

## Shape Control of Colloidal Semiconductor Nanocrystals through Thermodynamically Driven Aggregative Growth

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ABSTRACT: The optoelectronic properties of colloidal semiconductor nanocrystals					Aggregative growth

**ABSTRACT:** The optoelectronic properties of colloidal semiconductor nanocrystals (NCs) can be manipulated by changing their geometric shape. The precise synthetic control over particle morphologies, however, has remained elusive. Conventional growth techniques rely on the kinetic assembly of atomic units, where supersaturation and precipitation processes can lead to a broad distribution of particle shapes. In this paper, we demonstrate that replacing atomic precursors with small-size nanocrystals as building blocks for larger colloids offers an easier, more predictive control over nanoparticle shape evolution. The reported growth strategy is illustrated via shape.



selective syntheses of CdSe and CdS NC cubes, spheres, rods, as well as unprecedented "donut" and ring-like structures. Different particle morphologies were obtained through a thermodynamically driven growth, using a distinct combination of coordinating compounds that minimize the surface free energy. The demonstrated aggregative growth is explained using a thermodynamic model for interacting viscous colloids.

#### INTRODUCTION

Colloidal semiconductor nanocrystals (NCs) represent a promising class of inorganic nanomaterials for solution processing of optoelectronic devices.<sup>1–11</sup> The strong correlation between NC geometry and ensuing optoelectronic properties has been a prominent driving force behind the strong interest in these nanomaterials.<sup>1,12</sup> To that end, significant effort has been devoted to achieving a narrow particle size distribution,<sup>13–23</sup> while shape control of semiconductor NCs has received less attention<sup>24–27</sup> and, at present, is of great interest in the field.<sup>28</sup> The expected benefits of shape-selective NC syntheses include the ability to expose targeted NC facets for catalytic processes, to create nanostructures with a large fraction of surface atoms, and to design shapes suitable for close-packed, electricallycoupled NC assemblies.

Classically, the shape evolution of semiconducting nanocrystals has been precursor-driven. This dynamic environment of colloidal growth is strongly influenced by monomer kinetics (atomic building blocks with a neutral charge).<sup>29,30</sup> A continuous supply of monomers during synthesis causes monomer supersaturation.<sup>31</sup> As a result, nonequilibrium phases in the form of isolated clusters or surface growth are created. The presence of reactive monomers in the growth solution also leads to delayed nucleation, which further broadens the particle shape dispersion, making precise shape control more challenging.

In contrast to the conventional, precursor-driven NC synthesis, recent literature in the field  $^{32-44}$  reports the existence of a fundamentally different growth mechanism,

known as aggregative growth, which involves the coalescence of nanoparticles within the reaction mixture. This process has been known to contribute to the formation of metal nanoparticles<sup>45–48</sup> and was recently identified as an important mechanism contributing to the size evolution of semiconductor NCs.<sup>27,49</sup> Aggregative growth excludes monomer interactions, allowing the shape evolution to proceed in a thermodynamic regime.<sup>28</sup> The shape evolution of colloidal nanocrystals is driven by the minimization of surface energy. This leads to the formation of low-energy facets, whose indexes are determined by the Wulff method.<sup>50–52</sup>

Consequently, in thermodynamic equilibrium, the shape of a nanocrystal can be predicted as a function of its volume.<sup>25,53</sup> During aggregative growth, nanoparticles coalesce to form composite nanostructures with reduced surface free energy, whose shapes are determined solely by surface tension.<sup>54</sup> We have previously reported that the rate of aggregative growth is significantly increased in coordinating solvents.<sup>19</sup> This has been attributed to the role of bonds between coordinating solvent molecules and surface ions. The binding energy of ligands (Z-type, X-type, or L-type) can reduce the surface energy of a nanocrystal,<sup>25</sup> resulting in melting point depression of the corresponding NC facet (see Supporting Information

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**Figure 1.** Shape-selective synthesis of CdS NCs using the aggregative growth strategy. The four listed morphologies were fabricated via coalescence of ~3-nm zinc blende (ZB) CdS seeds in the presence of a unique coordinating surfactant: (a,b) Spherical CdS NCs grown at T = 260 °C in a oleylamine (OLAM)/CdCl<sub>2</sub> mixture, (c,d) Cubic CdS NCs grown in OA/C<sub>17</sub>H<sub>35</sub>COCl<sub>2</sub> at T = 300 °C, (e,f) rod-shaped CdS NCs fabricated in OLAM/CdCl<sub>2</sub> at T = 200 °C (the reaction is fully completed after 24 h), and (g,h) donut-like CdS NCs synthesized in NaOA at T = 245 °C. Scale bars are 20 nm.

(SI), eq S3), which makes it more susceptible to interparticle coalescence growth. Additionally, it has previously been demonstrated that NCs have suppressed melting points compared to bulk material.<sup>55</sup>

Here, we demonstrate that aggregative growth of colloidal semiconductor NCs enables a predictive control over nanoparticle shapes. In the present approach, the growth of colloidal NCs is achieved through the aggregation of small-size nanoparticles in coordinating solvents. Under these conditions, the shape of growing nanocrystals is determined primarily by the surface energy and, therefore, is tunable solely via the type of coordinating solvents/compounds used in the reaction mixture. This concept is illustrated in Figure 1, where different coordinating compounds result in different shapes of CdS NCs, including spheres (Figure 1a,b), cubes (Figure 1c,d), nanorods (Figure 1e,f), as well as unusual geometries, such as donut- and ring-shaped NCs (Figure 1g,h). The assemblydriven growth, as demonstrated, can be explained using existing theoretical models for interacting viscoelastic colloids.

#### RESULTS

The aggregative growth of CdSe and CdS NCs was explored in reaction mixtures containing different combinations of coordinating solvents and coordinating compounds, as shown in Figure 1. Reactions were carried out via a hot injection method, in which small-size colloidal NCs (less than 4 nm diameter, prepared separately) were injected into coordinating reaction mixtures, inducing coalescence growth. The reaction temperature was varied such that it was at or above the thermal threshold (Figure 2a) for a given reaction mixture. The onset of coalescence was explored by heating the reaction mixture, including original "seed" nanocrystals, from room temperature until growth was observed (evident from red-shifting of the lowest exciton peak in absorbance). The CdSe NC size evolution in a typical growth reaction is illustrated in Figure 2b. The photoluminescence (PL) peak gradually red-shifts during the reaction, indicating NC growth. The corresponding nanoparticle sizes, calculated according to ref 56, are indicated by red dots in Figure 2c.

Notably, during the growth reaction, the emission linewidth decreases, which suggests the size focusing of the NC population (Figure 2b). By assuming a constant single-particle linewidth, we estimate the NC size dispersion from the full width half maximum (FWHM) of the PL spectra (Figure 2c, red dots). The reduction in the CdSe NC size dispersion is consistent with the predictions of the aggregative growth model<sup>49</sup> (Figure 2c, red curve), which assumes nanoparticle growth by coalescence. In contrast to aggregative growth, the Ostwald ripening model<sup>57</sup> stipulates that NC growth is due to the dissolution of smaller NCs in favor of larger ones (Figure 2d), which causes initial broadening of the nanoparticle size dispersion (Figure 2c, blue curve). According to Figure 2c, our experimental size dispersion,  $\sigma(r)$ , closely follows the aggregative growth model. Furthermore, the PL spectra in Figure 2e demonstrates clear evidence that nanocrystal volume doubles and/or triples due to coalescence at the early stages of the growth reaction, which is consistent with the aggregative growth model. Similarly, volume increases at very early stages of the aggregative growth reaction were observed in the case of ultrasmall CdSe NCs (Figure SF1), showing evidence of 2-5 times volume increases within 5 s of growth.

The role of coordinating solvents in the aggregative growth of semiconductor colloids has been investigated by previous reports.<sup>36,41,49</sup> It is generally accepted that amines and carboxylates increase the rate of nanoparticle coalescence compared to non-coordinating solvents (e.g., 1-octadecence) due to increased driving force toward colloidal aggregation.<sup>49</sup> The head groups of coordinating solvent molecules render the



**Figure 2.** (a) Demonstration of the coalescence threshold for different reaction environments: OLAM/Se (yellow),  $OLAM/CdCl_2$  (red), OLAM/HCl (blue), and OLAM alone (green). The particle growth is monitored via the lowest-energy exciton absorption. (b) The evolution of the CdSe NC emission during aggregative growth in an  $OLAM/CdCl_2$  mixture. (c) Comparison of the experimental and theoretical NC size dispersion versus particle size. The two theoretical curves represent the predictions of the Ostwald ripening and aggregative growth models, calculated according to ref 49. (d) Graphic illustration of the Ostwald ripening and aggregative growth models, calculated plue) and during (red) aggregative growth with intermediate PL spectra showing the presence of CdSe NCs with 2 and 3 times the volume of the original seeds. To obtain the PL spectrum for early-time product of aggregation, the rate of coalescence was reduced by introducing a significant volume fraction of a non-coordinating solvent (octadecene).



Figure 3. Diagram showing a greater affinity of bound ion pairs (X-type ligands) over L-type amine ligands (i.e., oleylamine). The surface energy of CdX (X = S, Se) NCs is lower than that with L-type ligands.

solution more polar compared to alkyl-terminated colloidal nanoparticles, causing NC aggregation. The binding of amines and carboxylates to NC surfaces also increases the aggregative growth rate. The binding of these ligands reduces the surface energy of a NC facet (*hkl*) by the amount that is equal to the difference between binding and relaxed energies of a particular ligand,  $E_{\text{bound ligand}}$  (*hkl*) –  $E_{\text{free ligand}}$ .<sup>25</sup> The ligand-induced decrease in the surface energy of a NC facet lowers its melting point (Supporting Information, eq S3), which makes it more susceptible to interparticle coalescence onset temperatures, as shown in Figure 2a. The use of bound ion pairs, such as *n*-

alkylammonium chloride, is created by the addition of Lewis acids (i.e., HCl,  $CdCl_2$ , or stearoyl chloride (SC)) to coordinating solution and have previously been explored as strong ligands with high binding affinity onto CdSe NC surfaces (Figure 3).<sup>58</sup> The increased binding energy of bound ion pairs over classical L-type ligands (i.e., oleylamine) is what leads to the reduced surface energy and coalescence onset observed for CdX (X = S, Se) NCs.

The effect of *n*-alkylammonium chloride on the aggregative growth of NCs was further explored by heating NCs in OLAM to 260  $^{\circ}$ C without the addition of Lewis acid (i.e., no bound ion pair was present; Figure SF2). Upon maintaining the



**Figure 4.** (a–d) Evolution of CdS NC shapes during aggregative growth in OLAM/CdCl<sub>2</sub>. (e–h) Evolution of CdS NC shapes during aggregative growth in OA/ $C_{17}H_{35}$ COCl. In the latter case, two populations of NCs are observed at intermediate stages: original NC seeds and cube-shaped assemblies. After approximately 2–3 h at T = 300 °C, the original seeds are depleted, leaving cubes as the majority product. The crystal structure of cube-shaped NCs is ZB. In the case of OLAM/CdCl<sub>2</sub> mixture, a single population of NCs persists during consecutive growth stages. A low size dispersion is evident at intermediate reaction stages. The final product is represented by large spherical NCs with a WZ crystal structure.

temperature for several minutes, no change in the NC size is observed; however, upon addition of stearoyl chloride, immediate nanocrystal growth is observed, demonstrating the crucial role bound ion pair ligands have in reducing the onset temperature of coalescence. Furthermore, when the concentration of NCs versus n-alkylammonium chloride was investigated, it was found to have little effect (Figure SF3). The effect of *n*-alkylammonium chloride was investigated by hot injecting of 50-940 nmol of CdSe nanocrystals into 5 mL of OLAM and 20 mg of CdCl<sub>2</sub> at 260 °C and reacting for 40 min. There was a negligible effect on the FWHM of the emission linewidths, with a <6% deviation between all experiments and no clear trend. The position of the emission peak was found to vary slightly, with 50 nmol of NCs emitting at ~694 nm and 940 nmol emitting at ~685 nm, representing an approximately 1.5 nm diameter difference (~11.5 nm diameter using 940 nmol vs ~13 nm diameter using 50 nmol of CdSe NCs), or about 12% deviation. Overall, these experiments demonstrated that the amount of *n*-alkylammonium chloride present during the reaction is independent of the amount of NCs used, suggesting that the *n*-alkylammonium chloride is a type of initiator to aggregative growth and is not required to sustain growth. Finally, the temperature at which growth is performed was found to have a significant impact on the size of the final NCs (Figure SF4). When using nalkylammonium chloride in the coordinating solution (OLAM/CdCl<sub>2</sub> mixture), the size of CdS NCs ranged from 8.2 nm at 260  $^{\circ}\mathrm{C}$  to 16.8 nm at 325  $^{\circ}\mathrm{C}.$ 

The NC size evolution during an aggregative growth in an OLAM/CdCl<sub>2</sub> mixture is characterized in Figure 4a–d. The original zinc blende (ZB) CdS NCs gradually increase in size from 3.1 to 7.5 nm (in 30 min) when heated at T = 260 °C.

The shape of NCs appears to be spherical throughout the growth reaction and maintains a relatively low size dispersion at different growth stages (<8%, Figure 2b,c). A highresolution transmission electron microscopy (TEM) image of a characteristic NC in the final product reveals a wurtzite (WZ) lattice structure (Figure 4d), and the transformation of the ZB lattice to a WZ lattice was confirmed by powder X-ray diffraction (XRD) measurements (Figure SF5). The spherical shape of NCs is replaced by a hexagonal geometry when a particle size reaches 15-17 nm (Figure SF6). The growth of these larger structures requires higher reaction temperatures (T = 300 - 320 °C). An apparent mono-crystalline morphology of these nanoparticles suggests that the incorporated NC seeds anneal to form a uniform lattice during the synthesis. The shape evolution of CdSe NCs in OLAM/CdCl<sub>2</sub> coordinating solvent mixtures was similar to that of CdS. A 30-min aggregation growth reaction at T = 260 °C produces a 3.5–9 nm increase in the average particle size (Figure SF7a), caused by the coalescence of original ZB NC seeds. The final product exhibits a low particle size dispersion of <7%, which was consistent with a reduced PL linewidth ( $\Delta E = 86 \text{ meV}$ ) of coalesced CdSe NCs, compared to  $\Delta E = 125$  meV for the original 3.5 nm CdSe seeds (Figure SF7b).

Additionally, the aggregative growth of 3.1-nm ZB CdS was investigated in a coordinating solvent of oleic acid (OA) and chloride-based Lewis acid (Figure 4e–g). The onset temperature of coalescence in OA was found to be 220 °C, as previously reported.<sup>36</sup> With the addition of a chloride source, the cubic crystal facets became more prominent during growth, resulting in pristine-shaped cubes; however, with just OA present during the aggregative growth, the cube edges would not be as defined (Figure SF8). To obtain the well-defined



**Figure 5.** (a) Spherically shaped CdS nanoparticles forming through the aggregative growth of 2.6-nm ZB NCs in 5 mL of OLAM and 20 mg of CdCl<sub>2</sub>. (b) Spherically shaped CdS nanoparticles forming through the aggregative growth of 2.5-nm WZ NCs in 5 mL of OLAM and 20 mg of CdCl<sub>2</sub>. (c) Cube-shaped CdS nanoparticles forming through the aggregative growth of 2.6-nm ZB NCs in 5 mL of OA, 1 mL of 1-octadecene (ODE) with 0.2 mL of stearoyl chloride stock solution. (d) Rod-shaped CdS nanoparticles forming through the aggregative growth of 2.6-nm WZ NCs in 5 mL of OA, 1 mL of 0.6-nm WZ NCs in 5 mL of OA, 1 mL of 0.6-nm WZ NCs in 5 mL of OA, 1 mL of 1-octadecene NCs in 5 mL of OA, 1 mL of 0.6-nm WZ NCs in 5 mL of OA, 1 mL of 0.6-nm WZ NCs in 5 mL of OA, 1 mL of 0.6-nm WZ NCs in 5 mL of OA, 1 mL of 0.6-nm WZ NCs in 5 mL of OA, 1 mL of 0.6-nm WZ NCs in 5 mL of 0.6-nm WZ



**Figure 6.** (a) TEM image of the reaction product resulting from aggregative growth of 3.5-nm CdSe NCs in OLAM/Se mixture at T = 100 °C. After 20 h at this temperature, ring formation was observed (see inset). (b) TEM image of CdSe nanorods resulting from aggregative growth of 3.5 nm CdSe NCs in OLAM at T = 260 °C for 2–4 h. (c) TEM image of donut-like CdS NCs fabricated via the aggregative growth of 3-nm CdS NCs in NaOA at T = 240 °C. (d) Exciton fine structure changes for wurtzite CdSe NCs occurring during a transition from a dot (red) to a rod (blue) morphology.<sup>59</sup> *F* is the total angular momentum of an excitonic state (b = bright, d = dark). Adapted from ref 60. Copyright 2021 American Chemical Society. (e) Changes in the emission and absorption profiles of CdSe NCs caused by the aggregative growth in OLAM/Se mixture at T = 100 °C.

cube shapes, the temperature needed to reach above the threshold of coalescence, to  $\geq 270$  °C, and had to be maintained for up to an hour. The coalescence dynamics of CdX (X = S, Se) NCs in OA/Lewis acid differs significantly from that of an *n*-alkylammonium chloride and OLAM coordinating mixture (i.e., OLAM/CdCl<sub>2</sub>). In the OLAM/

 $CdCl_2$  environment, low dispersion of particle sizes persists throughout the entire growth reaction, while the aggregative growth in OA is distinguished by the formation of two NC populations at intermediate stages (Figures 4f and SF9a). The presence of two populations with distinct sizes is also evidenced by the double-peak profile of the CdSe PL spectra (Figure SF9b). The high-energy PL feature is attributed to original CdSe NC seeds, while the low-energy peak is assigned to cube-shaped nanoparticles. After approximately 60 min at T = 300 °C, the original seed population is nearly depleted, causing the size dispersion to drop below 10% (see Figure 4g). The final product consists primarily of cube-shaped NCs. A high-resolution image in Figure 4h reveals the zinc blende (ZB) crystalline lattice structure of cubic CdSe NCs.

The role of crystal structure in the original seed NCs is investigated by looking at the coalescence of wurtzite (WZ) nanocrystals in OLAM/CdCl<sub>2</sub> and OA coordinating solutions, which can be compared to the results from the ZB crystals. We find that the crystal structure of original NC seeds appears to play a unique role in determining the trajectory of the coalescence growth and overall final shape, as shown in Figure 5a-d. According to Figure 5a,b, both ZB and WZ NC seeds give rise to spherical WZ nanocrystals in n-alkylammonium chloride coordinating mixtures. However, in the case of the OA reaction solvent, original NC seeds with different lattice structures produced different NC geometries upon coalescence. For instance, aggregative growth seeded by ZB CdS NCs leads to the formation of ZB cubes (Figure 5c). Meanwhile, WZ CdS seeds in a OA mixture react to form WZ nanorods (Figure 5d). The rod thickness is broader than single NCs, which indicates that nanorods were not formed through the oriented attachment of original seeds but rather through thermodynamically driven shape formation. Additionally, using mixtures of OLAM and OA, it is possible to produce very thick (>4 nm diameter) rods, as shown in Figures 1e,f, and SF10.

Aggregative growth in a mixture of elemental chalcogenides and OLAM (i.e., a bound ion pair using Se<sup>2-</sup> in place of Cl<sup>-</sup>) exhibited the lowest thermal threshold for NC coalescence (Figure 2a). The fusion of CdSe NCs is achieved at temperatures as low as T = 90 °C when the concentration of Se in OLAM is 100 mM. In such a low-temperature regime, aggregative growth appears to resemble the fusion of NCs at molten surfaces,<sup>49</sup> resulting in characteristic, one-dimensional assemblies, as shown in Figure 6a. The elongated structures appear to grow in a curved pattern, which in some cases leads to the formation of CdSe rings, particularly at longer reaction times (Figure 6a, inset). While it is difficult to achieve specific shape homogeneity for such one-dimensional (1D) assemblies, the emission linewidth remains relatively narrow ( $\Delta E = 85$ meV, Figure 6e). However, upon injection of CdSe NCs into *n*-alkylammonium ion solution with Se/OLAM at 260  $^{\circ}$ C, the formation of large spherical NCs is observed, similar to that obtained for OLAM/chloride coordinating mixtures at ≥180 °C and OLAM only at 330 °C (Figure SF11).

The rate of NC coalescence in a  $OLAM/CdCl_2$  mixture slows significantly when the particle size reaches a particular threshold value. We attribute this suppression of aggregative growth to the increasing elasticity of the core components of the larger nanoparticles. It has been established that the solvent/solid tension in small-diameter NCs converts the entire nanoparticle into a molten phase,<sup>44,61</sup> which permits their coalescence into a single composite nano-object. In larger colloids, only the surface layer is affected by the solvent/solid tension,<sup>62</sup> causing the formation of a molten layer over the elastic core. In this case, nanoparticles can undergo a partial rather than the full coalescence. An example of such a partial coalescence is provided in Figure 6b, which shows a nanorodlike assembly of large-size CdSe NCs along the 0001 wurtize (WZ) axis. In this case, the attachment process is much slower than the coalescence of small-size seeds, requiring several hours at a minimum to produce nanorods with an aspect ratio of 2-3 (Figure SF10).

One-dimensional assemblies of CdSe NCs achieved in OLAM/Se reaction mixture (Figure 6a) represent an interesting type of semiconductor quantum dots (QDs), where the fine structure of lowest-energy excitons differs from that of zero-dimensional QDs. As illustrated in Figure 6d, eight lowest-energy transitions in CdSe NCs shift lower in energy and reorder when several dots are fused into a 1D assembly of the same diameter.<sup>60</sup> In spherical CdSe NCs, the upper  $F = \pm 1_{\text{bright}}$  states (F = S + J is the total angular momentum) carry most of the dipole strength for optical absorption, while the lower  $F = \pm 1_{\text{bright}}$  states are responsible for the room-temperature emission. When CdSe is elongated along the wurtzite *c*-axis, the upper  $F = \pm 1_{\text{bright}}$  states drop in energy (up to 80 meV, depending on the particle diameter), which is consistent with a red-shifted emission in coalesced CdSe NCs (Figure 6e).

The most unusual nanoparticle growth is observed in the NaOA reaction mixture at T = 240-260 °C. In this case, the aggregative growth of ~3 nm CdS seed NCs results in the formation of donut-shaped NCs, measuring ~7 nm in diameter. The "donut hole" is present in 95% of all structures, as shown in Figure 6c. Our analysis of high-resolution TEM images in Figure SF12 reveals a possible mechanism of the "hole" formation. The presence of partly closed rings suggests that NC seeds do not undergo a full coalescence but rather stick at hetero-interfaces in a ring-like pattern. Fully formed donuts, on the other hand, exhibit the same lattice fringe pattern throughout the entire structure, possibly as a result of thermal annealing across interfaces.

Our experiments demonstrate that aggregative growth of NCs leads to potential control of particle shapes. The final products of these reactions exhibit a remarkable homogeneity of particle shapes, which implies that the rate of coalescence falls abruptly when a maximum particle size for given experimental conditions is reached. This behavior, however, deviates from the predictions of classical aggregative growth models based on the classical Bomoluchowski rate equation (see Supporting Information).<sup>49,63-65</sup> Namely, the coalescence growth of any two particles  $A_i$  and  $A_j$ , each containing *i* and *j* numbers of primary particles  $(A_1)$ , can be described as  $A_i + A_j \xrightarrow{K_{ij}} A_k$ , where the collision rate,  $K_{ij}$  depends on particle sizes,  $R_i$ ,  $R_j$ , and their respective diffusion coefficients,

$$K_{ii} = 4\pi (R_i + R_i)(D_i + D_i)$$
(1)

Based on this model, the ultimate size of a NC in the reaction mixture is diffusion-limited. Since larger particles exhibit a lower diffusion coefficient, given by the Stokes–Einstein law, their growth rates subside with the particle size. Our simulations based on eq 1 (see Supporting Information) demonstrate that such a diffusion-limited aggregation cannot explain the distribution of particle shapes in the final product. Indeed, the predicted particle size dispersion  $\sigma(r)$  continues to increase with r (Figure SF13), which disagrees with the experimental data showing uniform particle distributions at long reaction times.

To reconcile the Smoluchowski model predictions with the experimentally observed particle size evolution, we consider

 $D_{i,i}$ , according to



**Figure 7.** Thermodynamic model explaining the formation of molten phases in spherical nanocrystals. (a) Graphical representation of reduction in the nanoparticle free energy ( $\Delta G$ ), which drives the formation of the molten layer with a thickness  $\delta$ . Melting is observed if the solid/solvent interfacial tension ( $\gamma_{SV}$ ) is reduced upon the insertion of a liquid layer:  $\gamma_{SL} + \gamma_{LV} - \gamma_{SV} < 0$ , where  $\gamma_{SL}$  and  $\gamma_{LV}$  are the solid/liquid and liquid/solvent interfacial tensions, respectively. (b) Illustration of the local and global minima of  $\Delta G$  that corresponds to melting of a surface layer (local minimum) and the entire particle (global minimum). (c, d) Dependence of  $\Delta G$ , on the molten layer width,  $\delta$ , for CdSe NCs at different solvent temperatures. Parameters for these calculations are provided in the SI section. For small sizes of CdSe NCs (d = 2 nm), such as those shown in (c), the global minimum of  $\Delta G$  at  $\delta/R \rightarrow 1$  suggests melting of the entire nanoparticle (i.e., without surface melting), whereas for larger CdSe NCs (d = 6 nm), a molten layer is energetically favorable at T = 140 °C. At this temperature, nanocrystals will undergo a partial coalescence into a rod-like structure (see Figure S4). Panels (a)–(d) adapted from ref 60. Copyright 2021 American Chemical Society. (e) Contour plot showing the dependence of molten layer thickness,  $\delta/R$ , on the nanoparticle size and the solvent temperature.

the effect of the nanocrystal viscosity on aggregative growth. A recent study<sup>44</sup> has suggested that particle coalescence results from a liquid-drop behavior of heated colloids caused by the formation of a molten inorganic phase. From a theoretical perspective, the melting of inorganic nanoparticles is driven by the reduction of the interfacial energy between the solid (nanoparticle) and matrix (solvent) phases. This concept is illustrated in Figure 7a, indicating that the reduction of free energy,  $\Delta G < 0$ , is caused by the reduction in the nanoparticle interfacial tension ( $\gamma_{SV}$ ) upon melting of the surface layer,  $\delta$ , such that  $\gamma_{SL} + \gamma_{LV} - \gamma_{SV} < 0$ , where  $\gamma_{SL}$  and  $\gamma_{LV}$  are the solidliquid and liquid-solvent tension terms. To estimate the corresponding change in the particle free energy as a function of the liquid layer thickness,  $\delta$ ,  $\Delta G(\delta) = G_{slv} - G_{sv}$ , we use the Kofman approximation<sup>62</sup> adapted for spherical nanoparticles in solution (see Supporting Information). A typical evolution of  $\Delta G$  with  $\delta$  is illustrated in Figure 7b. The local minimum of  $\Delta G(\delta, T)$  provides the expected thickness of the molten layer,  $\delta(T)$ . If  $\delta = R$ , the entire nanoparticle is considered to be in a liquid phase.

In the case of smaller-diameter CdSe nanoparticles, the onset of surface melting is strongly affected by the curvature of the particle<sup>66</sup> (see Supporting Information). According to Figure 7c, small-size CdSe NCs (d = 2 nm) exhibit no local minimum of  $\Delta G$  with increasing liquid layer thickness,  $\delta$ , indicating that the entire particle becomes molten at a threshold temperature (a global minimum at  $\delta/R \rightarrow 1$ ). Consequently, smaller-diameter NCs undergo full coalescence when the threshold temperature is reached. For larger NCs (e.g., d = 6 nm CdSe NCs in Figure 6d),  $\Delta G(\delta)$  exhibits both global and local minima, suggesting that melting of the surface layer is thermodynamically favorable in a certain solvent temperature range. Another effect of large particle size is that the melting of the entire particle  $(\delta/R \rightarrow 1)$  requires greater temperatures than those of smaller-size CdSe NCs. The increase in the full-particle melting threshold with the size of a

nanocrystal in Figure 7d suggests that the maximum particle size that can be achieved via coalescence growth is determined by the reaction temperature. Particles larger than this size are not fully molten and thus cannot undergo full coalescence. Partial coalescence, however, is possible. In the case of d = 6 nm CdSe,  $\Delta G$  exhibits a local minimum at  $\delta/R = 0.1$  (0.3 nm) at T = 140 °C, which implies that surface melting is energetically favorable at this particle size, as shown in Figure 7e. With molten surfaces, nanoparticles can form one-dimensional structures, such as rod-like or chain-like assemblies, which agrees with experimentally observed morphologies in Figures 6b and SF14.

#### CONCLUSIONS

We have demonstrated that the aggregative growth of colloidal semiconductor NCs provides a powerful strategy for tuning nanoparticle shapes. Unlike conventional growth techniques that rely on the reaction of atomic precursors, the present approach employs the coalescence of small-size nanoparticles into larger colloids. The absence of atomic species during aggregative growth prevents shape evolution by monomer precipitation, allowing nanoparticles to transform into a "lowest-energy" morphology. With this approach, controlling the shape of nanocrystals is achieved through the use of different reaction environments, which uniquely affect the final particle shape. This concept is conclusively demonstrated by performing a shape-selective growth of CdX (X = S, Se) cubes, spheres, nanorods, nanorings, and donut-like structures. The aggregative growth mechanism is explained using a thermodynamic model of interacting viscous colloids. We expect that the present growth strategy will provide a viable platform for the shape-selective synthesis of many other types of inorganic colloids, stimulating the discovery of novel optoelectronic properties.

#### METHODS

**Materials.** The following materials were used: cadmium oxide (CdO, 99% STREM), 1-octadecene (ODE, 90% Aldrich), *n*-octadecylphosphonic acid (ODPA, >99% PCI), octadecylamine (ODA, 90% Acros), oleic acid (OA, 90% Aldrich), sulfur (S, 99.99% Acros), chloroform (anhydrous, 99% Aldrich), oleylamine (OLAM, 70% Aldrich), hexane (anhydrous, 95% Aldrich), ethanol (anhydrous, 95% Aldrich), isopropyl alcohol (IPA, high-performance liquid chromatography (HPLC) grade, OmniSolv), tri-*n*-octylphosphine (TOP, 97% Strem), tri-*n*-octylphosphine oxide (TOPO, 99% Aldrich), selenium powder (Se, 200 mesh, Acros), acetone (anhydrous, Amresco, ACS grade), stearic acid (97% Aldrich), stearoyl chloride (SC, >97% TCI), and tributylphosphine (TBP, 97% Aldrich). All reactions were performed under argon atmosphere using the standard Schlenk technique. The centrifuge used for precipitation operated at 6500 rpm.

**Synthesis of Zinc Blende CdS Seed NCs.** CdS NCs were fabricated according to the previously reported procedure.<sup>67</sup> A mixture of 0.0768 g of CdO, 3.6 mL of OA, and 24 mL of ODE in a 50 mL three-neck flask was heated to 240 °C until the solution turned optically clear. Then, all of the sulfur precursor solution made by dissolving 0.02 g of sulfur powder in 10 mL of ODE at 200 °C was quickly injected. The reaction was finally stopped by removing the flask from the heating mantle after 4–5 min. CdS NCs were separated from the solution by precipitating with ethanol and redissolving the product in hexane.

Synthesis of Wurtzite CdS or CdSe Seed NCs. NCs were synthesized using the following procedure. A mixture of 0.06 g of CdO, 0.28 g of ODPA, and 3 g of TOPO (1.5 g of TOPO for CdS NC synthesis) was heated to 320 °C until the solution turned optically clear. Then, the mixture was heated up to 370 °C and kept at this temperature. In another flask, 0.73 mmol of chalcogenide powder (58 mg Se powder or 23.6 mg S powder) was dissolved in 1.5 mL of TOP at 120 °C. Finally, chalcogenide precursor was swiftly injected into the Cd flask and allowed to react for up to 3 min. The reaction was quenched by placing the flask in a water bath when the solution temperature was below 290 °C. CdS or CdSe NCs were cleaned via two successive precipitations with anhydrous ethanol and toluene, finally being suspended in hexane. The final NC product was centrifuged for 30 s to remove anything insoluble.

**Synthesis of Zinc Blende CdSe Seed NCs.** ZB CdSe NCs were synthesized by adapting a previously reported procedure from the literature.<sup>68</sup> Briefly, 80 mg of CdO, 2 mL of OA, and 18 mL of ODE were heated in a 50 mL flask to 250 °C until the solution turned clear. Next, 25 mg of Se powder was sonicated in 1 mL of ODE for at least 5 min to create a suspension. Once the Cd flask had reached 250 C, the Se suspension was swiftly injected and allowed to react for the desired amount of time. The flask was then removed from the heat and quenched in a water bath. The NCs were cleaned by precipitation with toluene/ethanol procedure, followed by centrifugation at 6500 rpm for up to 10 min. This cleaning procedure was performed twice before the final NCs were suspended in hexane.

Aggregative Growth in  $OLAM + CdCl_2$  (Spheres). In a typical growth, 5 mL of OLAM and 20 mg of  $CdCl_2$  (or equivalent molar amount of HCl or stearoyl chloride) were degassed at 120 °C for approximately 15 min. The flask was switched to an argon environment (using Schlenk line) and heated to the desired temperature (180–320 °C). Next, 70 nmol of CdX (X = S, Se) NCs in 1 mL of ODE were swiftly injected into the flask and allowed to grow for 30–60 min. The growth was stopped by quenching the reaction in a water bath. The product was cleaned by several precipitations with ethanol and resuspension in toluene. The final NC product was suspended in hexane and centrifuged for 30 s to remove anything insoluble.

Aggregative Growth in OLAM + OA (Nanorods). In a typical procedure, 2.5 mL of OA, 2.5 mL of OLAM, and 20 mg of  $CdCl_2$  were heated to the desired temperature (200–320 °C), followed by hot injection of 200–250 nmol of CdX (X = S, Se) NCs in 1 mL of ODE. Once the desired size (diameter of the rod) was reached, the

reaction mixture was cooled to 160–200 °C for 3–20 h to promote elongation via fusion of NCs. The NC product was cleaned via several successive precipitations with ethanol/toluene before being dispersed in hexane.

Aggregative Growth in OA + Stearoyl Chloride. Here, 50 mg of CdO, 5 mL of OA, and 1 mL of ODE were heated to 260  $^{\circ}$ C until a clear solution was achieved. The temperature was lowered to 120  $^{\circ}$ C and degassed for approximately 15 min. Switching to an argon environment, 0.2 mL of stearoyl chloride solution and 50 nmol of CdS NCs were added to the flask, followed by brief degassing to remove any solvent. The flask, under argon environment, was subsequently heated to 305–325  $^{\circ}$ C for 30 min. When using wurtzite NCs, the final product was rods and when using zinc blende NCs, the final product was cubes. Finally, the NCs were precipitated using excess isopropyl alcohol twice before being suspended in hexane and centrifuged for 30 s to remove anything insoluble.

**Aggregative Growth in NaOA (Donut-Shaped NCs).** For the formation of donut-shaped CdS NCs, 125 nmol of CdS seed NCs, 225 mg of sodium oleate, and 4 mL of OA were combined in a 25 mL flask and degassed at 150 °C for 10 min. The flask was then switched to an argon environment, placed on a Schlenk line, and heated to 245 °C for 10 min. The reaction was removed from the heat and allowed to cool to room temperature, finally being cleaned via three ethanol/ toluene precipitations. Final samples were redispersed in hexane.

**Aggregative Growth in OLAM + Se (Nanorings).** In a standard procedure, 200 nmol of CdSe NCs, 6 mL of OLAM, and 15 mg of selenium powder were placed into a flask and degassed at 100 °C. Following the degassing, the NC mixture was switched to an argon environment and maintained at that temperature for 20 h. The NC product was precipitated several times using ethanol/toluene method. The final product was suspended in hexane and centrifuged to remove any unreacted selenium powder.

**Stearoyl Chloride Stock Solution.** In a 25 mL flask, 10 mL of ODE was degassed at 120 °C for at least 30 min. It is important to remove any potential water to prevent the hydrolysis of the stearoyl chloride. Next, the flask was switched to an argon environment, removed from the heat, and 0.3 g of stearoyl chloride was added to the flask under positive argon pressure to prevent air from entering the flask. The stearoyl chloride would be fully dissolved within 10 min.

**Cleaning the Reaction Product.** After the reaction mixture had cooled to room temperature, equal amounts of solution (approximately 3 mL) were placed in two 15 mL centrifuge tubes. To precipitate the product, 2 mL of chloroform and 6 mL of ethanol were added to each tube, and the tubes were then inverted several times and centrifuged for 5 min at 6500 rpm. The clear supernatant was discarded, and the remaining precipitate was dissolved in 2 mL of chloroform, 6 mL of ethanol was added, and the centrifuge tubes were inverted several times and then centrifuged 5 min at 6500 rpm. Finally, the precipitate was dissolved in 5 mL of hexane and centrifuged for 3 min at 6500 rpm to remove any insoluble products. The final hexane solution was stored under ambient conditions and was stable for months.

**Characterization.** UV–vis absorption spectra were recorded using a Cary 60 scan spectrophotometer. High-resolution transmission electron microscopy (TEM) measurements were carried out using a Thermo Fisher Talos F200X G2 S/TEM instrument operated at 200 kV. Specimens were prepared by depositing a drop of NP solution in hexane onto a carbon-coated copper grid and allowing it to dry in air. Powder X-ray diffraction measurements were carried out with a Bruker D8 Advance PXRD. Energy dispersive X-ray (EDX) analysis was performed using Hitachi 2700 operated at 20 kV. Emission spectra were acquired using a 405-nm PicoQuant PDL 800-D pulsed laser and measured with an Andor newton<sup>EM</sup> SR-303i-A spectrograph. Time-resolved emission lifetime spectra were acquired using the same 405-nm pulsed laser, and photons were collected using ID Quantique's ID100-50 single-photon detector and processed using a SPC-130 TCSPC module from Beckler & Hickl.

#### ASSOCIATED CONTENT

#### **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00265.

Experimental section, additional figures, and details of calculation (PDF)

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#### **Author Contributions**

D.H., J.O., D.P., L.W., and B.S.L.N. contributed by performing experiments for the aggregative growth of nanocrystals. D.K. advised J.O. and provided editorial feedback on the manuscript. M.D.E.F. provided insight into experiments and provided editorial feedback for the manuscript. J.C. designed experiments, edited the manuscript, and performed aggregative growth experiments. M.Z. advised the project and wrote the manuscript.

#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Kovalenko, M. V.; Manna, L.; Cabot, A.; Hens, Z.; Talapin, D. V.; Kagan, C. R.; Klimov, V. I.; Rogach, A. L.; Reiss, P.; Milliron, D. J.; Guyot-Sionnnest, P.; Konstantatos, G.; Parak, W. J.; Hyeon, T.; Korgel, B. A.; Murray, C. B.; Heiss, W. Prospects of Nanoscience with Nanocrystals. *ACS Nano* **2015**, *9*, 1012–1057.

(2) Coe, S.; Woo, W.-K.; Bawendi, M.; Bulović, V. Electroluminescence from Single Monolayers of Nanocrystals in Molecular Organic Devices. *Nature* **2002**, *420*, 800–803.

(3) Shirasaki, Y.; Supran, G. J.; Bawendi, M. G.; Bulović, V. Emergence of Colloidal Quantum-Dot Light-Emitting Technologies. *Nat. Photonics* **2013**, *7*, 13–23.

(4) Dai, X.; Deng, Y.; Peng, X.; Jin, Y. Quantum-Dot Light-Emitting Diodes for Large-Area Displays: Towards the Dawn of Commercialization. *Adv. Mater.* **2017**, *29*, No. 1607022.

(5) Park, Y.-S.; Roh, J.; Diroll, B. T.; Schaller, R. D.; Klimov, V. I. Colloidal Quantum Dot Lasers. *Nat. Rev. Mater.* **2021**, *6*, 382–401.

(6) Yang, Z.; Pelton, M.; Fedin, I.; Talapin, D. V.; Waks, E. A Room Temperature Continuous-Wave Nanolaser Using Colloidal Quantum Wells. *Nat. Commun.* **2017**, *8*, No. 143.

(7) Clapp, A. R.; Medintz, I. L.; Mauro, J. M.; Fisher, B. R.; Bawendi, M. G.; Mattoussi, H. Fluorescence Resonance Energy Transfer Between Quantum Dot Donors and Dye-Labeled Protein Acceptors. *J. Am. Chem. Soc.* **2004**, *126*, 301–310.

(8) Beard, M. C.; Blackburn, J. L.; Johnson, J. C.; Rumbles, G. Status and Prognosis of Future-Generation Photoconversion to Photovoltaics and Solar Fuels. *ACS Energy Lett.* **2016**, *1*, 344–347.

(9) Porotnikov, D.; Zamkov, M. Progress and Prospects of Solution-Processed Two-Dimensional Semiconductor Nanocrystals. *J. Phys. Chem. C* 2020, 124, 21895–21908.

(10) Yang, Z.; Fan, J. Z.; Proppe, A. H.; de Arquer, F. P. G.; Rossouw, D.; Voznyy, O.; Lan, X.; Liu, M.; Walters, G.; Quintero-Bermudez, R.; Sun, B.; Hoogland, S.; Botton, G. A.; Kelley, S. O.; Sargent, E. H. Mixed-Quantum-Dot Solar Cells. *Nat. Commun.* 2017, 8, No. 1325.

(11) Mongin, C.; Garakyaraghi, S.; Razgoniaeva, N.; Zamkov, M.; Castellano, F. N. Direct Observation of Triplet Energy Transfer from Semiconductor Nanocrystals. *Science* **2016**, *351*, 369–372.

(12) Efros, A. L.; Brus, L. E. Nanocrystal Quantum Dots: From Discovery to Modern Development. *ACS Nano* **2021**, *15*, 6192–6210. (13) Voznyy, O.; Levina, L.; Fan, J. Z.; Askerka, M.; Jain, A.; Choi, M.-J.; Ouellette, O.; Todorović, P.; Sagar, L. K.; Sargent, E. H. Machine Learning Accelerates Discovery of Optimal Colloidal Quantum Dot Synthesis. *ACS Nano* **2019**, *13*, 11122–11128.

(14) Talapin, D.; Rogach, A.; Kornowski, A.; Haase, M.; Weller, H. Highly Luminescent Monodisperse CdSe and CdSe/ZnS Nanocrystals Synthesized in a Hexadecylamine–Trioctylphosphine Oxide– Trioctylphospine Mixture. *Nano Lett.* **2001**, *1*, 207–211.

(15) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. Highly Luminescent Monodisperse CdSe and CdSe/ZnS Nanocrystals Synthesized in a Hexadecylamine–Trioctylphosphine Oxide–Trioctylphospine Mixture. *Nano Lett.* **2001**, *1*, 207–211.

(16) Zhong, X.; Feng, Y.; Knoll, W.; Han, M. Alloyed Zn x Cd 1 - x S Nanocrystals with Highly Narrow Luminescence Spectral Width. J. Am. Chem. Soc. 2003, 125, 13559–13563.

(17) Li, J.; Wang, H.; Lin, L.; Fang, Q.; Peng, X. Quantitative Identification of Basic Growth Channels for Formation of Monodisperse Nanocrystals. J. Am. Chem. Soc. 2018, 140, 5474-5484. (18) Zhou, J.; Pu, C.; Jiao, T.; Hou, X.; Peng, X. A Two-Step Synthetic Strategy toward Monodisperse Colloidal CdSe and CdSe/CdS Core/Shell Nanocrystals. J. Am. Chem. Soc. 2016, 138, 6475-6483.

(19) Razgoniaeva, N.; Carrillo, L.; Burchfield, D.; Moroz, P.; Adhikari, P.; Yadav, P.; Khon, D.; Zamkov, M. Colloidal Synthesis of Monodisperse Semiconductor Nanocrystals through Saturated Ionic Layer Adsorption. *Chem. Mater.* **2016**, *28*, 2823–2833. (20) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Synthesis of Monodisperse Spherical Nanocrystals. *Angew. Chem., Int. Ed.* 2007, 46, 4630–4660.

(21) Dai, Q.; Wang, Y.; Li, X.; Zhang, Y.; Pellegrino, D. J.; Zhao, M.; Zou, B.; Seo, J.; Wang, Y.; Yu, W. W. Size-Dependent Composition and Molar Extinction Coefficient of PbSe Semiconductor Nanocrystals. *ACS Nano* **2009**, *3*, 1518–1524.

(22) Morris-Cohen, A. J.; Frederick, M. T.; Lilly, G. D.; McArthur, E. A.; Weiss, E. A. Organic Surfactant-Controlled Composition of the Surfaces of CdSe Quantum Dots. *J. Phys. Chem. Lett.* **2010**, *1*, 1078–1081.

(23) Smith, D. K.; Luther, J. M.; Semonin, O. E.; Nozik, A. J.; Beard, M. C. Tuning the Synthesis of Ternary Lead Chalcogenide Quantum Dots by Balancing Precursor Reactivity. *ACS Nano* **2011**, *5*, 183–190.

(24) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.;
Kadavanich, A.; Alivisatos, A. P. Shape Control of CdSe Nanocrystals. *Nature* 2000, 404, 59–61.

(25) Bealing, C. R.; Baumgardner, W. J.; Choi, J. J.; Hanrath, T.; Hennig, R. G. Predicting Nanocrystal Shape through Consideration of Surface-Ligand Interactions. *ACS Nano* **2012**, *6*, 2118–2127.

(26) Zhang, J.; Zhang, H.; Cao, W.; Pang, Z.; Li, J.; Shu, Y.; Zhu, C.; Kong, X.; Wang, L.; Peng, X. Identification of Facet-Dependent Coordination Structures of Carboxylate Ligands on CdSe Nanocrystals. J. Am. Chem. Soc. 2019, 141, 15675–15683.

(27) Lv, L.; Li, J.; Wang, Y.; Shu, Y.; Peng, X. Monodisperse CdSe Quantum Dots Encased in Six (100) Facets via Ligand-Controlled Nucleation and Growth. J. Am. Chem. Soc. **2020**, 142, 19926–19935.

(28) Xia, Y.; Chen, W.; Zhang, P.; Liu, S.; Wang, K.; Yang, X.; Tang, H.; Lian, L.; He, J.; Liu, X.; Liang, G.; Tan, M.; Gao, L.; Liu, H.; Song, H.; Zhang, D.; Gao, J.; Wang, K.; Lan, X.; Zhang, X.; Müller-Buschbaum; Tang, J.; Zhang, J. Facet Control for Trap-State Suppression in Colloidal Quantum Dot Solids. *Adv. Funct. Mater.* **2020**, *30*, No. 2000594.

(29) Sugimoto, T. Preparation of Monodispersed Colloidal Particles. *Adv. Colloid Interface Sci.* **1987**, *28*, 65–108.

(30) Hewavitharana, I. K.; Brock, S. L. When Ligand Exchange Leads to Ion-Exchange: Nanocrystal Facets Dictate the Outcome. *ACS Nano* **2017**, *11*, 11217–11224.

(31) Lifshitz, I. M.; Slyozov, V. V. The Kinetics of Precipitation from Supersaturated Solid Solutions. *J. Phys. Chem. Solids* **1961**, *19*, 35–50.

(32) Penn, R. L.; Banfield, J. F. Imperfect Oriented Attachment: Dislocation Generation in Defect-Free Nanocrystals. *Science* **1998**, 281, 969–971.

(33) Wang, F.; Richards, V. N.; Shields, S. P.; Buhro, W. E. Kinetics and Mechanisms of Aggregative Nanocrystal Growth. *Chem. Mater.* **2014**, *26*, 5–21.

(34) Kumar, S.; Davis, T. M.; Ramanan, H.; Penn, R. L.; Tsapatsis, M. Aggregative Growth of Silicalite-1. *J. Phys. Chem. B* 2007, 111, 3398–3403.

(35) Yu, K.; Ouyang, J.; Leek, D. M. In-Situ Observation of Nucleation and Growth of PbSe Magic-Sized Nanoclusters and Regular Nanocrystals. *Small* **2011**, *7*, 2250–2262.

(36) Razgoniaeva, N.; Yang, M.; Garrett, P.; Kholmicheva, N.; Moroz, P.; Eckard, H.; Royo Romero, L.; Porotnikov, D.; Khon, D.; Zamkov, M. Just Add Ligands: Self-Sustained Size Focusing of Colloidal Semiconductor Nanocrystals. *Chem. Mater.* **2018**, *30*, 1391–1398.

(37) Cheng, T.; Marin, R.; Skripka, A.; Vetrone, F. Small and Bright Lithium-Based Upconverting Nanoparticles. J. Am. Chem. Soc. 2018, 140, 12890–12899.

(38) Yu, L.; You, H.; Zhang, Q.; Zhang, L.; Fang, J. Digestive Ripening Mechanism Investigation in a Classical Lee–Meisel Method Based on in Situ UV-Vis Spectra. *CrystEngComm* **2019**, *21*, 1529–1533.

(39) Kim, M.-G.; Jeong, J.; Choi, Y.; Park, J.; Park, E.; Cheon, C.-H.; Kim, N.-K.; Min, B. K.; Kim, W. Synthesis of V-Doped In 2 O 3 Nanocrystals via Digestive-Ripening Process and Their Electrocatalytic Properties in CO 2 Reduction Reaction. *ACS Appl. Mater. Interfaces* **2020**, *12*, 11890–11897. (40) Cassidy, J.; Zamkov, M. Nanoshell Quantum Dots: Quantum Confinement beyond the Exciton Bohr Radius. *J. Chem. Phys.* 2020, 152, No. 110902.

(41) Kholmicheva, N.; Yang, M.; Moroz, P.; Eckard, H.; Vore, A.; Cassidy, J.; Pushina, M.; Boddy, A.; Porotnikov, D.; Anzenbacher, P.; Zamkov, M. Ion-Mediated Ligand Exchange and Size Focusing of Semiconductor Nanocrystals in Ligand-Saturated Solutions. *J. Phys. Chem.* C 2018, *122*, 23623–23630.

(42) Shimpi, J. R.; Sidhaye, D. S.; Prasad, B. L. V. Digestive Ripening: A Fine Chemical Machining Process on the Nanoscale. *Langmuir* **2017**, *33*, 9491–9507.

(43) Huang, X.; Parashar, V. K.; Ao, Z.; Gijs, M. A. M. Insight into the Growth of Anisotropic CdSe Nanocrystals: Attachment of Intrinsically Different Building Blocks. *J. Phys. Chem. C* **2020**, *124*, 27754–27762.

(44) Yuan, B.; Cademartiri, L. Growth of Colloidal Nanocrystals by Liquid-Like Coalescence. *Angew. Chem., Int. Ed.* **2021**, *60*, 6667–6672.

(45) Zheng, H.; Smith, R. K.; Jun, Y.-W.; Kisielowski, C.; Dahmen, U.; Alivisatos, A. P. Observation of Single Colloidal Platinum Nanocrystal Growth Trajectories. *Science* **2009**, *324*, 1309–1312.

(46) Yuk, J. M.; Park, J.; Ercius, P.; Kim, K.; Hellebusch, D. J.; Crommie, M. F.; Lee, J. Y.; Zettl, A.; Alivisatos, A. P. High-Resolution EM of Colloidal Nanocrystal Growth Using Graphene Liquid Cells. *Science* **2012**, 336, 61–64.

(47) Wang, F.; Richards, V. N.; Shields, S. P.; Buhro, W. E. Kinetics and Mechanisms of Aggregative Nanocrystal Growth. *Chem. Mater.* **2014**, *26*, 5–21.

(48) Polte, J.; Ahner, T. T.; Delissen, F.; Sokolov, S.; Emmerling, F.; Thünemann, A. F.; Kraehnert, R. Mechanism of Gold Nanoparticle Formation in the Classical Citrate Synthesis Method Derived from Coupled In Situ XANES and SAXS Evaluation. *J. Am. Chem. Soc.* **2010**, *132*, 1296–1301.

(49) Cassidy, J.; Ellison, C.; Bettinger, J.; Yang, M.; Moroz, P.; Zamkov, M. Enabling Narrow Emission Line Widths in Colloidal Nanocrystals through Coalescence Growth. *Chem. Mater.* **2020**, *32*, 7524–7534.

(50) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev.* 2005, 105, 1025–1102.

(51) Herring, C. Some Theorems on the Free Energies of Crystal Surfaces. *Phys. Rev.* **1951**, *82*, 87–93.

(52) Rempel, J. Y.; Trout, B. L.; Bawendi, M. G.; Jensen, K. F. Density Functional Theory Study of Ligand Binding on CdSe (0001), (0001), and (1120) Single Crystal Relaxed and Reconstructed Surfaces: Implications for Nanocrystalline Growth. *J. Phys. Chem. B* **2006**, *110*, 18007–18016.

(53) Sarkar, S.; Sharp, C. G.; Finn, S. T.; Macdonald, J. E. Cracking Shells and Scrambling Eggs: Intermediate Shell Formation and Anion Rearrangement in the Cation Exchange from p-SnS to Cu1.8S. *Chem. Mater.* **2021**, *33*, 3011–3019.

(54) Brilliantov, N. V.; Albers, N.; Spahn, F.; Pöschel, T. Collision Dynamics of Granular Particles with Adhesion. *Phys. Rev. E* 2007, *76*, No. 051302.

(55) Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. Melting in Semiconductor Nanocrystals. *Science* **1992**, *256*, 1425–1427.

(56) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15*, 2854–2860.

(57) Ostwald, W. On the Assumed Isomerism of Red and Yellow Mercury Oxide and the Surface-Tension of Solid Bodies. Z. Phys. Chem. 1900, 34U, 495–503.

(58) Chen, P. E.; Anderson, N. C.; Norman, Z. M.; Owen, J. S. Tight binding of carboxylate, phosphonate, and carbamate anions to stoichiometric CdSe nanocrystals. *J. Am. Chem. Soc.* **2017**, *139*, 3227–3236.

(59) Scholes, G. D. Controlling the Optical Properties of Inorganic Nanoparticles: Controlling the Optical Properties of Inorganic Nanoparticles. *Adv. Funct. Mater.* **2008**, *18*, 1157–1172.

(60) Cassidy, J.; Yang, M.; Harankahage, D.; Porotnikov, D.; Moroz, P.; Razgoniaeva, N.; Ellison, C.; Bettinger, J.; Ehsan, S.; Sanchez, J.; Madry, J.; Khon, D.; Zamkov, M. Tuning the Dimensionality of Excitons in Colloidal Quantum Dot Molecules. *Nano Lett.* **2021**, *21*, 7339–7346.

(61) Mei, Q. S.; Lu, K. Melting and Superheating of Crystalline Solids: From Bulk to Nanocrystals. *Prog. Mater. Sci.* 2007, *52*, 1175–1262.

(62) Kofman, R.; Cheyssac, P.; Aouaj, A.; Lereah, Y.; Deutscher, G.; Ben-David, T.; Penisson, J. M.; Bourret, A. Surface Melting Enhanced by Curvature Effects. *Surf. Sci.* **1994**, *303*, 231–246.

(63) Meakin, P. Formation of Fractal Clusters and Networks by Irreversible Diffusion-Limited Aggregation. *Phys. Rev. Lett.* **1983**, *51*, 1119–1122.

(64) Weitz, D. A.; Huang, J. S.; Lin, M. Y.; Sung, J. Limits of the Fractal Dimension for Irreversible Kinetic Aggregation of Gold Colloids. *Phys. Rev. Lett.* **1985**, *54*, 1416–1419.

(65) Yu, W. W.; Peng, X. Formation of High-Quality CdS and Other II–VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. *Angew. Chem., Int. Ed.* **2002**, *114*, 2474–2477.

(66) Buffat, P.; Borel, J.-P. Size Effect on the Melting Temperature of Gold Particles. *Phys. Rev. A* **1976**, *13*, 2287–2298.

(67) Yu, W. W.; Peng, X. Formation of High-Quality CdS and Other II–VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. *Angew. Chem., Int. Ed.* **2002**, *114*, 2474–2477.

(68) Pu, C.; Zhou, J.; Lai, R.; et al. Highly reactive, flexible yet green Se precursor for metal selenide nanocrystals: Se-octadecene suspension (Se-SUS). *Nano Res.* **2013**, *6*, 652–670.

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