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Separation-dependence evolution of inter-particle interaction in the oriented-attachment growth of nanorods: A case for hexagonal nanocrystals

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Abstract

Previous reports only evaluated the correlation between oriented-attachment growth and part of the interaction, *i.e.*, either van der Waals interaction or Coulombic interaction. By focusing on hexagonal nanorods, a relatively complex form of 1D nanocrystals, this Letter takes into account both dominant interactions and systematically investigates their countering effects on the separation dependence of the inter-particle interaction in the oriented-attachment growth of 1D nanocrystals. As elucidated by the Arrhenius equation, the growth kinetics and thermodynamics of oriented-attachment nanocrystals can thus be evaluated with such quantitatively-resolved inter-particle interactions between the attaching objects.

Introduction

Oriented-attachment (OA) growth has now become a major research focus in the crystal growth field since the OA mechanism was first uncovered by Banfield *et al.*¹⁻⁶ The OA mechanism has been employed to realize various nanorods^{7,8} and quantum dots^{9,10}. Nevertheless, as illustrated by the authors' previous reports, the theoretical aspects of the fundamental interaction between the attaching nanocrystals have received much less attention compared with the extensive experimental findings in the field.¹¹⁻¹⁸ To facilitate the theoretical investigation into the OA growth mechanism, the authors have recently derived the analytical expressions of the inter-particle interactions between the growing 1D nanocrystals (NCs) and the short attaching precursor NCs.^{12,19} With the expressions, the correlation between the inter-particle interactions, mainly including the attractive van der Waals interaction (vdW) and the repulsive Coulombic interaction (CI) has been evaluated. However, to our best knowledge no report has been focused systematically on both interactions which impact simultaneously on the growth of various OA NCs.¹¹ By taking the OA growth of hexagonal NCs, a relatively-complex form of NCs, as a platform, this work derives and analyzes the countering effects of vdW and CI on the 1D evolution of NCs. The results, as obtained by the means of numerical evaluation, reveal the NC-NC separation dependence of the inter-particle interactions with detailed insight into the effects of charge density, Hamaker constant and aspect ratio (AR), and thus facilitate the fundamental investigation into the thermodynamics and kinetics of the oriented-attachment growth of 1D NCs.

Theoretical models

Only vdW and CI are taken into account in this report by agreeing with the known assessment that the inter-particle dipolar interaction (DI) can play an insignificant role in OA growth and be negligible.^{11,20} In addition, the magnitude of the CI between the surface of the growing hexagonal NR and the surface of the attaching precursor NC is dependent on the strength and distribution of the surface charges. The correlation between the surface charge density σ and the surface electrical potential ψ_0 of a planar surface can be established according to the Debye–Hückel model of electrical double layer, as shown in Eq. 1,

$$s = e(y_0 / k^{-1}) \quad (1)$$

where ϵ represents the absolute permittivity of the solvent and κ^{-1} is Debye-Hückel length. According to Eq. 1, the distribution of surface charges is equivalent to the distribution of surface electrical potential as the absolute permittivity ϵ and the Debye-Hückel length κ^{-1} remain constant at the room temperature.²¹ Moreover, the correlation between the surface potential ψ_0 and the potential-determining ion concentration c in the solution can be expressed by Nernst equation, which is depicted in Eq. 1,

$$y_0 = \frac{k_B T}{e} \ln\left(\frac{c}{c_{zp}}\right) \quad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature, e represents the charge of a single electron and c_{zp} denotes the concentration of the ions when the electrical potential on the surface is zero.²¹ By substituting Eq. 2 into Eq. 1, we obtain Eq. 3.

$$s = \frac{e}{k^{-1}} \frac{k_B T}{e} \ln\left(\frac{c}{c_{zp}}\right) \quad (3)$$

Based on Eq. 3, the distribution of the surface charge density σ on the growing NR and the attaching NC only depend on the distribution of the potential-determining ions in the specific solution which should be uniform and unchanged as the OA growth system maintains in equilibrium. Therefore, it is appropriate to assume a few points: 1. the surface charge density on hexagonal nanorods and precursor NCs is uniform; 2. the repulsion which arises from the CI of surface charge is treated as the effect of net charge on electrical double layer; 3. Brownian motion and rotation of precursor NCs generate merely slight fluctuation of interaction energy and can be neglected as the precursor NCs approach the growing nanorods.

vdW interaction, CI and energy barrier

The vdW interaction between two spherical NP containing q atoms/ cm^3 is expressed in Eq. 4,

$$E = - \int_{V_1} dv_1 \int_{V_2} dv_2 \frac{q^2 \lambda}{r^6} \quad (4)$$

where V_1 , V_2 are the volumes of the two attaching NCs, r represents the separation between the volume elements dv_1 and dv_2 of two NCs, respectively, and λ is the London-vdW constant.²²

Consider a hexagonal NR with a length L_1 and center O_1 , and a random point P at a distance $O_1P=C$, as shown in Fig. 1. A spherical surface around P with radius r is sketched to cut out a partial spherical surface inside the hexagonal NR. Thus, the expression of this surface area can be obtained *via* surface integral, which yields Eq. 5,

$$[\text{surface}] = 12 \left[r^2 \arctan\left(\frac{\sqrt{3r^2 - 3R^2}}{r}\right) + \frac{\sqrt{3}}{2} rR \arctan\left(\frac{R}{2\sqrt{r^2 - R^2}}\right) - \frac{1}{3} \pi r^2 \right] \quad (5)$$

where R denotes the side length of the hexagon.

Similarly, another sphere with radius $O_1P = C$ around the center O_1 of the elongated hexagonal NR can be sketched to cut out a surface in the hexagonal precursor NC with length L_2 and center O_2 . Based on Eq. 5, the volume integral in Eq. 4 equals an expression *via* Eq. 5 and the vdW between the elongated hexagonal NR and short hexagonal precursor is given by Eq. 6. Here A denotes the Hamaker constant ($A = \pi^2 q^2 \lambda$) and the center-center separation O_1O_2 is equal to D.

$$E = -\frac{A}{\pi^2} \int_{D-\frac{1}{2}L_2}^{D+\frac{1}{2}L_2} [\text{surface}]_{r=c} dC \int_{C-\frac{1}{2}L_1}^{C+\frac{1}{2}L_1} [\text{surface}] \frac{1}{r^6} dr \quad (6)$$

The CI between two arbitrary points with separation r is depicted in Eq. 7,

$$E = \frac{1}{4\pi\epsilon} \frac{Q_1 Q_2}{r} \quad (7)$$

where Q_1 and Q_2 are the values of net charges and ϵ represents the absolute permittivity of the solvent. Thus, the CI between the elongated hexagonal NR and the short hexagonal precursor NC can be viewed as a double summation of eight facets and derived *via* surface integration. Nevertheless, the derivation of CI is rather complicated (see Supporting Information).

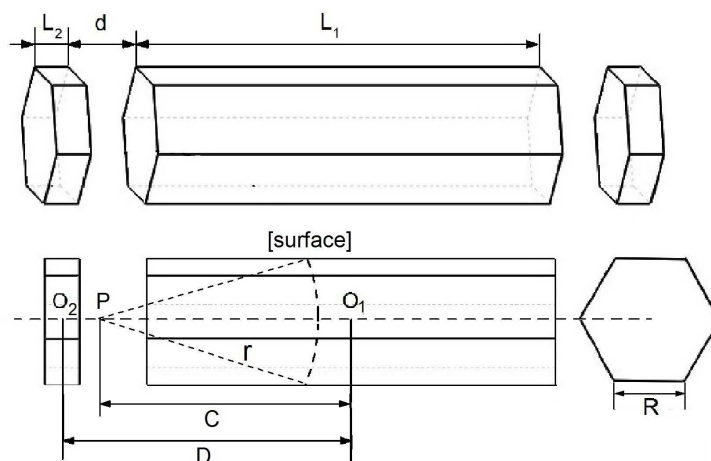


Figure 1 | Configuration of a hexagonal precursor and a hexagonal NR. O_1 and O_2 are the geometric centers of the hexagonal NR and the hexagonal precursor NC, respectively. L_1 and L_2 are the respective lengths of the hexagonal NR and the hexagonal precursor NC, R is the side length of hexagon, d is surface-to-surface separation and D is the separation between O_1 and O_2 . The center of the curved surface with radius r inside the hexagonal NR is located on the central axis. The separation between P and O_1 is noted as C.

Results and Discussion

The energy barrier associated with an OA growth is regarded as the activation energy (E_a) of the OA growth in the form of Arrhenius equation to determine the rate constant k of this process, as described in Eq. 8,

$$k = Ae^{-E_a/RT} \quad (8)$$

where R is the ideal gas constant, T is the absolute temperature, and A denotes the frequency factor. Based on Eq. 8, CI increases E_a , lowers the growth rate, and thus impedes the OA growth. Yet, the enhancement in vdW owns an opposite effect on OA growth.²³

We then employ numerical integration *via* adaptive Simpson quadrature to evaluate the inter-particle interaction in the growth of 1D NCs.

As shown in Fig. 2, all the interactions are negligible as the NC-NC separation tends to be infinite. But CI varies much slower than vdW, and is still a few times kT in magnitude as the NC-NC separation is ~ 40 nm while the magnitude of vdW can be negligible as the separation exceeds 15 nm. This indicates CI dominates potential energy in the initial state of the OA growth as the precursor concentration is relatively high. Contrarily, as the hexagonal precursor NC continuously approaches the hexagonal NR and the separation is below 10 nm, CI increases slightly with decreasing separation while vdW decreases abruptly into quite negative values, which induces a sudden drop in the total potential energy and generates an energy barrier with the magnitude of 10 kT in the process. As a consequence, CI contributes to the major magnitude of the energy barrier although vdW should also be taken into account when determining the critical NC-NC separation d_c associated with the energy barrier E_a .

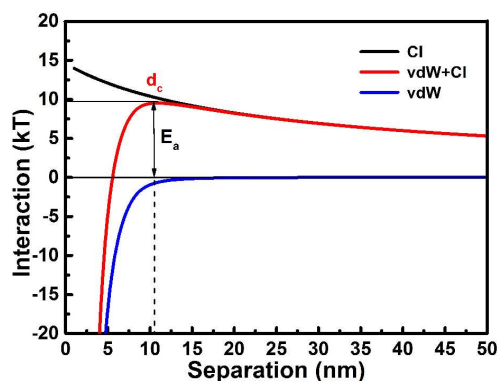


Figure 2 | Plots of inter-particle interaction included vdW, CI and total potential energy *versus* surface-to-surface separation between the hexagonal NR and the precursor NC. The plots assume $AR=5$, surface charge density $\sigma=0.01$ electrons/nm², relative permittivity of solvent $\epsilon=80$, Hamaker constant $A=10^{-19}$ J, and $T=300$ K.

Impact of parameter on the inter-particle interaction

Due to the opposite effects of vdW and CI on the OA growth, it is necessary to further analyze the impact of various parameters on total potential energy in the process of OA growth, including the surface charge density, the Hamaker constant associated with CI and vdW, respectively.

Figure 3a illustrates the correlation of total potential energy with different surface charge densities. The increase of surface charge density brings about a striking increase in the energy barrier E_a and results in a substantial decrease in d_c , which can be disastrous to the OA growth. It is desirable to control the surface charge density under a certain level. With excessively low surface charge density, the precursor NC with sufficient thermal energy at room temperature has a high possibility to overcome the energy barrier, but can also destroy electrostatic stabilization of the colloidal growth system. Hence, one can introduce suitable ligands to regulate the surface charge density in a proper range to facilitate the OA growth.¹¹ In addition, as surface charge density increase further, the shift in the energy barrier appears to be weak and d_c is nearly fixed at 8 nm. Unlike the effect by the surface charge density, the increase of Hamaker constant induces

the opposite effect on the total potential energy, which is shown in Fig. 3b. With increase in Hamaker constant, the energy barrier reduces slightly and d_c shifts to small values. Therefore, an increase in the atomic density of the precursor NC, according to $A=\pi^2 q^2 \lambda$, is beneficial for the OA growth.

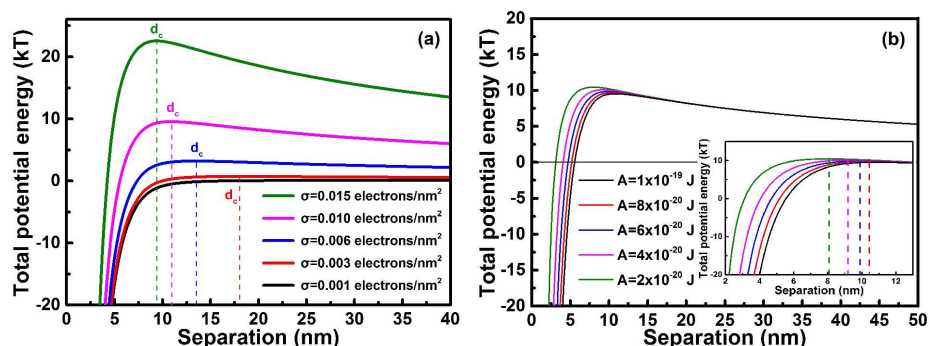


Figure 3 | Plots of total potential energy *versus* the surface-to-surface separation with AR=5, relative permittivity of solvent $\epsilon=80$ and $T=300$ K: (a) total potential energy *versus* separation at different surface charge densities, (b) total potential energy *versus* separation at different Hamaker constants.

As OA growth proceeds, AR increases with the hexagonal NR elongation. Fig. 4a illustrates that with the increase of AR, the energy barrier rises by several kT, which suggests that an upper boundary of E_a must exist and is equal to the maximal kinetic energy of the hexagonal precursor NC. The attachment of the precursor with elongated hexagonal NR is thus hindered as this energy barrier reaches this boundary. Thus there is a limiting length of elongated NRs for the OA growth, which is consistent with experimental result.⁶ In addition, there is no shift in the energy barrier as AR varies, which means that AR is independent on d_c . Figure 4b shows the detailed correlation between total potential energy with AR. The total potential energy increases rapidly at the initial state of the OA growth, and the increase gets gradual as AR exceeds 20. This suggests again that the further OA elongation of hexagonal NRs with already a large length is not thermodynamically favorable. In particular, the unsmooth black curve in Fig. 4b with $d=5$ nm exhibits fluctuation features as AR decreases below 20. This phenomenon is induced by the approximation made in the derivation of vdW, as demonstrated in detail in the Supporting Information.

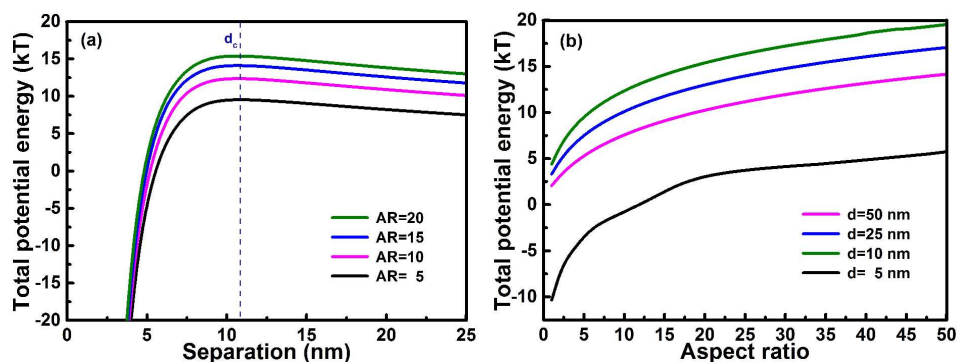


Figure 4 | Plots of total potential energy *versus* AR with surface charge density $\sigma=0.01$ electrons/nm², relative permittivity of solvent $\epsilon=80$, Hamaker constant $A=10^{-19}$ J, and $T=300$ K: (a) total potential energy *versus* separation at different ARs, (b) total potential energy *versus* AR at different surface-to-surface separations (d).

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3 It should be noted that our analysis assumes that the crystal structure of the NR and precursor
4 NC is centrosymmetric so that the inter-particle dipolar interaction is negligible. In addition, our
5 work introduces net charge to approximate the effect of the electrical double layer (EDL) and
6 simplify the derivation. Non-centrosymmetric crystal structure, inter-particle interaction including
7 the effects of DI and EDL, and the associated kinetics and thermodynamics in the growth of such
8 NCs are subject to our future research.
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11 **Comparison with previous reports**

12 The vdW and the CI are predominant factors in the OA growth of nanorods and nanowires.
13 The CI dominates the total potential energy as the separation between the attaching precursor NC
14 and the growing nanorod is large. But the vdW is a more dominant interaction as the separation is
15 below 10 nm. Nevertheless, previous reports evaluate either the vdW interaction in the short
16 separation range or the CI in the long separation range with the magnitude. Furthermore, previous
17 reports only emphasize the impact of the nanorod size on the OA growth, but the effect of the
18 interaction parameters like surface charge density and Hamaker constant are neglected.^{12,19} Our
19 work avoids these defects and for the first time evaluates the evolution of the total inter-particle
20 potential energy with respect to the separation. Energy barrier E_a and critical separation d_c are
21 introduced into our model, based on which the countering effects of the CI and the vdW on the 1D
22 OA growth can be analyzed quantitatively.
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28 **Conclusions**

29 In this report, both van der Waals interaction and Coulombic interaction in the
30 oriented-attachment growth of hexagonal nanocrystals have been evaluated quantitatively. The
31 separation dependence of the main inter-particle interactions correlates with the parameters
32 associated with the interactions, including the surface charge density, the Hamaker constant and
33 the aspect ratio of growing nanocrystals. The results indicate that low surface density and high
34 atomic density of the precursor NCs can facilitate the OA growth and increase the growth rate of
35 1D NCs. The work facilitates the fundamental understanding on the underlying kinetic and
36 thermodynamic factors in the growth of 1D nanocrystals.
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Table of Contents entry

By focusing on hexagonal nanorods, the countering effects of van der Waals interaction and Columbic interaction on the oriented attachment growth of 1D nanocrystals are investigated.

