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Symmetry-Breaking for Formation of Rectangular CdSe Two-Dimensional Nanocrystals in Zinc-Blende Structure

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Abstract: Formation of CdSe nanocrystals with two-dimensional quantum confinement (CdSe 2D nanocrystals) was studied with pre-formed CdSe nanocrystals in the size range between 1.7-2.2 nm as seeds. Specifically, the 2D CdSe nanocrystals were encased with six {100} facets of the zinc-blende (face-center-cubic) structure, i.e. 1.5 nm in thickness with quite large atomically-flat {100} basal planes (~8 nm width X~45 nm length). Symmetry breaking between the thickness and lateral directions occurred in the early stage by rapid formation of single-dot intermediates with flat yet polar {100} basal planes and the desired thickness from the seeds through intra-particle ripening. Two single-dot intermediates fused together through their reactive side facets—mostly the nonpolar {110} ones—to form 2D embryos with the same thickness. Such oriented attachment continued selectively onto the reactive side facets of the 2D embryos. Simultaneously, intra-particle ripening occurred slowly on the side facets of the 2D nanocrystals, which converted unstable side facets gradually to four stable {100} ones. When ~3 stable {100} side facets were developed, oriented attachment would continue on the remaining active one, resulting in the second symmetry breaking between two lateral directions. Cadmium acetate assisted both formation of single-dot intermediates and oriented attachment. Cadmium alkanoates with a long hydrocarbon chain selectively stabilized polar {100} facets on the nanocrystals including single-dot intermediates and shuttled insoluble acetate to the reactive surface of the nanocrystals.

Introduction

Colloidal semiconductor nanocrystals are attracting tremendous attention because of their dimensiondependent optical properties.¹ With their three-dimensions in the quantum-confinement size regime, dot-shaped semiconductor nanocrystals are known as quantum dots or zero-dimensional (0D) nanocrystals.¹ Rod-shaped nanocrystals with their long axis as the only dimension beyond the exciton size of the corresponding bulk materials are considered as quantum rods, *i.e.*, one-dimensional (1D) nanocrystals.² Colloidal nanocrystals with only one dimension smaller than the quantum-confinement threshold of the bulk exciton are established as two-dimensional (2D) nanocrystals.³ Synthesis of high-quality colloidal 0D nanocrystals have been advanced rapidly since the early 1990s, ^{4,5} and monodisperse quantum rods became available in 2000.² Rapid progress on 0D and 1D nanocrystals is greatly benefited by active studies of their corresponding growth mechanisms, which are reasonably unified at least for the most studied systems, *i.e.*, CdSe and other II-VI nanocrystals. ⁶⁻¹⁸ In comparison, 2D nanocrystals are under-developed. For the mostly developed II-VI 2D nanocrystals, the first report on CdSe 2D nanocrystals in wurtzite structure appeared in 2006³ and those in zinc-blende structure were reported in 2008.¹⁹ The predicament on colloidal synthesis of 2D nanocrystals is related to poor understanding of their formation mechanism, especially the necessary symmetry breaking. ^{20,21} Symmetry breaking here refers to the preferred growth along one of symmetry-equivalent and isotropic directions. For instance, II-VI semiconductors are typically in either wurtzite (hexagonal) or zincblende (face-center-cubic) phases, whose symmetry does not support formation of 2D nanocrystals with atomically flat basal planes with significantly different dimensions on thickness, width, and length.

Though it is challenging to synthesize II-VI 2D nanocrystals, their optical properties are qualitatively

different from those of the corresponding 0D and 1D nanocrystals. For instance, the homogeneous peak width of photoluminescence (PL) of 0D and 1D nanocrystals is quite similar, but that of the corresponding 2D nanocrystals with similar PL peak position can be reduced by one-half. ^{22,23} The PL decay dynamics of the 2D nanocrystals is also a magnitude faster than that of the corresponding 0D and 1D nanocrystals. ^{24,25} The Stoke's shift of all 2D cadmium chalcogenide nanocrystals is nearly zero ²⁶⁻²⁸ while that of the corresponding 0D and 1D ones is quite large. ^{2,5} All these intriguing optical features are believed to be associated with their atomically-flat basal planes, which are perpendicular to the quantum-confinement direction of the 2D nanocrystals. For II-VI nanocrystals, only those tiny "magic-size clusters" are confirmed to possess atomically-flat facets. ²⁹⁻³¹

As the most developed system, formation mechanisms of CdSe 2D nanocrystals in wurtzite and zincblende structures are suggested to be completely different from each other. Wurtzite CdSe 2D nanocrystals are proposed to be formed by assembly/attachment of pre-formed magic-size clusters within the soft templates of alkylamine-alkanoates layer structures. ^{22,32} Conversely, formation of zincblende CdSe 2D nanocrystals has been suggested by lateral extension of properly pre-formed seeds selective addition of the monomers onto the sides of seeds. ^{23,27,28,33} While symmetry-breaking is suggested through the layer-structures of the templates for the wurtzite case, it is largely an unanswered question for the zinc-blende case. It is interesting to notice that both basal planes and lateral side facets of zinc-blende CdSe 2D nanocrystals can be the same, *i.e.*, {100} facets of the face-centercubic (fcc) structure, ^{23,33} which makes the symmetry-breaking more bewildering.

The Weller's group has studied formation of colloidal PbS 2D nanocrystals (nanosheets), which is also

in a face-center-cubic structure (rock salt). They have suggested oriented-attachment ³⁴—the crystal growth through fusion of primary nanocrystals with their lattices aligned to each other—as the formation mechanism, and the symmetry-breaking is achieved by direction of attachment, namely by fusing their reactive {110} facets of adjacent nanocrystals. ³⁵

Though distinguishable mechanisms are proposed for zinc-blende CdSe and rock salt PbS 2D nanocrystals, there are quite some similarities between these two systems. Firstly, both zinc-blende CdSe and rock salt PbS are face-center-cubic crystal structure. Secondly, synthesis of relatively thick CdSe 2D nanocrystals—only available for zinc-blend ones yet—and PbS 2D nanosheets both require pre-formation of nanocrystal seeds, ^{23,35} which are significantly larger than the thickness of the final 2D nanocrystals (see below). Thirdly, in both cases, some adventitious reagents are required to initiate formation of the 2D nanocrystals from the seeds, namely chlorine-containing organics for the PbS system and metal acetates for the CdSe system. Noticeably, acetates were found to be the key reagents to initiate oriented attachment of copious types of inorganic nanocrystals by reducing their surface passivation. ³⁶⁻⁴⁰

The analysis above implies that oriented-attachment might be a plausible mechanism for formation of zinc-blende CdSe 2D nanocrystals, instead of simple lateral extension by selective monomer addition. This work intends to systematically investigate this alternative mechanism. Different from previous studies, the pre-formed CdSe nanocrystal seeds with a range of sizes are purified from the residual precursors and side products using an established procedure. ⁴¹ Emphasis are on identification of symmetry breaking between three directions, given the dimensions of the thickness, width, and length

being substantially different from each other for the CdSe 2D nanocrystals.

Results and discussion

Design of experimental system. Figure 1a illustrates the general scheme of the experiments. CdSe quantum dots with their diameter varied between 1.7 and 2.2 nm—with 1.8 nm as the default size (see Figure S1, Supporting Information)—were applied as the seeds. These nanocrystal seeds were synthesized with cadmium *n*-alkanoates and elemental Se as the precursors in octadacene (ODE). The nanocrystal seeds were purified using a recently developed procedure that quantitatively removed the unreacted precursors and free fatty acids. ⁴¹ The purified seeds were injected into a growth solution

with designated compositions and temperature. During the growth, aliquots with a known volume were taken at different time intervals from the reaction solution and used for monitoring the reaction. To ensure dissolution of the reaction mixture for



Figure 1. (a) Schematic illustration of the synthetic protocol for the CdSe 2D nanocrystals. (b) UV-Vis absorption spectra of purified CdSe seeds and the assynthesized 2D nanocrystals. (c) Typical TEM image of the CdSe 2D nanocrystals. (d) Side view of the atomic model for the CdSe 2D nanocrystals. (e) HRTEM image of a CdSe 2D nanocrystal with the corresponding FFT pattern (inset).

quantitative measurements, the aliquots were diluted with a known amount of toluene with $\sim 0.2\%$ oleic acid (or octanoic acid), which should convert the surface ligands into entropic type to promote solubility. ⁴²

The scheme in Figure 1a was modified from a synthetic procedure originally developed by the Dubertret group. ¹⁹ Without purification of the seeds, the original procedure introduced metal acetates into the solution of the pre-formed seeds, which was confirmed to yield zinc-blende CdSe 2D nanocrystals with alternating stacking of 6 monolayers of Cd cations and 5 monolayers of Se anions, namely 5.5 monolayers of CdSe unites along the thickness direction and 1.5 nm in thickness from the top to bottom basal planes (Figure S2, Supporting Information).⁴³ Both atomically-flat basal planes were {001} facets terminated with Cd ions coordinated with alkanoate ligands. To ensure the growth of 2D nanocrystals via lateral extension, Dubertret et al. suggested that the size of seeds should be identical to (or similar with) the thickness of the resulting 2D nanocrystals, *i.e.*, 1.5 nm for 5.5-monolayer CdSe 2D nanocrystals. ^{23,28} We noticed that this value was significantly smaller than the seeds observed under transmission electron microscope (TEM) (see example in Figure S1, Supporting Information), *i.e.*, 1.8-2.2 nm in diameter. These results suggested that lateral extension through addition of monomers might not be the growth mechanism of the 2D nanocrystals.

UV-Vis spectrum (Figure 1b) of the as-synthesized 2D nanocrystals using the purified seeds through the scheme in Figure 1a was found to resemble that of high-purity 5.5-monolayer 2D nanocrystals obtained in the original synthesis (Figure S2, Supporting Information). In comparison, the UV-Vis spectrum of the purified seeds in Figure 1b was typical for CdSe quantum dots. The absorption peak

was found to be consistent with that of dot-shaped CdSe 0D nanocrystals with the size being ~1.8 nm. ⁴⁴ The TEM measurements revealed that the top view of 2D nanocrystals synthesized using the purified seeds (Figure 1c) was nearly identical to that of the 2D nanocrystals synthesized with the unpurified seeds (Figure S2, Supporting Information). Specifically, the average dimensions of the width and length were ~8 and ~45 nm (Figure S3, Supporting Information), respectively. As shown in the highresolution TEM images and corresponding selected-area FFT (fast Fourier transform) patterns (Figures le and S4 in Supporting Information), two groups of d-spacing along <100> and <110> directions could be observed, which identified the thickness direction (perpendicular to the view plane under those TEM images) and lateral directions in Figure 1d and 1e. Specifically, the side facets of the rectangles were the same as the basal planes, *i.e.*, {100}. Though all thickness, width, and length directions were <100> of the zinc-blende structure, their dimensions were significantly different from each other (Figures 1d, 1e, S4 (Supporting Information)).

Results discussed above clearly indicated that growth of the CdSe 2D nanocrystals, specifically the symmetry-breaking between thickness, width, and length directions, did not require existence of cadmium and selenium precursors. Thus, these preliminary results suggested that oriented attachment should be a plausible mechanism for the transition from the nanocrystal seeds to the 2D nanocrystals.

Ligands on growth of the CdSe 2D nanocrystals. Oriented attachment implies critical importance of the surface ligands of nanocrystals. It was reported that, upon reduction of ligand protection, several types of nanocrystal systems would become unstable and form complex structures by oriented attachment. $^{36-40}$ For the current system, while cadmium acetate (Cd(Ac)₂) and cadmium stearate $(Cd(St)_2)$ were both in the solution, introduction of the purified seeds into the solution could generate 2D nanocrystals with high purity at 250 °C (Figure 2a). $Cd(St)_2$ alone would keep the seeds stable in the growth solution, but $Cd(Ac)_2$ would drastically destabilize the seeds (Figure 2b). Some of the seeds

remained unchanged with the Cd(Ac)₂-only reaction while relatively large and irregular species were observed in the UV-Vis and PL measurements (Figure 2b). The minor sharp feature at ~550 nm in the PL spectrum of the resulting nanocrystals of the Cd(Ac)₂only reaction, and TEM image in Figure S5 (Supporting Information) showed that there are a small fraction of the 2D nanocrystals in the mixed products.

It was reported that fatty amines were necessary ingredients for formation of CdSe 2D nanocrystals in wurtzite structure. ^{3,22,32,45} Conversely, organophosphine ligands were found to hinder the growth of CdSe 2D nanosheets in zinc-blende structure. ⁴⁶ Those two types of ligands and organophoshpine oxides—another type of common ligands—were tested in the reactions with the purified



Figure 2. With the same (purified) CdSe seeds, UV-Vis and PL spectra of CdSe nanocrystals prepared with the existence of (a) both cadmium acetate $(Cd(Ac)_2)$ and cadmium stearate $(Cd(St)_2)$, (b) either $Cd(Ac)_2$ or $Cd(St)_2$, (c) $Cd(Ac)_2$ mixed with either oleylamine $(NH_2Ol),$ (TBP),tributylphosphine or trioctylphosphine oxide (TOPO), respectively. For clarity, PL spectra are not shown in (c).

seeds. Results in Figure 2c revealed that none of these three types of ligands would efficiently promote formation of 2D nanocrystals by mixing them with $Cd(Ac)_2$. When phosphine oxide and $Cd(Ac)_2$ were

in the solution, no sign of the 2D nanocrystals was detected. The other two types of ligands seemed to promote random aggregation caused by $Cd(Ac)_2$, indicated by complete disappearance of the original seeds (compare Figures 2c with 2b).

Free fatty acids were found to be somewhat similar to the corresponding cadmium fatty acid salts (Figure S6, Supporting Information). Under elevated temperatures in octadecene, stearic acid would partially replace acetate in $Cd(Ac)_2$ and the resulting salts with mixed carboxylate groups would become soluble. Presumably, this would convert the growth solution to be similar with the typical growth system in Figure 1a.

Replacement of cadmium acetate by acetic acid for typical reaction was not effective to promote

formation of the 2D nanocrystals (data not shown). Presumably, the boiling point of acetic acid was too low to keep it in the reaction solution under the necessary high reaction temperatures.

Different roles of cadmiumacetateandcadmiumstearate.Results in the above



Figure 3. (a) Relative CdSe-unit yield of 2D nanocrystals versus the concentration of $Cd(Ac)_2$, with a fixed amount of $Cd(St)_2$. (b) UV-Vis spectra of the final products for three representative reactions in (a). (c) Relative CdSe-unit yield of 2D nanocrystals versus the concentration of $Cd(St)_2$, with a fixed amount of $Cd(Ac)_2$. (d) UV-Vis spectra of the final products for three representative reactions in (c).

sub-section suggested that both cadmium acetate and cadmium stearate (or other *n*-alkanoates with a long hydrocarbon chain, see Figure S7, Supporting Information) were necessary for conversion of the seeds to the 2D nanocrystals. However, additional results revealed that these two reagents likely played different roles (Figure 3).

Figure 3a reveals that, at a fixed concentration of cadmium stearate, the final yield of the 2D nanocrystals for each reaction increased rapidly in the beginning and reached a plateau as the concentration of cadmium acetate increased. The CdSe-unit yield of the 2D nanocrystals was represented by the absorbance at 550 nm. This was so because the molar extinction coefficients at the peak position of the CdSe 2D nanocrystals with a given thickness, *i.e.*, 550 nm for 5.5-monolayer CdSe 2D nanocrystals, were reported to be approximately linearly related to their area of the basal planes. ⁴⁷ Evidently, the low conversion yield of the reactions with limited amounts of cadmium acetate was accompanied with the remaining of the 0D nanocrystals (Figure 3b).

For the reactions with a fixed concentration of cadmium acetate, the final yields of the 2D nanocrystals increased rapidly to a peak and followed by a steady decrease as the concentration of cadmium stearate increased (Figure 3c). Figure 3d shows that no 0D nanocrystals were left at the peak of conversion. However, on both sides of the conversion peak, existence of 0D nanocrystals was clearly evidenced.

By varying the hydrocarbon chain length of *n*-alkanotes from 14 to 22, the general trend in Figure 3 remained. Interestingly, though no 0D seeds left in the solution, the final yield of 2D nanocrystals increased steadily as the hydrocarbon chain length increased (Figure S7, Supporting Information),

 indicating existence of some not fully developed nanostructures (see further discussion below). Furthermore, the longer the hydrocarbon chain of the *n*-alkanotes, the slower the initial conversion rate was observed (Figure S7, Supporting Information).

The results in Figures 2, 3, S6, and S7 suggested that cadmium *n*-alkanotes with a long hydrocarbon chain played two roles for the formation of 2D nanocrystals. Firstly, it assisted cadmium acetate to convert the 0D nanocrystals to 2D nanocrystals. In the current reaction solution, cadmium acetate was found to be insoluble. It was confirmed that the existence of cadmium *n*-alkanotes with a long hydrocarbon chain would greatly improve the solubility of cadmium acetate by formation of cadmium salts with mixed carboxylate groups. Secondly, it stabilized the 0D nanocrystal seeds. The first role was dominating at low concentrations of the cadmium *n*-alkanotes with a long hydrocarbon chain, while the second one became more and more important when their concentration passed the conversion peak.

Conversion process from 0D seeds to 2D nanocrystals. With optimized concentrations, the conversion process was studied. Figure 4 illustrates the temporal evolution of UV-Vis/PL spectra (left panel) and the morphology (right panel) of the nanocrystals for a reaction at 250 °C.

Quantitative results of the UV-Vis spectra are summarized in Figure S8 (Supporting Information), which determined that the absorbance at 320 nm during the entire reaction course remained nearly constant. This means that a constant CdSe unit yield in the form of nanocrystals throughout the entire conversion process. ⁴⁸ Consistent with this conclusion, a constant yield of CdSe units was also obtained

by using the extinction coefficients of the 0D seeds and 2D nanocrystal final products (Table S1, Supporting Information). A constant yield of CdSe units in the form of nanocrystals excluded growth from free precursors in solution, in accordance with the effective purification mentioned above.

Alternatively, instead of oriented attachment, a constant CdSe-unit yield during the conversion reaction might be explained by a special pathway, *i.e.*, a very small portion of the seeds growing rapidly by slow dissolution of the other seeds. Against this hypothesis, the size evolution of 0D nanocrystals

followed an opposite trend, *i.e.*, rapid increasing in size within the first ~30 s and then remaining at a nearly constant size (see Figure 4 left and discussions below).

During the first 30 s of the reaction in Figure 4, the UV-Vis peak shifted from 480 nm to 490 nm, and the PL peak evolved from a symmetric and



Figure 4. Temporal evolutions of UV-Vis/PL (left) and TEM images (right) of CdSe nanocrystals at 250 °C. The dashed line (left panel) indicates the absorption peak position of the persistent 0D nanocrystals.

narrow peak to a peak with shoulders on both sides. During the entire conversion process, the absorption peak at ~490 nm was observable except at the very end of the reaction (see the UV-Vis spectrum at 1200 s). Under TEM, the size of the nanocrystals in the first 30 s was found to increase

slightly to ~2.0 nm from ~1.8 nm seeds, and their two-dimensional projection on TEM remained approximately spherical (Figure S1, Supporting Information). As the reaction proceeded beyond 300 seconds, population of tiny 0D nanocrystals decreased and gradually became scarcely observable (Figure 4, right panel).

The results described in the above paragraph implied that the 0D nanocrystals with their first excitonic absorption peak at ~490 nm were the critical intermediates for attachment. Given their nearly spherical shape and similar sizes of the seeds, we named them as "single-dot intermediates" for attachment. To confirm existence of such special intermediates, the 0D seeds with their first excitonic absorption peak in the range between 470 to 520 nm were examined (Figure S9, Supporting Information). All those reactions demonstrated formation of the single-dot intermediates during the early stage of a conversion reaction, which had the first excitonic absorption peak at 490 ± 2 nm. Interestingly, for the 0D seeds with their first excitonic absorption peak at ~490 nm, formation of the single-dot intermediates from the seeds was still needed prior to formation of the 2D nanocrystals (Figure S9, Supporting Information). Furthermore, for those reactions with different seeds, it was possible to identify similar transient stages with nearly identical UV-Vis and PL spectra, *i.e.*, with both absorption features for the single-dot intermediates and 2D nanocrystals (Figure S9, Supporting Information).

The TEM images in Figure 4 (right panel) revealed that the lateral dimensions of 2D nanocrystals increased gradually and the relative population of the single-dot intermediates decreased. Though the distribution of lateral dimensions was not monodispersed at all stages, it gradually narrowed by the time nearly all small particles—presumably the single-dot intermediates—were completely consumed.

The lateral dimensions of the 2D nanocrystals in the early stage (before 120 s for the reaction in Figure 4) was mostly irregular in shape and smaller than the final values. During the middle stage (between \sim 180 and \sim 300 s), the width for the large ones in the solution was almost fully developed but the length was noticeably smaller than the final value.

Interestingly, two or three side facets of the large 2D nanocrystals in the middle stage were quite well developed as {100} facets but one or two of their side facet(s) remained as {110} ones. Their interesting morphology was well resolved by Scanning Transmission Electron Microscope and high-resolution TEM (Figure S10, Supporting information). The polar {100} facets of zinc-blende CdSe nanocrystals should be terminated with cadmium ions that would be well coordinated with carboxylate ligands. ³³ Conversely, ligands passivation on the nonpolar {110} facets would be comparatively poor. Thus, these large 2D nanocrystals in the middle stage should grow by particle attachment onto the active {110} facet(s), which would eventually result in 2D nanocrystals in rectangular shape with four {100} side facets. It was interesting to notice that formation of PbS nanosheets was also identified through oriented attachment of the {110} facets of the 0D nanocrystals. ³⁵

The PL spectra in Figure 4 (left panel) revealed additional evidences for particle attachment, instead of growth through lateral extension by monomer addition. In principle, the smallest volume increase for particle attachment should be one nanocrystal (the precursor) and that for lateral extension by monomer addition should be one atom/molecule. The former would show a significant peak jumping in the evolution of PL spectra, and the PL peak of the latter should shift continuously. Evidently, the experimental results in Figure 4 (left panel) was consistent with that of particle attachment. Four PL

peaks dominated all PL spectra in Figure 4 (left panel), namely ~490 nm for the seeds, ~505 nm for the single-dot intermediates, ~538nm for another intermediate species (to be discussed below), and 550 nm for the 2D nanocrystals. These four peaks appeared sequentially. As mentioned above, the PL spectra of all reactions with different size seeds were qualitatively the same after disappearance of the original seeds (Figure S9, Supporting Information). The PL peak of the seeds disappeared after ~1 min of the reaction, and that for the single-dot intermediates lasted roughly from 30 s to nearly the end of the conversion, which was consistent with the UV-Vis spectra described above. The PL peak for the 2D nanocrystals at 550 nm became more and more dominating along the reaction. The peak at ~538 nm became evident shortly after the appearance of the ~505 nm peak associated with the single-dot intermediates, and lasted to the end of a reaction though the intensity became very faint after ~600 s for the reaction in Figure 4. Furthermore, the PL peak at ~538 nm (varied between 530 nm to 540 nm for different reactions) was always observed regardless of size of the seeds used.

All the results in the above paragraph not only supported the particle-attachment mechanism but also suggested some structural information about the species related to the PL peak at ~538 nm. These species should be associated with the smallest ones grown by particle attachment of the single-dot intermediates. Thus, we would denote them as "2D embryos" and shall devote an entire subsection to study their structure.

The spectral features related to Figure 4 and described above were observed for all reactions with different cadmium n-alkanoates and/or different reaction temperatures. For the reactions with different cadmium carboxylate concentrations, the features in Figure 4 were also observed once the reaction

resulted in significant conversion. Further experiments revealed that, for the original synthesis without purification of the seeds, the temporal evolution of optical properties and shape of the nanocrystals was quite similar to those in Figure 4 (Figure S11, Supporting Information). All these results suggest a universal mechanism for formation of the 2D nanocrystals with absorption peak at 550 nm from the 0D seeds.

Temperature effects on formation of 2D nanocrystals. Results in Figure 5(a) illustrate the temporal evolution of the conversion yield—the CdSe unit yields in 2D nanocrystals—of the reactions at different reaction temperatures. As pointed out above, this conversion yield would not include the 2D embryos because it was measured by the absorbance at 550 nm of reaction aliquots. Evidently, the conversion yield increased rapidly by increasing the reaction temperature. The initial inductive time approximately corresponded to formation of the single-dot intermediates from the seeds, which

decreased with the increase of reaction temperature.

All curves in Figure 5(a) evidently did not follow mono-exponential increase, indicating a complex kinetics involved in the formation of 2D



Figure 5. (a) The relative conversion yield of CdSe units from 0D to 2D nanocrystals under different temperatures. (b) Arrhenius plot for the conversion from the single-dot intermediates to the 2D nanocrystals with t^1 as the time to reach a fixed CdSe-unit yield in 2D nanocrystals. (c) Arrhenius plot for the conversion from the seeds to the single-dot intermediates with t^0 as the inductive time in Figure 5(a).

nanocrystals from the single-dot intermediates. This seemed to be reasonable, considering the complicated chemistry involved in oriented attachment. Nevertheless, one could obtain experimental activation energy (E_a) by Arrhenius plot as a semi-quantitative indicator of the temperature-dependence of two processes, namely formation of the single-dot intermediates from the seeds as well as conversion of the single-dot intermediates to the 2D nanocrystals. The rate for the former case at a given temperature was calculated as the inverse of the inductive time in Figure 5(a), and the rate for the latter case was estimated as the inverse of reaction time to reach a fixed CdSe-unit yield of the 2D nanocrystals given in Figure 5(a). The E_a values in Figures 5(b) and 5(c) imply that conversion of the single-dot intermediates to 2D nanocrystals should be noted that the single-component fitting in Figure 5, especially in Figure 5b, is not perfect, which should only be applied for determining the temperature-dependence of the related process and does not exclude complex chemical kinetics for the corresponding process.

It is interesting to notice that formation of CdSe wurtzite 2D nanocrystals occurred under relative low temperatures, *i.e.*, between 60-140 °C. ^{3,22,32,45} Based on the results in Figure 5, neither formation of the single-dot intermediates from the seeds nor conversion of the single-dot intermediates to the 2D nanocrystals could be observed if the reaction was below 140 °C within the experimental timeframe. The substantially low reaction temperatures for formation of wurtzite 2D nanocrystals should be related to two factors. Firstly, the seeds for the wurtzite CdSe 2D nanocrystals were believed to be tiny "magic size clusters", which are thermodynamically less stable than the seeds and single-dot intermediates in this work. Secondly, formation of the wurtzite CdSe 2D nanocrystals was suggested

to rely on the soft templates composed of alkylamine-carboxylate layer structures, which would become unstable at elevated temperatures.

Characterization of the 2D embryos. Results above suggested that the conversion of seeds to 2D nanocrystals went through two intermediates with reasonably defined structures, *i.e.*, the single-dot intermediates and 2D embryos. In this sub-section, we shall discuss the 2D embryos, which should help us to illustrate the structure of single-dot intermediates in the following sub-section.

As discussed above, attachment of the single-dot intermediates lasted until the end of the conversion process. The 2D embryos might thus exist towards the end of the conversion process.—_Though the

population would be very low, the 2Dembryos would likely be able to be separated from the 2D nanocrystals, given their very distinctive sizes. high-speed By centrifugation of the final product



Figure 6. (a) UV-Vis spectra of supernatant and precipitate separated by centrifugation of aliquots of the final solution. (b) high resolution TEM image with a few representatives_{110} and {100} facets labeled. The FFT pattern was obtained from all nanocrystals. (c) UV-Vis spectra of the seeds, single-dot intermediates, and 2D embryos. (d) Overlapping comparison of absorption features between single-dot intermediates and 2D embryos after aligning the main peak.

of a reaction (see Experimental for detail), we obtained a large amount of materials as precipitate and a light-color supernatant. The precipitate was re-dispersed into solution and its UV-Vis was found to be consistent with high-purity 2D nanocrystals (Figure 6a). In comparison to that of the aliquots before separation, the UV-Vis spectrum of the re-dispersed precipitate showed a reduced absorbance at ~528 nm and missed two minor peaks at ~410 and 429 nm (Figure 6a). Though the supernatant had a very small amount of nanocrystalline materials, it was sufficient for recording UV-Vis spectrum and TEM measurements.—

The UV-Vis of the 2D embryos in the supernatant, with its main absorption peak at ~528 nm, was found to be qualitatively different from that of the 2D nanocrystals (Figure 6a). Furthermore, the two missing minor peaks at ~410 and 429 nm in UV-Vis spectrum of the re-dispersed precipitate versus that of the original aliquots were fully recovered in the spectrum of the supernatant. The tail to the low energy side of the main peak was likely associated with the presence of a minor amount of the random aggregates caused by cadmium acetate (see Figure 2b).

TEM measurements (Figure S1, Supporting Information) identified that the 2D embryos were significantly larger than the single-dot intermediates. For the reaction using the 1.8 nm seeds (UV-Vis peak at 480 nm), the average size of the single-dot intermediates and the 2D embryo was ~2.0 nm and ~3.0 nm (Figure S1, Supporting Information), respectively. Assuming the dimension perpendicular to the TEM substrate was similar for single-dot intermediates and the 2D embryos, one would conclude that one 2D embryo should be produced by two single-dot intermediates.

High-resolution TEM images of the 2D embryos (Figure 6b) revealed that nearly all nanocrystals possessed a clear lattice fringes, which is unusual for spherical dots in zinc-blende structure. ⁴⁹ Furthermore, the zone axis of the ensemble in Figure 6b was identified as <100>. Furthermore, the average size of 3 nm for the 2D embryos was found to be significantly larger than a typical dot with the same absorption peak position. ⁴⁴ These facts strongly imply a possible morphology for the 2D embryos, *i.e.*, thin disks with their basal planes as well-developed {100} facets.

While the basal planes should be well developed and atomically flat, the top view of these 2D embryos was mostly irregular (Figure 6b). These were thought to be consistent with oriented attachment of two single-dot intermediates. Consistent with flat yet relatively large basal planes and thin thickness, the lattice fringes of nearly all nanocrystals in Figure 6b were single-crystalline. Majority of the side facets could be identified as {100} and {110} (see representative ones in Figure 6b). Given the high reactivity of the {110} facets versus the {100} facets mentioned above, such types of side facets of the 2D embryos were found to be reasonable. Both their formation from two single-dot intermediates and their further growth into 2D nanocrystals should have gone through oriented attachment at the {110} side facets.

Structure of single-dot intermediates. The single-dot intermediates appeared slightly larger than the typical seeds under TEM, specifically ~2.0 nm for the single-dot intermediates versus ~1.8 nm for the typical seeds (Figure S1, Supporting Information). As mentioned above, assuming the same dimension along the direction perpendicular to the TEM substrates, each 2D embryo (Figure 6b) was approximately equivalent to two single-dot intermediates in total CdSe units.

Figure 6c illustrates that the single-dot intermediates possessed a set of distinguishable absorption features (~490 nm, ~441 nm, ~392 nm, and ~374 nm). While the main absorption peaks in the UV-Vis spectra for the seeds and single-dot intermediates were close in energy, the spectral contour of the single-dot intermediates was found to be distinguishable from that of the seeds. Instead, the contour of UV-Vis spectrum for the single-dot intermediates was found to be quite similar to that of the 2D embryos (Figure 6c). In fact, the UV-Vis absorption spectra and fluorescence excitation spectra of the single-dot intermediates and 2D embryos could almost overlap with each other by aligning their first excitonic peaks (see Figures 6d and S12 in Supporting Information). Specifically, both single-dot intermediates and 2D embryos possessed a pair of absorption peaks separated by ~18 nm, namely \sim 392/374 nm for the single-dot intermediates and \sim 410/427 nm for the 2D embryos. These spectral features along with dimensions estimated by TEM suggested that the single-dot intermediates might likely possess 2D-like structure, meaning with well-developed {100} facets as atomically flat basal planes and thin dimension perpendicular to the basal planes. To confirm this hypothesis, an early-stage (60 s) aliquots—presumably enriched in single-dot intermediates as shown in Figure 4—was studied by high-resolution TEM.

Results in Figure S13 (Supporting Information) demonstrated that, similar to Figure 6b, nearly all nanocrystals of this early-stage aliquots possessed clear lattice fringes and the zone axis of the ensemble was also <100>. In addition to a few of those relatively large nanocrystals—supposedly the 2D embryos and other 2D nanocrystals, there were quite some small nanocrystals (~2 nm in size) in Figure S13 (Supporting Information). The zone axis of these small nanocrystals was <100> and the

side facets included both {100} and {110} ones, which was found to be consistent with the structure of single-dot intermediates discussed in the above paragraph.

Results discussed above implied that formation of the single-dot intermediates from the seeds was likely intra-particle ripening. ⁸ Through such an intra-particle ripening process, a typical seed (1.8 nm in all three dimensions) shrank one dimension to the thickness of a 2D nanocrystal (1.5 nm) and expanded the other two directions to ~2.0 nm. At the same time, two atomically flat {100} basal planes were developed. Such surface reconstruction was not completely surprising, given the high concentration of cadmium carboxylates in the reaction solution. It was observed that, with a high concentration of cadmium carboxylates, CdSe nanocrystals in zinc-blende structure preferred to be faceted with exposure of their low index facets (mostly {100} and {110}, and minor contributions of {111}). ⁴⁹ Presumably, the {110} side facets could survive in the single-dot intermediates (Figure S13, Supporting Information) and the 2D embryos (Figure 6b), but would be gradually eliminated in the final 2D nanocrystals (Figure 1) by either oriented attachment or intra-particle ripening.

Formation mechanism of the 2D nanocrystals from the seeds. With all results disclosed in this report, it should be possible to conclude that 5.5-monolayer CdSe 2D nanocrystals in zinc-blende structure were formed through a complex mechanism involving oriented attachment. The conversion of the 0D seeds to the 2D nanocrystals involved several key steps and two symmetry-breaking events.

In the first step, seeds with the sizes somewhat larger than the thickness of the targeting 2D nanocrystals—between 1.7 and 2.2 nm applied in this work for 5.5-monolayer CdSe 2D nanocrystals

with 1.5 nm thickness—would adjust their shape through intra-particle ripening at elevated temperatures (> ~200 °C). This would result in single-dot intermediates with nearly flat {100} basal planes and thickness similar to that of the final 2D nanocrystals (1.5 nm for 5.5-monolayer CdSe 2D nanocrystals). The shrinkage along the thickness dimension would slightly expand the lateral dimensions of the single-dot intermediates (Figure S1, Supporting Information), and their side facets include stable {100} ones and other reactive ones, such as {110} facets (Figure S13, Supporting Information). Formation of this type of single-dot intermediates required existence of extra cadmium carboxylates. Cadmium fatty acid salts with a long hydrocarbon chain were the critical reagent for this step (Figure 3, right). Cadmium acetate would accelerate this step but could induce uncontrolled aggregation without existence of the long-chain alkanoates (Figure 3, left).

In the second step, two single-dot intermediates fused together through oriented attachment to form one 2D embryo. This step was substantially slower than the first step (Figure 4). Because the {100} facets, especially the atomically flat basal planes, were well passivated with carboxylate ligands, the oriented attachment occurred at the reactive side facets of the single-dot intermediates, such as {110} ones. Such oriented attachment continues between the single-dot intermediates and 2D embryos (or other reactive 2D nanocrystals), resulting in irregular lateral dimensions in the early stage of oriented attachment (Figure 4, right panel). This would complete the first symmetry breaking on the basis of the first step, which differentiated the thickness direction—one of three <100> direction—and the two lateral directions. The Weller group also suggested a similar facet-selective oriented attachment for the face-center-cubic lattice. ³⁵ Different from their proposed mechanism, structure characterization of

CdSe 2D embryos and single-dot intermediates in Figures 6 and S13 (Supporting Information) strongly suggested that the CdSe nanocrystals developed their atomically flat basal planes at least in the form of 2D embryos, possibly in the form of the single-dot intermediates. A key factor for completing the first symmetry-breaking at this step was the relatively fast formation of single-dot intermediates and very slow oriented attachment, which was ~60 s for the first step and > 600 s for the second step as revealed by Figure 4. Such rate difference between two processes could be achieved as long as the reaction temperature was not excessively high, given their significantly different activation energies (Figure 5). A slow second step further allowed oriented attachment to occur with one single-dot intermediate at one time and leave sufficient time for adjusting the side facets in the third step. Different from the first step, oriented attachment in this step as well in the next step would require small carboxylates, specifically acetates, on the surface of the nanocrystals to ensure insufficient-ligand-protection through rapid ligand dynamics. ^{38,39,50,51} Because of insolubility of cadmium acetate in the solvent, cadmium alkanoates with a long hydrocarbon chain were needed to act as shuttles to bring acetates onto the surface of nanocrystals (Figures 2 and 3).

In the third step, single-dot intermediates continuously attached onto the 2D embryos as well as other reactive 2D nanocrystals with irregular lateral shape. Simultaneously, the resulting 2D nanocrystals adjusted their side facets to {100} ones through intra-particle ripening (Figure 4, right panel). Possibly, oriented attachment between 2D embryos and other small 2D nanocrystals might also occur in this step, but it should have not played a major role because the shape and lateral dimensions of the final 2D nanocrystals were reasonably monodisperse. Similar to the second step, oriented attachment should occur on the {110} or other active side facets, which would retain the first symmetry-breaking achieved

in the second step. The remaining {110} and other reactive side facets of the resulting 2D nanocrystals would gradually be eliminated through intra-particle ripening, which should be somewhat similar to that proposed by the Weller group for formation of PbS nanosheets. ³⁵ Such an intra-particle ripening process would gradually start to define the top view of the 2D nanocrystals when their lateral dimensions reached ~8 nm in the current reaction system. Not surprisingly, the slow intra-particle ripening did not develop four {100} side facets simultaneously, which would cause the second symmetry-breaking (see 180 s TEM in Figure 4 and high-resolution TEM in Figure S10, Supporting Information). The oriented attachment barely occurred onto three well-developed {100} side facets and continued onto the remaining {110} side facet(s), which would result in significant elongation along one of two lateral dimensions (Figures 1 and 4).

The first and second steps had minimum overlapping in the time domain but the second and third step overlapped for the majority period of a reaction. As a reaction proceeded, the second step became less and less competitive because concentration of the single-dot intermediates decreased rapidly. At the same time, the concentration and the reactive surface area of the 2D nanocrystals increased significantly to promote the third step. As a result, the width and length of the 2D nanocrystals were reasonably monodispersed.

Conclusion

In conclusion, for zinc-blende CdSe (face-center-cubic), it is possible to grow 2D nanocrystals encased with six {100} facets with distinctive dimensions of thickness, width, and length through a complex

mechanism involving oriented attachment. By applying purified seeds with their sizes between 1.7 and 2.2 nm for growth of 5.5-monolayer CdSe 2D nanocrystals (1.5 nm in thickness), growth through lateral extension by monomer addition onto existing seeds was excluded. The first symmetry breaking (between the thickness and lateral directions) was realized by rapid formation of single-dot intermediates through intra-particle ripening of the seeds, which possessed a reduced thickness (1.5 nm) perpendicular to the atomically flat {100} basal planes and expanded lateral dimensions in comparison to diameter of the initial seeds. The second symmetry breaking (between two lateral dimensions) originated from unequal development of the polar and well passivated {100} side facets during the oriented attachment. Cadmium acetate assisted both formation of single-dot intermediates and oriented attachment. Cadmium alkanoates with a long hydrocarbon chain also played two roles in the conversion of the seeds to 2D nanocrystals, namely, selectively stabilizing polar {100} facets of the nanocrystals and shuttling insoluble acetate to the surface of the nanocrystals. Preliminary results implied that oriented-attachment mechanism also worked for other types of zinc-blende cadmium chalcogenide 2D nanocrystals (data not shown). Understanding symmetry breaking in highly symmetric crystal structures should help to open a door for synthesis of a diverse group of 2D nanocrystals with unique optical and optoelectronic properties.

Experimental Section:

Materials. Cadmium acetate dihydrate (Cd(Ac)₂ • 2H₂O, 99.999%), selenium powder (Se, 200 mesh, 99.999%), stearic acid (HSt, 90+%), oleic acid (HOl, 90%), butylamine (98%), octanoic acid (HOc, 98+%), and 1-octadecene (ODE, 90%) were purchased from Alfa-Aesar. Oleylamine (NH₂Ol, C₁₈

content 70%) was purchased from Aldrich. Tributylphosphine (TBP) was purchased from Shanghai Titan Chem. Tri-n-octylphosphine oxide (TOPO) was purchased from J&K. Acetone (analytical reagent), methanol absolute and chloroform (analytical reagent) were purchased from Sinopharm Reagents. All chemicals were used without further purification.

Synthesis of cadmium stearate (Cd(St)₂). Typically, 20 mmol of HSt and 20 mmol of tetramethylammonium hydroxide were dissolved in 200 ml of methanol. To this solution, $Cd(Ac)_2 2H_2O (10 \text{ mmol})$ dissolved in 50 ml of methanol was added dropwise under vigorous stirring. White $Cd(St)_2$ then precipitated from the reaction mixture. After the addition was completed, the mixture was kept on stirring for another 20 min. The white precipitate was separated by centrifugation, washed three times with methanol, and dried under vacuum overnight for usage.

Synthesis of other types of cadmium fatty acid salts was carried out using the same procedure described above. Stearic acid was replaced by an equal molar amount of the corresponding fatty acid.

Direct synthesis of 5.5-monolayer CdSe 2D nanocrystals. In a typical synthesis, $Cd(St)_2$ (0.2 mmol) and ODE (3 ml) were loaded in a 25 ml three-neck flask. After degassing for 10 min, the mixture in the flask was heated to 250 °C under Ar protection. A total amount of 8 mg (0.1 mmol) Se dispersed in 1 mL ODE were swiftly injected. When the lowest energy absorption peak of the product in the UV-Vis spectrum reached at ~490 nm, 40 mg Cd(Ac)₂ 2H₂O (0.15 mmol) was introduced. The reaction was kept at 250°C for several minutes and aliquots were taken out for monitoring the reaction by UV-Vis. The reaction was stopped by allowing the reaction mixture to cool down in air.

Synthesis and purification of CdSe nanocrystals (seeds) of three different sizes (the first excitonic absorption peak at 473 nm, 488 nm, 502 nm, respectively). A typical synthesis of CdSe nanocrystals was conducted by injecting a 2.0-mL Se-octadecene suspension (0.1 mol/L) into a hot (260 °C) mixture of Cd(St)₂ (0.2714 g, 0.4 mmol) and 13 mL ODE in a 50-mL three-neck flask. The reaction was kept at 240°C for several minutes. Needle-tip aliquots were taken for UV–vis and PL measurements to monitor the reaction. When the targeted size of nanocrystals was achieved, the reaction mixture was cooled rapidly to room temperature for purification using a procedure in literature.⁴¹

The reaction mixture was centrifuged at 12000 rpm for 10 min, and the precipitate was dissolved in a mixture of chloroform (4 ml) and butylamine (60 μ l), and then kept at 60 °C to form a clear solution. Acetonitrile with equivalent volume to chloroform/butylamine mixture was added into the vial. The vial was centrifugated at 4000 rpm for ~1 min, while the solution temperature was still at ~50 °C. The supernatant was quickly removed, with precipitate dissolved in ~1.0 mL chloroform at 60 °C. 1.2 mL acetonitrile was then added into it again to start another cycle of precipitation, centrifugation, and decantation. The final products were re-dispersed in 2 ml ODE at 65 °C, and low boiling point residuals were removed from the solution by Ar bubbling at 65 °C.

Synthesis of CdSe 2D nanocrystals using purified CdSe nanocrystal seeds. Typically, Cd(St)₂ (variable amount) and ODE were loaded in a 25 ml three-neck flask. After bubbling for 10 min, the mixture in the flask was heated to a designated temperature (250 °C as the default) under Ar protection. Pre-crushed Cd(Ac)₂ suspended in 1 mL ODE was injected into the mixture, followed by the stock

solution of CdSe nanocrystal seeds. The amount of seeds was usually the same as that used in the direct synthesis of 2D nanocrystals without purification of the seeds. The reaction temperature was set at a designated value (250 °C as the default) and the total volume of solution was controlled at 5 ml. Needle-tip aliquots were taken and dispersed in 0.2% oleic acid (or octanoic acid) solution in toluene for UV–vis and PL measurements to monitor the reaction. When the reaction was completed, several drops of oleic acid were added to the flask prior to the cooling of mixture.

Purification and separation of CdSe 2D nanocrystals and 2D embryos. The finial product of a reaction was centrifugated at 10000 rpm for 5 min. The precipitate was obtained by decantation and dissolved in chloroform. Acetonitrile was added and the precipitate was isolated by centrifugation at 12000 rpm for 3 min. The precipitate containing CdSe 2D nanocrystals and supernatant with the 2D embryos were isolated from each other by decantation. To improve the purity of either 2D nanocrystals or 2D embryos, the cycle of dissolution, precipitation, centrifugation, and decantation might be repeated multiple times for the designated component.

Measurements. UV-vis spectra were taken on Agilent Technologies Cary 4000 UV-Vis spectrophotometer. PL spectra were recorded by Edinburgh Instruments FLS920 spectrometer. TEM images were taken on a Hitachi 7700 transmission electron microscope operating at 100 kV, and the nanocrystals were deposited onto a copper grid with ultrathin carbon film. HRTEM images were taken on a JEM 2100F transmission electron microscope operating at 300 kV.

Supporting Information

Additional UV-Vis, PL spectra, XRD pattern, TEM images, and quantitative calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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TOC Figure—_-

