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Necking Formation during Oriented Attachment of PbSe Nanocrystals

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ABSTRACT: Oriented attachment of nanocrystals has been recognized as an important strategy to construct epitaxially connected superlattices for various applications. The necking formation between semiconductor nanocrystals during oriented attachment, which largely determines the properties of the final superlattice structure, is still poorly understood. Here, with in situ liquid cell transmission electron microscopy (TEM) our direct observation reveals the nucleation and growth of necking between PbSe
nanocrystals with atomic details. We find that nanocrystals first approach each other until the gap distance is down to 0.6 nm, and a neck between two nanocrystals nucleates within 10 sec. Once the neck width is above the critical size of 0.9 nm, it grows into a 3-nm-wide neck in 15 sec. The atomic structure of the neck was further confirmed through ex situ statistic characterization of large-area superlattices with aberration-corrected scanning TEM. The neck formation mechanisms are elucidated through the additional DFT calculations. These findings not only provide critical insights into the atomic pathways of necking formation during oriented attachment, but also open the opportunities to synthesize nanocrystal superlattices with improved connectivity and properties.

KEYWORDS: PbSe nanocrystals, necking, oriented attachment, liquid cell TEM, superlattices
INTRODUCTION

Oriented attachment of colloidal nanocrystals has been found in a variety of natural and synthetic systems, in which nanocrystals preferentially connect along specific crystal facets to form a single crystal lattice. During oriented attachment, the inter-nanocrystal connectivity, which is achieved through a “necking” process, is essential for regulating the coherent coupling effects in superlattices and thus enabling the emergence of various novel properties. For instance, the epitaxially connected superlattices of semiconductor nanocrystals show remarkable electronic phenomena including topological states and Dirac cones. The key step to attain these phenomena lies in the construction of uniform inter-nanocrystal necks to increase the electron delocalization length. To understanding the necking phenomenon in semiconductor superlattices, recent efforts have been focused on using X-ray scattering and ex situ TEM to characterize the superlattice structures before and after oriented attachment. These measurements indicate an elongated center-to-center distance between neighboring nanocrystals that is larger than the diameter of initial nanocrystals. Tentative models have been proposed to explain the neck formation accordingly. However, the mechanisms of neck nucleation and growth during the formation of semiconductor superlattices are still largely unknown due to the lack of direct observation. Revealing of necking formation mechanisms is significant not only for interpreting semiconductor crystallization pathways through orientated attachment, but also for improving the inter-nanocrystal connectivity in semiconductor superlattices to achieve the predicted novel electronic properties.

Here, we report real-time atomic-resolution imaging of the necking process in oriented attachment of PbSe nanocrystals by liquid phase TEM. During the superlattice
transformation from hexagonal PbSe nanocrystal monolayers into connected square superlattices, we find that the necking process has three stages: (I) nanocrystals first approach each other with the superlattice angle changing from near 60 degree towards near 90 degree, indicating the geometry change from hexagonal to square. (II) When the neighboring nanocrystals reach a gap distance of approximately 0.6 nm, they stop approaching and start to build a neck. Atomic-resolution imaging allows us to directly observe the nucleation and growth processes of necking, which indicates that it takes 5 to 10 sec to form a stable neck nucleus over the critical size of 0.6 × 0.9 nm (neck length and width). (III) After nucleation, the neck grows to 3 nm in width in 15 sec. Using scanning TEM, we further confirm the formation of two-atomic-layer necks during superlattice transformation. The mechanisms of neck nucleation and growth are elucidated through the additional density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

The self-assembly and oriented attachment of PbSe nanocrystals are often performed in a single step by evaporating solutions of oleate-capped nanocrystals on the surface of an immiscible high-polar solvent, typically ethylene glycol (EG). To avoid the evaporation process during in situ TEM imaging, we separate the oriented attachment process from self-assembly through a superlattice transformation approach. First, an unconnected monolayer of oleate-capped PbSe nanocrystals (6.2 nm) are self-assembled through drop-casting 4 µL of a 0.5 mg/mL hexane solution on a 10 nm thick carbon-film TEM grid. We further deposit 100 nL of anhydrous EG on another similar TEM grid, and then sandwich two TEM grids together to form a carbon-film liquid cell for in situ TEM imaging. Before loading the PbSe nanocrystals and EG, the carbon-film TEM grids are pretreated with oxygen/argon plasma for 30 s to increase the wetting
of high-polar EG solution on the carbon film and improve the sealing ability of liquid cell. The flow of EG liquid during in situ observation initiates the oriented attachment of PbSe nanocrystals, enabling the real-time imaging of the complete necking process with up to atomic resolution (Movie S1–S4). Due to EG solution forms pockets/domains inside the liquid cell, it has been a challenge to achieve large-area ordered square superlattices as that formed ex situ. Nevertheless, we observe domains of hexagonal-like superlattice transform into connected square geometry.

The image series in Fig. 1A and Movie S1 depict the oriented attachment of six nanocrystals (1 to 6). At 0 sec, nanocrystals 2 and 3 have already been connected whereas the other nanocrystals are discrete in a hexagonal-like geometry. In the next 50 sec, the discrete nanocrystals move towards the neighboring nanocrystals and further fuse into an almost square superlattice. The trajectory of nanocrystal centers and the nanocrystal connectivity are shown in Fig. 1B, from which we analyze the change of four representative superlattice angles (α to δ). As shown in Fig. 1C, all the four superlattice angles shift from near 60 degree towards 90 degree, indicating the superlattice symmetry changes from hexagonal to square upon the approaching of nanocrystals.

The change of gap distances between five initially unconnected nanocrystal pairs is plotted in Fig. 1D. As a representative pair, nanocrystals 1 and 2 approach each other from a gap distance of 4.5 nm at 0 sec with a speed about 0.3 nm·s⁻¹. Then, they slow down and stop at a critical gap distance of 0.6 nm at 21 sec. As shown in the third image (20 sec) in Fig. 1A, there is a clear gap between nanocrystals 1 and 2. It further takes approximately 10 sec to build a discernible neck, which we consider as the neck nucleation process. Although other nanocrystal pairs have different initial gap distances
and different approaching speeds, they follow the same oriented attachment mode with three stages (Fig. 1C), i.e., (I) approaching each other until forming a gap distance of approximately 0.6 nm, (II) forming a neck nucleus in 5 to 10 sec, (III) neck growing in the lateral direction (width). This three-stage oriented attachment is also demonstrated by other two movies (Movie S2 and S3) and analyzed in Figs. S* and S*, showing very similar critical gap distances (~ 0.6 nm) and neck nucleation time (5 to 10 sec).

Atomistic pathway of the neck nucleation and growth is further revealed, see the image series in Fig. 2A and Movie S4. The clear lattice fringes throughout the movie enable us to reconstruct the atomic models of the neck nucleation and growth (right column in Fig. 2A), in which only Pb atoms are shown for clarity and a closer comparison to TEM images. We find that nanocrystal alignment occurs before the neck nucleation. As in the image at 2.0 sec, two unconnected nanocrystals have already reached the critical gap distance of 0.6 nm, showing matched \{200\} lattices aligned in the same direction with the same $d$-spacing of 3.1 Å. The 3.1 Å $d$-spacing keeps constant during the neck formation, indicating no strong lattice distortion. Counting the \{200\} lattices, we find both nanocrystals initially have 20 atomic layers along inter-nanocrystal direction, and after the oriented attachment, two extra layers along \{200\} lattices formed in the initial 0.6 nm gap. As reflected by the edge trajectories of nanocrystals (Fig. 2B), the nanocrystal centers barely change during the necking process, however, the nanocrystal width (perpendicular to inter-nanocrystal direction) decreases slightly during the neck growth. This is probably caused by the atom migration from the lateral faces into the gap through surface diffusion.

A closer scrutiny on the necking area reveals that the neck nucleation involves the formation of metastable PbSe filament (snapshot at 3 s as an example) before the
formation of a stable nucleus. Fig. 2C records the size change of the filament or neck. During the whole necking process, the neck length is fixed to 0.6 nm as the same as the initial gap distance. However, the neck width fluctuates between 0 to 0.9 nm from 2 to 7 sec due to the formation and cleavage of thin PbSe filaments. After this nucleation process, a stable nucleus with width larger than 0.9 nm forms, and keeps growing to a width approximate to 2.7 nm in 20 sec.

We further employ high-angle annular dark field scanning TEM (HAADF-STEM) to investigate the ex situ neck formation during large-area superlattice transformations. We perform the superlattice transformation with a similar procedure used in situ, i.e., first forming hexagonal monolayer on carbon-film TEM grid, and then immersing the grid in EG for 30 sec. The large-area structures before and after EG treatment are characterized by HAADF-STEM and analyzed by home-developed computer vision scripts (Fig. 3A–E). We observe that the nanocrystal center-to-center distance is larger than the initial nanocrystal diameter during the superlattice transformation, similar to that reported in a one-step square superlattice preparation through evaporating nanocrystals in hexane or toluene solution on top of EG layer. We note that the precise neck length should not be directly calculated as the difference between center-to-center distance and nanocrystal diameter, instead, it should be calculated as difference between center-to-center distance and the nanocrystal size along <100> directions. The precondition to obtain the neck size with atomic-level precision relies on the high monodispersity of initial nanocrystals. Statistical analysis on nanocrystal diameter (Fig. 3A,C) shows that the initial hexagonal packed monomers are high monodisperse: 95% nanocrystals have a diameter of 6.2 ± 0.1 nm. This high monodispersity is essential to determine that nanocrystal monomers contain 20 layers of {200} lattices along the <100> directions, which is consistent with the nanocrystal size measured in Fig. 2. After EG
treatment, a square superlattice (Fig. 3B) forms with an average center-to-center distance of 6.7 nm (Fig. 3D). Therefore, the neck length is calculated as the difference between the center-to-center distance (6.7 nm) and the nanocrystal size along <200> direction (20 layers of \{200\} lattices, 6.1 nm), i.e., 0.6 nm (2 layers of \{200\} lattices).

In addition, Fig. 3E shows the histogram of neck width, indicating an average width of 3.0 nm, comparable to the neck width measured in situ at 20 sec (Fig. 2).

The necking of two extra \{200\} lattices is confirmed by direct atomic-resolution imaging (Fig. 2F,G). Fast Fourier transformation (FFT, Fig. 2F insert) shows the uniform oriented attachment in the connected superlattice. Drawing boxes with 20 \times 20 atomic layers helps to show the necks clearly (Fig. 2G) and it enables us to count the newly formed extra lattices. The result (Fig. 2H) also shows most necks are formed with two extra layers of \{200\} lattices.

Previous studies on gold crystallization found that oriented attachment of gold nanocrystals may also involves the necking of nanoparticles with a gap distance approximate to 0.5 nm [ref]. It was proposed that the gold nanocrystals stop at the small gap distance because of the separation of solvent, i.e., water. Our recent atomic-resolution in situ TEM study on gold nanocrystals suggests the ligands could play an important role in separating gold nanocrystals during oriented attachment [ref]. We speculated that the necking between semiconductor nanocrystals may also involves a similar stage of solvent or ligand separation. Since we have observed that the approaching PbSe nanocrystals stop at a gap distance of 0.6 nm, we consider the gap results from ligand residual instead of solvent. This is because we start the superlattice transformation from completely dried nanocrystal monomers and there is no hexane or toluene solvents between nanocrystals, which is different from the toluene/EG
interfacial assembly method [ref]. In addition, once the oleate ligands are removed from
the nanocrystal surface, they tend to form a molecular monolayer to separate the
nanocrystals from EG as oleate ligands have a surfactant structure with a high-polar
carboxylic head and a long non-polar alkyl tail. Therefore, it is more likely that the
PbSe nanocrystals are separated by oleate-ligand residuals when they stop and start to
build a neck.

We perform DFT calculations to support this hypothesis and to further understand
the necking mechanism. In order to reduce the calculation expense while retaining the
main structures of oleate ligands and PbSe nanocrystals, we construct the structure with
an oleic acid fragment (without the alkyl tail after the alkene group) sandwiched in two
{001} faceted salt-rock PbSe crystals (Fig. 4A). Upon two crystals approaching each
other, the system energy first decreases and then increases when they start to squeeze
the oleic acid fragment. Note that, the distance between outmost layers to the gap is one
{002} layer (0.3 nm) larger than the gap distance that we refer to in the TEM image
analysis. The system has a lowest energy with the gap distance between 0.6 to 0.7 nm,
in accord with the stop distance that we observed in the in situ and ex situ experiments.
We further evaluate the critical nucleus size by adding Pb and Se atoms into the 0.6 nm
gap (Fig. 4C). The energy differences as moving Pb and Se atoms from bulk into the
gap are calculated as shown in Fig. 4D. When adding the first 9 pairs of Pb and Se
atoms, ΔE generally increases with considerable fluctuations. Upon further addition of
Pb and Se atoms, ΔE decreases as well as fluctuates, indicating that nucleation needs to
overcome an energy barrier for forming a stable nucleus. The critical nucleus contains
9 pairs of Pb and Se atoms, which has a size of 3×3 {200} layers, i.e., 0.9 nm in width.
This is also consistent with the in situ observation of necking formation in Fig. 2.
To summarize, we report the first in situ observation of the necking formation of semiconductor nanocrystals and it reveals the atomic pathways of necking between PbSe nanocrystals. We show three stages of necking process, i.e., (I) nanocrystals approaching each other, (II) they stop and start to build a neck (nucleation), (III) the growth of neck. In addition, we provide the kinetics data (e.g., nucleation time) and critical spatial information (e.g., separation gap distance and critical nucleus size) that can only be obtained through in situ investigations. We confirm the neck structure by the statistics of ex situ formed large-area superlattices with atomic precision. Moreover, we elucidate the nucleation and growth mechanisms by DFT calculations. By revealing the necking phenomenon in an unprecedented atomic level, this study provides critical insights into the oriented attachment of nanocrystals. Our improved understanding on the neck nucleation and growth will facilitate the synthesis of nanocrystal superlattices with better coupling connectivity, leading to the potential to achieve their predicted novel properties.
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Fig. 1. Neck formation between PbSe nanocrystals during the transformation from unconnected hexagonal to connected square superlattices. (A) Sequence of in situ TEM images showing the approaching and necking of six nanocrystals. Images are extracted from movie S1 and shown in false color. Scale bar, 5 nm. (B) Trajectories of the nanocrystal centers showing the approaching of nanocrystals and the transformation from hexagonal to square geometries. Dashed or solid lines between six nanocrystal pairs indicate they are separated or epitaxial connected, respectively. Four representative superlattice angles are marked with α to δ. (C) Plot of the four superlattice angles versus time. (D) Analysis of the gap distances between six nanocrystal pairs showing a three-stage necking pathway. Pair of nanocrystals 1 and 2 (orange dots and lines) is emphasized to show the three stages of (I) approaching, (II) stop and neck nucleation, (III) neck growth. When gap distance falls into 0 nm (gray bar), it indicates a stable nucleus formed between the nanocrystal pair.
**Fig. 2.** Atomistic pathway of neck nucleation between two PbSe nanocrystals. (A) Sequence of in situ TEM images (left column), extracted from movie S4, showing the atomistic pathway of neck nucleation. Zoom-in view (middle column) and atomic models (right column) showing the necking details. Both scale bars are 2 nm. (B) Trajectories of the nanocrystal edges showing the nanocrystal shape change during neck formation. (C) Plot showing the change of neck length and width during the neck nucleation and growth stages (separated by dash line).
Fig 3. HAADF-STEM characterization on neck structure in large-area superlattices formed ex situ. (A, B) HAADF-STEM images of the hexagonal monolayer and the connected square superlattice. Right columns show the recognitions of nanocrystal diameter (red circles), center-to-center distance (blue lines), and neck width (green lines) on half of the images. Recognitions are performed through computer vision, and the full recognition results and methods are shown in Figure S*. (C) Histogram showing the distribution of nanocrystal diameter in the hexagonal monolayer in (A). (D, E) Histograms showing the distributions of center-to-center distance and neck width in the connected square superlattice in (B). (F) Atomic-resolution image and inserted FFT show the uniform nanocrystal orientation and neck connectivity in a square superlattice. Cyan boxes with a size of $20 \times 20$ \{200\} layers are drawn to better visualize the extra layers formed through necking. (G) Zoom-in image showing the two extra \{200\} layers formed through necking. (H) Histogram of neck length in the unit of atomic layers, obtained by counting extra \{200\} layers between nanocrystals as indicated by (G). Scale bars are 20 nm in (A, B), 5 nm in (F), and 2 nm in (G).
Fig. 4. DFT calculations on the critic gap distance during nanocrystal approaching and the critic nucleus size during neck nucleation. (A) Sandwich structure with an oleic acid fragment in two \{001\} faceted salt-rock PbSe crystals. Note that, the layer-to-layer distance indicated by gray arrow is one \{002\} layer (0.3 nm) larger than the gap distance (blue arrow) that we refer to in the TEM image analysis. (B) System energy change upon two crystals approaching each other. (C) Representative structure with a neck between two PbSe crystals formed by 9 pairs of Pb and Se atoms. When filling atoms into the two-atomic-layer gap, the Pb and Se atoms are adding in pairs and packed closely. (D) \(\Delta E\) change as moving different pairs of Pb and Se atoms from bulk into the gap, showing the instability of thin filaments with few atom pairs and the increased stability of necks with more than 9 atom pairs.