# Crystal Structure Control of CdSe Nanocrystals in Growth and Nucleation: Dominating Effects of Surface versus Interior Structure

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Ⓢ *Supporting Information*

ABSTRACT: For the most studied nanocrystal system in the literature, experimental results in this paper revealed that formation of either zinc blende or wurtzite CdSe nanocrystals was dominated by the ligand—surface interaction, instead of the interior structure difference. This conclusion was considered to be reasonable, given the very small energy difference between wurtzite and zinc blende CdSe (only 1.4 meV per CdSe unit and about 1000 times smaller than the energy of a single cadmium—ligand bond). Cadmium carboxylate ligands in the form of cadmium fatty acid salts promoted formation of the zinc blende structure. Conversely, cadmium phosphonate ligands with a long hydrocarbon chain favored the formation of the wurtzite structure. The effects of either cadmium carboxylate or cadmium phosphonate ligands were found to play a determining role during both nucleation and growth. Different from our expectation, fatty amine was found to be only a secondary factor for crystal structure determination. With an appropriate choice of capping ligands, it was possible to achieve precise control of the crystal structure of the CdSe nanocrystals in both nucleation and growth for either the zinc blende or wurtzite structure.
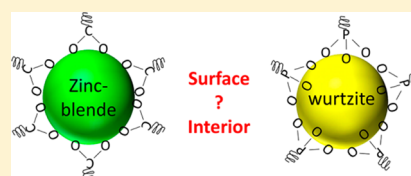
■ INTRODUCTION

The synthesis of size- and shape-controlled colloidal semiconductor nanocrystals in their quantum confinement size regime has achieved great success in the past couple decades.[1,2] Extensive studies revealed that, to fully realize their size-dependent optical properties, semiconductor nanocrystals should be not only monodisperse in size but also single-crystalline with identical crystal structures.[3−5] This has inspired great interest in identification of parameters that control the crystal structure of semiconductor nanocrystals in both nucleation[6,7] and growth.[8−13] Unfortunately, even for the most studied CdSe nanocrystal system, perfection of the crystal structure of the nanocrystals has not reached a satisfactory level yet, especially in the wurtzite structure.[14,15] The results described below suggest that, instead of considering the interior structure difference, it is necessary to take surface effects into account. In the specific case of the CdSe nanocrystal system, in this paper we will reveal that the surface effects dominated the structural difference during both nucleation and growth of CdSe nanocrystals for either the wurtzite (hexagonal) or zinc blende (face-centered cubic) structure.

II—VI and III—V binary systems, at present, are the main focus of both fundamental study and technical applications of semiconductor nanocrystals. These binary compounds can all appear in either the zinc blende or wurtzite crystal structure. In both types of crystal structures, each cation (anion) is coordinated with four counterions in a tetrahedral configuration. While the local coordination and bond length in both crystal structures are identical, the hexagonal planes—along the (111) direction for the zinc blende structure and the (001) direction for the wurtzite structure—are rotated 60° with

respect to each other. Although this structural difference seems to be subtle, it breaks the inversion symmetry in the wurtzite structure and thus makes the optical properties of the two types of nanocrystals differ from each other, which was suggested by both theoretical and experimental studies.[3−5,16] Therefore, if the nanocrystals were synthesized with an imperfect structure, a new type of unnecessary inhomogeneity of their optical properties would result.

The difficulty in controlling the structural perfection of either zinc blende or wurtzite is their quite small structural difference discussed in the above paragraph, which in turn results in a very small energy difference. For CdSe, theoretical calculations revealed that the energy difference between its zinc blende and wurtzite structures is only 1.4 meV per CdSe unit.[17] Because the phase transition temperature from zinc blende (room temperature stable) to wurtzite (high temperature stable) is about 100 °C for the bulk,[18] the entropy difference between the two phases should also be quite small. It is interesting to notice that synthetic methods for good quality zinc blende as well as wurtzite CdSe nanocrystals were all established at a temperature significantly above 100 °C,[1,2] and the structural perfection of zinc blende nanocrystals (typically formed between 200 and 300 °C) seemed to be at least as good as that of their wurtzite counterparts.

There is a substantial difference between a bulk crystal and a nanocrystal, which is the role of surface coordination. To achieve satisfactory optical properties and colloidal stability, good quality semiconductor nanocrystals available today were

all synthesized with a monolayer of organic ligands, such as carboxylate, amine, phosphonate, and phosphine ligands.[19] The bonding energy between the surface cadmium ions and surface ligands must be substantially larger than the energy difference between zinc blende and wurtzite crystal structures (for details see the Results and Discussion). This suggested to us that control of the crystal structure of the CdSe nanocrystal system should be dominated by the ligand bonds with the surface ions of the nanocrystals.

A systematic study was carried out to test the hypothesis outlined in the above paragraph, i.e., formation of a specific crystal structure being determined by capping ligands. By judiciously designing the reaction system, it was possible to separate the initial formation (or nucleation) stage and the following growth stage, which demonstrated somewhat different trends of ligand effects. While the main hypothesis was generally verified, this work also revealed some other interesting results. Unlike the studies described in the literature,[20,21] this study showed that synthesis of stable wurtzite CdSe nanocrystals in the commonly known nucleation size regime, i.e., ~2 nm, was possible with proper choices of the ligands. Using these newly discovered wurtzite CdSe small particles as the seeds, it will be demonstrated below that high crystal purity wurtzite CdSe nanocrystals could be synthesized at relatively low temperature.

■ RESULTS AND DISCUSSION

Choice of Systems for Study. The CdSe nanocrystal system, including both the wurtzite and zinc blende structures, has been the most studied system up to now. In this study, as the noncoordinating solvent approach in various forms gave the best performance,[22,23] it was applied. Octadecene (ODE) was the noncoordinating solvent. Organic ligands studied by this work mainly included the three most common ones, namely, cadmium carboxylates, amines, and cadmium phosphonates with a long hydrocarbon chain. The cadmium precursor was either CdO reacting with fatty acids in situ or isolated cadmium fatty acid (phosphonic acid) salts. The Se precursor was mostly a suspension of Se in ODE (Se-SUS),[24] a Se−ODE solution,[7,23,25] or a Se−amine solution. The commonly used Se−phosphine precursors[14] were also tested as well. The reactions were typically carried out at temperatures between 200 and 300 °C under an Ar flow. The details are provided in the Experimental Section.

For simplicity, we employ an expanded abbreviation system suggested previously[26] for fatty amine, fatty acid, and fatty acid salts. Fatty amines are abbreviated as NH_2Xy, where Xy is the first two letters of the common name of the corresponding amine. In this abbreviation system, the first letter of the common name is capital and the second is lower case. For example, oleylamine would be abbreviated as NH_2Ol. For fatty acid and cadmium fatty acid salts, the abbreviations are quite similar to those of fatty amines, but the "NH_2" in the abbreviation is replaced by either "H" or "Cd", respectively. For instance, stearic acid and cadmium stearate would be written as HSt and $Cd(St)_2$, respectively.

Estimation of the Transition Enthalpy and Entropy from Zinc Blende to Wurtzite CdSe Nanocrystals. For CdSe, theoretical calculations revealed that the energy difference between its zinc blende and wurtzite structures is only 1.4 meV per CdSe unit,[17] which corresponds to about 0.14 kJ/mol of CdSe units. For the CdSe nanocrystal system, the bonding energy between the surface cadmium ions and surface

ligands varies from case to case. As a rough reference, a typical metal−ligand coordination bond should be between ~50 to 150 kJ/mol, which is extremely large in comparison with the energy difference between the zinc blende and wurtzite crystal structures.

For the case of nucleation, the size of the particles should be 2 nm (or smaller). Taking a 2 nm CdSe particle coated with carboxylate ligands—usually from fatty acids—as an example, the total energy difference between the zinc blende and wurtzite interior structures for this particle is only ~0.11 eV. This value is even smaller than the energy of a single hydrogen bond, which is roughly 20 kJ/mol (or 0.21 eV/bond). As the total number of carboxylate−Cd bonds for a 2 nm CdSe particle should be around 40−50, the energy difference between two crystal structures would thus unlikely play a significant role in the nucleation stage.

For the growth stage after nucleation, the energy difference contributed by the interior structures was further reduced in comparison to that of the surface ion−ligand coordination. Let us consider a layer-by-layer growth model for conservative reasons. The number of bonds formed in the middle of a layer is proportional to its area, and the number of coordinations on the surface should be proportional to the number of dangling bonds at the edge of the layer. Therefore, with this conservative model, one could safely conclude that the role of surface coordination in the growth stage should be at least as important as in the case of nucleation. For an aggressive model, one could argue that every step of growth involves surface ion−ligand bonds.

The entropy difference of the interior structures would also unlikely play a decisive role in control of the crystal structure for the CdSe nanocrystal system. An early work reported that the phase transition temperature from zinc blende (room temperature stable) to wurtzite (high temperature stable) for bulk CdSe is about 100 °C.[18] From this and the enthalpy of the phase transition, one could roughly estimate the entropy difference between two phases should be ~0.38 J/(K mol), which is very small. A computational work supported this estimation, which reported the entropy difference between zinc blende and wurtzite bulk CdSe is negligible.[27]

The Rosenthal group[28] reported that sub ~2 nm CdSe nanocrystals could be amorphous even at room temperature. They suggested that, as the energy difference between the zinc blende and wurtzite structures is so small, nanoparticles with such small sizes have a somewhat difficult time choosing a structure. Because the reaction temperature in a typical synthesis for good quality CdSe nanocrystals is always significantly higher than room temperatures, it is thus not possible for the CdSe nanocrystals to make a choice based on the energy difference between the two structures. As a result, the final structure of the nuclei and the growth of additional materials might be solely determined by the surface ligands.

Effects of Fatty Amine on the Growth of Wurtzite CdSe Nanocrystals. Fatty amines have been widely used in the synthesis of wurtzite CdSe and other types of II−VI (or III−V) semiconductor nanocrystals. However, in terms of control of the crystal structure of a given type of nanocrystal, different studies usually led to different conclusions.[9,29] To clarify this issue, a systematic study was carried out with a fixed solution composition other than the concentration of the amine.

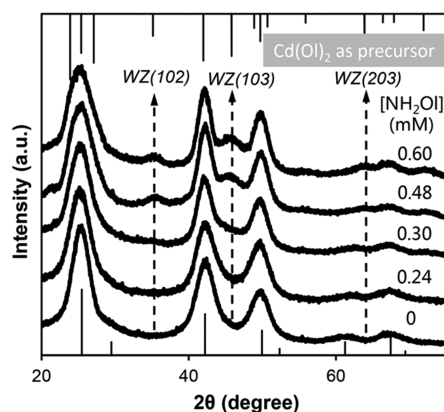Figure 1 illustrates a series of powder X-ray diffraction (XRD) patterns of CdSe nanocrystals (~5 nm in size for all

Figure 1. XRD patterns of CdSe nanocrystals (∼5 nm in size) synthesized with different oleylamine (NH₂Ol) concentrations varied from 0 to 0.6 mM. Three unique diffraction peaks of the wurtzite structure are indicated by dashed arrows (WZ(102), WZ (103), and WZ(203)) in the plot. The short bars on the top (bottom) of the plot represent the diffraction pattern of the bulk wurtzite (zinc blende) CdSe structure.

Figure 2. Representative TEM images, high-resolution TEM images, and SAED patterns of CdSe nanocrystals synthesized with either 0.60 mM (left panel) or 0 mM (right panel) NH₂Ol.

cases) formed with different NH_2Ol concentrations. In all reactions, the cadmium precursor $(Cd(St)_2)$ was formed by reaction of 0.1 mmol of CdO and 0.4 mmol of HSt in 4 mL of ODE, and the Se precursor was a Se solution made by dissolving Se in ODE and NH_2Ol. Introduction of amine from the Se precursor was found to be beneficial in terms of controlling the stability of the cadmium carboxylates in the reaction system. To make all reactions comparable, the reaction temperature was controlled between 280 and 300 °C until the size of the nanocrystals reached ∼5 nm (see the transmission electron microscopy (TEM) images in Figure 2 as examples).

The XRD patterns in Figure 1 reveal a gradual change of the CdSe nanocrystals from zinc blende to wurtzite structure with an increase of the NH_2Ol concentration. All diffraction peaks in Figure 1 support this trend. As the NH_2Ol concentration gradually increased in Figure 1, the (111) peak of the zinc blende structure at about 26° evolved into a broad envelop due to the overlap of the (100), (002), and (101) Bragg peaks of the wurtzite structure. Unlike the completely indistinguishable diffraction peaks between the zinc blende and wurtzite structures, the unique Bragg peaks of the wurtzite structure, namely, the (102), (103), and (203) peaks, are all identifiable by the patterns associated with reactions with a reasonably high amine concentration.

When no NH_2Ol was present in the reaction solution, the XRD pattern (the lowest pattern in Figure 1) matched quite well with the standard zinc blende diffraction pattern. It should be noticed that even the XRD pattern with the highest NH_2Ol concentration in Figure 1 reveals significant imperfection in comparison to the standard wurtzite diffraction pattern. A further increase of the NH_2Ol concentration apparently did not improve the quality of the samples as judged by XRD diffraction. This imperfection is evidently similar to that of the common XRD patterns of wurtzite CdSe nanocrystals reported in the literature.[14,15] Furthermore, selective area electron diffraction (SAED) patterns shown in Figure 2 also confirm the perfection of the zinc blende nanocrystals and imperfection of the wurtzite nanocrystals.

High-resolution TEM was applied to further examine the structure of the nanocrystals. Consistent with the hypothesis illustrated in the above paragraph, the nanocrystals were found
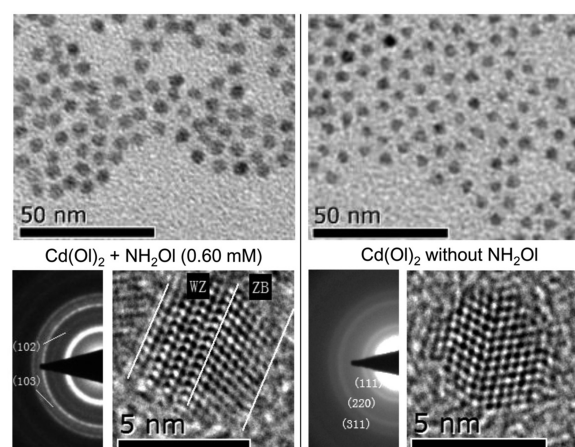
to be wurtzite nanocrystals with a significant number of stacking faults. Interestingly, the stacking faults were not randomly distributed. The high-resolution TEM picture of a typical CdSe nanocrystal synthesized with a high NH_2Ol concentration is shown in Figure 2 (left panel) and reveals that the particle actually has a section of zinc blende at one end. Also consistent with the XRD analysis, the zinc blende nanocrystals were found to be of good quality, with one stacking fault on average along the (111) direction per dot (see Figure 2, right panel for one example with a single stacking fault). With such atomic level information from the high-resolution TEM measurements, one could simulate the XRD pattern (simulation details to be provided below) with good confidence (see Figure S1, Supporting Information).

The above observation is consistent with the suggestion that nucleation of zinc blende CdSe nanocrystals is relatively easy.[20,21,30] Thus, a plausible interpretation of the results illustrated above is that the initial seeds—or nuclei—of CdSe nanocrystals were zinc blende seeds. When no amine was present in the reaction solution, the nanocrystals were grown in zinc blende structure with only fatty acid salts (fatty acids excluded by late experiments; see the next subsection) as the ligands. When amine was added as an additional ligand, the system was promoted to the growth of the wurtzite structure. Because the reaction temperature was significantly below the phase transition temperature needed for the nanocrystals in this size range,[11] the zinc blende structure remained as a section along with the wurtzite section in the final nanocrystals.

Growth of CdSe Nanocrystals on Existing Zinc Blende Seeds. Though the addition of amine leads to the growth of wurtzite CdSe, one could argue that amine may activate the Cd precursor, leading to a faster growth. According to the literature,[11] the growth rate might dictate the crystal structure of the final nanocrystals. Thus, the results in Figures 1 and 2 cannot distinguish whether the structure is the effect of either the ligands or the reaction rate.

A set of comparative experiments were designed to clarify the issue discussed in the above paragraph. In this set of reactions, zinc blende CdSe nanocrystals with only 2.5 nm size were synthesized without addition of amine. The as-synthesized seeds were purified according to the literature[5] to remove unreacted precursors. As shown in Figure S2 (Supporting Information), no shift of the first peak of absorption was

observed after the purification. The purified seeds were mixed with 2 mL of NH$_2$Ol and 4 mL of ODE and heated to 220 °C under an Ar flow. A slight blue shift (2 nm) of the first absorption peak was observed, indicating the partial displacement of metal carboxylate complexes by amine.[31] Other than that, the system was found to be stable upon prolonged heating. At this temperature, 0.6 mL of 0.1 M Se-SUS was injected into the reaction flask. According to a recent study,[24] Se powder in the suspension would immediately yield very reactive H$_2$Se, and the reactive H$_2$Se would attack the Cd−carboxylate bonds on the surface of the nanocrystals. In the current system, this rapidly initiated the growth of the nanocrystals through the Ostwald ripening process. In this process, CdSe monomers were dissolved from small dots and grown on the bigger ones, which resulted in the red shift of the first peak of UV−vis absorption (Figure S2).

The comparative experiment was performed by simply replacing NH$_2$Ol with oleic acid (HOl). Again, the nanocrystals remained stable by heating the mixture of the 2.5 nm zinc blende seeds, HOl, and ODE to 220 °C. However, the amount of Se-SUS with the same volume fraction of Se was reduced to 0.2 mL. Injection of the same amount of Se-SUS used in the first reaction described in the above paragraph caused rapid aggregation of CdSe nanocrystals. Infrared (IR) measurements suggested that the nanocrystal precipitate was nearly naked (Figure S3, Supporting Information). Because there was a large amount of HOl in the solution, the precipitation of the nanocrystals implied that HOl could not be a good ligand for the nanocrystals. This seems to be reasonable if one notices that free fatty acids cannot coordinate well with either the surface cations or surface anions.

The XRD patterns of the final products (∼5 nm in size) of two comparative reactions are plotted in Figure 3a. The pattern for the reaction with NH$_2$Ol resembled the pattern with a high concentration of amine in Figure 1, namely, a pattern with all wurtzite features and a certain degree of structural imperfection. The corresponding high-resolution TEM picture (see Figure 3b as one example) also showed a combination of a zinc blende section and a wurtzite section. In comparison, the XRD pattern and high-resolution TEM picture for the reaction with HOl (instead of NH$_2$Ol) revealed the final CdSe nanocrystals had the zinc blende structure.

Moreover, parts d and e of Figure 3 suggest that two comparative reactions, though they resulted in growth of either the wurtzite structure (with NH$_2$Ol) or zinc blende structure (with HOl), occurred at about the same growth rate. This means that the growth rate was not the determining parameter for growth in either the wurtzite or zinc blende structure. Instead, it would be safe to conclude that amine ligands induced the growth of the wurtzite structure on these zinc blende seeds through ligand−surface interaction.

It is worth noting that the results above contradict a recent proposal that Ostwald's rule of stages dictates the isolated phase of the final nanocrystals without a structure-directing ligand.[11] There could be two reasons for this inconsistency. First, their system possessed a relatively complex ligand composition, i.e., a mixture of amine, cadmium carboxylate, and tributylphosphine. Second, the variation of the Cd:Se ratio and Cd(St)$_2$ concentrations in their system could also lead to an uncontrolled surface.

Attempts To Control Nucleation by Amine Ligands.
The experimental results shown in Figures 1−3 reveal that fatty amine promoted growth of the wurtzite structure while fatty
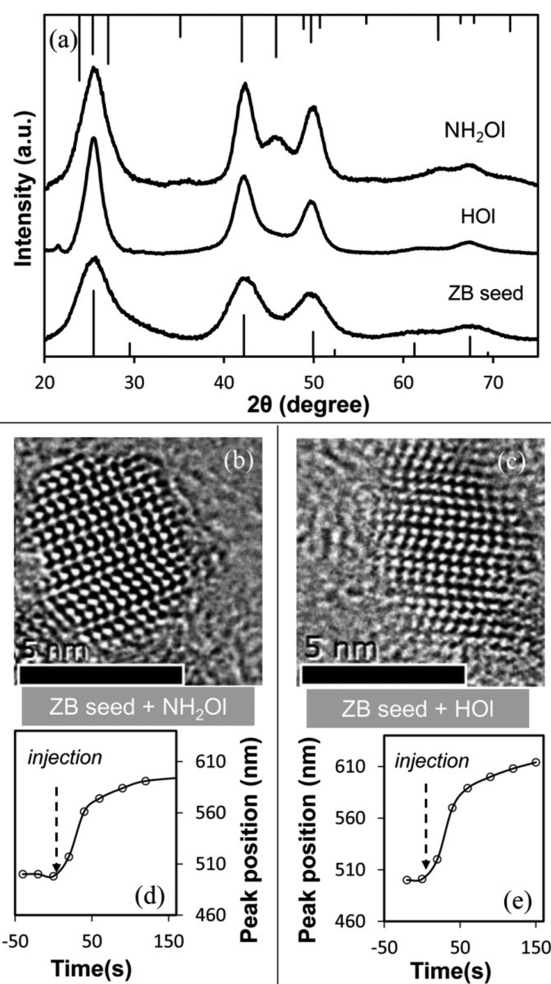

Figure 3. (a) XRD patterns of the 2.5 nm zinc blende (ZB) core and 6 nm final nanocrystals formed with different ligands. (b, c) HR-TEM images of the final samples. (d, e) Time evolution curves of the absorption peak of the nanocrystals for the growth reactions with different ligands.

acids did not. This fact inspired an extensive amount of work to achieve structure-controlled nucleation by fatty amine ligands.

Several types of cadmium precursors were tested, including cadmium nitrate, cadmium acetylacetonate, Cd(Ac)$_2$, and Cd(Fa)$_2$. Unfortunately, none of the reactions with these nonligand Cd precursors gave us positive results on nucleation control. Usually, the reaction was often too fast to be controlled, which reveals that fatty amines are much weaker ligands in comparison to cadmium fatty acid salts.

Reactions attempted to consume the carboxylate groups from long-chain fatty acids during formation of CdSe nanocrystals were also unsuccessful. Although formation of amides by the reaction of cadmium fatty acid salts with amine was observed, the XRD patterns of the resulting CdSe nanocrystals were still not much better than those with a high amine concentration in Figure 1. Furthermore, employment of other noncharge ligands, such as trioctylphosphine oxide (TOPO) and tributylphosphine (TBP), did not improve the situation, too.

Nucleation in Wurtzite Structure by Cadmium Phosphonate Ligands. The results discussed above suggest that, with cadmium carboxylates and/or fatty amines, it would not be possible to obtain wurtzite CdSe nanocrystals with a

high structural purity. Likely, the problem is a lack of ligand-dominated structure control for wurtzite CdSe during the nucleation stage. By going through the literature, it is found that cadmium phosphonate often fostered growth of wurtzite rods and tetrapods out of a zinc blende core with good crystal quality.[32,33] More importantly, the side facets of the wurtzite rods and tetrapods were typically nonpolar ones.[32,33] This implies that, though cadmium phosphonate ligands are also negatively charged, they might be able to stabilize all facets of the wurtzite structure of CdSe nanocrystals. The difference between carboxylate and phosphonate ligands might be a result of their distinguishable coordinating habits. Usually, a phosphonate group can coordinate with three or more cation centers, instead of one (or two) for the carboxylate group.[34,35]

Fortunately, employment of cadmium phosphonate as the Cd precursor (Se-SUS as the Se precursor) indeed yielded small-sized wurtzite nanocrystals with very high structure purity. The XRD pattern matched well with a pure wurtzite stacking sequence (Figure 4, top). The reaction temperature
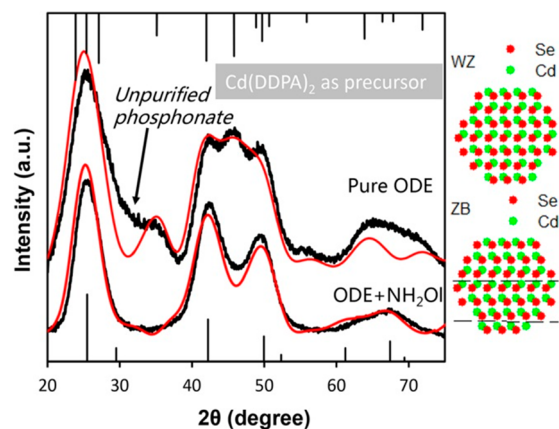

Figure 4. XRD patterns of 2.5 nm CdSe nanocrystals synthesized with (bottom) and without (top) NH$_2$Ol using cadmium dodecylphosphonate (Cd(DDPA)$_2$) as the Cd precursor. Red lines are the computer simulation results. Stacking sequences (shown to the right of the plot) applied to the simulations are ABABABA (ABC*BAC*A) for particles synthesized without (with) NH$_2$Ol.

was typical, i.e., 250−280 °C, about 100 °C lower than the temperature (∼370 °C) used for formation of wurtzite CdSe nanocrystals reported in literature.[36]

Interestingly, when fatty amine was introduced into this new system, zinc blende CdSe nanocrystals with at least two stacking faults were obtained (Figure 4, bottom). Considering there were only seven atom layers in such a small nanocrystal, "polycrystalline" may be a more appropriate description of the dots synthesized with amine added to this new system.

High-resolution TEM could directly offer structural information on nanocrystals at the atomic level, especially with the help of exit wave reconstruction.[37] However, a particle with a specific orientation on the substrate would be required to give a definite answer. For CdSe nanocrystals with wurtzite and zinc blende structures, such a specific orientation does not occur frequently on TEM substrates. Thus, a more conclusive method is to combine high-resolution TEM experiments with XRD simulation, which could give a global picture of the entire sample. The XRD patterns in this work were all simulated following a literature method.[14] The nanocrystals were built by layering either the (111) plane of zinc blende or the (001) plane of wurtzite one by one. The bulk bond length (2.63 Å for CdSe) was used. The sequence used for zinc blende was ABCABC..., while ABABAB... was used for the wurtzite structure. Atoms falling within the defined sphere of a given size were selected and calculated using a discrete form of the Debye equation:[38]

$$I(S) = I_0 \frac{f^2(S)}{2\pi S} \sum_k \frac{p(r_k)}{r_k} \sin(2\pi r_k S) \tag{1}$$

where $I(S)$ is the diffracted intensity, I_0 is the incident intensity, $f(S)$ is the scattering factor, S is the scattering parameter ($S = 2 \sin(q)/\lambda$ for X-rays of wavelength λ diffracted through angle q), r_k is the interatomic distance, and $p(r_k)$ is the number of times a given interatomic distance r_k occurred.

Simulation of the XRD patterns (Figure 4) confirmed that cadmium phosphonate ligands indeed behaved differently from cadmium carboxylate ligands. Surprisingly, the effect of amine revealed in Figure 4 was actually to promote formation of the zinc blende structure, instead of the wurtzite structure suggested in the literature.[9] Moreover, the results in Figures 1−3 definitely reveal amine-promoted growth of the wurtzite
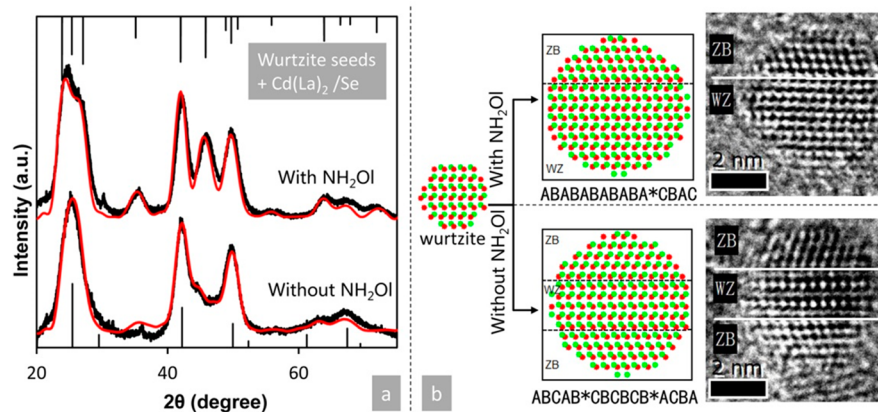

Figure 5. (a) XRD patterns of CdSe nanocrystals (5 nm in size) grown with wurtzite seeds using a cadmium carboxylate precursor with (or without) amine. Red lines are the computer simulation results. (b) Schematic diagram of the CdSe nanocrystals used for XRD simulations and the corresponding typical HR-TEM images.
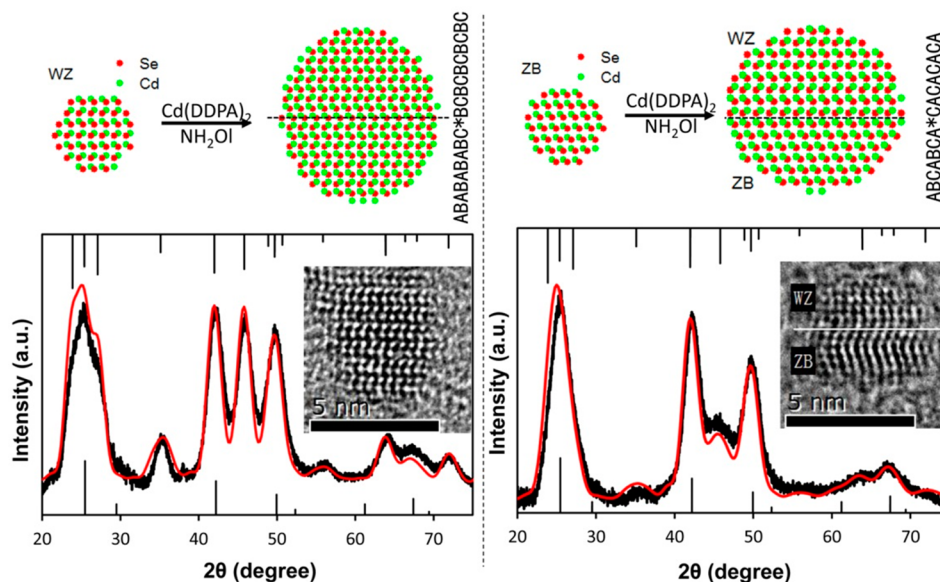
Figure 6. XRD pattern and a representative high-resolution TEM image of 5 nm CdSe nanocrystals formed by seeded growth with cadmium dodecylphosphonate (Cd(DDPA)$_2$) as the Cd precursor and NH$_2$Ol added. Red lines are the computer XRD simulation results using the sequence and shape in the corresponding schematic diagram. Left: 2.5 nm wurtzite seeds. Right: 2.5 nm zinc blende seeds.

structure in the growth stage. Evidently, the main difference between the reactions associated with Figure 4 and those shown in Figures 1−3 was the cadmium precursor used—also potentially the major ligands. Presumably, the existence of amine in either the cadmium phosphonate or cadmium carboxylate system would change the composition of the ligands, which in turn would weaken the structure choice of the nuclei for both cases. The experiments below further confirm this suggestion.

Growth onto Wurtzite Seeds with Cadmium Carboxylate. After the wurtzite CdSe nanocrystals were obtained in the nucleation stage, it became possible to complete the study on ligand-induced structure control in the growth stage with cadmium carboxylate. Such studies using zinc blende seeds in the literature[29] as well as this study (see Figures 1−3 as examples) are already in place.

The purified wurtzite CdSe nanocrystal seeds (~2.5 nm in size) synthesized using cadmium phosphonate (Figure 4, no amine) with known concentration[39] were mixed with Cd(La)$_2$ and NH$_2$Ol in ODE. The mixture was heated to 220 °C under Ar and was found to be stable. The growth was initiated by injection of Se-SUS into the flask (see the Experimental Section for details). For comparison, a reaction without any amine was performed in parallel with all other conditions the same. The XRD patterns show a dramatic difference between the nanocrystals obtained in this set of comparative reactions (Figure 5a). The XRD pattern of the final CdSe nanocrystals grown with the existence of NH$_2$Ol was likely among the best quality diffraction patterns reported up to now for wurtzite CdSe nanocrystals.[10,15] Conversely, the XRD pattern for the reaction without amine was quite similar to that of zinc blende with some stacking faults. The analytical technique with XRD simulation (Figure 5a) coupled with high-resolution TEM (Figure 5b) was applied to yield more quantitative structural information for both cases. The simulation results indicated that, though the quality of the XRD pattern of the nanocrystals grown with amine in place (top curve in Figure 5a) was among the best in the literature for wurtzite CdSe nanocrystals, it still

had a zinc blende section on one edge of the particle. For the nanocrystals grown without amine, high-resolution TEM showed CdSe nanocrystals with a small section of wurtzite structure sandwiched in the middle of two zinc blende regions (Figure 5b). More quantitatively, the maximum size of the wurtzite section in the sandwich structure was found to be ~7 atomic layers according to the simulation results. This was the size of the seeds used in the growth (see Figure 4). It should be mentioned that, as amine could also be a ligand in the system, the final Cd:Se ratio in such reactions should not exceed 1:1. Otherwise, the cadmium carboxylate ligands would be converted into fatty acid. Similar experimental results were also obtained if the Se precursor was the traditional selenium tributylphosphine (Figure S4, Supporting Information) instead of Se-SUS.

The results in this subsection combined with the results about growth on zinc blende seeds (see the text related to Figures 1−3) reveal that the ligand effects at the growth stage could be separated from that in the nucleation stage. Independent of the crystal structure of the seeds, cadmium carboxylate ligands promoted the growth of zinc blende CdSe nanocrystals. The existence of amine along with cadmium carboxylate ligands would alter the growth habit from zinc blende to wurtzite nanocrystals. Again, similar to what was proposed for amine in altering the nucleation habit of cadmium phosphonates, amine in the current case could also affect the ligand environment dictated by the cadmium carboxylate ligands in the solution. This in turn would change the growth habit of the nanocrystals. The results above further imply that, if a high concentration of amine and an excess of Se precursor are in place, the CdSe nanocrystals obtained will be in a structure close to wurtzite with zinc blende stacking faults. This was actually the condition mostly used for synthesis of such a type of CdSe nanocrystals in the literature.[15]

Synthesis of Wurtzite CdSe Nanocrystals with Different Types of Seeds. Initially, we suspected that cadmium phosphonate (or cadmium phosphonate with some free phosphonic acid) would yield high-purity wurtzite CdSe

nanocrystals with different sizes under certain conditions. However, this was not successful. The system was often found to be too reactive when excess phosphonic acid was added (or produced by the reaction of the Se precursor with excess cadmium phosphonate), which would thus induce Ostwald ripening rapidly. Because phosphonic acid is a pretty strong acid, we thought it should be possible to neutralize it by fatty amine. The results in Figure 6 (right) reveal that, by addition of NH_2Ol to the reaction system with wurtzite seeds formed by the approach shown in Figure 4, large-sized CdSe nanocrystals with a high-purity wurtzite crystal structure were indeed obtained. The XRD pattern with very sharp (102) and (103) peaks in Figure 6 (left) was substantially better in comparison to that shown in Figure 5 (top curve). High-resolution TEM and computer simulation of the XRD pattern gave us wurtzite nanocrystals with at most one stacking fault per dot (the high-resolution TEM image in Figure 6 (left) shows a wurtzite nanocrystal without any stacking fault).

It should be noted that this approach is not optimized yet for production (see the Experimental Section for details), though it does yield high-purity wurtzite CdSe nanocrystals. At present, the Se precursor is selenium tributylphosphine as the greener Se-SUS would result in rapid nucleation of small-sized CdSe nanocrystals. This is very likely because cadmium phosphonates are bound onto the surface of nanocrystals quite tightly. As a result, when active Se precursors are added to the system, they react with cadmium phosphonates in solution.

Experimental results further revealed that the high-purity wurtzite CdSe nanocrystals in large sizes also depended on the structure of the seeds. As shown in Figure 6 (right), the structural purity of the final nanocrystals grown on the zinc blende seeds using cadmium phosphonate and amine was quite poor. Quantitatively, the final nanocrystals grown with zinc blende seeds were identified as having one section of zinc blende and one section of wurtzite. More importantly, the size of the zinc blende region agreed with the size of the seeds used (Figure 6, right).

The combined results in Figure 6 (left and right) reveal that cadmium phosphonate promotes growth of wurtzite CdSe no matter what the crystal structure of the seeds is. This is consistent with our hypothesis that the crystal structures of CdSe nanocrystals in both nucleation and growth should be mostly determined by the ligands. However, this result contradicts the suggestions in the literature. Cadmium phosphonate was usually thought to "arrest" the structure of the nuclei due to the strong bonding feature and thus should yield final nanocrystals with the same structure as the seeds.[12,40]

CONCLUSION

In summary, instead of the interior crystal structure, surface ion–ligand coordination was found to be the key factor in determining the crystal structure of CdSe nanocrystals, i.e., wurtzite versus zinc blende. Overall, the results above showed that cadmium phosphonate ligands (cadmium carboxylate ligands) promoted formation of the wurtzite (zinc blende) CdSe structure in both nucleation and growth. Conversely, fatty amines, fatty acids, phosphonic acids, and phosphines did not show decisive effects. After extensive and systematic studies, it was found that fatty amines usually act as a secondary factor in structure determination likely due to their weak bonding[41] and highly dynamic[42] nature. Experimental results further revealed that structure conversion from wurtzite (zinc blende) to zinc blende (wurtzite) would not occur in typical reaction

conditions at least when the size of the nanocrystals was 2.5 nm or larger. By controlling both nucleation and growth ligand systems, it was possible to obtain high-purity CdSe nanocrystals for both the wurtzite and zinc blende structures. Selection of one crystal structure over the other was found to be independent of the reaction rates, and in fact, formation of high-purity wurtzite CdSe nanocrystals with a decent size (~5 nm) could only be achieved with a very low growth rate in this work. Although the exact ligand–surface coordination is unknown due to limited access to the surface structure of nanocrystals at present, the results shown in this work shed new light on the precise control of the crystal structure of the nanocrystals. This is not only important for synthesis of nanocrystals with desired properties, but also of interest for understanding crystallization in general. In principle, any crystallization event starts from crystals in the nanometer size regime.

EXPERIMENTAL SECTION

Chemicals. Stearic acid (HSt; 90+%), lauric acid (HLa; 99.5%), tetramethylammonium hydroxide (98%), octylamine (98%), cadmium oxide (CdO; 99.998%), selenium powder (200 mesh, 99.999%), 1-dodecylphosphonic acid (DDPA; 95%), 1-octadecene (ODE; 90%), and oleic acid (HOl; 90%) were purchased from Alfa-Aesar. Oleylamine (NH_2Ol; C_{18} content 70%) was purchased from Aldrich. Tributylphosphine (TBP) was purchased from Shanghai Titanchem. Cadmium acetate dihydrate ($Cd(Ac)_2 \cdot 2H_2O$; 98.5%) was purchased from Shanghai Tingxin Reagents. All organic solvents were purchased from Sinopharm Reagents. All chemicals were used directly without any further purification.

Synthesis of Cadmium Stearate ($Cd(St)_2$). The synthetic procedure was similar to the room temperature synthesis of $Mn(St)_2$ reported in the literature.[43] Typically, HSt (20 mmol) and 20 mmol of tetramethylammonium hydroxide were dissolved in 200 mL of methanol. To this solution was added dropwise under vigorous stirring $Cd(Ac)_2 \cdot 2H_2O$ (10 mmol) dissolved in 50 mL of methanol. White $Cd(St)_2$ immediately precipitated, and the mixture was stirred for another 20 min to ensure the reaction was completed. The precipitate was washed three times with methanol and dried under vacuum overnight.

Synthesis of $Cd(La)_2$. The procedure was similar to the synthesis of $Cd(St)_2$ described above, except the substitution of HSt by HLa.

Preparation of the Se Precursor. Se solutions in ODE and in NH_2Ol (0.1 mM for both cases) were prepared by mixing 1 mmol of Se powder with 10 mL of ODE and NH_2Ol, respectively. The mixtures were degassed for 10 min and heated to 180 °C, and the reactions were stopped after the full dissolution of Se. A 0.1 mM Se suspension was prepared by dispersing 0.5 mmol of Se powder in 5 mL of ODE by sonication for 5 min. A 0.5 mM TBP–Se solution was made by dissolving 5 mmol of Se powder in 1.18 g of TBP in a glovebox and further dilution with 7.5 g of ODE.

Synthesis of 5 nm CdSe Nanocrystals under Different NH_2Ol Concentrations. CdO (0.1 mmol), 0.4 mmol of HSt, and 4 mL of ODE were mixed in a 25 mL flask. After the mixture was stirred and argon was bubbled for 10 min, the contents of the flask were heated to 300 °C to get a clear solution. A Se solution was made by mixing the desired volumes of 0.1 M Se–ODE and 0.1 M Se–NH_2Ol. A 1 mL sample of the Se solution was injected into the reaction flask at 300 °C, and the temperature was dropped from 300 to 280 °C. The temperature remained the same until the nanocrystals grew to 5 nm.

Synthesis of 2.5 nm Zinc Blende CdSe Seeds. Zinc blende CdSe nanocrystals were synthesized using a modified procedure reported in the literature.[24] $Cd(St)_2$ (0.1 mmol) was loaded into a 25 mL flask with 3 mL of ODE. After the mixture was stirred and argon was bubbled for 10 min, the contents of the flask were heated to 260 °C. A 1 mL sample of 0.1 M Se-SUS was swiftly injected into the flask at 260 °C, and the reaction temperature was set to 240 °C for further growth of the nanocrystals. After 5 min of growth, the particle reached

the desired size (with the first excitonic absorption peak at 500 ± 5 nm), and further annealing at 240 °C for 5 min was carried out to obtain a stable surface. Needle-tip aliquots were taken and dissolved in toluene for monitoring the reaction using UV−vis.

Synthesis of 2.5 nm Wurtzite CdSe Seeds. In a typical synthesis, CdO (0.1 mmol) and 0.2 mmol of DDPA were loaded into a 25 mL flask with 2 mL of ODE. After the mixture was stirred and argon was bubbled for 10 min, the contents of the flask were heated to 280 °C to get a clear solution. A 1 mL sample of 0.1 M Se-SUS was swiftly injected into the flask at 280 °C, and the reaction temperature was set to 250 °C for further growth of the nanocrystals. The reaction was stopped at 30 s to get 2.5 nm nanocrystals.

In Situ Purification of Seed Nanocrystals. For zinc blende CdSe seeds, octylamine (0.2 mL), hexane (4 mL), and methanol (8 mL) were added to the reaction flask at 50 °C and stirred for 1 min. After stirring, the colorless methanol layer was separated from the top ODE/hexane layer by a syringe. This extraction procedure was repeated three times. The hexane left in the ODE layer was removed by argon bubbling at about 70 °C. For wurtzite CdSe seeds, TBP (0.2 mL), octylamine (0.2 mL), hexane (3 mL), and methanol (6 mL) were added to the reaction flask at 50 °C and stirred for 5 min. TBP was used to get rid of the unreacted elemental Se, considering the very short reaction time. After stirring, the colorless methanol layer was separated from the top ODE/hexane layer by syringe. This extraction procedure was repeated three times, but neither TBP nor octylamine wes added for the last purification. The hexane left in the ODE layer was removed by argon bubbling at about 70 °C.

Synthesis of CdSe Nanocrystals on Wurtzite Seeds with Carboxylate. Purified 2.5 nm wurtzite seeds (3.0×10^{-7} mol) were mixed with 0.2 mmol of $Cd(La)_2$ and 1 mL of NH_2Ol, and the mixture was further diluted by ODE to 4 mL of total volume. The mixture was degassed for 10 min and heated to 220 °C, and 0.3 mL of 0.1 M Se-SUS was swiftly injected into the flask. More Se-SUS was added dropwise to get 5 nm quantum dots at 240 °C. Control experiments were carried out by simply exchanging NH_2Ol with the same volume of ODE.

Growth of CdSe Nanocrystals on Different Seeds with Cadmium Phosphonate. CdO (0.2 mmol) and 0.4 mmol of DDPA (stoichiometric ratio) were loaded into a 25 mL flask with 2 mL of ODE. After 10 min of degassing, the mixture was heated to 280 °C to get a clear solution. The $Cd(DDPA)_2$ precursor was cooled to room temperature and mixed with 1 mL of NH_2Ol and 3.0×10^{-7} mol of 2.5 nm CdSe seeds with either the zinc blende or wurtzite crystal structure. The mixture was degassed for 10 min and heated to 220 °C, and then 0.4 mL of 0.5 mM Se−TBP was injected into the flask. After injection, the temperature was reset to 240 °C for the growth of CdSe nanocrystals. When the first peak of absorption did not shift any further, 0.2 mL of 0.5 mM Se−TBP was added dropwise to the solution to reach the desired size.

X-ray Powder Diffraction (XRD). XRD patterns were acquired using a Rigaku Ultimate-IV X-ray diffractometer operating at 40 kV/30 mA using the Cu Kα line (λ = 1.5418 Å). To get high-quality XRD patterns, purification of the nanocrystal products was carried out before the measurements. Nanocrystals synthesized with cadmium carboxylate were purified using the same procedure for zinc blende seeds described above. Nanocrystals synthesized with cadmium phosphonate were precipitated by ethanol. Precipitates collected by centrifugation and decantation were redissolved in toluene, and unreacted phosphonate was separated by centrifugation at 8000 rpm for 5 min. Powder samples for XRD measurements were prepared by precipitation of the nanocrystals from the solution using ethanol as the precipitant, and the precipitate was separated by decantation of the solution waste. Collected precipitates were redissolved in hexane and precipitated by ethanol again. The final precipitates were transferred onto a glass slide for XRD measurements.

Optical Measurements. UV−vis spectra were recorded on an Analytik Jena S600 UV−vis spectrophotometer. Before measurement, the nanocrystal sample was diluted to an optical density below 0.2.

Transmission Electron Microscopy (TEM) and High-Resolution TEM (HR-TEM). TEM images were taken on a Hitachi 7700 transmission electron microscope at 100 kV using copper grids coated with a pure carbon support film. HR-TEM images were taken on a JEM 2100F transmission electron microscope at 300 kV using a copper grid coated with an ultrathin carbon film as the substrate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing the XRD patterns of 5 nm CdSe nanocrystals synthesized with or without amine, evolution of UV−vis spectra of 2.5 nm zinc blende CdSe nanocrystals ripened in oleylamine and oleic acid, FT-IR spectra of the precipitate yield with excess Se suspension with oleic acid and the corresponding washed precipitate, and isomaterial seeded growth on wurtzite seeds with $Cd(La)_2$ and Se-TBP. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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