need to form simultaneously and continue to grow at the same rate, which means nucleation and growth stages must be separated.

Nucleation rate could be diminished via a sudden change in the monomer concentrations or temperature, while the growth could also be restricted by limiting monomer flux to the particle surface through adjusting experimental parameters, for example, temperature or precursors, to control the reaction in the diffusion-controlled regime. One of the successful methods is the so-called hot-injection technique. In the first part of this technique, in order to diminish the nucleation rate, a cold precursor of one component (e.g., Se) is injected into a hot precursor of the second component (e.g., Cd) dissolved in a surfactant solvent, leading to an explosive nucleation that decreases the monomer concentration below the critical concentration. The growth is then

placed in a diffusion-growth mode due to the limited monomer content, so finally narrow size-distributed NCs are obtained. Unfortunately, experimentally the nucleation in the hot-injection technique is not completely separated from the growth process where stable particles are still generated when the particle average size increases.¹¹ A possible reason for this is a limitation in the experimental design as the kinetics of the nucleation is too fast to control. As a result, NCs sizes are always dispersive to some extent due to the nonuniform growth process for particles.

A kinetic approach to focusing size distribution of NCs has been presented by Peng et al., who made a second injection of monomers for refocus of the size distribution in the late stage of growth and attributed the size-focusing to the faster growth rate of small NCs at a high monomer concentration.^{5,12} This technique is based on the fact that the consumption of monomers broadens size distribution so a group of growing monomers can recover size distribution to the initial stage. In the kinetic size-focusing approach, both size and size distribution vary during the process, so size distribution of NCs may be only narrowed at the later stage of NCs growth. In this letter, we demonstrate a thermodynamic-based method for achieving size narrowing for NCs, which only leads to a decrease in size distribution but keeps average size constant.

Experimental Section. The method involves three stages, including the growth of NCs to the sizes corresponding to the chemical potential well, a quenching process to remove thermal energy to keep NCs in the chemical potential well, and an isothermal annealing process to reduce a size deviation. In the stage I, CdSe NCs were first grown to the sizes corresponding to stable configurations, for example, 3.4–3.6 nm corresponding to the magic closed-shell structure, by a general hot injection approach.^{13–15} TOPSe was prepared with 1.5 mmol of Se, 2.3 mmol of trioctylphosphine (TOP), and 1.2 mL of toluene. One milliliter of TOPSe was injected into the hot Cd precursor obtained by mixing 0.5 mmol of CdO, 2 mmol of stearic acid (SA), 25 mmol of trioctylphosphine oxide (TOPO), and 40 mmol of hexadecylamine (HDA) at 280 °C. In the present study, the reaction conditions to obtain 3.6 nm NCs were 300 °C/280 °C and 4 min for injection/growth temperatures and reaction time, respectively. In the stage II, the reaction system was immediately quenched by a cold wet cloth to 120 °C to suspend the growth as the desired size of NCs, that is, 3.6 nm obtained.¹⁶ In the stage III, an isothermal annealing process was conducted at 150 °C for 800 s. In the kinetic perturbation experiment, the Se precursor was

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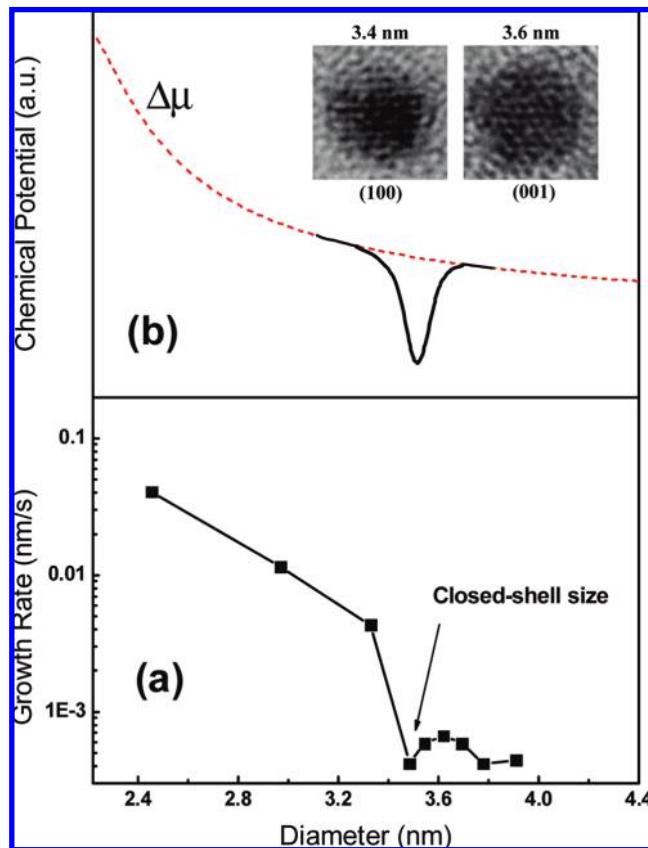


Figure 1. (a) Growth rate vs diameter curve of CdSe NCs at 280 °C (CdO/SA/TOPO/HDA = 0.5/2/25/40 mmol, Se/TOP = 1.5/2.3 mmol, injection = 300 °C).¹⁷ (b) Schematic representation of the chemical potential as a function of the diameter of CdSe NCs. Red dashed curve represents the classic growth curve from conventional thermodynamics. Black curve marks the chemical potential well. The inset pictures show TEM images of the CdSe NC at around the magic closed-shell size.

prepared by dissolving 2 mmol of Se into 2.75 mmol of TOP and diluting by toluene to 7 mL. CdSe NCs were first produced by an injection of 1 mL of TOPSe into the Cd precursor, followed by a series of five 1-mL TOPSe injections that were carried out every minute in succession.

NCs size and size distribution were analyzed by transmission electron microscopy (TEM, JEOL 2010). In photoluminescence (PL) measurements, 0.2 mL of aliquots was taken from solution and dispersed in 10 mL of toluene. For the kinetic perturbation and the isothermal annealing process, size variations of the magic closed-shell CdSe NCs were in the atomic scale. As images of particles edge may lose contrast leading to some error, TEM failed to analyze the variation of particle size. Instead, observation of variations in size and size distribution was made by changes in PL wavelength according to the calibration curve from TEM results.^{2,5,8} In the observation, short wavelength at half-maximum (SWHM) and long wavelength at half-maximum (LWPM) were defined. All samples measured by PL were raw solutions taken from the reaction mixture without any purification or size separation to avoid any loss of particles.

Results and Discussion. Figure 1 presents the growth rate (a) and the chemical potential curve (b) as a function of the diameter of CdSe NCs exhibiting a decrease with an increase in size as predicted by conventional thermodynamics.¹⁷ As NCs size approaches 3.4–3.6 nm (corresponding to a PL peak position of 580–588 nm), the growth rate of the CdSe NCs dramatically decreases, which is considered that

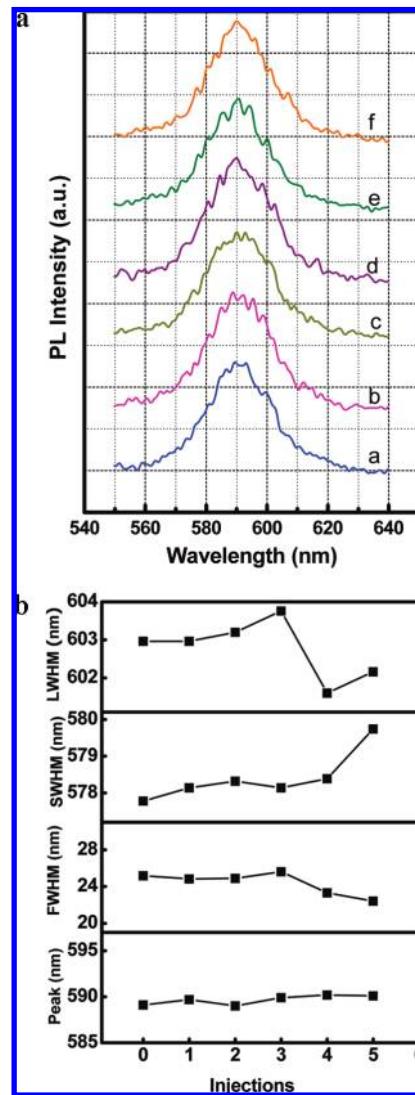


Figure 2. (a) PL spectra from the magic closed-shell CdSe NCs grown at 280 °C and quenched to 120 °C (curve a) and with 1–5 injections of monomers every minute (curves b–g) at 120 °C. (b) Variations of the peak position, the FWHM the SWHM, and the LWPM.

the NCs are in a thermodynamically stable configuration, that is, the magic closed-shell configuration as reported previously.^{18,19} The closed-shell structure, containing a well-defined number of atoms, the fewest surface dangling bonds and displaying maximum stability, is a case of magic-structured NCs. The magic-structured closed-shell NCs are in relatively stable thermodynamic state, which provides a local barrier preventing the NCs from changing their original state. This stable configuration can be considered as a potential well in the classic chemical potential curve. As growing into the magic structure, the NCs meet the chemical potential well that has an energy barrier, which can block the NCs growth to a certain extent. Any change in morphology, for instance, growth or dissolution, can make the magic-structured NCs unstable. Thus, in order to carry on the crystal growth any further the monomers must overcome an energy barrier by forming a stable cluster on the NCs surface.¹⁷ The insets in Figure 1 show TEM images of CdSe NC at around the magic closed-shell sizes.

Figure 2a displays PL spectra of CdSe NCs at around the magic closed-shell size in the kinetic perturbation experiment. Only slight oscillations in the PL peak positions between 588–591 nm appears

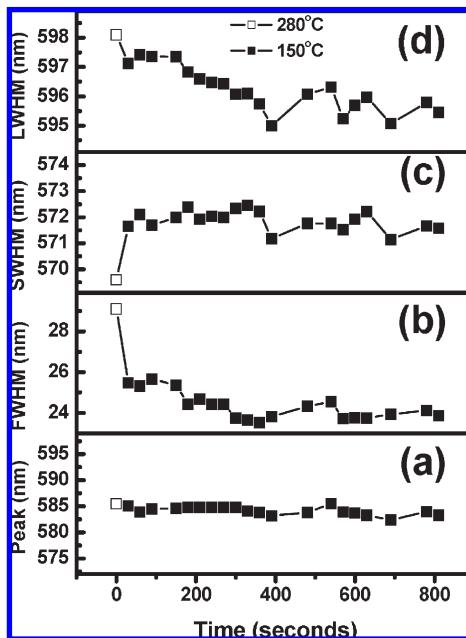


Figure 3. Variations of PL peak position (a), the FWHM (b), the SWHM (c), and the LWHM (d) for magic closed-shell CdSe NCs.

as the extra injections of monomers are carried out, indicating the average size of the NCs is not affected by the kinetic disturbance. This result demonstrates that the NCs are reserved in the chemical potential well. In addition, rearrangement of PL subpeaks during the perturbation process is considered an adjustment of the morphology of NCs. Variations of the PL FWHM, SWHM, and LWHM are shown in Figure 2b. The FWHM of the NCs remains stable in the first three injections because both of the SWHM and the LWHM increase in a similar fashion. But after the fourth injection is carried out, the FWHM reduces as the LWHM dramatically decreases and SWHM still increases, as shown in Figure 2b. This event elucidates that larger and smaller NCs in the ensemble tend to stay at the relative stable closed-shell size. The kinetic perturbation experiment suggests that the magic-structured NCs can sustain a certain amount of the kinetic disturbance, and NCs tend to concentrate at the magic closed-shell size having the enhanced stability that will contribute to a reduction in FWHM or size distribution.

It is thus possible that under a modest external perturbation all NCs slightly deviating from the magic closed-shell sizes could be restored to the stable configurations, which means truly monosized NCs may be obtained in a suitable experimental operation. A methodology is investigated that involved a thermal treatment first by the quenching to suspend the NCs growth, followed by the isothermal annealing to restore the magic closed-shell structure. Figure 3 shows variations in PL peak position, FWHM, SWHM, and LWHM for the magic-structured NCs during a thermal treatment process. In Figure 3a, the PL peak position nearly fixes, indicating that the magic-structured NCs show no significant variation in size in the process and have a high stability. This phenomenon suggests that the monomers have deficient thermal energy to form stable clusters on the NCs surface so that the NCs can continue to grow. Results in Figure 3b show that any NCs slightly deviating from the magic size can achieve a reduction in size distribution during the isothermal annealing and recover to their most stable configuration. The annealing process at 150 °C provides moderate energy for aiding relatively unstable NCs that deviates from the magic size to shrink or enlarge to gain the stable magic structure, presented in Figure 3c,d, which show that NCs concentrate to the magic closed-shell size of the annealing process.

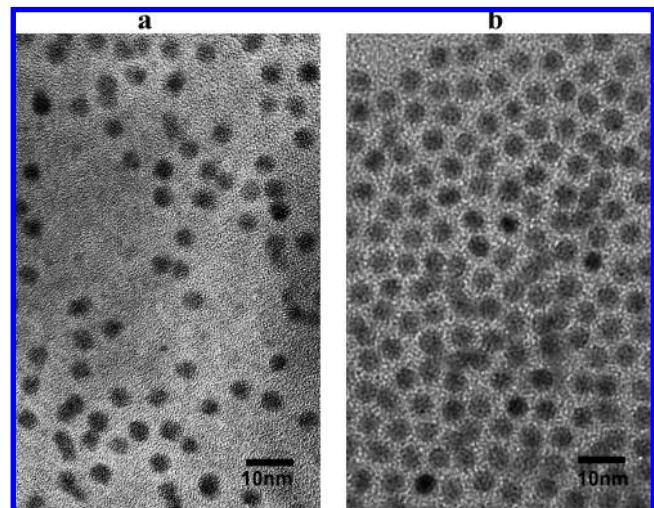


Figure 4. TEM images of CdSe NCs with 3.6 nm in diameter. (a) A sample is collected at 280 °C, with SD = 7.6%. (b) A sample first quenched to 150 °C and annealed for 300 s with SD = 4.2%.

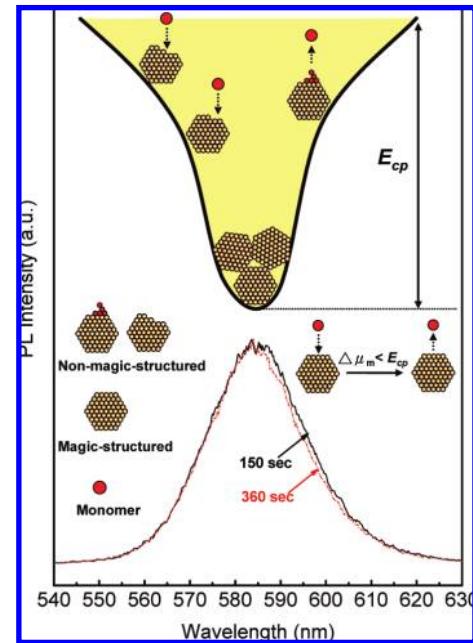


Figure 5. PL spectra of magic CdSe NCs annealed at 150 °C for 150 and 360 s. Inset: a plausible mechanism of the process. E_{cp} is the chemical potential well energy. $\Delta\mu$ is the chemical potential of monomers relative to the surface of NCs.

The experiments carried out between 400–500 s reveal that the oscillation of the NCs size is caused by a temperature fluctuation arising from the heating source, which is found to strongly affect final size deviation, as shown in Figure 3b. A similar event was also observed in optical absorption data (see Supporting Information). During the isothermal process, the absorption spectra shows no significant change in peak position, while the FWHM exhibits some variations, implying that the size distribution changes during the process. The size distribution of NCs broadens as temperature fluctuates.

By this strategy, CdSe NCs, isothermally annealed at 150 °C for 300 s and subsequently cooled to room temperature with rate of about 2 °C per minute, are prepared. As shown in Figure 4a, a sample was collected at 280 °C without isothermal annealing process with a size at 3.6 nm with the standard deviation of 7.6%. With isothermal annealing, CdSe NCs with a size at 3.6 nm with

the standard deviation of 4.2% (reduce \sim 45%) are shown in Figure 4b and in the Supporting Information section. It is believed that a limitation of the degree of the reduction in size deviation is eventually determined by the temperature fluctuation of the heating source. This approach is expected to be able to extend to other material systems that have the magic size state or the immediate stable state. To utilize the immediate state, careful control of the thermodynamic factors of the process is intrinsically necessary. Also, the stability of materials in the states (i.e., energy of the chemical potential well), which relates to the surface/volume free energy and the crystallography, may be considered. Detailed discussion will be published elsewhere.

Variations of PL curves in the isothermal process are responsible for the morphological changes of NCs, as shown in Figure 5. Blue shift of the LWHM of CdSe NCs annealed at 150 $^{\circ}$ C from 150 to 360 s indicates that larger particles in the CdSe NCs ensemble shrink; that is, magic CdSe NCs desorb or detach monomers. A plausible mechanism of the process is illustrated in Figure 5 (inset). As the thermal energy is partially removed, the larger particles cannot overcome the energy barrier built by the chemical potential well, and hence the additional adsorbed monomers are detached, while smaller NCs can grow into the stable configuration. Any NCs slightly deviating from the relative stable sizes will adjust to the magic structures or a relatively stable state by reducing or increasing their sizes or morphology to gain more stability. This adjustment may correspond to variations of subbands in the PL spectra.

The above results reveal a fact that the size narrowing takes place in two ways. One is the kinetic narrowing, and the other is the thermodynamic narrowing. For the first type, the reduction in size deviation is achieved by a faster growth rate of smaller NCs. In this case, both of the NCs average size and size distribution change during the process. For the later case (present study), the reduction is based on the thermodynamic equilibrium, which only narrows down the size distribution while the average size remains a constant. Accordingly, NCs in any relatively stable configuration, for instance, magic closed-shell structures in lower energy states, can be used to prepare monosized particles if precise control of thermal parameters could be achieved. The relatively stable intermediate states should exist in maximal quantities for the NCs; for example, the PL spectra showing subpeaks may indicate the NCs have preferences in the specific sizes, as shown in Figure 2a.

Conclusion. We have presented a concept of the chemical potential well and recommended a thermodynamically controlled process to narrow size distribution of NCs. In a controlled exercise, the size deviation of CdSe NCs with a diameter of 3.6 nm has been reduced from 7.6% to 4.2%. The final size distribution is limited by the temperature fluctuations of the heating source.

Supporting Information Available: Size histograms of nanocrystals obtained by analysis of TEM images. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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