

# Growth of ultrasmall nanoparticles based on thermodynamic size focusing

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Received: 17 July 2012 / Accepted: 15 September 2012  
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**Abstract** This study presents a new concept to synthesize quantum dots or nanoparticles with smaller size (<2 nm) based on the thermodynamic size focusing. Conventionally, control over crystal size is achieved by interrupting crystal growth and/or limiting the reaction rate at lower temperature. Alternatively, we synthesized ultrasmall nanoparticles via a simple thermal quenching-isothermal annealing process called the thermal size focusing. This approach, avoiding the difficulty of controlling the rapid nanoparticles' growth in the interruption method or long synthesis time in the low-temperature process, provides an efficient way for obtaining ultrasmall nanoparticles.

**Keywords** CdSe · Magic size · Nanoparticles · Nanocrystals · Quantum dots · Ultrasmall

## Introduction

In the past two decades, the hot-injection method has been developed to synthesize colloidal semiconductor

quantum dots (QDs) or nanoparticles (NPs) with high quality and high emission efficiency (Murray et al. 1993; Hines and Guyot-Sionnest 1996; Peng et al. 1998, 2000; Peng and Peng 2001; Puntes et al. 2001; Chen et al. 2004; Kim et al. 2005; Zhang et al. 2011; Chen et al. 2011; Kim et al. 2012). Recently, the attention has been directed to the synthesis of ultrasmall nanoparticles (e.g., <2.5 nm) such as magic molecular clusters (Soloviev et al. 2000; Nguyen et al. 2010) and magic-sized QDs (Kudera et al. 2007; Yu and Liu 2009). Magic-sized QDs, which are similar to magic molecular clusters, have a relatively stable thermodynamic state due to specific crystallographic configuration (Yu et al. 2007). For instance, CdSe QDs at around 3.4–3.6 nm in diameter have the closed-shell morphology and the relatively lower surface energy which generates the so-called free energy or chemical potential well during the QD growth (Chen and Kumar 2009a). This unique property has revealed a new synthetic strategy to control particle size and size distribution for QDs, i.e., by constraining QDs in the chemical potential well, where the QDs are relatively stable, to make them gain an extraordinary size and size distribution. For example, one-pot synthesis of QDs with controllable multimodal size distribution was recently reported (Chen and Kumar 2009b). Based on a controlled kinetic-thermodynamic process, QDs with two or three size groups could be sequentially preserved into different chemical potential wells so multimodal-size-distributed QDs ensemble with controllable size distribution can be directly

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obtained in a one-pot synthesis. Moreover, the synthesis of truly monosized QDs has also been proposed by employing a similar strategy. By confining QDs in the chemical potential well via thermal quenching followed by isothermal annealing, nearly mono-sized QDs have been prepared (Chen and Kumar 2009c). In that process, the most stable state of QDs corresponds to the magic size so particles in the QD ensemble will automatically adjust their size or surface morphology to the magic size/morphology via attaching or detaching loose lattices or monomers at the surface in the thermodynamic regime. This thermal curing process is also called thermodynamic size recovery or thermodynamic size focusing (Chen and Kumar 2009c).

In the hot-injection process, smaller QDs or ultrasmall NPs are generally synthesized by interrupting crystal growth via an injection of a cold reagent (Capek et al. 2009) immediately after the precursor injection (e.g., 5 s). Although ultrasmall NPs prepared from hot-injection have the advantages of high crystallinity due to relatively high reaction temperature (e.g., 200–350 °C) and a fairly short reaction time (approximately minutes), however, an interruption of crystal growth may unexpectedly lead to crystal defects at the NP surface and also the process is hard to control since the size enlargement of nanocrystals usually carries out within seconds in the initial growth stage of the hot-injection process. Another synthetic approach, in which ultrasmall CdSe NPs were size selected from magic-sized NP families prepared at a relatively lower temperature (e.g., 80 °C), was also presented (Kudera et al. 2007). In this low-temperature synthetic process (e.g., 80–100 °C), the crystal growth normally underwent a very slow process (days to weeks) and ultrasmall CdSe nanoparticles grown were usually in co-existence with larger particles (Riehle et al. 2009). If the growth time is long enough to reach equilibrium (e.g., weeks), the CdSe nanoparticles could be grown into the magic structure with complete decomposition of larger particles (Kucur et al. 2008). For a system with lower reaction rate, the thermodynamics is more dominant for the crystal growth so nanocrystals synthesized are of good quality and with a stable configuration. Unfortunately, this kind of synthesis normally takes very long time and more energy consumption.

In this paper, we present a synthetic approach to synthesize ultrasmall NPs based on the concept

derived from the chemical potential well, called thermodynamic size focusing. The approach combines the advantage of shorter time of the interruption method with the advantage of high crystal quality of the thermodynamics-dominated crystal growth. The synthetic process involves a thermal quenching to create nanocrystals with higher surface energy and an isothermal curing process to remove the higher-energy surface part of NPs to recover their most stable size.

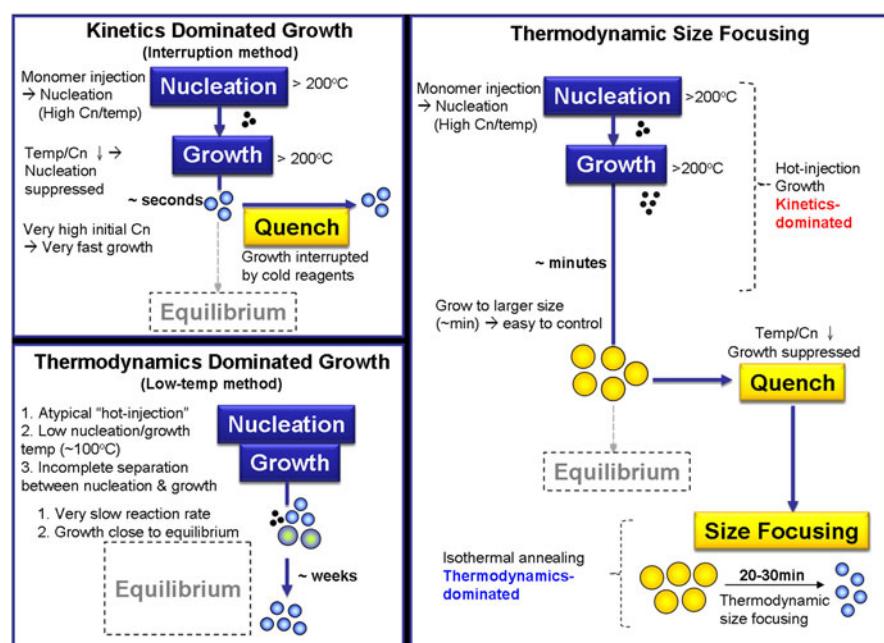
Synthetic process includes three steps, growth of large NPs at a high temperature, quenching of the reaction system to “freeze” the large NPs in a non-magic size, and isothermal annealing to shrink the large NPs via a size focusing. Step I follows the conventional hot-injection method (Qu et al. 2001). Briefly, a cadmium precursor (0.5 mmol CdO, 2 mmol stearic acid, 25 mmol trioctylphosphine oxide, and 40 mmol 1-hexadecylamine) was prepared at 150 °C in a flask. Cold selenium precursor TOPSe (1.5 mmol Se, 2.3 mmol trioctylphosphine, and 1.2 ml toluene) was prepared at room temperature. Both the TOPSe injection and growth temperatures were set 270 °C and magnetic stirring was set to 250–300 rpm. In step II, at about 2 min of the growth time, the stirring was switched off and a quench process was applied for the system to 180 °C with cooling rate ~240 °C/min by an air condenser. In step III, an isothermal heat treatment was applied for the system for 30 min at the same temperature, while the stirring rate was doubled (500–600 rpm) to speed the size focusing. In the isothermal annealing process, the stirring was set to a higher rate to speed up the size reducing process and to avoid the core growing, but it should be noted that the NPs’ surface may be damaged using the stirrer with a very high stirring rate (e.g., ≥1,000 rpm). The overcoating of ZnS shell could be carried out at the same temperature as the isothermal annealing by a typical overcoating process using diethyl zinc and bis(trimethylsilyl) sulfide as precursors (Chen et al. 2004). All samples measured by UV-vis optical absorption and photoluminescence (PL) were in the same concentration and without any size separation to avoid losing any particles. For PL measurement, a blank curve of the precursor collected before the TOPSe injection was used as the baseline to eliminate disturbance of the organic molecules. Particle sizes are translated from UV first excitonic peak energy according to the calibration curve from the experimental data in the literature (Peng et al. 1998;

Yu et al. 2003; Jun and Jang 2005). The PL efficiency of NPs was estimated by comparing with Stilbene 420 in methanol of the same optical density (0.01).

Figure 1 schematically shows the syntheses of ultrasmall NPs by the interruption method (Capek et al. 2009), low-temperature process (Riehle et al. 2009; Kucur et al. 2008), and thermodynamic size focusing process employed in the present study. In the interruption method, both the nucleation and crystal growth take place at higher temperature and the nucleation-growth less overlapped with each other because of a temperature/concentration drop, which suppresses the nucleation process. The interruption method keeps the advantages of the hot injection, i.e., fairly short synthesis time and higher core crystallinity for NPs. In the low-temperature method, the reaction occurs at a lower rate and nanoparticles initially grown are either in a larger size distribution (Kudera et al. 2007) or in coexistence with large particles process (Riehle et al. 2009; Kucur et al. 2008). For thermodynamic size focusing method, in this study, larger CdSe NPs (between 2 and 3 nm) are first grown and then quenched to a lower temperature ( $\sim 180$  °C), followed by isothermal annealing to carry out the size focusing for the sample. Smaller CdSe NPs can be produced from the size reduction of the larger CdSe NPs in the isothermal annealing process.

Experimentally, we first observed that after the initial TOPSe injection into a reaction vessel containing Cd precursor (between 2 and 4 min), the orange reaction liquid changed to light yellow one under room light when a quenching process along with an isothermal treatment were applied for the reaction system, implying that the bandgap energy of the product blue shifted. Figure 2a shows the UV-vis spectra of a NP sample collected at 270 °C with a reaction time of 2 min. The first excitonic absorption is at 543 nm (curve u1), corresponding to  $\sim 3.1$ -nm CdSe NPs in diameter. As the reaction system is quenched to 180 °C, collected NP sample shows a similar PL curve to the above one (data not shown). When the system is further isothermally treated for 10 min, the first excitonic peak of NPs shifts about 90 nm to the high energy region ( $\sim 452$  nm), indicating that the NPs with average diameter  $\sim 1.7$  nm are obtained (curve u2). The UV absorption peak becomes broad due to the disturbance of the released monomers from the dissolution of the larger NPs. Longer isothermal treatment shows no significant effect on the particle size (curve u3), but slightly narrows the peak width. The absorbance of NPs at the high energy side decreases together with a slight increase at about 452 nm after the isothermal heat treatment (470–600 nm, curve u2  $\rightarrow$  u3), showing that the

**Fig. 1** Preparation of ultrasmall NPs or smaller QDs by three different synthetic approaches



treatment not only reduces the concentration of 3.1 nm NPs but also increases that of 1.7 nm NPs.

Corresponding PL spectra of the NPs are shown in Fig. 2b. The NPs initially display a yellow emission at  $\sim 560$  nm together with a broad band at  $\sim 480$  nm caused by a slower injection of TOPSe, which was normally used to produce seeds for growing multi-modal-size-distributed NPs (curve p1) (Chen and Kumar 2009b). After the NPs are quenched to  $170$  °C, followed by the isothermal heat treatment, the intensity of the 560-nm PL peak weakens, while the 480-nm band intensifies and sharpens (curve p2). The FWHM of the 480-nm band narrows from 106 nm (curve p1) to 40 nm (curve p2) and 31 nm (curve p3), exhibiting a size focusing event. Moreover, longer heat treatment leads to an enhancement of the 480-nm PL peak (curve p3) together with decreasing intensity of the 560-nm PL peak. The result is consistent with the UV-vis spectra, demonstrating that the production of the 1.7-nm NPs are based on the size reduction of the 3.1-nm NPs. Inset in Fig. 2b displays a photo of CdSe NPs taken in different stages (270, 180 °C as quenched, and 180 °C after the isothermal annealing). The color changes from yellowish to blue under 365-nm UV light irradiation.

CdSe NPs from thermal size focusing process have similar PL spectra to those prepared by the conventional method and could be directly overcoated with a high bandgap shell in the later stage of isothermal

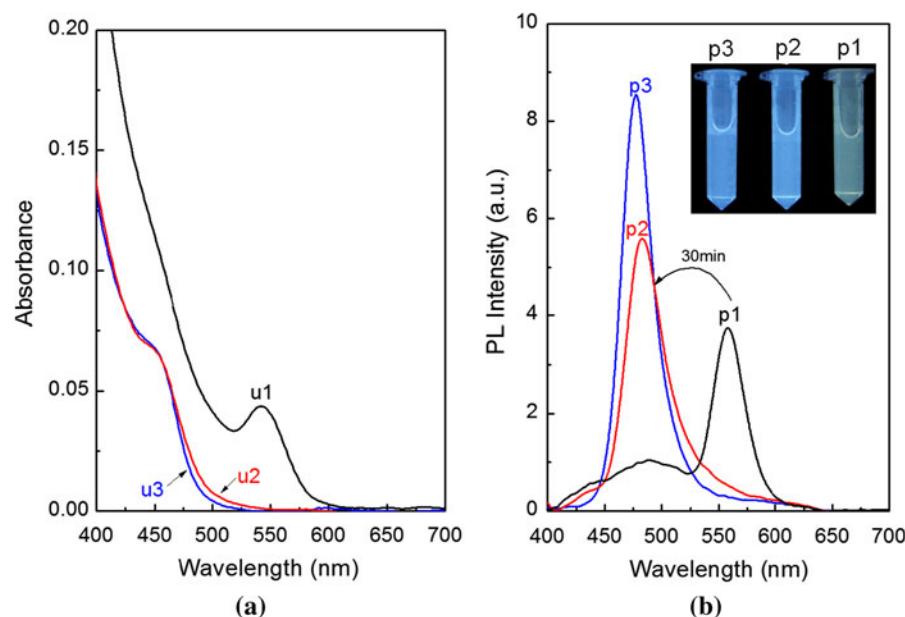
annealing. Figure 3 gives PL spectra of the 1.7-nm CdSe NPs (curve a) and the NPs overcoated by ZnS (curve b and c, excited by 365- and 325-nm UV source, respectively) grown by *in situ* overcoating. Slight red shifts in both PL and UV spectra (inset in Fig. 3) for CdSe/ZnS NPs prove that Zn and S elements did not alloy with CdSe. The PL efficiency of bare CdSe NPs estimated to be 17.2 %. With the ZnS overcoat, PL efficiency of the NPs increases up to 72.5 %, indicating that CdSe NPs are of high quality and ZnS effectively passivates CdSe cores.

Shrinkage of large colloidal NPs toward small ones in the growth process is interesting since a small particle is normally less stable than a large one according the classic thermodynamics. For example, in the Ostwald ripening process, small particles dissolve in a solution and feed large particles to grow because of the relatively high solubility of the small particles. Note that Ostwald ripening takes place close to equilibrium between monomers and particles, and the particles in the system are assumed to have smooth surface and the variation of the solubility between particles is simply caused by different surface curvature. The size reduction of the larger crystals in the present system is caused by the swap of growth to dissolution due to the thermal quenching process. The thermal quenching is used to produce 3.1-nm NPs with more surface lattice defects because the interruption of the crystal growth could lead to structural defects, as

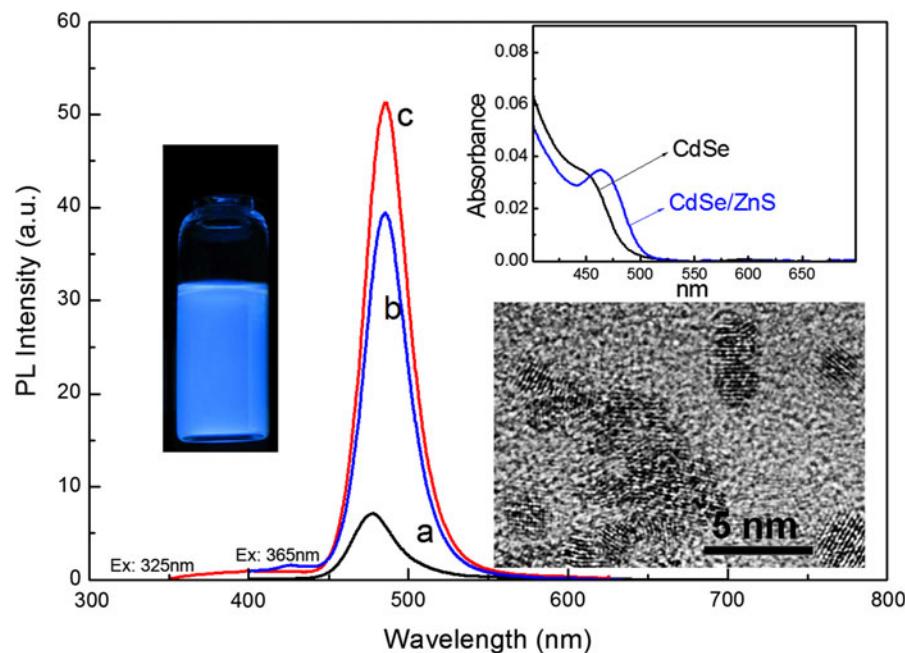
**Fig. 2** **a** UV-vis absorption

spectra of CdSe NPs prepared at 270 °C (curve u1) and isothermally annealed at 180 °C for 10 min (curve u2) and 20 min (curve u3). All samples were without purification.

**b** Corresponding photoluminescence spectra; curves p1, p2, and p3 correspond to curves u1, u2, and u3. Inset in **b** is a photo of CdSe NPs dispersed in hexane loaded in centrifuge tubes irradiated by 365 nm UV light. The solution emits mixed yellow/blue light and changes to sole blue light ( $p1 \rightarrow p3$ ). (Color figure online)



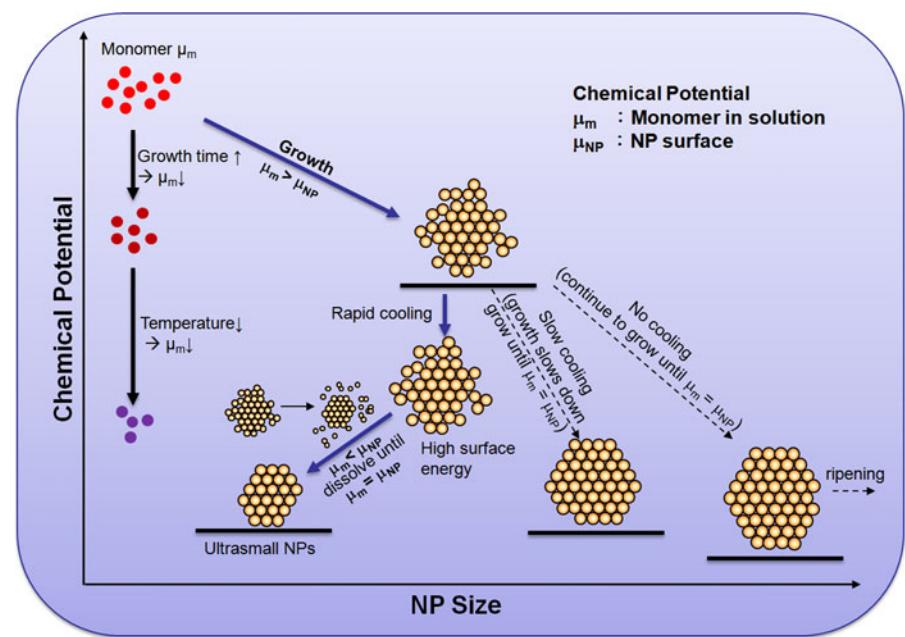
**Fig. 3** PL spectra from CdSe (curve a) and CdSe/ZnS NPs (curves b and c, excited at 365- and 325 nm, respectively) synthesized by size focusing at the magic state via post-annealing. Inset (up) is UV spectra of CdSe and CdSe/ZnS NPs. All samples were without purification. The inset image (down) shows a high resolution TEM image and a digital photo of CdSe/ZnS NPs in toluene under 365 nm UV (left)



shown in Fig. 4. In that situation, the larger particles could have higher solubility than those smaller ones having stable crystallographic configuration. In addition, the temperature drop can also result in decreasing monomer concentration. So, the chemical potential at the NP surface ( $\mu_{NP}$ ) could be higher than that of monomer ( $\mu_m$ ) in the solution and thus the monomer

flux could reverse to the other side. Finally, the isothermal treatment provides gentle environment for relatively unstable larger particles to recover their more stable form through detaching loosely surface lattices or attached monomers. Therefore, a negative growth rate occurs and larger NPs shrink in the solution. On the other hand, for those which undergo a

**Fig. 4** Plausible mechanism of formation of QDs or NPs with a smaller size via control over a thermal quench-isothermal annealing process (thermodynamic size focusing)



slower cooling process, the crystal growth mechanism such as grain growth or lattice reorganization still continues so the final particle size slightly increases after the cooling (middle image in Fig. 4). If there is no cooling applied, the crystal growth carries on and ends when  $\mu_{NP}$  is equal to  $\mu_m$ , i.e., equilibrium between the crystal surface and monomer of the solution establishes.

In summary, ultrasmall NPs have been synthesized by thermodynamic size focusing method. The process includes two essential steps; larger unstable NPs created by a thermal quenching process, followed by an isothermal heat treatment to reduce NP size. The approach, which avoids the difficulty of controlling the rapid growth of NPs in the initial growth stage and has fairly short time ( $\sim 1$  h), provides an alternative way to obtain ultrasmall NPs.

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