

Quantitative evaluation of Coulombic interactions in the oriented-attachment growth of nanotubes†

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The Coulombic interaction in the oriented attachment growth of one-dimensional nanotubes is evaluated *via* a newly-derived analytical expression of the Coulombic interactions between a spherical attaching nanoparticle and a growing nanotube. The correlation between the interaction and the important growth parameters, including nanoparticle/nanotube size, aspect ratio, and nanoparticle-nanotube separation has been analyzed. Our work provides, for the first time, an efficient platform to investigate the growth kinetics and mechanisms of oriented attachment growth of nanotubes.

The oriented-attachment (OA) growth mechanism has been extensively investigated since its first cited observation by Banfield *et al.* in 1998.^{1,2} The OA growth mechanism has developed into a key component in the scientific community's understanding of materials synthesis and crystal growth. Progress in the OA growth mechanism investigation has been multifold, and many insightful application potentials and growth details of the OA growth of nanocrystals (NCs) have been revealed in recent years. For instance, Cao *et al.* obtained promising electrical properties from zero-dimensional (0D) CdS nanoparticles (NPs) grown *via* the OA mechanism.³ Adachi, Talapin *et al.* achieved pronounced electronic and optical properties from one-dimensional (1D) OA growth of TiO₂ and

PbSe nanowires, which can be used in the transistor and solar cell devices.^{4,5} Two-dimensional (2D) PbS nanofilms grown *via* the OA mechanism, as reported by Schliehe *et al.*, exhibit excellent photoelectronic properties and are proposed to be used as photodetectors.⁶ *In situ* transmission electron microscopy (TEM) has frequently been employed to investigate the growth details of OA of NCs. For instance, the OA growth of sub-5 nm Fe₂O₃ NPs was observed *via in situ* TEM, as reported by Li *et al.*⁷ Liao *et al.* observed the *in situ* growth of 1D Pt₃Fe nanorods.⁸ Zheng *et al.* investigated the OA growth of Pt NPs with 0.1 seconds time resolution.⁹ Compared to the aforementioned findings among other experimental breakthroughs, fundamental theoretical research on the kinetics and thermodynamics in the OA growth is still at an early stage. Such a lag is mainly attributed to two factors. First, the correlation between the kinetic models and the thermodynamic activation energy, which is typically investigated *via* the Arrhenius equation, can be allusive in the OA growth.¹⁰ Second, analytical expressions of interparticle interactions for many classical OA growth systems are still subject to insightful exploration although such interactions can possibly be computed at a few nanometer scale *via* first-principles calculations.^{11,12} As a matter of fact, quantitatively evaluating the interparticle interactions between isotropic and anisotropic objects is of fundamental significance in a number of analytical areas. For instance, high-resolution atomic force microscopy (AFM) is based on a quantitative understanding of van der Waals (vdW) interactions between the AFM tip and the surface to be characterized.¹³ To facilitate the theoretical investigation into the OA growth of 1D nanocrystals, the authors derived the analytical expressions of the vdW and the Coulombic interaction (CI) between an attaching nanoparticle and a growing OA nanorod in the authors' recent reports.^{14,15} The authors evaluated the correlation between the growth kinetics of OA nanorods and the important parameters, including nanoparticle-nanorod separation, the diameter of the nanoparticle and the aspect ratio of the growing nanorod.¹⁶ These theoretical investigations greatly improved our

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fundamental understanding of 1D OA growth of nanocrystals. Recently, the growth of another class of important 1D nanocrystals has been demonstrated; nanotube (NT) formation can also be governed *via* the OA growth mechanism.¹⁷ To our knowledge, an adequate analytical investigation into the OA growth of nanotubes remains lacking. In this report, we derived the analytical expression of CI between an attaching NP and a growing OA NT. Subsequently, we evaluated, for the first time, the CI between an NP and an NT with respect to important OA growth parameters, such as the NP-NT separation, the radius of the NP, and the aspect ratio (AR) of the growing NT.

Initially, we derive the analytical expression of the CI between an NP and an NT. The configuration of the NP and the NT, as well as the integration route, is demonstrated in Fig. 1. This derivation is similar to the derivation of the expression of the CI between an NP and an NR.^{14,15} The CI between the NP and the two ends of the NT is shown in eqn (1), and the CI between the NP and the two cylindrical (inner/outer) sides of the NT is expressed in eqn (2).

$$E_1 = \frac{q_0 q_3}{2\pi\epsilon r_1^2} \left[\sqrt{r_1^2 + \left(c + \frac{l}{2}\right)^2} + \sqrt{r_1^2 + \left(c - \frac{l}{2}\right)^2} - 2c \right] - \frac{q_0 q_4}{2\pi\epsilon r_2^2} \left[\sqrt{r_2^2 + \left(c + \frac{l}{2}\right)^2} + \sqrt{r_2^2 + \left(c - \frac{l}{2}\right)^2} - 2c \right] \quad (1)$$

$$E_2 = \frac{q_0 q_1}{4\pi\epsilon l} \left[\ln \left(c + \frac{l}{2} + \sqrt{\left(c + \frac{l}{2}\right)^2 + r_1^2} \right) - \ln \left(c - \frac{l}{2} + \sqrt{\left(c - \frac{l}{2}\right)^2 + r_1^2} \right) \right] + \frac{q_0 q_2}{4\pi\epsilon l} \left[\ln \left(c + \frac{l}{2} + \sqrt{\left(c + \frac{l}{2}\right)^2 + r_2^2} \right) - \ln \left(c - \frac{l}{2} + \sqrt{\left(c - \frac{l}{2}\right)^2 + r_2^2} \right) \right] \quad (2)$$

In eqn (1) and (2), r_0 is the radius of the NP, r_1 (r_2) represents the radii of outer (inner) cylindrical sides of the NT, c is the separation between the NT and the NP, l represents the length of the NT, and ϵ is the dielectric constant of the growth medium. Since a growing NT can be attached by two NPs at both ends of the NT, the total CI associated with the OA growth of the NT is the CI between the NT and two NPs, which is equal to $2(E_1 + E_2)$. The detailed derivations of eqn (1) and (2) along with the physical meanings of the various symbols are given in the ESI.†

The concentration of the starting material, *i.e.*, the precursor, is a crucial synthetic parameter of a colloidal synthetic system.^{18–20} Evaluating its correlation with CI is of particular importance and can provide practical guidance to design and control the growth mechanism and kinetics of the OA growth. With the analytical expression of the CI between the NP and the NT, the correlation between the CI and the NP-NT separation is readily evaluated, as shown in Fig. 2. It is noted that the plots in Fig. 2 and all the following figures are based on the calculation of the CI between a growing NT and two attaching NPs at both ends of the NT.

For the four considered ARs (5, 10, 15 and 20), the CI is very large when the NP-NT separation is small and decreases abruptly as the separation approaches a critical distance (d) that exists as an inflection point in the graph. This critical distance (the inflection point) indicates the distance at which too large a precursor concentration, regardless of the aspect ratio, becomes detrimental to the OA growth of NTs. Above this distance, the CI decreases as c increases, and the difference among the CI for the four ARs rapidly becomes negligible. The corresponding magnitude of d increases as the AR increases; therefore, the OA growth of NTs becomes more sensitive to the increase in precursor concentration as the OA growth evolves. However, the sensitivity with increasing AR appears to become less pronounced as the AR increases, as suggested by the plot of the inflection point *versus* AR in Fig. 2b.

The physical and chemical properties of nanocrystals are largely coupled to their sizes.^{21–24} Quantum confinement effects are typically observed as the size is below 100 nm. Further, as the size of nanocrystals is small enough, fundamental property transitions can occur. For instance, nonmagnetism–magnetism transition was observed from ultra-thin europium oxysulfide nanorods, and insulator–conductor transition was observed from 40 nm SiO₂:Pt films.^{25,26} Recently, the authors also reported the superantiferromagnetic properties of 5 nm rare earth chalcogenide semiconductor EuTe nanocrystals. This motivated

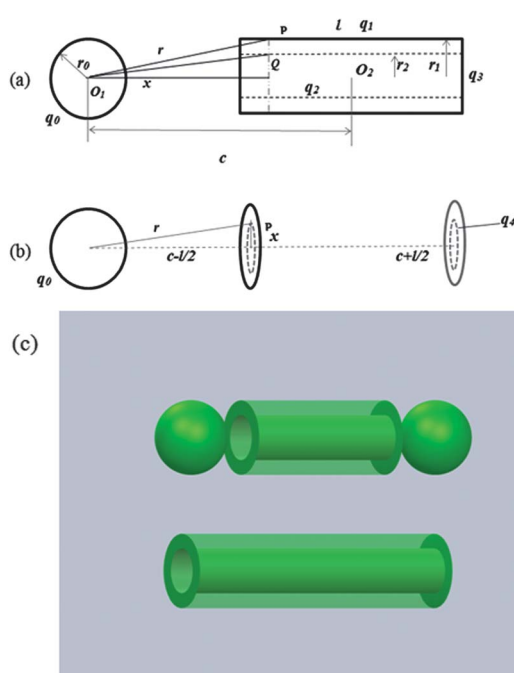


Fig. 1 (a) and (b) derivation route of the analytical expression of CI between an NP and an NT. (c) A 3D demonstration of attaching NPs and a growing NT.

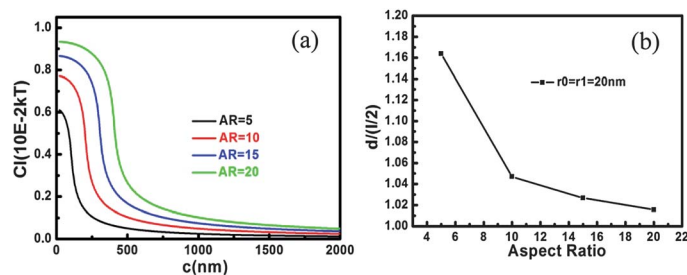


Fig. 2 (a) Plots of CI versus c for NTs of different ARs, assuming a fixed $r_2/r_1 = 0.5$ ($r_2 = 20$ nm, and $r_1 = r_0 = 10$ nm), $l = 2$ AR r_1 , $T = 300$ K, dielectric constant of water solvent = 80, and charge density = $30000/\pi$ electrons per nm^2 , and (b) graph of AR versus the ratio of d to $l/2$.

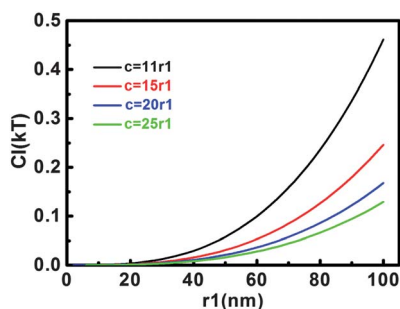


Fig. 3 Plots of CI versus r_1 for NTs of different NP-NT separations based on eqn (1) and (2), assuming AR = 10, $r_2/r_1 = 0.5$, $l = 20$ r_1 , $r_0 = r_1$, $T = 300$ K, dielectric constant of water solvent = 80, and charge density = $30\,000/\pi$ electrons per nm^2 .

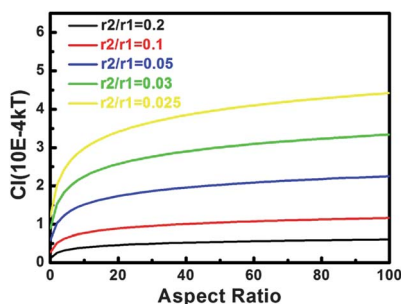


Fig. 4 Plots of the CI versus AR based on eqn (1) and (2), assuming the NT and the NP are attaching, $r_0 = r_2 = 2.5$ nm, and $l = \text{AR } r_1 + r_0$.

us to evaluate the dependence of the CI on the nanoparticle's size under certain ambient conditions. Fig. 3 depicts the plots of the CI versus the outer NT radius. (Given the construct of our growth mechanism, the outer NT radius and the NP diameter correspond to each other.) The graph confirms that the CI increases with increasing outer NT radius, which suggests that large NTs experience a larger growth energy barrier compared with small NTs. Comparing the CI versus r_1 plots for different NP-NT separations, the CI for smaller NP-NT separations is larger than the CI for larger NP-NT separations. This disparity appears to be more obvious when the outer radius of the NTs is larger than 60 nm. This strongly suggests that dilute precursor systems are highly preferable for the OA growth of NTs with relatively large outer radii.

In a given OA growth colloidal system, a certain growth time will mark the cessation of the OA growth. From an energetics point of view, the growth of 1D nanocrystals is terminated by the increased energy barrier that the elongation of OA nanocrystals experiences at a critical length value. An intuitive explanation for this growth termination phenomenon asserts that CI increases as the length increases. To investigate quantitatively the CI evolution as a function of the increasing length of 1D NTs, we plotted the CI as a function of NT length (Fig. 4) based on our calculations of CI between the growing NT and two attaching NPs *via* the derived expression.

For the five inner radius to outer radius ratios, the CI first increased abruptly with increasing AR; thereafter, the increase became much less pronounced as the AR approaches ~ 10 . This suggests that the energy barrier of the OA growth of NTs experiences a critical transition at an AR ~ 10 . NTs that grow beyond this AR value are expected to grow smoothly only if CI is the dominant interaction in the OA growth. The growth of thicker NTs experiences larger CI, as shown in Fig. 4, is consistent with the authors' earlier reports, which indicated that the OA growth of thicker nanorods experiences larger CI compared with the OA growth of thinner nanorods.^{14,15} The CI versus AR plots with a fixed outer radius are shown in Fig. S1;† these plots are comparable to those in Fig. 4 except that the magnitudes of those plots are substantially closer for different inner radius to outer radius ratios.

Our quantitative investigation as reported in this article can help advance the basic research and the application of nanotubes in various fields. For instance, understanding the interparticle interaction facilitates the design and realization of nanotubes with desired crystallinity and morphology. The well-resulted nanotubes can then find applications in a number of areas including bio-sensing, AFM characterization and transistors, *etc.*^{13,27}

Conclusions

In summary, the Coulombic interaction expression for a growing nanotube was derived in this report. Using the expression, the CI was evaluated as a function of the important parameters of the OA growth, including the nanoparticle/nanotube size, aspect ratio of the nanotube, and the nanoparticle-nanotube separation. Our work broadens the opportunity for the OA research community to evaluate the growth

mechanisms and kinetic models of the OA growth of nanotubes.

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