

Using Interaction of Nano Dipoles to Control the Growth of Nanorods

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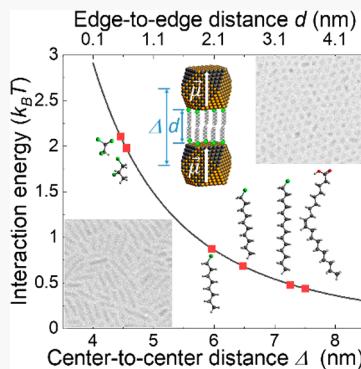
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ABSTRACT: Charged facets of a nanocrystal can form an intrinsic nanometer-size electric dipole. When the spacing between these nano dipoles is adjusted, the dipolar interaction energy is tuned from a fraction to a multiple of the thermal energy. Consequently, the one-dimensional oriented attachment can be switched on or off, as is the growth of nanorods. This kinetically controlled growth is achieved at relatively low reaction temperatures while the thermodynamically controlled growth dominates at higher temperatures. The synthesized PbSe nanorods are branchless, exhibiting a single-exponential photoluminescence decay trace with an e-folding lifetime of 1.3 μ s and a photoluminescence quantum yield of 35%.



Oriented attachment of nanoparticles in a colloidal solution is one of the important processes in the formation of larger-scale anisotropic nanostructures.¹ Banfield and co-workers first invented the concept when they studied the growth of iron oxyhydroxide crystal.² The proposed mechanism has been used to explain a variety of material systems including TiO₂,^{3,4} ZnO,⁵ CdTe,⁶ CdSe,⁷ and PbSe.⁸ Among them, we are interested in lead selenide (PbSe). Bulk PbSe is a classic high-performance thermoelectric material known since the 1950s.⁹ Its figure of merit can be further enhanced in anisotropic one-dimensional structures.¹⁰ On the other hand, recent reports of high multiple-exciton-generation^{11–13} rate and slow Auger recombination rate^{14,15} in PbSe nanorods finds them another promising application in highly efficient photovoltaic devices.

The driving forces for oriented attachment, similar to the forces to assemble the colloidal nanocrystals into superlattices, include van der Waals, electrostatic, magnetic, molecular, and entropic interactions.¹⁶ Many methods including tuning the ligands,^{17–20} solvents,^{21–23} and evaporation speed²⁴ have been reported to assemble quantum-dot superlattices. However, it is still challenging to quantitatively reveal the specific driving force that is responsible for the self-assembly and the oriented attachment. Consequently, it is difficult to exploit this process for the rational design of desired nanostructures.

In this work, we demonstrate that the interaction of the nano dipoles can be exploited to control the attachment of colloidal PbSe quantum dots and so the growth of the nanorods. We find that the strength of the dipolar interaction between the quantum dots can be accurately tuned by using

the surface ligands of different lengths. In consequence, we can turn on or off the one-dimensional growth of the nanorod by changing the length of the surface ligand. At higher reaction temperature, the thermodynamic process overpasses this kinetically controlled process, reducing the aspect ratio of the nanorods or turning them into nanodots.

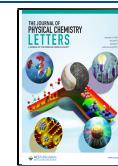
Though PbSe is a centrosymmetric material, an electronic dipole can form in a PbSe quantum dot under a proper arrangement of its {111} facets. If one side of the quantum dot has four Pb-rich (+) {111} facets and the other side has four Se-rich (−) {111} facets (Figure 1c), an effective electric dipole is formed in the quantum dot.⁸ The magnitude of the dipole moment can be a few hundred debye.²⁵ In consequence, the dipole–dipole attraction energy between the two quantum dots can exceed the thermal energy $k_B T$ (k_B is the Boltzmann constant, and T is the temperature in kelvin) at the reaction temperature.²⁵ This strong interaction likely drives quantum dots to align and attach to form one-dimensional (1D) nanorods.

The magnitude of the screened dipole moment of a PbSe quantum dot is^{6,26}

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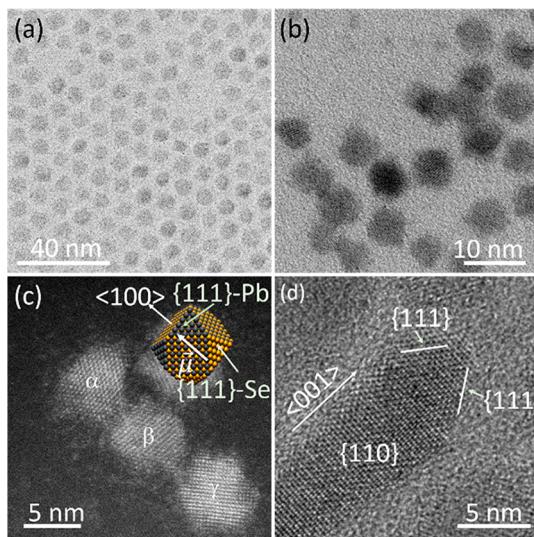


Figure 1. Transmission electron microscopy (TEM) images of the colloidal PbSe quantum dots treated with (a) 1-chlorotetradecane (CTD) and (b) 1,1,2-trichloroethane (TCA). (c) High-resolution TEM (HRTEM) dark-field image of the PbSe quantum dots after the TCA treatment. Quantum dot α and β , but not γ , are aligned and fused along the $\langle 100 \rangle$ direction. Inset: a PbSe nanocrystal model showing Pb-rich and Se-rich $\{111\}$ facets, and the electric dipole moment $\vec{\mu}$. (d) HRTEM image of a PbSe nanorod showing its $\{110\}$ facet (facing-up) and two $\{111\}$ facets (standing-up) at its tip.

$$\mu = \frac{6\epsilon_2 qr}{\epsilon_2 + 2\epsilon_1}$$

where ϵ_1 is the dielectric constant of the solvent; ϵ_2 is the dielectric constant of the quantum dot; q is the charge of the dipole; r is the radius of the quantum-dot sphere. Then the dipole–dipole interaction energy of two head-to-tail aligned dipoles is³⁵

$$V = \frac{-2\mu^2}{4\pi\epsilon_1\epsilon_0\Delta^3}$$

where ϵ_0 is the vacuum dielectric constant and Δ is the interdot spacing (center-to-center distance between two quantum dots).

Among all the parameters affecting the dipolar interaction strength, the interdot spacing, Δ , is most significant because it is inversely proportional to Δ^3 . In experiments, Δ can be tuned by changing the length of the capping ligands on the quantum dots.^{27–29} In this work, we use chloroalkane as the surface ligands for nanocrystals and demonstrate that the length has a critical role in the growth of the nanorods.

We first demonstrate that the chloroalkane molecules can adsorb on the surface of PbSe nanocrystals and modulate the interdot spacing (Δ). We treated the oleic-acid capped PbSe quantum dots using two different chloroalkane molecules: CTD and TCA. After the ligand exchange with CTD, the quantum dots drop-casted onto a TEM substrate remain well separated from each other (Figure 1a). The average interdot spacing (edge to edge) reduces from 3.5 to 3.0 nm (Supporting Information A). The chloroalkane molecules likely replace the original oleic-acid ligands instead of removing them. Otherwise, attachment of quantum dots will occur as those treated with $(\text{NH}_4)_2\text{S}$ ²⁸ or oleylamine.³⁰ The quantum

dots treated with TCA are closer to each other (Figure 1b). Some of them have attached (Figure 1c).

The dipole–dipole interaction at a small interdot spacing distance makes the neighbor quantum dots align. As shown in Figure 1c, quantum dot α and β with their $\{110\}$ facets facing up are aligned along $\langle 100 \rangle$ direction, which is likely due to the interaction of the electric dipoles (Figure 1c, inset). The strong interaction can push away the capping molecules in between the quantum dots (α and β in Figure 1c) so that they fuse,^{22,28,30} termed “necking”.^{27,31–33}

Our first-principles computation using density functional theory (DFT) supports the experimental results. The binding energies of the chloroalkane molecules to the different facets of the PbSe quantum dot are in the same order of magnitude (a few meV/Å²) as the original oleic acid (OA) capping ligands (Supporting Information B). Therefore, chloroalkane molecules in the quantum dot solution can bind to all the facets of the quantum dot or replace the surface oleic-acid ligands. The binding energies of lead oleate [$\text{Pb}(\text{OA})_2$] to the reconstructed³⁴ Pb-rich and Se-rich $\{111\}$ facets are both around 10 meV/Å². This makes it possible to form an equal number of Pb-terminated and Se-terminated $\{111\}$ facets and thus the electric dipole.

The binding of the chloroalkane molecules on the $\{111\}$ facets of the quantum dots suppresses the fast growth of the $\{111\}$ facet to avoid their elimination⁸ so that the electric dipole moment remains within the quantum dot. Without the suppression, the $\{111\}$ facets grow and diminish, resulting in cubic nanocrystals terminated by six $\{100\}$ facets.⁸ Further growth of the $\{100\}$ facets results in a hexapod structure (Supporting Information C). The overall growth of the nanocrystal is also slowed down. In our experiment, cosolvent TCA slows down the growth of PbSe nanocrystals by a factor of 6 as indicated by the change of the solution color. This provides time for the long-range but weak dipolar interaction to take effect for oriented attachment before the nanocrystal grows three-dimensionally.

Many quantum-dot superlattices were assembled using such an *ex situ* method while tuning the ligands,^{17–19} solvents,^{21–23} and evaporation speed.²⁴ When the assembly and attachment occur in the reaction environment of a synthesis, smooth and singly crystalline nanostructures form. In our synthesis (Supporting Information D), the greater Brownian motion at elevated solution temperatures makes the dipole–dipole interaction more effective to align and attach quantum dots one-dimensionally. The formed nanorods have an increasing aspect ratio but a fixed diameter by reaction time (Supporting Information E), confirming that the oriented attachment is the growth mechanism.³⁵ The attached quantum dots still have “dents” formed by the $\{111\}$ facets of each dot (Figure 1c). With the lead and selenium precursors in the reaction solution, the $\{111\}$ facets keep growing until eliminated,⁸ resulting in smooth nanorods (Figure 1d). The HRTEM image shows the nanorod is singly crystalline with its longitudinal axis along the $\langle 100 \rangle$ direction (Figure 1d). The nanorod has a sharp tip with two opposite $\{111\}$ facets making an acute angle of 71°. The existence of the large $\{111\}$ facets supports the explanation of the formation of the electric dipole moment in a PbSe quantum dot.

At room temperature, the as-synthesized nanorod exhibits a single-exponential photoluminescence decay trace with an e-folding lifetime of 1.3 μs (Supporting Information F). The absolute quantum efficiency of the nanorods is 35 \pm 3%

(Supporting Information F). These superior optical properties are likely due to the minimal defects and well-passivated surfaces. The long photoluminescence lifetime (as is the exciton lifetime) is in favor of charge separation and transfer, which is advantageous for photovoltaic applications. The high photoluminescence quantum efficiency is critical for the application in light-emitting devices and photonic devices.

Because the chloroalkane molecule ligands can tune the interdot spacing, it is expected to control the attachment of quantum dots to grow nanorods. A series of chloroalkane capping ligands with different lengths are used to systematically tune the interdot distance. The ligands, including TCA, 1,2-dichloropropane (DCP), 1-chlorooctane (COE), 1-chlorodecane (CDE), and CTD, have lengths ranging from 0.3 to 1.9 nm. The results show that only PbSe quantum dots formed when the longest capping ligand (CTD) is used in the synthesis (Figure 2d). When the shorter ligand CDE is used (Figure 2c), a mixture of nanorods and quantum dots form. As the length of ligands gets shorter, only nanorods form (Figure 2a,b).

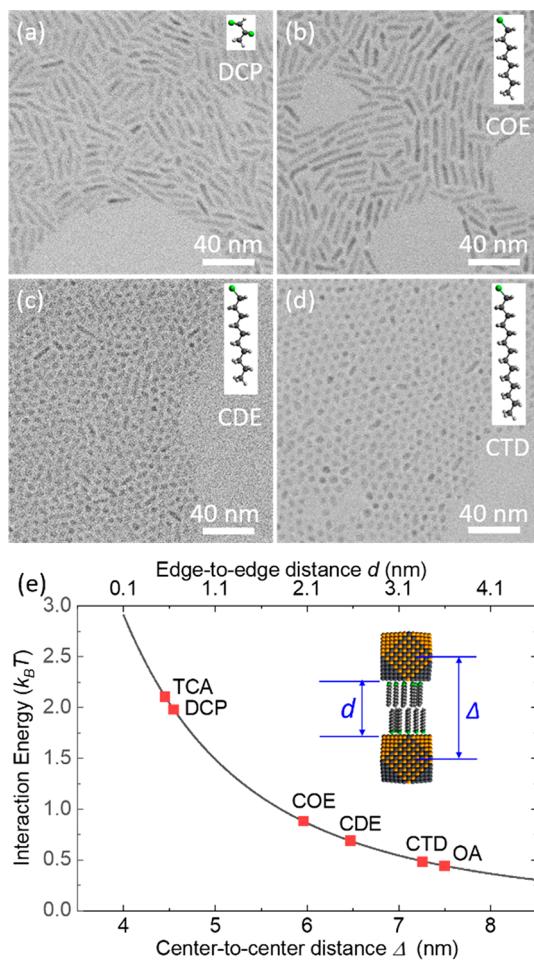


Figure 2. TEM images showing the PbSe nanocrystals synthesized with cosolvents (a) DCP, (b) COE, (c) CDE, and (d) CTD. The inset in each image shows the molecular structure of the chloroalkane. (e) Dependence of dipole–dipole interaction energy (magnitude) on the distance Δ (solid line). The solid squares indicate the estimated distance and the corresponding interaction energy between the quantum dots capped by different chloroalkanes: TCA, DCP, COE, CDE, CTD, and OA.

The experimental results are well-explained by the dipolar interaction of the nano dipoles. The equivalent charge (q) on a PbSe quantum dot of diameter ~ 6.8 nm is about 1 e .²⁵ Assuming the surface charge density is the same for the quantum dots of different sizes, the average effective charge q on 3.9 nm large quantum dots in our experiment is estimated to be $\sim 0.33\text{ e}$. Given the dielectric constants of the diphenyl-ether solvent ($\epsilon_1 = 3.9$) and PbSe ($\epsilon_2 = 23$), the electric dipole moment ($\mu = \frac{6\epsilon_2 qr}{\epsilon_2 + 2\epsilon_1}$) is calculated to be 138 D. It is in the same order of magnitude of the dipole moment of 10 nm PbSe nanocrystal as estimated by Sashchiuk et al.³⁶

The dipolar interaction energy ($V = \frac{-2\mu^2}{4\pi\epsilon_1\epsilon_0\Delta^3}$) is then determined by the interdot distance Δ which can be calculated from the diameter of the quantum dots and the thickness of the capping-ligand layer d (d is assumed to be twice the length ligand), as shown in Figure 2e. When the quantum dots are capped by oleic acid (OA, 1.8 nm),³⁷ the interdot distance is estimated to be 7.5 nm (Supporting Information G). The magnitude of the corresponding interaction energy is about 1.4 kJ/mol, equivalent to $0.4k_B T_{\text{A}}$ (T , reaction temperature ~ 383 K; N_{A} , Avogadro constant). It is not enough to stabilize the chain of quantum dots.^{6,38} Our result shows that all nanocrystals grow into star-shaped crystals (Supporting Information C) instead of nanorods. When the quantum dots are capped by TCA, the interdot distance Δ is about 4.5 nm (Supporting Information G), resulting in the interaction energy 6.7 kJ/mol (equivalent to $2.1 k_B T_{\text{A}}$). The interaction energy is between the two extremes when DCP, COE, CDE, or CTD caps the quantum dot.

This long-range interaction exerts a consistent force on each quantum dot in Brownian motion. Though its magnitude is typically less than short-range ligand–ligand interaction, it is sufficient¹⁶ to align and attract the nanocrystals to attach. The threshold of the interaction energy (magnitude) for the formation of nanorods is $\sim 0.7k_B T$ when CDE is used as the spacing ligands. Longer (shorter) ligands result in smaller (larger) magnitude of the interaction energy, turning off (on) the oriented attachment. The total dipole moment of the attached nanocrystals increases linearly as its length, while the dipole–dipole interaction energy is proportional to μ^2 . In consequence, the one-dimensional attachment process gets enhanced as the nanorods get longer until there is no nanocrystal to attach or stopped by the steric hindrance.

The reaction temperature has a significant effect on the growth of nanorods. High reaction temperatures result in fast growth and a large diameter of nanorods (Figure 3a-d). The corresponding photoluminescence peak of each sample also shifts to longer wavelength as the reaction temperature increases (Supporting Information H). The red-shift of the photoluminescence peak is due to the reduction of quantum confinement at a large diameter.³⁹ More importantly, the average length of the nanorods decreases as the reaction temperature increases, which indicates that 1D attachment is less efficient at higher reaction temperatures.

It is likely the growth of the nanorods is controlled by two different mechanisms: kinetic and thermodynamic. In the kinetic (thermodynamic) process, the growth is activated at lower (higher) activation energy but ends up with a less (more) stable product.⁴⁰ In our case, the growth of the nanorods is kinetically controlled at a reaction temperature of 110 °C but more thermodynamically controlled at 150 °C.

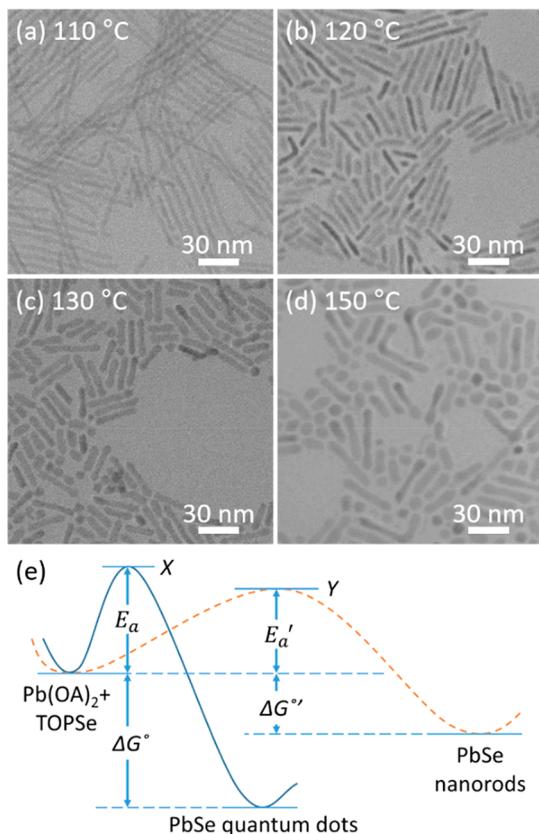


Figure 3. TEM images of PbSe nanorods synthesized at (a) 110 °C, (b) 120 °C, (c) 130 °C, and (d) 150 °C. (e) The energy landscape illustrating the thermodynamically controlled (solid line) and kinetically controlled (dashed line) reaction pathways. The chloroalkane cosolvent reduces activation energy from E_a to E_a' , resulting in nanorods.

The product from thermodynamically controlled growth tends to have a low aspect ratio which is more stable. The two mechanisms can simultaneously occur in one synthesis but may dominate the crystal growth at different stages.

Reducing the activation energy E_a (Figure 3e) promotes kinetically controlled growth. It is realized by using a chloroalkane cosolvent in our synthesis. Our DFT calculations show that the binding of the chloroalkane molecule (TCA) on the surfaces of a PbSe nanocrystal increases the surface energy (Supporting Information B). Meanwhile, shorter capping ligands enhance the dipolar interaction, which effectively reduces the energy barrier of attachment. Both factors reduce the overall energy barrier (E_a') of the pathway from the reactants “ $\text{Pb}(\text{OA})_2 + \text{TOPSe}$ ” through Y to product PbSe nanorods (Figure 3e). Because the rate constant is exponentially dependent on the activation energy ($k \sim e^{E_a/RT}$), the reaction corresponding to pathway Y can be significantly faster than pathway X, resulting in PbSe nanorods as the main product. At higher reaction temperatures, the reactions through both X and Y pathways are viable, resulting in quantum dots and nanorods (Figure 3d).

The nanorod growth mechanism developed for PbSe—one-dimensional oriented attachment modulated by dipole–dipole interaction—can be applied for other centrosymmetric crystals. One of them is PbS which also has a cubic rock-salt crystal structure. In a similar reaction condition as for the synthesis of PbSe nanorods, the presence of chloroalkane can also turn PbS

quantum dots into PbS nanorods (Supporting Information I), which is likely driven by the same aforementioned dipolar interaction. Interestingly, two-dimensional oriented attachment also occurs during the growth of colloidal PbS nanosheets,^{37,41–44} which might be due to a stronger antiparallel dipolar interaction.⁴⁵

In summary, we demonstrate that the growth of nanorods can be controlled by modulating the interaction of nano dipoles in colloidal quantum dots. This interaction can be accurately tuned by changing the interdot distance in the reaction solution. The one-dimensional attachment can be turned on or off so that the growth of the nanorod can be well-controlled. This control is achieved at relatively low reaction temperatures while the thermodynamically controlled growth dominates at higher temperatures. The synthesized PbSe nanorods exhibit excellent optical properties that may find applications in optoelectronic, thermoelectric, and photonic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c03276>.

Interdot spacing, DFT calculations, synthesis of PbSe nanocrystals without chloroalkane, synthesis of PbSe nanorods, time-dependent aspect ratio, time-resolved photoluminescence and absolute photoluminescence quantum yield, ligand length, electric dipole moment, dipolar interaction energy, photoluminescence spectra from PbSe nanorods synthesized at different temperatures, and synthesis of PbS nanorods (PDF)

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Notes

The authors declare no competing financial interest.

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