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The evaluation of van der Waals interaction in the oriented-attachment growth of nanotubes

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Abstract

Taking the advantage of nanomaterials to protect the environment and avoiding the side effect need a fundamental understanding of the growth mechanism of the nanomaterials. Here, the van der Waals interaction between a nanoparticle and a nanotube in the oriented-attachment growth of nanotubes is quantitatively evaluated for the first time. In particular, the correlation between van der Waals interaction and the growth parameters is investigated in depth. Our work opens up the opportunity of studying the important interparticle interactions in the oriented attachment growth of nanotubes.

Keywords: Environment; Oriented-attachment Growth; van der Waals Interaction; Nanotube; Nanoparticle

Introduction

Nanotubes (NTs) have been extensively studied and show great application potentials in the fields of environmental science and engineering, especially, in the area of environmental protection.[1] For instance, due to the high surface area and the hollow structures, NTs can act as adsorbents of radionuclides and heavy metals to clean the soil and water supplies;[2-7] NTs are also investigated to detect, catalytically degrade organic pollutants and remove biological substances.[8-16] On the other hand, the big amount of solvents and other harmful chemicals used for manufacturing nanotubes along with nanotubes themselves may cause serious health effects and environmental problems.[17-22] To synthetize these novel nanomaterials via non-toxic methods, tune their properties by controlling their structures, apply them to various fields while avoiding their potential adverse effects on environment and human health, a fundamental understanding on the growth mechanism of the nanomaterials is necessary. Ostwald ripening is widely used to describe the growth of nanomaterials in solvents.[23] However, Ostwald ripening cannot explain the growth of certain crystals, especially the growth of certain nanostructures.[24-28] Penn *et al.* proposed an alternative crystal growth mechanism, *i.e.* oriented-attachment (OA), which has largely facilitated the general understanding of the crystal growth of various crystals.[25, 29-32] Recently, high-resolution *in-situ* observation of the critical OA growth steps of nanocrystals has elevated the OA field to an ever high research level. For instance, using a fluid cell Li *et al.* explored a way to investigate the *in-situ* growth of iron oxyhydroxide nanoparticles (NPs). The high-resolution transmission electron microscopy reveals that, the NPs keep rotating and interacting until a perfect lattice match is reached.[33] The direct observation technique provides an efficient route to the evaluation of the interparticle interactions in the 'jump-to-contact' OA growth. However, analytical forms of interparticle interactions still need to be developed to rationalize the OA phenomena as observed via the aforementioned *in-situ* techniques. The authors have recently derived the analytical expressions of the repulsive Coulombic interaction (CI) and the attractive van der Waals interaction (vdW) to investigate the OA growth of nanorods (NRs).[34-36] In this paper, for the first time we apply the expression of vdW between a NP and a NR to study the vdW in the OA growth of nanotubes (NTs), which has been observed in experiments.[37] Theoretical investigations have been carried out, to evaluate the correlation between the vdW and the important growth factors including aspect ratio (AR), NT-NP separation and sizes of the attaching objects.

Results and Discussion

In the OA growth of a nanotube, as shown in Figure 1, two nanoparticles attach to both ends of the nanotube to facilitate the nanotube growth along the axial direction.

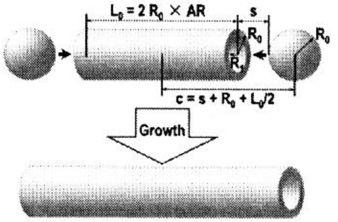

Figure 1. A 3D demonstration of the OA growth of a nanotube.

We first study the dependence of the vdW on the NT-NP separation based on the analytical expression of vdW between a NP and a NR.[36] Assuming that the outer radius (R_0) of the nanotube is the same as the radius of the nanoparticles, that the aspect ratio ($AR=L_0/2R_0$, as shown in Fig. 1) of the nanotube is 10 and that the inner radius (R_1) of the nanotube is 1 nm, we calculate vdW *versus* the center-to-center separation (c) between the growing nanotube and the two attaching nanoparticles with different outer radii. Figure 2 shows the calculated results. For all the R_0s, as the NT-NP separation increases, vdW decreases. With c fixed, the slope of the plot increases as R_0 increases. For each curve, we note the existence of a transition point; as the NT-NP separation is larger than the transition separation, the slope of the curve is quite small. As the NT-NP separation is smaller than the transition separation, vdW increases abruptly with decreasing c. The transition points are determined in the plots with different R_0s and plotted as the head-to-head NT-NP separation (s) *versus* R_0, as shown in Fig. 2b. The plot in Figure 2b shows a linear relation between R_0 and the transition separation s and the extension line crosses the origin where R_0 and s are both zero. This linear increasing relation shows that the separation at the transition point for larger NT/NP is larger, suggesting that the OA growth of larger NTs is more energetically favorable than that of smaller NTs if the repulsion forces such as the Coulombic force are less dominant.

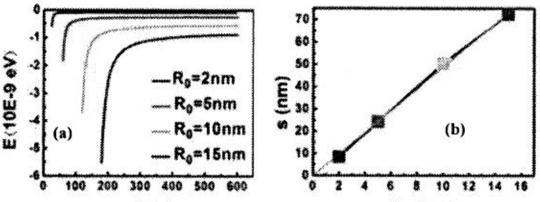

Figure 2. (a) Plots of vdW *versus* the center-to-center NT-NP separation, with a fixed aspect ratio of 10, and an inner radius of 1 nm; (b) Plot of head-to-head transition separation *versus* the outer radius of the NT.

Similar to Figure 2a, for various ARs but a fixed outer radius of 15 nm and inner radius of 10 nm, we obtain the plots of vdW *versus c*. As shown in Figure 3, the slope of the vdW plot increases as the aspect ratio of the NT increases and thus, the OA growth of long NTs is more energetically favorable compared to the OA growth of short NTs.

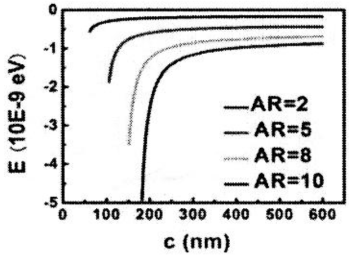

Figure 3. Plots of vdW *versus c* between the nanoparticle and the nanotube with AR equal to 2, 5, 8, and 10, and assuming that the outer radius of the NT is 15 nm and that the inner radius of the NT is 1 nm.

Figure 4a illustrates the correlation between *c* and vdW for NTs with a fixed outer radius of 15 nm and a fixed length of 300 nm, but various inner radii (1 nm, 1.5 nm, 2 nm, and 5 nm). The slope of the curve always increases as *c* decreases. The increase tends to be more obvious as *c* is below the transition point. With *c* fixed, the slope decreases with increasing R_1. The correlation between the transition-point separation and R_0/R_1 is plotted in Figure 4b. The trend that *s* decreases as R_1 increases is noted, indicating that the growth of the nanotube with a larger R_1 is not thermodynamically favorable. Such results are consistent with the data in Figure 2a and Figure 3.

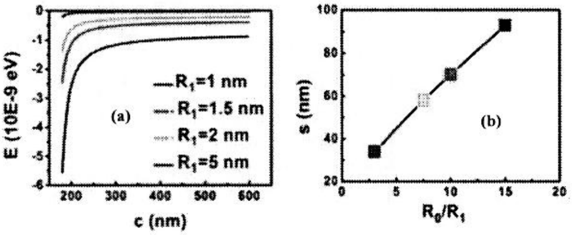

Figure 4. (a) Plots of vdW *versus c* between the nanoparticle and the nanotube, assuming that AR=10, R_0=15 nm, and L_0=300 nm. (b) Plot of *s versus* R_0/R_1.

In the above discussion, we evaluate the correlation between vdW and the center-to-center NT-NP separation with different variables. All the plots experience a process from rapid change in vdW to slow change in vdW as the NP-NT separation increases. As the nanoparticle and the nanotube are closer, the change of separation has an increased effect on vdW, but with large NP-NT separations, the center-to-center separation and other variables do not appear to impact much on vdW.

Figure 5 illustrates the correlation between inner radius and vdW with outer radii of 5 nm, 10 nm, 20 nm, and 30 nm, respectively, while keeping the NT length fixed at 300 nm and the center-to-center separation at 240 nm. Here, we set R_1 in the range of 1 nm~R_0. For each R_0, with the increase in inner radius R_1, vdW changes to zero rapidly, and the change is more apparent as R_1 is small. With the inner radius fixed, the slope increases with increasing outer radius of the NT, which is consistent with the result in Fig. 2b.

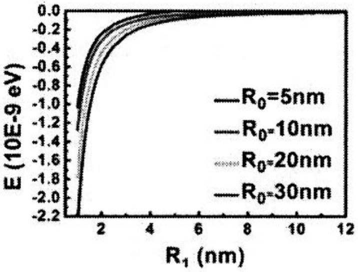

Figure 5. Plots of vdW *versus* inner radius with a fixed center-to-center separation of 240 nm and a nanotube length of 300 nm.

Figure 6 shows the plots of vdW *versus* the length of the NT with fixed R_1 of 2 nm and c of 150 nm. vdW does not appear to vary much till L_0 increases to a certain point, as noted in the figure. However, after the point, increasing L_0 leads to a rapid vdW increase as L_0 increases, which suggests that the growth of the nanotube tends to be more energetically desirable as its length evolves. Furthermore, the transition point of L_0 decreases as R_0 increases, indicating that increased vdW can largely facilitate the OA growth of thicker NTs with larger outer radii.

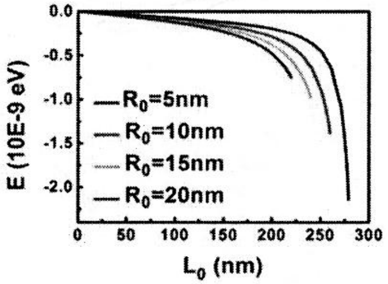

Figure 6. Plots of vdW *versus* L_0 with R_1 = 2 nm and c = 150 nm.

In the synthesis of OA NTs, the thermodynamic feasibility of the growth and the growth termination state must be evaluated with careful consideration of other factors including Coulombic interaction, solvent, capping agent and surfactant, etc.[37-39] Combined with such practical growth factors, our theoretical analysis as presented in this report is expected to facilitate largely the rational design of

OA growth systems for the synthesis of nanotubes and other important forms of nanostructures. In addition, we only focus on the on-axis attachment of NPs onto NTs in this report. NPs can also approach NTs in an off-axis fashion in practical synthetic environment, and the torque is a significant factor for the off-axis attachment. Although the predominance of the vdW interaction in the OA growth of nanorods with the on-axis approach configuration was found in our previous work, [36, 39] the torque based on the vdW interaction between a growing NT and an attaching NP with the off-axis approach configuration is still unknown. Such a topic with much complexity will be investigated in detail in our future efforts.

Conclusion

The recently-derived expression of van der Waals interaction between a nanoparticle and a nanorod is employed to investigate the van der Waals interaction in the oriented-attachment growth of nanotubes. Our work provides the opportunity of evaluating the fundamental interparticle interactions in the oriented-attachment growth of nanotubes, known to exhibit intriguing electrical, optical, magnetic and catalytic properties, which will promote the application of nanotubes to the environmental remediation.

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