Coulombic interaction in the colloidal oriented-attachment growth of tetragonal nanorods*

Li Jun-Fan(李峻樊)[a)b)†], Wen Ke-Chun(文克春)[a)b)†], He Wei-Dong(何伟东)[a)‡],
Wang Xiao-Ning(王晓宁)[a)], Lü Wei-Qiang(吕维强)[a)], Yan Peng-Fei(严鹏飞)[a)], Song Yuan-Qiang(宋远强)[a)],
Lu Hong-Liang(路红亮)[c)], Lin Xiao(林 晓)[c)§], and Dickerson J. H.[d)e)]

[a)] *School of Energy Science and Engineering, University of Electronic Science and Technology, Chengdu* 611731, *China*
[b)] *School of Life Science and Technology, University of Electronic Science and Technology, Chengdu* 611731, *China*
[c)] *School of Physics, University of Chinese Academy of Sciences, Beijing* 100049, *China*
[d)] *Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY* 11973, *US*
[e)] *Department of Physics, Brown University, Providence, RI* 02912, *US*

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In this report, the analytical expression of Coulombic interaction between a spherical nanoparticle and a tetragonal nanorod is derived. To evaluate the Coulombic interaction in the oriented attachment growth of tetragonal nanorods, we analyze the correlation between the Coulombic interaction and the important growth parameters, including: nanoparticle–nanorod separation, aspect ratio of the nanorods, and surface charge density. Our work opens up the opportunity to investigate interparticle interactions in the oriented attachment growth of tetragonal nanorods.

Keywords: Coulombic interaction, oriented-attachment growth, tetragonal nanorod, nanoparticle

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1. Introduction

One-dimensional (1D) nanocrystals (NCs) have only one macroscopic dimension and, thus, typically exhibit the quantum effects in two dimensions.[1–4] The 1D NCs exhibit size-dependent physical properties, including: optical properties, electrical properties, and magnetic properties.[5–9] Due to these intriguing properties, the 1D NCs have shown great application potentials in electronic, magnetic, and optical devices.[10–12] Due to the anisotropic crystallinity of tetragonal crystals, it is energetically favorable for tetragonal NCs to grow into 1D nanorods (NRs) in most instances.[13–15] There are two NRs growth mechanisms,which are: Ostwald ripening and oriented attachment (OA).[16–18] In particular, oriented attachment has evolved to be the key focus in the NC growth field in recent years. In parallel to the extensive experimental investigations, the interparticle interactions (including the van der Waals interaction and the Coulombic interaction) in the oriented attachment growth of cylindrical NRs have recently been studied.[19–21] In order to investigate the growth details of oriented attachment tetragonal NRs, we must also know the growth mechanism and analyze the interparticle interactions.[22–25] In this article, we derive the analytical expression of the Coulombic interaction between a spherical nanoparticle (NP) and a tetragonal NR. In addition, theoretical calculations are performed based on the expression, and the correlations between the Coulombic interaction and the important growth parameters, including the nanoparticle–nanorod separation, the aspect ratio (AR) of nanorods, and the surface charge density are evaluated.

2. Theory and methods

In the oriented attachment growth of tetragonal NRs, the growth proceeds via the attachment of precursor NPs onto the end sides of the growing NRs, as demonstrated in Fig. 1(a), where the attaching NPs can be cubic or in an irregular morphology other than spherical. A random point $P(x,z)$ on the front side plane of the tetragonal NR is taken as an integration unit (Fig. 1(b)). The Coulombic interaction between a spherical NP and a tetragonal NR consists of the Coulombic interaction between the spherical NP and the four rectangular side planes of the tetragonal NR, and the Coulombic interaction between the NP and the two end sides of the NR. The expression of the total Coulombic interaction (E_t) between a spherical NP and a tetragonal NR is

$$E_t = \frac{\delta_1\delta_2}{\pi\varepsilon}4\pi r^2\left[2a\ln\left(\frac{\sqrt{2a^2+c^2}+a}{\sqrt{c^2+a^2}}\right) - c\arctan\left(\frac{a^2}{c\sqrt{2a^2+c^2}}\right)\right] + \frac{\delta_1\delta_2}{\pi\varepsilon}4\pi r^2\left[2a\ln\left(\frac{\sqrt{2a^2+(c+l)^2}+a}{\sqrt{(c+l)^2+a^2}}\right)\right.$$

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†These authors contributed equally to this work.
‡Corresponding author. E-mail: weidong.he@uestc.edu.cn
§Corresponding author. E-mail: xlin@ucas.ac.cn
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$$
\begin{aligned}
&-(c+l)\arctan\left(\frac{a^2}{(c+l)\sqrt{2a^2+(c+l)^2}}\right)\Bigg]\\
&+\frac{2\delta_1\delta_2}{\pi\varepsilon}4\pi r^2\Bigg[a\ln\left(\frac{\sqrt{2a^2+(2c+l)^2}+2c+l}{\sqrt{2a^2+(2c)^2}+2c}\right)\\
&+(2c+l)\ln\left(\frac{\sqrt{2a^2+(2c+l)^2}+a}{\sqrt{a^2+(2c+l)^2}}\right)\\
&-2c\ln\left(\frac{\sqrt{2a^2+(2c)^2}+a}{\sqrt{a^2+(2c)^2}}\right)\\
&-a\arctan\left(\frac{2c+l}{\sqrt{2a^2+(2c+l)^2}}\right)\\
&+a\arctan\left(\frac{2c}{\sqrt{2a^2+(2c)^2}}\right)\Bigg], \qquad (1)
\end{aligned}
$$

where δ_1 is the surface charge density of the NP, δ_2 is the surface charge density of the tetragonal nanorod, ε is the dielectric constant of the medium, r is the separation between two points, a is half of the length of the square base of the tetragonal nanorod, c is the separation between the NP and the front end face of the tetragonal nanorod, and l is the length of the tetragonal nanorod (Fig. 1(c)). The detailed derivations of Eq. (1) are given in Appendix A.

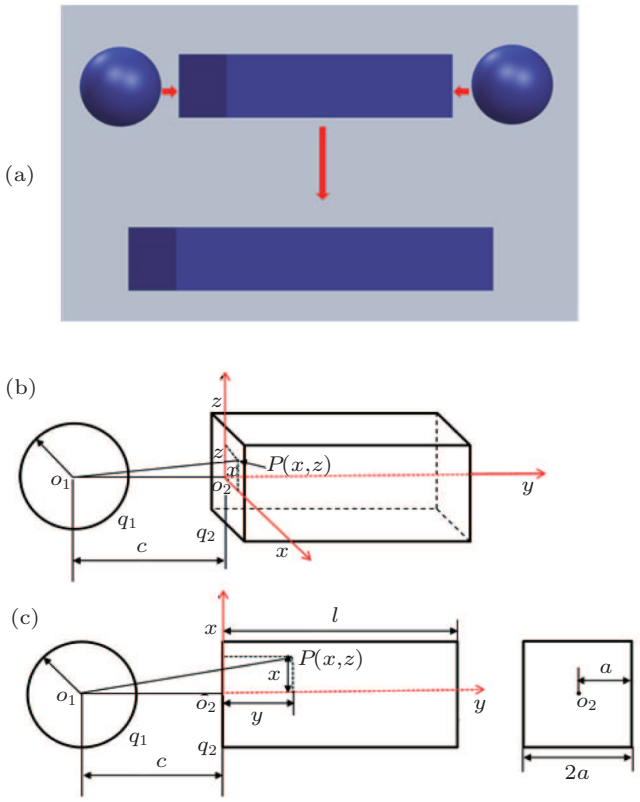


Fig. 1. (color online) (a) A 3D demonstration for the oriented attachment crystal growth of a tetragonal NR. Two NPs attach to the two end sides of the growing NR. (b) The configuration of a tetragonal NR and a spherical NP for the integration of the Coulombic interaction between the spherical NP and one end plane of the tetragonal NR. (c) A configuration of the spherical NP and one side plane of the tetragonal NR for the integration of the Coulombic interaction between the spherical NP and one side plane of the tetragonal NR.

3. Results and discussion

Due to the similarity in the dimensionality and the symmetry of tetragonal NRs with respect to cylindrical NRs, which were studied in our recent reports, we expect that the Coulombic interaction behaves similarly in the growth of the two classes of NRs.[15,20] Based on Eq. (1), we first evaluate the Coulombic interaction as a function of the NP–NR separation. From the four plots of the Coulombic interaction versus c for different radii (r_1) of the NPs shown in Fig. 2, it is seen that the Coulombic interaction gradually decreases by ~92% as c increases by ~ 18 times for the considered radii. As shown in Fig. 2(a), as c increases from 11 nm to 199 nm, the Coulombic interaction decreases by ~92 % for 1 nm NPs and NRs. In Fig. 2(b), as c increases from 55 nm to 995 nm, the Coulombic interaction also decreases by ~92 % for 25 nm NPs and NRs. In Fig. 2(c), as c increases from 550 nm to 9900 nm, the Coulombic interaction decreases by ~ 92% for 50 nm NPs and NRs. Similarly, in Fig. 2(d), as c increases from 1100 nm to 19800 nm, the Coulombic interaction also decreases by ~ 92% for 100 nm NPs and NRs. Above all, we can see that the degree of the Coulombic interaction decrease is independent of the range of c. Thus, the decrease of the Coulombic interaction with increasing c is more gradual for larger nanoparticles. Furthermore, with the same c, the Coulombic interaction increases dramatically as r_1 increases, the oriented attachment growth of thick tetragonal NRs is thus more sensitive to the change in Coulombic interaction compared to the oriented attachment growth of thin tetragonal NRs. Thus, due to the more obvious increase in Coulombic interaction as r_1 increases, the OA growth of thick tetragonal NRs is expected to be less thermodynamically favorable compared to the OA growth of thin tetragonal NRs. The as calculated results here are qualitatively consistent with our previous evaluation of CI in the OA growth of cylindrical NRs.[15]

Figure 3 shows the plots of the Coulombic interaction versus AR for NRs with different sizes. It is noted that Coulombic interaction increases with increasing AR. When AR $<$ 10, the Coulombic interaction increases rapidly, and when AR $>$ 10, the Coulombic interaction increases gradually. The saturation of the Coulombic interaction with increasing AR suggests that the growth of ultra-long tetragonal oriented attachment NRs is not thermodynamically favorable if the Coulombic interaction is the dominating interparticle interaction in the oriented attachment growth. In addition, the Coulombic interaction also increases with increasing r_1. As r_1 increases from 5 nm to 50 nm, the Coulombic interaction increases by ~ 1000 times, verifying the high sensitivity of the Coulombic interaction to the size variation of the attaching NP and NR. However, as the growth of tetragonal oriented attachment NRs proceeds, the average density of NPs in the solution becomes smaller and, consequently, the separation between NP and NR becomes

larger. Therefore, the Coulombic interaction increase with increasing AR can be balanced, to some extent, by the Coulombic interaction decrease with consuming reaction precursors as the oriented attachment growth proceeds. When synthesizing tetragonal oriented attachment NRs, such a balance is expected to mitigate the devastating monotonous increase or decrease in Coulombic interaction with certain diameters and ARs.

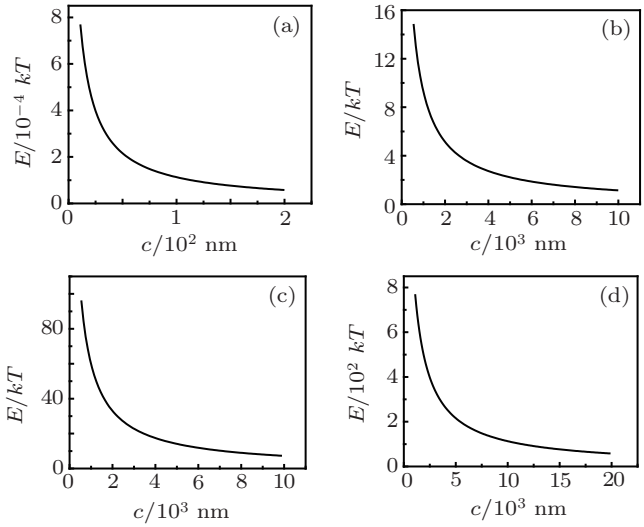


Fig. 2. Plots of Coulombic interaction versus c for NPs with different radii: (a) $r_1 = 1$ nm, (b) $r_1 = 25$ nm, (c) $r_1 = 50$ nm, (d) $r_1 = 100$ nm. We assume that the length of the tetragon side $(2a)$ is equal to $\sqrt{2}r_1$. The four plots assume $T = 300$ K, AR = 10, dielectric constant = 80 (water solvent), and charge density = $5000/\pi$ electrons/nm^2.

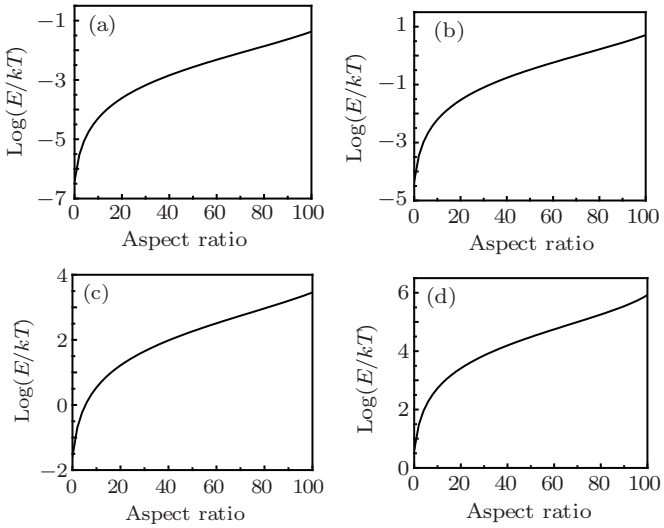


Fig. 3. Plots of Coulombic interaction versus AR $(= l/(2a))$ for NRs with different sizes: (a) $r_1 = 5$ nm, (b) $r_1 = 10$ nm, (c) $r_1 = 25$ nm, (d) $r_1 = 50$ nm. We assume that the length of the tetragon side $(2a)$ is equal to $\sqrt{2}r_1$, $T = 300$ K, dielectric constant = 80 (water solvent), and charge density = $5000/\pi$ electrons/nm^2. The relation between c and x is $c = c_0 - x \cdot r_1/2$, c_0 is the initial separation ((a) $c_0 = 300$ nm, (b) $c_0 = 600$ nm, (c) $c_0 = 1500$ nm, (d) $c_0 = 2700$ nm), and x stands for the AR.

Figure 4 shows the plots of the Coulombic interaction versus the charge density (δ) with the radii of 5 nm, 10 nm, 25 nm, and 50 nm. For the four considered radii, the Coulombic interaction increases as δ increases. In particular, as the charge density is lower than 18 electrons/nm^2, the Coulombic interaction increases much more abruptly with increasing δ compared to the Coulombic interaction increase when $\delta > 18$ electrons/nm^2 for all the radii. Therefore, increasing the charge density of the NP and NR system in the range of 0–18 electrons/nm^2 can dramatically increase the Coulombic interaction, which is detrimental to the oriented attachment growth of the NR. Nevertheless, based on our quantitative analysis, appropriate surfactants, solvents, and capping agents can be selected to maintain suitable surface charges on the tetragonal NR and the NP to facilitate the efficient formation of tetragonal oriented attachment NRs.

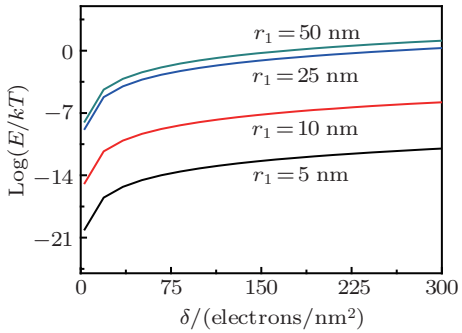


Fig. 4. (color online) Plots of Coulombic interaction versus charge density for NRs and NPs with different radii.

In this work, we provide calculations of the Columbic interaction in the oriented attachment growth of one-dimensional tetragonal nanorods, where we mainly consider the one-dimensional length evolution of the nanorods. In such a case, we believe that in the growth, the change in the size ratio between the nanoparticle and the nanorod is much less obvious over time compared to the change in the length of the nanorods. For simplicity, we thus assume that the length of the tetragon side equals $\sqrt{2}r_1$ in the growth. The calculation on the Coulombic interaction in more complex systems is subject to future research.

4. Conclusion

In summary, the analytical expression of the Coulombic interaction between a spherical NP and a tetragonal NR has been derived. Based on the expression, we have investigated the analytical effects of nanoparticle–nanorod separation, aspect radio, and charge density on the Coulombic interaction. Obtaining the effective ranges of the important growth parameters enables us to design the efficient synthesis of the tetragonal NRs, which can be used as promising building blocks for various applications.

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Appendix A

The expression of the Coulombic interaction between two random points can be expressed with the Coulomb's law as

$$E = \frac{1}{4\pi\varepsilon}\frac{q_{\rm a}q_{\rm b}}{r}, \tag{A1}$$

where $q_{\rm a}$ and $q_{\rm b}$ are the charges on the two points, ε is the dielectric constant of the medium, and r is the separation between the two points. Here, we assume that the surface charge density of the tetragonal nanorod is homogeneous and equal to δ_2 while the surface charge density of the nanoparticle is δ_1. Firstly, we derive the expression of the Coulombic interaction between a spherical NP and the front end side of a tetragonal nanorod (E_1). In addition, the total surface charge of the NP can be equivalent to the charge existing in the center of the NP in derivation progress, so E_1 can be obtained by

$$E_1 = \frac{q_1\delta_2}{4\pi\varepsilon}\int_{-a}^{a}{\rm d}x\int_{-a}^{a}\frac{{\rm d}z}{\sqrt{c^2+z^2+x^2}}, \tag{A2}$$

where q_1 is the total charge on the NP, a is half of the length of the square base of the tetragonal nanorod, and c is the separation between the NP and the front end face of the tetragonal nanorod.

With $\theta = \arctan(z/\sqrt{x^2+c^2})$, E_1 can be expressed as

$$\begin{aligned} E_1 &= \frac{q_1\delta_2}{\pi\varepsilon}\int_0^a{\rm d}x\int_0^{\arctan\frac{a}{\sqrt{x^2+c^2}}}\frac{\sqrt{c^2+x^2}\sec^2\theta\,{\rm d}\theta}{\sqrt{c^2+x^2}\sec\theta} \\ &= \frac{q_1\delta_2}{\pi\varepsilon}\left[a\ln\left(\frac{\sqrt{2a^2+c^2}+a}{\sqrt{c^2+a^2}}\right)\right. \\ &\quad \left.+\int_0^a\frac{a}{\sqrt{a^2+c^2+x^2}}-\frac{ac^2}{(c^2+x^2)\sqrt{a^2+c^2+x^2}}{\rm d}x\right]. \end{aligned} \tag{A3}$$

With $\beta = \arctan(x/\sqrt{a^2+c^2})$, then the solution of Eq. (A3) is expressed as

$$\begin{aligned} E_1 &= \frac{q_1\delta_2}{\pi\varepsilon}\left[a\ln\left(\frac{\sqrt{2a^2+c^2}+a}{\sqrt{c^2+a^2}}\right)\right. \\ &\quad +\int_0^{\arctan\frac{a}{\sqrt{a^2+c^2}}}\left(\frac{a\sqrt{a^2+c^2}\sec^2\beta}{\sqrt{a^2+c^2}\sec\beta}\right. \\ &\quad \left.\left.-\frac{ac^2\sqrt{a^2+c^2}\sec^2\beta}{[c^2+(a^2+c^2)\tan^2\beta]\sqrt{a^2+c^2}\sec\beta}\right){\rm d}\beta\right] \\ &= \frac{\delta_1\delta_2}{\pi\varepsilon}4\pi r^2\left[2a\ln\left(\frac{\sqrt{2a^2+c^2}+a}{\sqrt{c^2+a^2}}\right)\right. \\ &\quad \left.-c\arctan\left(\frac{a^2}{c\sqrt{2a^2+c^2}}\right)\right]. \end{aligned} \tag{A4}$$

Replacing c with $c+l$ in Eq. (A4), where l is the length of the tetragonal nanorod, we obtain the Coulombic interaction between the NP and the back end side of the NR

$$\begin{aligned} E_2 &= \frac{\delta_1\delta_2}{\pi\varepsilon}4\pi r^2\left[2a\ln\left(\frac{\sqrt{2a^2+(c+l)^2}+a}{\sqrt{(c+l)^2+a^2}}\right)\right. \\ &\quad \left.-(c+l)\arctan\left(\frac{a^2}{(c+l)\sqrt{2a^2+(c+l)^2}}\right)\right]. \end{aligned} \tag{A5}$$

The integration form of the Coulombic interaction between the NP and the four side planes can be given as

$$E_3 = 4\times\frac{q_1\delta_2}{4\pi\varepsilon}\int_{-a}^{a}{\rm d}x\int_{c}^{c+l}\frac{{\rm d}y}{\sqrt{a^2+x^2+(c+y)^2}}. \tag{A6}$$

With $\gamma = \arctan[(c+y)/\sqrt{x^2+a^2}]$, we then obtain

$$\begin{aligned} E_3 &= \frac{2q_1\delta_2}{\pi\varepsilon}\int_0^a{\rm d}x\int_{\arctan\frac{2c}{\sqrt{a^2+x^2}}}^{\arctan\frac{2c+l}{\sqrt{a^2+x^2}}}\frac{\sqrt{a^2+x^2}\sec^2\gamma}{\sqrt{a^2+x^2}\sec\gamma}{\rm d}\gamma \\ &= \frac{2q_1\delta_2}{\pi\varepsilon}\left[\int_0^a\ln(\sqrt{a^2+(2c+l)^2+x^2})+(2c+l)\,{\rm d}x\right. \\ &\quad \left.-\int_0^a\ln(\sqrt{a^2+(2c)^2+x^2})+(2c)\,{\rm d}x\right]. \end{aligned} \tag{A7}$$

The two terms in Eq. (A7) resemble and own the same integration form, as given by

$$E = \frac{2q_1\delta_2}{\pi\varepsilon}\int_0^a[\ln(\sqrt{a^2+n^2+x^2})+n]\,{\rm d}x. \tag{A8}$$

With $\varphi = \arctan(x/\sqrt{a^2+n^2})$, equation (A8) can be expressed as

$$\begin{aligned} E &= \frac{2q_1\delta_2}{\pi\varepsilon}\left[a\ln(\sqrt{2a^2+n^2}+n)-a+\frac{\pi}{4}a\right. \\ &\quad +n\int_0^{\arctan\frac{a}{\sqrt{a^2+n^2}}}\sec\varphi\,{\rm d}\varphi \\ &\quad \left.-\int_0^{\arctan\frac{a}{\sqrt{a^2+n^2}}}\frac{na^2\sec\varphi}{a^2+(a^2+n^2)\tan^2\varphi}{\rm d}\varphi\right]. \end{aligned} \tag{A9}$$

Therefore, the Coulombic interaction between the NP and the four side planes of the NR can be given as

$$\begin{aligned} E_3 &= \frac{2\delta_1\delta_2}{\pi\varepsilon}4\pi r^2\left[a\ln\left(\frac{\sqrt{2a^2+(2c+l)^2}+2c+l}{\sqrt{2a^2+(2c)^2}+2c}\right)\right. \\ &\quad +(2c+l)\ln\left(\frac{\sqrt{2a^2+(2c+l)^2}+a}{\sqrt{a^2+(2c+l)^2}}\right) \\ &\quad -2c\ln\left(\frac{\sqrt{2a^2+(2c)^2}+a}{\sqrt{a^2+(2c)^2}}\right) \\ &\quad -a\arctan\left(\frac{2c+l}{\sqrt{2a^2+(2c+l)^2}}\right) \\ &\quad \left.+a\arctan\left(\frac{2c}{\sqrt{2a^2+(2c)^2}}\right)\right]. \end{aligned} \tag{A10}$$

With Eqs. (A4), (A5), and (A10), we then obtain the total Coulombic interaction ($E_{\rm t}$) between the spherical NP and the tetragonal NR, which is given in Eq. (1).

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