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Thermodynamic Equilibrium-Driven Formation of Single-Sized Nanocrystals: Reaction Media Tuning CdSe Magic-Sized versus Regular Quantum Dots

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A concept for the fundamental science of nanoparticle synthesis, thermodynamic equilibrium-driven formation of colloidal single-sized nanoparticle ensembles, is proposed and demonstrated in this manuscript, which addresses the controlled formation of CdSe magic-sized and regular quantum dots (MSQDs and RQDs). During formation, the former are magic-sized nuclei without further growth in size, while the latter experience nucleation and growth. Both MSQDs and RQDs exhibit bandgap emission, while the former have homogeneous spectra broadening only and the latter both homogeneous and inhomogeneous spectra broadening. The former are single-sized and the latter have size distribution. With continuous and homogeneous nucleation, the thermodynamically driven formation of MSQDs was realized via our one-pot noninjection approach, which features highly synthetic reproducibility and large-scale capability. With the proper tuning of the synthetic parameters, such as the nature of the reaction medium, that affect the thermodynamic equilibria, various CdSe MSQDs and RQDs were synthesized discriminately under otherwise identical synthetic formulation and reaction conditions; the reaction media were noncoordinating 1-octadecene, coordinating trioctylphosphine, and mixtures of the two. The nature of Cd precursors, affected also by the reaction media, plays a major role in the formation of MSQDs versus RQDs. The present investigation on the thermodynamically driven formation of CdSe single-sized nanoparticles via tuning of the reaction medium, mainly, brings novel insights into the formation mechanism and into the surface ligands of the resulting colloidal nanocrystals. More importantly, the present study provides novel experimental design and approaches to single-sized nanoparticles desired for various applications.

1. Introduction

The leading-edge research in the synthesis of high-quality nanocrystals aims at production of single-sized quantum dots (QDs).^{1–3} Colloidal semiconductor photoluminescent (PL) QDs have attracted significant attention due to their unique optical properties, which are tunable through their sizes, compositions, and structures.^{4–7} These properties give rise to significant potential in a wide range of technological applications. For the past decade, the QD synthesis has been explored intensively for both fundamental research and application-oriented research, such as for biolabeling and bioimaging,⁵ light-emitting diodes (LED),⁶ and photovoltaic devices.⁷ Both research and application efforts demand high-quality QDs with narrow size distribution, and ideally single-sized QDs without inhomogeneous spectra broadening.⁸ Several research groups have developed various wet-chemistry approaches to high-quality QDs with size distribution; they are termed as regular QDs (RQDs). The most

successful and widely used hot-injection method involves a rapid precursor injection at relatively high temperature and the subsequent growth at a relatively low temperature.^{9,10} However, compared to a noninjection approach, the hot-injection approach can be problematic, regarding its scale-up capability and reproducibility.^{11,12} Meanwhile, there is an outstanding need for a large quantity of high-quality QDs aiming at various commercialization opportunities such as in optoelectronic devices. Therefore, it is of particular importance in the QD research field to develop advanced synthetic methods.

The formation of nanocrystals involves crystallization processes which consist of, typically, nucleation and crystal growth.¹³ The nature of the nucleation and growth of a crystal is governed by both thermodynamic and kinetic factors, which play significant roles on the size and size distribution of resulting crystals. Thus, typical crystallization processes are highly variable and difficult to control, leading to crystals with broad size distribution. Without preferential nucleation sites, homogeneous nucleation occurs randomly and spontaneously in a uniform and supersaturated solution. With the formation of nuclei, nucleation is normally accompanied by the creation of interfaces at the boundaries of the newly formed solid phase.^{14,15} Therefore, nucleation involves the very first solid-phase evolution with a phase transformation from solution to solid. For the occurrence of a spherical nucleus with radius of r , there is

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change in Gibbs free energy described by classical nucleation theory

$$\Delta G = (4/3)\pi r^3 G_v + 4\pi r^2 \sigma$$

G_v is the free energy per unit volume, and σ is the free energy per unit area. When ΔG , the overall change in free energy, is negative, nucleation is favored. For a small hypothetical nucleus, the decreased energy $(4/3)\pi r^3 G_v$ is not sufficient to overcome the $4\pi r^2 \sigma$ needed to form the interface, and nucleation does not take place. For the nucleation to proceed, the nucleus size must reach a critical value, r^* , where $dG/dr = 0$, $r^* = -2\sigma/G_v$. When the solution-solid phase transformation is fully reversible, the size of the nucleus is usually determined by the thermodynamic conditions, such as the equilibrium concentrations of solute molecules and the nanocrystals (in terms of population or number per unit volume of the solution). This classical nucleation theory only describes a “static” picture on the nucleation (i.e., whether or not a particular size nucleus could form and exist) but does not provide any insight into control of the nucleation dynamic processes. After nucleation, the mechanisms of crystal growth in size could be due to monomer addition or nanocrystal aggregation/recrystallization. Traditionally, it has been acknowledged that the formation of nanocrystals with narrow size distribution requires fast nucleation followed by slow growth without any further nucleation.^{16,17}

When a chemical reaction is involved in a crystallization process, it is particularly important to understand and to separate, if possible, the thermodynamic and kinetic processes of the formation of the final crystal particles.^{18,19} Often, the kinetics of a chemical reaction plays a critical role on the size and size distribution of the nanocrystal ensemble; thus, it is difficult to scale up even with complicated process control. The challenge is to design a novel synthetic approach that is simple in process control and leads to colloidal nanocrystals that are identical in size and thus free of size distribution.

Here, we propose a pioneering concept to the fundamental science of nanoparticle synthesis, thermodynamic equilibrium-driven formation of single-sized nanoparticles without size distribution. Such a concept can be accomplished readily with an experimental approach taking advantage of the effect of thermodynamic equilibria that can be tuned by simple synthetic conditions including reaction media and temperature to control the nucleation. In an ideal system, the formation of single-sized nanocrystals would be determined by the thermodynamic equilibria via the reactant precursors, with little effect of the chemical reaction kinetics involved. In other words, chemical reactions are not the dominant or controlling step in the nucleation event, but the chemical equilibria among the reactant precursors and nanocrystal products are. Such an equilibrium-driven process could be readily scaled up due to the simplification of process operation and control.

Our research team has been actively developing one-pot noninjection approaches to various high-quality PL QDs, including CdSe, CdTe, CdTeSe, CdS, CdZnS, PbS, and CdP.^{1,2,12} Such a synthetic protocol features easy handling with high synthetic reproducibility, resulting in the formation of MSQDs and RQDs. The various MSQDs exhibiting bright bandgap emission can be engineered in pure form. The colloidal MSQDs are single-sized essentially and their bandwidth is similar to that of a corresponding single QD with only homogeneous line broadening.^{1,2,8} For example, one magic-sized CdSe nanocrystal ensemble with bandgap emission was produced in pure form

in 1-octadecene (ODE) and named Family 463, according to its bandgap absorption peaking at 463 nm.¹ This MSQD ensemble exhibits a bandwidth of ~ 8 nm in full width at half-maximum (fwhm), which is similar to that of a CdSe single dot.⁸ It has been acknowledged that the size and concentration of colloidal QDs can be estimated readily by their absorption peak position and absorbance from their absorption spectra, respectively.²⁰ For example, the absorption peak position redshifts when there is an increase in the nanocrystal size, while the optical density at the peak varies when there is any change in the nanocrystal concentration. Accordingly, the absorption spectra of colloidal QDs provide valuable information on their development during synthesis. It is important to point out that there is no growth in size for these MSQDs after homogeneous nucleation, as indicated by their fixed absorption peak position.^{1,2} The MSQDs are thus magic-sized nuclei, whose formation is thermodynamically driven and controlled. At present, there is little information available about the atomic structure of these nuclei; the present study does not address such a structure issue but focuses on their formation mechanism.

Meanwhile, it is necessary to point out that different opinions were expressed about the nanocrystals that exhibited a similar absorption doublet with the lowest energy peaking at ~ 463 nm and the second lowest at ~ 433 nm: magic-sized quantum dots (whose size was argued to be 2.1 nm based on diffusion ordered spectroscopy (DOSY) NMR),¹ magic-sized clusters (whose size was claimed to be unknown),^{21a} and 2D platelets (whose thickness was ~ 1.97 nm).^{21b} Nanoribbons or nanosheets were also recommended to an absorption doublet with first excitonic transition at 449 nm and second at 423 nm.^{21c} It is questionable that the 2D platelets and nanoribbons observed under transmission electron microscopy (TEM) were dispersed exhibiting the absorption doublets. We deem that it is the magic-sized clusters/quantum dots (MSQDs) that exhibit such absorption.^{1,21a}

In this manuscript, we present a systematic description on the concept of the thermodynamic equilibrium-driven formation of single-sized nanocrystals, illustrating how the equilibria could be tuned to become dominant factors via controlling the reactant precursors, and thus, achieving the control of the nucleation dynamics and the size of nuclei without further growth. Specifically, this concept is demonstrated with the formation of CdSe MSQDs versus RQDs in a noninjection-based process, whose synthetic parameters were controlled including the nature of the reaction medium. We are proposing a nonclassical model on the formation of single-sized nanocrystals that only involves nucleation without the next growth stage. Besides the classical nucleation theory based on the Gibbs free energy, we believe that the nucleation can be controlled through tailoring the thermodynamic equilibria by the reactant precursors, with little effect by the chemical reaction kinetics. With the noninjection synthesis approach, the formation of the MSQDs can be achieved by proper chemical formulation and simple temperature control. Cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) and elemental selenium (Se) were used as Cd and Se sources, respectively, and an acid was used (such as myristic acid (MA) to produce Cd reactant precursor, $\text{Cd}(\text{OAc})-(\text{OOC}-(\text{CH}_2)_{12}-\text{CH}_3)$, whose reactivity with Se reactant precursor was tunable). Experiments were conducted with fixed feed molar ratios of 2.7MA–4Cd–1Se and a Se concentration of 10 mmol/kg. The control of the formation of the pure-form MSQDs and RQDs was accomplished by varying the coordinating nature of the reaction medium, which was noncoordinating 1-octadecene (ODE), coordinating trioctylphosphine (TOP), and mixtures of the two at different weight ratios. The development of the

nanocrystals was monitored by the temporal evolution of the optical properties of the QDs sampled at temperatures ranging from 120 to 240 °C or at a constant temperature such as 150 °C with different growth periods. Several interesting results have been found. (1) In ODE, CdSe MSQD Family 463 was developed. (2) In ODE and TOP mixtures with less than 10% TOP (by weight), both MSQD Family 395 and Family 463 were produced. (3) In the mixtures of 10–50% TOP, only RQDs were formed. (4) In the mixtures of 65% TOP and up and in pure TOP, another single-sized ensemble, Family 408 was detected in pure form at ~120 °C. With these results, it is clear that the effect of the reaction medium and temperature on the controlled formation of the CdSe MSQDs and RQDs is significant. The present study brings insights on the formation mechanism of the MSQDs into thermodynamic equilibrium driven rather than reaction kinetics driven. The present investigation provides the first example of the thermodynamic equilibrium effect of the reaction medium on the formation of single-sized nanocrystals with only nucleation and no subsequent growth.

2. Experimental Section

2.1. Synthesis of CdSe Nanocrystals. All chemicals used are commercial available and were used as received. Cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 99.999%) and selenium powder (325 mesh, 99.5%) were from Alfa Aesar. The acids used included butanoic acid (C04), hexanoic acid (C06), octanoic acid (C08), 5-(4-biphenyl)valeric acid (BVA), myristic acid (MA, C14), lignoceric acid (C24), melissic acid (C30), 2-*n*-hexadecyl stearic acid (HSA), and tetradecylphosphonic acid (TDPA); they were purchased from Sigma-Aldrich Canada (with the highest purity available). 1-Octadecene (ODE, tech. 90%), trioctylphosphine (TOP, tech. 90%), and trioctylphosphine oxide (TOPO, 99%) used were purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI).

For a typical synthesis, 0.20 mmol cadmium acetate dihydrate and 0.13 mmol MA were loaded in a reaction flask together with ODE (or TOP or a mixture of the ODE and TOP); the flask was heated to 120 °C under vacuum and kept for 2 h. Meanwhile, the Se precursor TOPSe was freshly prepared by sonicating 0.05 mmol elemental Se in TOP at 60 °C. The freshly prepared TOPSe solution was transferred into the Cd precursor solution in ODE (at ~100 °C). The resulting mixture was heated at 120 °C for 1 h under a flow of purified nitrogen; afterward, the reaction was heated up to 240 or 150 °C at a rate of ~10 °C/min and carried out at 240 °C for 40 min or 150 °C for 60 min. A detailed description of the noninjection approach could be found elsewhere.^{1,2}

2.2. Optical Properties. To monitor the growth of the nanocrystals, the temporal evolution of the absorption and emission of the as-synthesized nanocrystals was examined. The absorption spectra were collected with a Perkin-Elmer Lambda 45 ultraviolet–visible (UV–vis) spectrometer with a 1 nm data collection interval. The photoemission spectra were collected with a Fluoromax-3 spectrometer (Jobin Yvon Horiba, Instruments SA, equipped with a 450 W Xe lamp as the excitation source); an excitation wavelength was 350 nm (if not specified) and an increment of data collection 1 nm (if not specified) and the slits 3 nm (if not specified).

2.3. XRD and TEM. The CdSe nanocrystal samples were purified for powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). For the purification, a toluene/methanol (1:1 by volume) mixture was used, and centrifugation was carried out at 4000 rpm for 30 min. The precipitate was washed twice with the toluene/methanol mixture.

Powder XRD (PXRD) patterns were collected at room temperature on a Bruker Axs D8 X-ray diffractometer using $\text{Cu K}\alpha$ radiation in a θ – θ mode. Data were collected between 5 and 75° in 2θ with a step size of 0.1° and a counting time of 5 s per step; the generator was operated at 40 kV and 40 mA. A XRD sample was prepared by depositing a suspension of a purified nanocrystal sample in toluene on a low-background quartz plate with subsequent solvent evaporation. TEM was performed on a JEOL JEM-2100F electron microscope operating at 200 kV and equipped with a Gatan UltraScan 1000 CCD camera. A TEM sample was prepared by depositing a dilute dispersion of a purified sample in toluene onto a 300 mesh carbon-coated TEM copper grid and dried in air.

3. Results and Discussion

In the studied model system producing the CdSe nanocrystals, Cd reactant precursor + Se reactant precursor \rightarrow CdSe, various synthetic parameters, such as the nature of the reaction medium, and the interplay between them affect the nanocrystal formation. Note that in a synthetic batch, thermodynamic equilibria can exist between the reactant monomers and the CdSe nanocrystals produced. The concentration of the reactant monomers together with temperature may affect both the chemical reaction kinetics and the thermodynamic equilibria. Also, the reaction medium affects the reactivity of the reactant precursors leading to the formation of the reactant monomers, as well as the thermodynamic properties, such as solubility and chemical stability, of nanocrystals produced. Regarding the nature of the two reactant precursors, the Se source, elemental Se, forms ODE/Se precursor in pure ODE, or TOPSe precursor in TOP and when the medium contains TOP. The Cd source, cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), is not very soluble in ODE, and thus needs to complex with myristic acid (MA) or TOP to form the Cd precursor, such as $\text{Cd}(\text{OAc})(\text{MA})$ or Cd–P complex. The Cd precursor controls the thermodynamic equilibria leading to the formation of MSQDs and/or RQDs. Below, various detailed experimental scenarios are presented to illustrate how the reaction medium together with temperature manipulate such equilibria and the thermodynamic properties of CdSe nanocrystals produced, and ultimately tune the formation of MSQDs versus RQDs. Although the reactions may not be done at steady-state equilibrium conditions, such as at a fixed temperature with time long enough, our systematically experimental approach demonstrates the trend of the formation and disappearance of the single-sized nanoparticles. We address the equilibrium formation but not the rate constant to reach the equilibrium and not a reaction condition to reach a steady-state under a particular temperature. Thus, we did not decouple the effect of temperature from that of time for the present study, which is not about quantitative study of dynamics but about the conceptual mechanism of the formation of single-sized nanoparticles.

3.1. Nanocrystal Development in ODE, Mixtures of ODE and TOP, and TOP. The effect of the reaction medium on the controlled formation of MSQDs versus RQDs is summarized and demonstrated in Figure 1. Figure 1 shows the temporal evolution of the absorption of the growing nanocrystals from 12 synthetic batches with identical feed molar ratios of 2.7MA–4Cd–1Se and Se feed concentration of 10 mmol/kg in five gram reaction medium. The total amount of TOP and ODE was maintained at 5 g for the 12 reaction batches with the TOP amount by weight ($\text{TOP}/(\text{TOP} + \text{ODE})$) of 0% (in this case, Se was dissolved in ODE first), 1.1, 1.8, 3.6, 7.0, 13, 20, 40, 50, 65, 85, and 100%. From each batch, there were 10 samples obtained along the reaction with the same growth

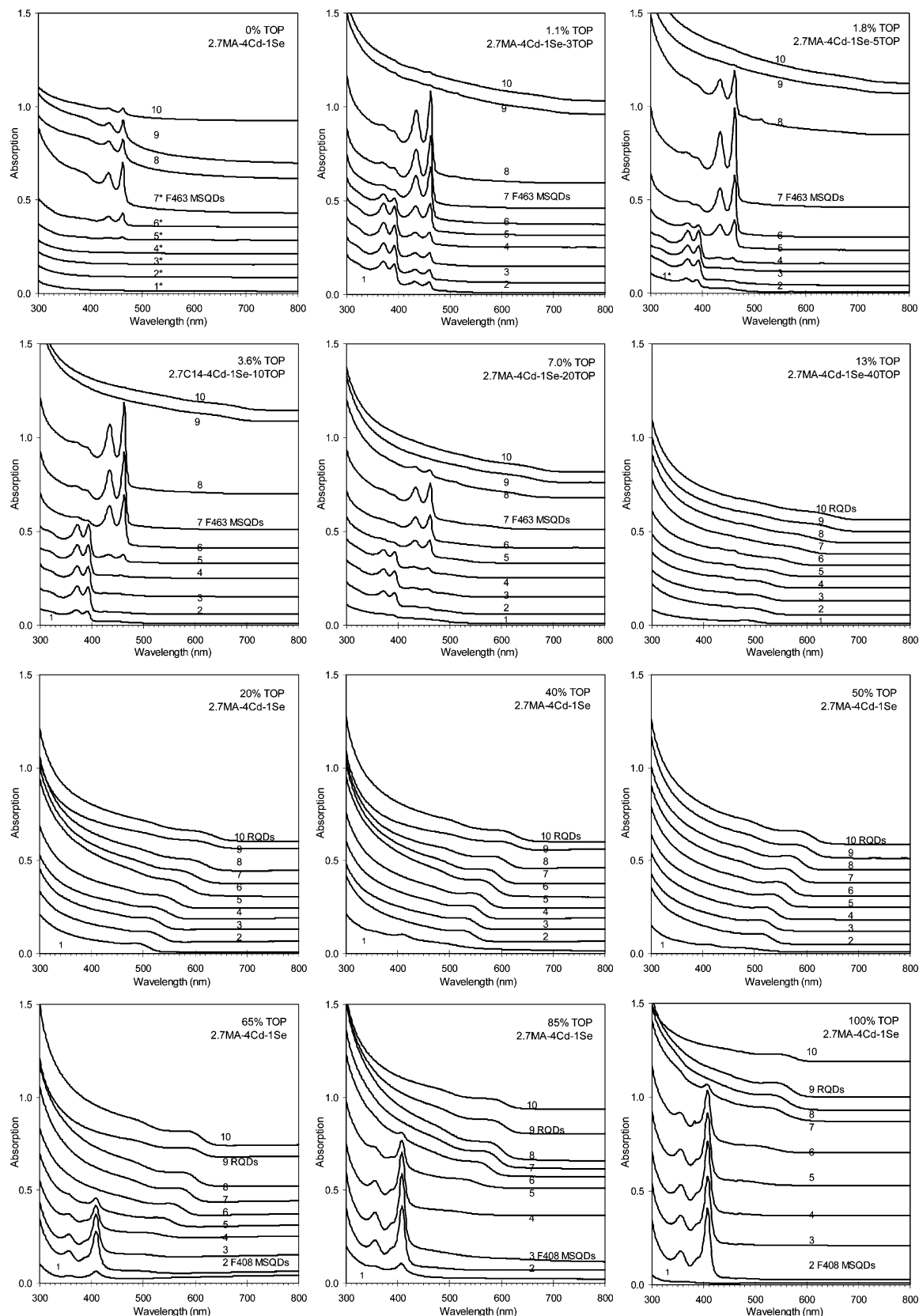


Figure 1. Temporal evolution of the absorption spectra (offset) of CdSe nanocrystals sampled from the 12 synthetic batches with the fixed feed molar ratio of 2.7MA–4Cd–1Se and [Se] of 10 mmol/kg. The weight percent of TOP in the TOP/ODE reaction media for each batch is indicated. Ten samples were obtained from each batch with their growth periods and temperature of 0 min/120 °C (Sample 1), 60 min/120 °C (Sample 2), 0 min/140 °C (Sample 3), 0 min/160 °C (Sample 4), 0 min/180 °C (Sample 5), 0 min/200 °C (Sample 6), 0 min/220 °C (Sample 7), 0 min/240 °C (Sample 8), 20 min/240 °C (Sample 9), and 40 min/240 °C (Sample 10). The as-synthesized nanocrystal samples were cooled to room temperature and dispersed in toluene. The absorption spectra were collected with a concentration of 15 $\mu\text{L}/1\text{ mL}$ (which means 15 μL as-synthesized nanocrystal solution in 1 mL toluene), except for Batch 0% TOP Samples 1*–7* (60 $\mu\text{L}/1\text{ mL}$) and Batch 1.8% TOP Sample 1* (30 $\mu\text{L}/1\text{ mL}$) (please note that the asterisk is used here to indicate the concentration difference of these samples from others).

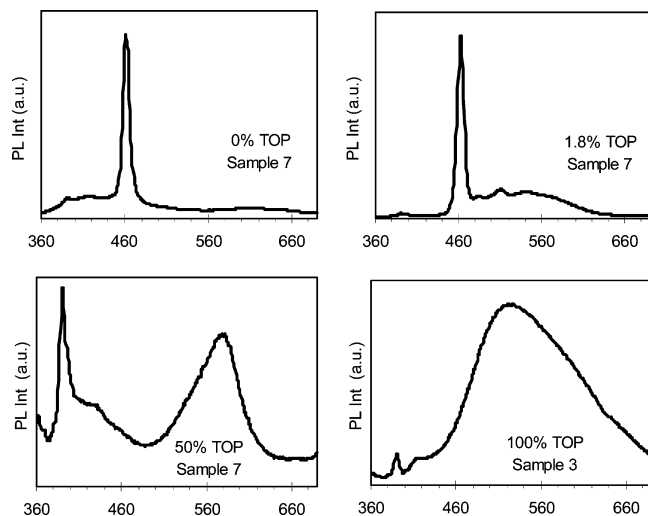


Figure 2. Emission spectra (excited at 350 nm) of the growing CdSe nanocrystals sampled from four synthetic batches shown in Figure 1; the TOP amount is indicated. The growing nanocrystals samples are indicated as Sample 3 (with the growth period and temperature of 0 min/140 °C) and Sample 7 (0 min/220 °C). The x -axis is wavelength with the unit of nm. Note that the feed molar ratios of 2.7MA-4Cd-1Se are not good for RQDs with bright bandgap emission; thus, the RQDs (left-bottom) exhibit very weak emission and the peak at 390 nm is from toluene.

periods and temperature ranging from 120 to 240 °C. Figure 2 shows the emission properties of the as-synthesized CdSe QDs from the four representative batches with the reaction media of 0, 1.8, 50, and 100% TOP. Interestingly, CdSe MSQD Family 395 and Family 463 exhibit bandgap emission, while Family 408 does not. The present study focuses on the thermodynamic effect of the reaction medium affecting the selective formation of the CdSe MSQDs and RQDs; therefore, attention is concentrated on the absorption properties. For comparison, the absorption of the QDs with the same growth periods and temperature sampled from the 12 batches is plotted together and presented in Supporting Information, Figure S1. Note that the development of the nanocrystals at a constant temperature (150 °C) in TOP is presented in Supporting Information, Figures S2 and S3. It is clear that the MSQDs are stable without growth in size, in a wide temperature range and over long reaction periods at a certain temperature.

For Batch 0% TOP shown in Figure 1, there were few QDs detected at temperature ranging from 120 to 140 °C. When the reaction temperature reached 160 °C (Sample 4*), CdSe MSQD Family 463 was detected and increased in number until the temperature reached 220 °C (Sample 7*); as the temperature was increased further, Family 463 decreased in number. Such decrease in nanocrystal number is indicated by the decrease of absorption peak intensity for Samples 8, 9, and 10. For Batch 1.1% TOP, CdSe MSQD Family 395 and Family 463 started to form simultaneously at 120 °C, indicating the bimodal nucleation of the magic-sized nuclei. Each MSQD ensemble exhibited an absorption doublet that is sharp and similar to that of the CdSe MSQDs prepared in ODE.²⁰ It is noteworthy that Family 395 formed at 120 °C (Sample 1) and increased in number to ~140–160 °C and decreased in number afterward. When the temperature was ~200 °C (Sample 6), Family 395 disappeared almost completely, while Family 463 continued to increase in number until 220 °C (Sample 7) and started to disappear afterward. The smaller sized nanocrystal nuclei (Family 395) have less thermal stability than the larger sized nuclei (Family 463). The development of RQDs with lower

bandgap energy was noticed at 240 °C for Batch 1.1% TOP (and not for Batch 0% TOP).

For Batch 0% TOP and Batch 1.1% TOP, the thermodynamic effect of the reaction media on the formation of the CdSe MSQDs is clearly seen, with the particular influence on the Se precursors and the solubility/thermal-stability of the CdSe MSQDs. For the two batches, the Cd precursor was Cd(OAc)(MA), which should be less reactive in 0% TOP than in 1.1% TOP. Meanwhile, the Se precursor was Se/ODE for Batch 0% TOP and TOPSe for Batch 1.1% TOP (and for the rest of the 10 batches shown in Figure 1). Se/ODE is less reactive than TOPSe. The presence of the magic-sized nuclei, Family 463, in Batch 0% TOP started at ~160 °C, while Family 395 and 463 appeared in Batch 1.1% TOP at lower temperature (120 °C). The bimodal nucleation of Family 395 and Family 463 in Batch 1.1% TOP is noteworthy. Furthermore, Family 463 at 220 °C was much less in number for Batch 0% TOP (Sample 7*) than for Batch 1.1% TOP (Sample 7); however, the lower solubility and/or higher thermal stability of Family 463 at 240 °C in Batch 0% TOP (Samples 9 and 10) than in Batch 1.1% TOP (Samples 9 and 10) is remarkable. SeTOP, more reactive than Se/ODE, leads to the bimodal nucleation at lower temperature; at the same time, TOP tends to increase the solubility of the CdSe magic-sized nuclei produced, thus decreasing the chemical/thermal stability and the equilibrium population in the reaction medium. Although the present study does not address the emission properties of the resulting CdSe QDs, we would like to point out that CdSe MSQD Family 463 developed at 220 °C from Batch 0% TOP exhibited a smaller degree of trap emission than that from Batch 1.1% TOP, as shown in Figure 2. Note that magic-sized nanocrystals can exhibit bandgap and/or trap emission, while that latter can lead to white-light emitters.^{3a}

From Batch 1.1% TOP to Batch 100% TOP (in Figure 1), the thermodynamic effect of the reaction media with particular consequence on the nature of the Cd precursor (as symbolized in eqs 1a and 1b) on the formation of the CdSe MSQDs, is evidently demonstrated. Essentially, when the TOP amount increases, the polarity of the reaction medium and the TOP coordination to Cd (via its headgroup phosphine) increase. Thus, the nature of the reaction medium plays an essential role on the thermodynamically driven formation of the MSQDs via tuning first the nature of the Cd precursor, second its reactivity with the Se reactant precursor TOPSe at 120 °C, and third the solubility/thermal stability of the resulting single-sized nuclei.

For the batches with the reaction media up to 7.0% TOP, as shown in eq 1a



the Cd precursor can be expressed as Cd(OAc)(MA), which reacted with the Se precursor in a controlled manner due to its own solubility in the reaction medium and the strong interaction between Cd²⁺ and CH₃-COO⁻.¹ (Note that in the reaction media with higher TOP amounts, a different Cd precursor becomes dominant, as discussed later). The presence of TOP led to the formation of CdSe MSQD Family 395 and Family 463. It is easy to understand that the more the TOP present (with higher polarity than ODE), the higher the solubility of the Cd precursor and the more reactive with the Se precursor. In addition to the reaction medium, the reactivity was affected by the reaction temperature, which was relatively low at low temperature (such as 120 °C) as compared to that at high temperature (such as at 220 °C). Furthermore, the solubility/

thermal stability of the magic-sized nuclei was also influenced by the reaction medium and temperature. For these four batches with the reaction media of 1.1–7.0% TOP, CdSe MSQD Family 395 disappeared at ~ 200 °C and Family 463 at 240 °C; meanwhile, RQDs evolved with the growth periods longer than 20 min at 240 °C. We believe that the reactivity of the reactant precursors regulated by the TOP amount is crucial for the thermodynamically driven formation of our CdSe MSQDs. Thus, the TOP presence affects both the nucleation/formation and dissolution/disappearance of the MSQDs. When the TOP wt % gets higher, its effect tends to be more dominant on the dissolution than on the formation. The population of CdSe MSQD Family 395 and 463 decreases in Batch 7.0% TOP is noteworthy.

For the four batches with the reaction media of 13–50% TOP, RQDs were present with their continuous growth in size along the reaction. Family 463 in Batch 13% (Samples 5 and 6) is much smaller in population than that in Batch 7.0% TOP. The RQDs from the reaction media with 20–50% TOP were developed in pure form without the coexistence of any MSQDs. The distinct absorption peaks of these RQDs together with their bandwidth reveal their narrow size distribution. Therefore, the presence of TOP increases the reactivity of the two reactant precursors, leading to the growth in size of the nuclei produced. It is necessary to point out that the present syntheses were carried out with the feed molar ratios of 2.7MA–4Cd–1Se; therefore, it is understandable that the RQDs did not exhibit bright bandgap photoemission (as shown in Figure 2 bottom-left). With the knowledge acquired from the present study that the mixtures of ODE and TOP are good choices in the preparation of RQDs via our noninjection protocol, the synthesis of high-quality RQDs with bright bandgap emission and narrow size distribution is being investigated in our laboratories with higher acid–Cd feed molar ratios.

For the three batches with the reaction media of 65–100% TOP, amazingly, another single-sized ensemble with its first excitonic absorption peaking at 408 nm was monitored. The persistent absorption fixed at 408 nm during the reaction, together with its narrow bandwidth of ~ 15 nm in fwhm, strongly suggests that this ensemble is single-sized. This family, termed as Family 408, is different from our previously reported CdSe MSQDs: the energy separation between its two absorption peaks, 408 and 356 nm, is ~ 444 meV, while the energy separation between the two transitions of the absorption doubles (which are 1S(e)–1S_{3/2}(h) and 1S(e)–2S_{3/2}(h)) of CdSe Family 513, 463, and 395 is ~ 161 , 173, and 185 meV, respectively.^{1,22} Similar to many of previously reported MSQDs,^{3a,23} Family 408 exhibited little bandgap emission but significant trap emission (as shown in Figure 2 bottom-right). For these batches, the Cd precursor can be expressed as Cd–P complex, which is resulted from the coordination competition of TOP (with the overwhelmingly large amount) to Cd and carboxylic acid (with the limited amount) to Cd. As presented by eq 1b



phosphorus in the Cd–P complex represents coordinating molecules such as TOP and TOPO (trioctylphosphine oxide). This Cd precursor reacted with the Se precursor at low temperature such as 120 °C, leading to the formation of CdSe Family 408; clearly, the nature of Cd precursors plays an essential role in the formation single-sized nanoparticles.

With a 60 min reaction period at 120 °C, Family 408 increased in population from Batch 65% TOP, to Batch 85%,

and to Batch 100% TOP. When the reaction temperature was raised, this single-sized ensemble dissolved/decomposed while RQDs grew. Thus, higher temperature enhances the dissolution of Family 408. Family 408 disappeared completely at 200 °C in Batch 65% TOP (Sample 6), at 220 °C in Batch 85% (Sample 7), and at 240 °C in Batch 100% (Sample 8). Meanwhile, the RQDs started to develop at 140 °C in Batch 65% TOP (Sample 3), at 160 °C in Batch 85% (Sample 4), and at 180 °C in Batch 10% (Sample 5); the RQDs kept growing in size as the reaction progressed. Thus, the TOP effect on Family 408 formation is superior to its dissolution effect (on the solubility and thermal stability). The disappearance of Family 408 supports the existence of the thermodynamic equilibrium between the counterbalancing nucleation and dissolution events. The developed single-sized nuclei were reversibly dissolved back into the system, leading to the presence of more available reactants, which might be in the form of monomers, dimers, trimers, and so forth, and which became available for the growth of the RQDs that were larger in size and more stable thermodynamically with lower solubility.

3.2. Nanocrystal Development in 100% TOP with (0–16) Acid-4Cd-1Se Feed Molar Ratios. It is noteworthy that the nature of the Cd precursor is regulated by the reaction medium (i.e., the TOP wt % in ODE), as illustrated with eqs 1a and 1b. Furthermore, for the batches with 65–100% TOP the surface ligands of the QDs formed are not the acid used anymore but TOP and TOPO. For example, in 100% TOP the formation kinetics of Family 408 and the RQDs in the absence of MA, as shown in Figure 3 (left, Batch 0MA-4Cd-1Se), was similar to that with the presence of MA, as shown in Figure 3 (middle, Batch 2.7MA-4Cd-1Se). Therefore, with the present synthetic protocol, MA is not necessary for the synthesis of CdSe Family 408 and RQDs in 100% TOP. Without the use of acid, the formation of Family 408 and/or RQDs in coordinating solvent TOP is worthy of notice. We demonstrated before the formation of Cd-based RQDs in TOP without the use of any acid while the Cd source was CdO.^{10,24,25}

Meanwhile, careful exploration of Batch 0MA–4Cd–1Se and Batch 2.7MA–4Cd–1Se suggests that MA enhanced the reactivity of the reactant precursors at 120 °C, leading to Family 408 with more population in the latter (Samples 2–3) than in the former. Moreover, too much MA in 100% TOP, as shown in Figure 3 (right, Batch 16MA-4Cd-1Se), inhibited the formation of Family 408, and thus, resulted in less population. It could be reasoned that the presence of more MA enhanced the solubility (or decomposition) of Family 408 in the reaction medium. Accordingly, it is easy to understand the existence of the thermodynamic equilibrium between the soluble species and Family 408 is affected by the presence of MA. In this sense, the formation of Family 408 is indeed driven thermodynamically with its population determined by the thermodynamic equilibrium of the reaction system.

The thermodynamic equilibrium-driven formation of Family 408 in 100% TOP is also demonstrated with the presence of tetradecylphosphonic acid (TDPA), as another example shown in Figure 4. TDPA is a commonly used acid in the synthesis of CdSe QDs.^{9b} The feed molar ratios were 1TDPA–4Cd–1Se (left), 2.7TDPA–4Cd–1Se (middle), and 16TDPA–4Cd–1Se (right). The effect of the TDPA amount on the formation of Family 408 is very much similar to that of MA, as shown in Figure 3, suggesting the existence of the reversible thermodynamic equilibrium between the soluble species and Family 408, no matter what type acids are used.

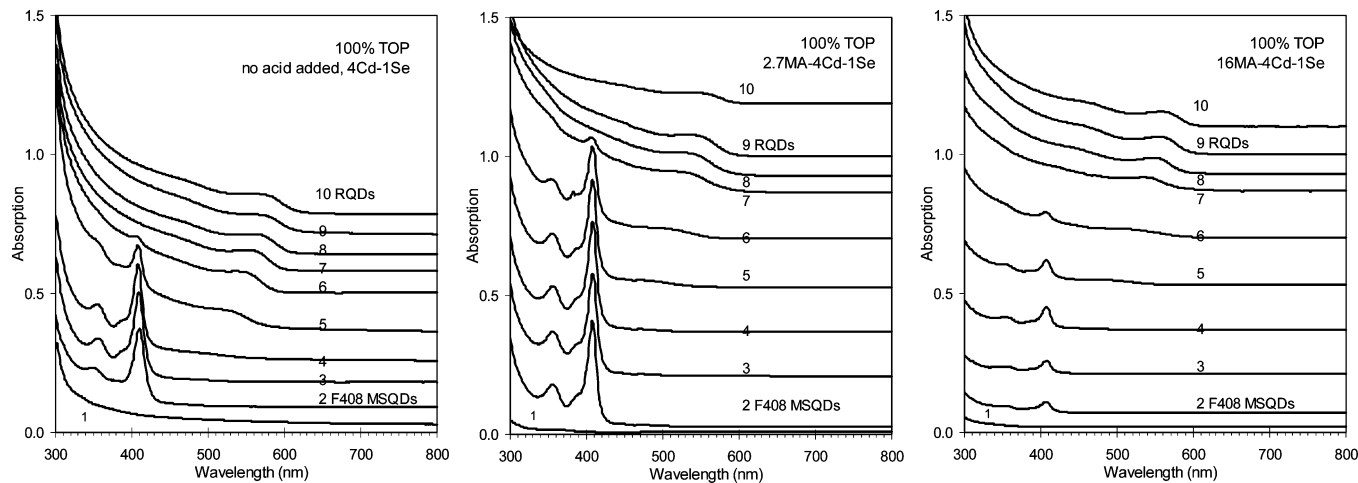


Figure 3. Temporal evolution of the absorption spectra (offset) of the growing CdSe nanocrystals sampled from three synthetic batches in 100% TOP, indicating the presence of the Cd precursor in the form of Cd–P complex. The feed molar ratio was fixed at 4Cd–1Se, with [Se] of 10 mmol/kg in 5 g TOP. The amount of MA is indicated. The growth periods and temperature are 0 min/120 °C (Sample 1), 60 min/120 °C (Sample 2), 0 min/140 °C (Sample 3), 0 min/160 °C (Sample 4), 0 min/180 °C (Sample 5), 0 min/200 °C (Sample 6), 0 min/220 °C (Sample 7), 0 min/240 °C (Sample 8), 20 min/240 °C (Sample 9), and 40 min/240 °C (Sample 10). The nanocrystals were dispersed in toluene. The absorption spectra were collected with 15 μ L/1 mL (which means 15 μ L as-synthesized nanocrystals media in 1 mL toluene).

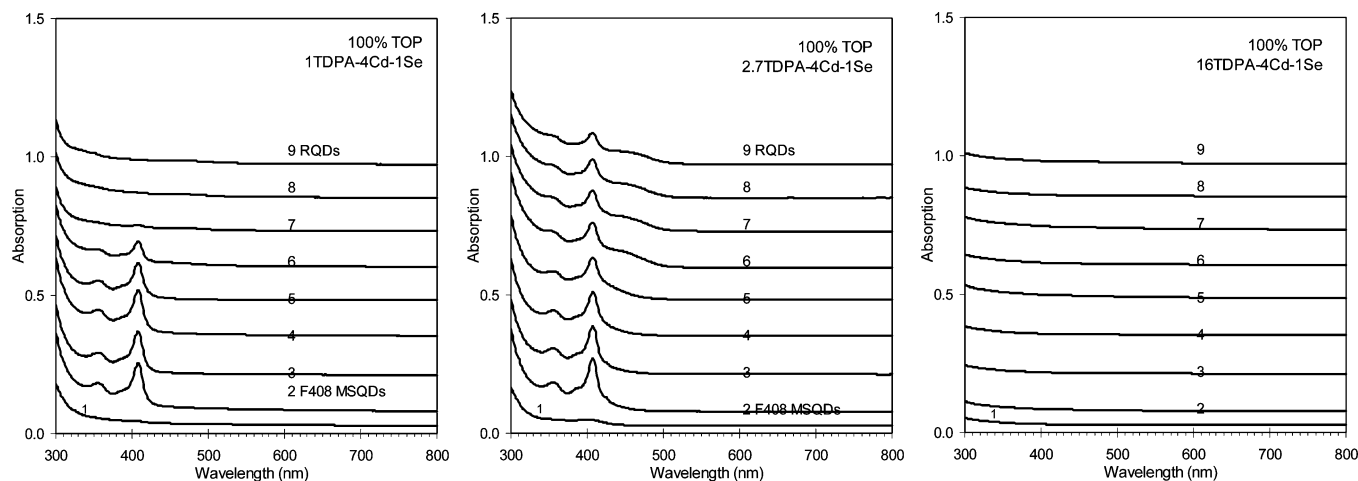


Figure 4. Temporal evolution of the absorption spectra (offset) of the growing CdSe nanocrystals sampled from three synthetic batches in 100% TOP in the presence of TDPA, indicating the presence of the Cd precursor in TOP in the form of Cd–P complex and not Cd–TDPA complex. The feed molar ratio was fixed at 4Cd–1Se, with [Se] of 10 mmol/kg in 5 g TOP. The amount of TDPA used is indicated. The growth periods and temperature are 0 min/120 °C (Sample 1), 60 min/120 °C (Sample 2), 0 min/130 °C (Sample 3), 0 min/140 °C (Sample 4), 0 min/150 °C (Sample 5), 10 min/150 °C (Sample 6), 20 min/220 °C (Sample 7), 30 min/150 °C (Sample 8), and 60 min/150 °C (Sample 9). The nanocrystals were dispersed in toluene. The absorption spectra were collected with 15 μ L/1 mL (which means 15 μ L as-synthesized nanocrystals in 1 mL toluene).

To further test the Cd precursor in the form of Cd–P complex (shown in eq 1b) and the thermodynamically driven formation of Family 408, various acids were used to synthesize Family 408 in 100% TOP with the fixed feed molar ratios of 2.7acid–4Cd–1Se and [Se] of 10 mmol/kg in five gram TOP. The temporal evolution of the optical properties of the developing nanocrystals (at 150 °C) was monitored and shown in Supporting Information Figures S2 and S3. Clearly, the presence of the nine acids in 100% TOP only affected the population of Family 408. Therefore, the acids used mainly affected the reactivity of the reactant precursors at 120 °C and thus the thermodynamic equilibrium between the soluble species and Family 408. Although the nine different acids used could interact with the Cd source compound (in ODE¹ and in the TOP/ODE mixtures with low TOP amounts, as shown in eq 1a), the significantly large amount of TOP (together with TOPO) molecules in the batches shown in Supporting Information

Figure S2 led to the formation of the Cd–P complex (in TOP) and eventually the TOP/TOPO-capped CdSe nanocrystals. As shown in Supporting Information Figure S4, the 2D DOSY-¹H NMR spectrum suggested that the surface ligand of Family 408 was TOP instead of MA presented in the reaction medium. The absence of the acid MA as the surface ligand of the resulting Family 408 is interesting and worthy of notice.

3.3. Nanocrystal Development in 1.1% TOP. The nature of the acid plays an important role in the formation of the CdSe QDs in the reaction media with low amounts of TOP. For example, in the 1.1% TOP reaction medium, as shown in Supporting Information Figure S5, the use of TDPA instead of MA modified significantly the reaction and led to the formation of the RQDs (Supporting Information Figure S5 top right, Batch TDPA) instead of the MSQDs (Supporting Information Figure S5 top left, Batch MA). When the limited amount of the acid was presented in the 1.1% TOP reaction medium, the Cd

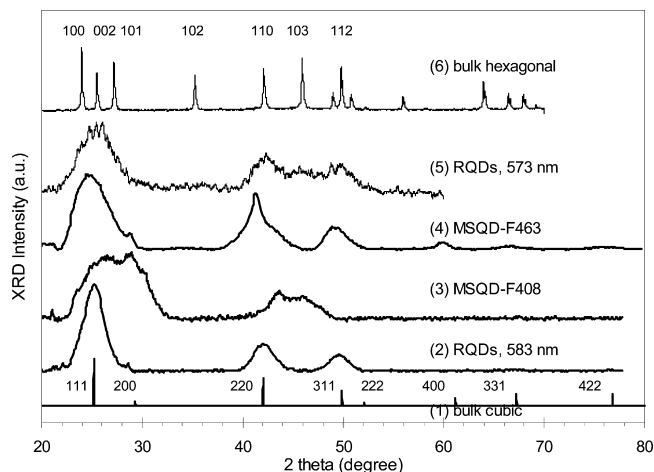


Figure 5. Powder X-ray diffraction (XRD) data. (1) Cubic bulk CdSe with the diffraction peaks index, (2) regular CdSe QDs via our noninjection approach with the reaction medium of 7.0% TOP (and with 16MA-4Cd-1Se feed molar ratios) and exhibiting absorption peak at 583 nm, (3) CdSe F408 MSQDs from a batch with 100% TOP (and with 2.7C06-4Cd-1Se feed molar ratios whose TEM is shown in Supporting Information Figure S6-a), (4) CdSe F463 MSQDs from a batch with 1.8% TOP (and with 2.7MA-4Cd-1Se feed molar ratios whose TEM is shown in Supporting Information Figure S6-b), (5) regular CdSe QDs via our hot-injection approach (with the injection at 300 °C and growth at 250 °C for 10 min and the reaction medium of 100% TOP) and exhibiting absorption peaking at 573 nm,^{12b} and (6) hexagonal bulk CdSe with the diffraction peaks index.

precursor should be in the form of Cd(OAc)(acid). It is reasonable that the reactivity of the Cd precursor Cd(OAc)(acid) depends on its nature: the reactivity of Cd(OAc)(TDPA) in the 1.1% TOP reaction medium at 120 °C was higher than that of Cd(OAc)(MA). In the future, we will make efforts to obtain the information on the solubility of the nanocrystals with the various acids as surface ligands and at different temperature.

The easy oxidation of TOP into TOPO was concerned, during the present investigation on the thermodynamically driven formation of single-sized nanocrystals. Do TOP and TOPO play similar roles in our noninjection-based protocol? Accordingly, the syntheses with the similar amount of TOP and TOPO added into the 1.1% TOP reaction medium were carried out and presented in Supporting Information Figure S5 (bottom-left and bottom-right, respectively.) The experimental data suggested that the effect of TOP added was similar to that of TOPO added.

3.4. Characterization with XRD and TEM. Now, let us turn our attention to the nanocrystal structure of the CdSe MSQDs and RQDs synthesized in the different reaction media at different temperatures. Figure 5 shows the powder X-ray diffraction (XRD) patterns of cubic CdSe bulk crystal as a reference (Curve 1), CdSe RQDs obtained with our noninjection approach (Curve 2), CdSe Family 408 (Curve 3), CdSe Family 463 (Curve 4), CdSe RQDs obtained with a hot-injection approach in TOP (Curve 5), and hexagonal bulk CdSe as a reference (Curve 6). The XRD result suggests that Family 408 is, evidently, smaller in size than Family 463 based on the broadness of the diffraction peaks. Also, according to the absorption peak positions, the size of Family 408 is calculated as ~ 1.62 nm and Family 463 is calculated as ~ 2.05 nm.^{20a} For ultrasmall clusters/nanocrystals, there is little distinction between wurtzite and zinc blende crystal structures due to a lack of atoms for cores.^{9a} Taking the hexagonal structure for Family 408, the two θ values are larger than those of the bulk for (100), (002), (101), and (110) planes and smaller for (112) plane. Therefore, the deformation in crystal structure was significant, indicating

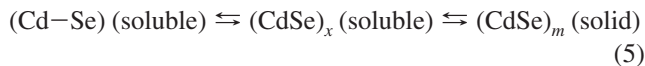
surface reconstruction and contribution from the surface atoms to the diffraction pattern; such deformation should be directly related to the high surface/volume ratio of these ultrasmall nanocrystals with high surface curvature. For Family 463, the (110) peak is relatively sharp, indicating a certain degree of elongation along the [110] direction, which is perpendicular to (110) plane.

High-resolution TEM images (as shown in Supporting Information Figure S6) of these nanocrystals show well-resolved crystal lattice fringes, revealing their highly crystalline nature. The aggregation of Family 408 was obvious (in Supporting Information Figure S6-a); such aggregation could take place during the TEM sample preparation. It is of particular importance to mention that nearly all reported MSQDs are either too small to be seen by TEM or tend to aggregate during their TEM sample preparation.^{1,2,17d,21a,26} The formation of quantum wires could be facilitated by the tendency of the aggregation of CdSe MSQDs.^{21a} TEM (shown in Supporting Information Figure S6) supports the hexagonal structure of the CdSe MSQDs.

3.5. Thermodynamic Equilibrium-Driven Formation of Single-Sized Nanoparticles—A Novel Concept to Nanoparticle Sciences. Finally, we would like to address the thermodynamically driven formation of the single-sized nanoparticles achieved with our noninjection protocol. The CdSe single-sized nanoparticles, whose crystallization processes only consist of nucleation without subsequent crystal growth, were observed in a wide window of formulations and conditions. The synthetic parameters investigated include the feed molar ratios of acid-Cd-Se, [Se], reaction temperature and growth periods, the nature of the acid, and the nature of reaction medium. The investigation on the control of the MSQD formation via various reaction media has brought us insights into the possible mechanism, the thermodynamically driven formation, which can be expressed by the following equations describing the thermodynamic equilibria and chemical reactions involved



Equation 2 represents the formation of reactant monomers (Cd-Se);^{27,28} note that the Cd precursor may exist in different forms (eq 1a or 1b). Equations 3 and 4 represent the thermodynamic equilibria among the reactant monomers (Cd-Se) in the solution phase and the nuclei (CdSe)_m in the solid phase. Equation 3 stands for the chemical reactions in the solution phase: the production of the soluble species of cadmium selenide (CdSe)_x and the decomposition of (CdSe)_x into (Cd-Se). Equation 4 denotes the thermodynamic equilibrium of the nucleation and dissolution processes: the homogeneous and continuous nucleation leading to the formation of the magic-sized nuclei, (CdSe)_m (solid; *m* is a magic number) from the soluble (CdSe)_x and the dissolution of the solid (CdSe)_m into the soluble (CdSe)_x. Regarding the number of the CdSe pairs, *x* could be 1, 2, ... and *m*, depending on the formulation and temperature. At present, it is not comprehensible whether the formation of the solid magic-sized nuclei (CdSe)_m involves the formation of the soluble and transient species (CdSe)_x. In the case of only one magic-sized species (CdSe)_m formed, eqs 3 and 4 could be combined into eq 5 and simplified to eq 6



Equation 6 describes the formation of the magic-sized nuclei $(CdSe)_m$ from the reactant monomers $(Cd-Se)$ (soluble), namely the formation and existence of the $(CdSe)_m$ nuclei might be related directly to their equilibrium with the surrounding $(Cd-Se)$ monomers in the solution phase. Equation 6 is valid only when the chemical reaction kinetics is not a determining factor on the formation of the magic-sized nuclei $(CdSe)_m$ (solid); thus, the equilibrium-driven formation is mainly determined by the thermodynamic properties (solubility/stability) of the nuclei. These properties are thermodynamically affected by the nature/concentration of the reactant monomers $(Cd-Se)$ (soluble), which are regulated by synthetic parameters including the nature of the reaction medium, temperature, and the nature/amount of the acid used. Accordingly, the model eq 6 helps us understand easily that the population and size of $(CdSe)_m$ (solid) is a matter of balance/competition between the effect of the synthesis parameters on the solubility/stability of $(CdSe)_m$ (solid) and on the nucleation. To achieve such an equilibrium between the magic-sized nuclei $(CdSe)_m$ (solid) and the reactant monomers $(Cd-Se)$ (soluble), in principle the temperature increase needs to be slow enough to realize the thermodynamically driven “quantized nucleation” with no subsequent growth. Within the synthesis condition window developed to produce single-sized nanoparticles, the nature/concentration of the reactant monomer $(Cd-Se)$ was controlled by factors including the nature of the two reactant precursors, the reaction medium, and the reaction temperature.

Note that in eqs 2–6, $(Cd-Se)$ (soluble), $(CdSe)_x$ (soluble), and $(CdSe)_m$ (solid) are represented for simplicity; they are stabilized with ligands.^{27,28} It was proposed that the Cd and Se precursors reacted with each other leading to the formation of the $(Cd-Se)$ monomer via an intermediate complex; the reactivity was affected by the reaction medium (such as the presence of water).²⁷ It is easy to understand that the chemical reaction kinetics and the thermodynamic equilibriums described by eqs 2 to 6 are influenced also by the reaction medium together with reaction temperature. The kinetics of the chemical reactions has little influence on the size of the magic-sized nuclei, although the nature and concentration of the reactant monomers $(Cd-Se)$ (soluble) together with temperature affect the formation kinetics. Rather than the chemical reaction kinetics, several equilibria regulate the equilibrium level of the reactant monomer concentration as well as the nucleation and dissolution to determine the size and population of the magic-sized nuclei. The overall thermodynamic equilibrium-driven mechanism is schematically illustrated in Figure 6.

We believe that the nature of the reactant monomer determines the formation of magic-sized nuclei and/or RQDs. However, the present study does not address the nature of $(Cd-Se)$ (soluble), while the investigation on the formation of the monomer in several RQD systems can be found elsewhere.^{27,28} Regarding the formation of RQDs instead of single-sized nanoparticles, it is reasonable to consider that the high reactivity of the reactant precursors leads to the formation of the reactant monomers with also high reactivity; with fast chemical reaction kinetics and nucleation rates, nucleation with various-sized nuclei takes place together with their growth leading to RQDs with certain size distribution. For the batches with the formation of RQDs, such as Batches 13–50% TOP in Figure 1, the

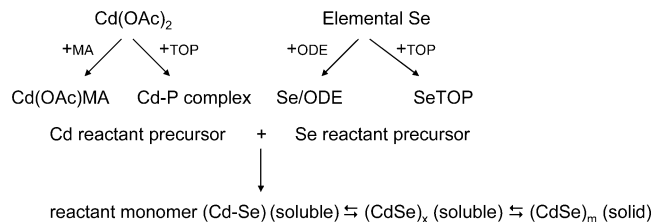


Figure 6. Schematic illustration of the thermodynamic equilibriums existing in the synthesis system that determine the formation of single-sized nuclei $(CdSe)_m$. Note that $(Cd-Se)$ (soluble), $(CdSe)_x$ (soluble), and $(CdSe)_m$ (solid) are represented for simplicity; they are likely stabilized with ligands.

chemical reaction kinetics and nucleation/growth rates play a significant role.

For the formation of single-sized nanoparticles via the control of the reactant monomers to ensure the existence of the thermodynamic equilibriums, our practical synthetic operation involved the separate preparation of the two precursor solutions, together with slow heating of the reaction. In principle, a critical “chemical reaction temperature” is required to overcome the activation energy barrier needed for the CdSe-forming reaction (eq 2). It is critical that the chemical reaction kinetics influences little the size of the nuclei $(CdSe)_m$; accordingly, the synthetic formulations with a reason window of reaction temperature and time should minimize such reaction kinetic effect. With the various formulations and reaction conditions, the present study has demonstrated successfully the production of single-sized nanoparticles which are magic-sized nuclei with no further growth in size.

Experimentally, the nature of the Cd precursor, which depends on the acid-to-Cd feed molar ratio as well as the nature of the reaction medium, plays an essential role regarding the formation of MSQDs and/or RQDs. Equations 2–6 and Figure 6 explain and support our experimental data nicely. For example, when the Cd precursor formed in ODE was in the form of $Cd(OAc)(OOC-(CH_2)_n-CH_3)$,^{1,2} myristic acid was found to be a good choice for CdSe Family 463 with a high yield.¹ It is easy to understand that the reactivity of the Cd precursor $Cd(OAc)(OOC-(CH_2)_n-CH_3)$ is different, regarding different $(OOC-(CH_2)_n-CH_3)$; also the concentration of the resulting reactant monomer is different. Accordingly, the reactivity of the Cd precursor is essential in determining the formation of magic-sized nuclei without further growth in size.

The formation of the CdSe MSQDs involves only the nucleation process with no further growth; conventionally, the formation of CdSe RQDs involves both nucleation and growth stages and is very sensitive to the chemical reaction kinetics. During syntheses, the MSQDs only change in population and not in size; therefore, the continuous and homogeneous nucleation can be slow and lengthy. At any time, the concentration of $(Cd-Se)$ (soluble) is determined by the competition between the consumption for nucleation and the dissociation of the nuclei. Single-sized MSQDs in pure form are produced through monomodal nucleation. In some cases, multiple families of single-sized nuclei could be generated simultaneously, indicating the presence of bimodal and/or multimodal nucleation. With longer reaction periods or at higher temperature, smaller-sized nuclei could disappear while larger-sized nuclei could survive. The larger-sized MSQDs are more stable thermodynamically than the smaller-sized MSQDs.

All these experimental observations suggest that within our synthesis window (including chemical formulation and temperature) for single-sized nanoparticles, the variation of chemical

reaction kinetics due to the change of the reaction formulation and temperature does not affect the size of the magic-sized nuclei. Meanwhile, the thermodynamic equilibria, tuned via the chemical formulation and temperature control, affect the presence or disappearance as well as the population of the single-sized nanoparticles. When the temperature exceeds the critical temperature of the solubility/stability of the magic-sized nuclei, they can reversibly dissolve/decompose back into the reaction medium (in the form of monomers and/or dimers and/or trimers, and so forth, which may become available to grow larger-sized MSQDs and/or RQDs). The population of the single-sized nanoparticles at any time should be determined by the dissolution and nucleation equilibria described by eqs 3–6. Dissolution, which is usually slow and gradual, is a thermodynamic equilibrium issue of eq 4. However, decomposition, which can be instantly fast, is a thermal stability issue of the chemical reaction described by eq 3. In the present study, “disappearance/disappear” was used sometimes with no distinction between the two words “dissolution/dissolve” and “decomposition/decompose”, since we consider the simplified eq 6, which only emphasizes nucleation-dissolution equilibrium rather than reactive formation–decomposition. The simplified equilibrium of eq 6 should provide a good description of the overall process and conceptually explain our experimental results observed.

4. Conclusions

We have proposed a thermodynamic equilibrium driven approach for the formation of single-sized nanoparticles and have demonstrated such a concept with the selectively controlled synthesis of CdSe MSQDs versus RQDs via our one-pot noninjection synthesis process that involves only proper chemical formulation and simple temperature control. MSQDs and RQDs were controllably synthesized by simply tuning the nature of the reaction medium under otherwise the same reaction conditions including the acid-to-Cd feed molar ratios and [Se] concentration. The thermodynamic effect of the reaction medium can be explained by the nucleation and dissociation between the reactant monomers and the single-sized nuclei. The reaction medium regulates the nature of the Cd and Se precursors and thus their reactivity; accordingly, the reaction medium influences strongly the size and yield of the resulting magic-sized nuclei via homogeneous nucleation. Importantly, our thermodynamically driven approach leads to magic-sized nuclei which involve only continuous and homogeneous nucleation without subsequent growth. The key is to control the thermodynamic conditions. When the conditions are satisfied, there should be little difference between injection and noninjection approaches. However, from an engineering point of view, our noninjection-based approaches are more suitable for scale-up than hot injection-based approaches, with prospects for simpler operations and process control.

For the present noninjection-based approach, the starting materials included cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) and elemental selenium (Se) as Cd and Se sources, respectively, and myristic acid (MA). The reaction media were noncoordinating ODE, coordinating TOP, and mixtures of the two. To realize the thermodynamic equilibrium-driven approach, the Cd and Se precursor solutions were prepared separately, and slow heating was performed after their mixing. Both efforts are expected to warrant sufficient time to reach thermodynamic equilibria described by eqs 3–6, among the reactant precursors, the resulting soluble-phase species including the reactant monomers, and the solid-phase nanocrystals. The thermodynamic equilibria, which are affected by the formulation and

temperature, determine ultimately the formation of the single-sized nanocrystals, whose sizes are determined “magically” by their unique thermodynamic properties such as solubility/thermostability. Practically, the synthesis of the single-sized nanocrystals was carried out at temperatures ranging from 120 to 240 °C for hours (or at one temperature such as 150 °C for a certain periods), and was monitored by the temporal evolution of the optical properties of the evolving QDs during synthesis. With the fixed feed molar ratios of 2.7MA-4Cd-1Se and [Se] of 10 mmol/kg in five gram reaction media, CdSe MSQD Family 463 started to form at ~ 160 °C in ODE. In the mixtures of less than 10% TOP (by weight), both Family 395 and Family 463 were developed with Family 395 as a main product from 120–160 °C and Family 463 dominating at temperatures of 180–220 °C. In the mixtures of 10–50% TOP, RQDs were produced at ~ 120 °C with growth in size as the reaction progressed. In the mixtures of 65% TOP and up to pure TOP, another single-sized ensemble, whose bandgap absorption peaking at 408 nm (and was thus named Family 408), was detected in pure form when the reaction temperature was raised from 120 to 140 °C; this family consistently disappeared as the reaction temperature increased, and RQDs formed consistently. For our experimental batches, the Se precursor was Se/ODE in pure ODE while TOPSe when TOP was used; the reactivity of Se/ODE was lower than that of TOPSe. For the reaction media with 0–10% TOP leading to Families 395 and 463, the Cd precursor was in the form of $\text{Cd}(\text{OAc})(\text{MA})$. For the reaction media with 65–100% TOP leading to Family 408, the Cd precursor was in the form of Cd–P complex. For the reaction media with 10–50% TOP leading to RQDs, the reactivity of the Cd and Se precursors should be very high, leading to the reactant monomer with significantly high concentration. As the TOP amount increased, the diffusion mobility enhanced. Note that the nature of the reactant monomers, leading to the single-sized nanoparticles and RQDs, should be different; there are thermodynamic equilibria existing between the reactant monomers and the single-sized nuclei. The formation of the RQDs with size distribution is affected by the reaction kinetics and nucleation rate; the high reactivity of the Cd precursor and/or high reaction temperature result in the nucleation with different-sized nuclei together with the growth of these nuclei. It is easy to understand that when the reactant monomer concentration is above a critical concentration and the reaction temperature is high enough, the kinetics of the chemical reaction and the nucleation would be affected significantly and would play a major role on the size and size distribution of the resulting nuclei, as well as the subsequent growth of the nuclei. Therefore, the present investigation on the thermodynamic effect of the reaction medium provides insights into the formation mechanism of the single-sized nanoparticles together with the nature of their surface ligands and gives the nanocrystal community a new experimental approach and design capability for the single-sized nanoparticles needed in various practical applications.

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Supporting Information Available: Temporal evolution of the optical properties of the growing nanocrystals from the various synthetic batches and the comparison, DOSY NMR, and high-resolution TEM characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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