An Energy Investigation into 1D/2D Oriented-Attachment Assemblies of 1D Ag Nanocrystals

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In the field of oriented-attachment crystal growth, one-dimensional nanocrystals are frequently employed as building blocks to synthesize two-dimensional or large-aspect-ratio one-dimensional nanocrystals. Despite recent extensive experimental advances, the underlying inter-particle interaction in the synthesis still remains elusive. In this report, using Ag as a platform, we investigate the van der Waals interactions associated with the side-by-side and end-to-end assemblies of one-dimensional nanorods. The size, aspect ratio, and inter-particle separation of the Ag precursor nanorods are found to have dramatically different impacts on the van der Waals interactions in the two types of assemblies. Our work facilitates the fundamental understanding of the oriented-attachment assembling mechanism based on one-dimensional nanocrystals.

The oriented-attachment (OA) growth mechanism, different from the Ostwald ripening (OR) growth mechanism, has evolved to be a key nanocrystal (NC) growth mechanism in the crystal field.[1–4] In the OA growth of NCs, small NC precursors approach and attach one another along a certain crystal direction. The growth of NCs with various shapes through the assembly of smaller precursor NCs has been frequently reported.[5–9] The anisotropic growth of one-dimensional (1D) nanorods (NRs), commonly seen in the crystal field, has been observed for various materials systems.[10–13] In the OA growth of 1D NRs, nanoparticles (NPs) attach at the two ends of growing NRs to grow larger aspect-ratio (AR) NRs. In addition, NPs can attach at their ends to form longer NRs (end-to-end growth),[14,15] or attach each other side by side (side-by-side growth) to form 2D nanoplates (NPts) and 3D nanostructures.[16–18]

The driving force of the OA growth is mainly related to the interactions between the attaching NCs, including Coulombic interaction (CI), van der Waals interaction (vdW), and dipolar interaction (DI).[19–21] There are two research trajectories investigating the fundamental inter-particle interactions. One trajectory is to experimentally investigate the inter-nanoparticle interactions. For instance, in situ high-resolution transmission electron microscopy (HR-TEM) techniques have been employed to monitor the motions of NCs and analyze the interactions associated with such motions.[22–24] The other trajectory is to theoretically compute the interactions. These simulations mainly include density functional theory (DFT), molecular dynamics (MD) and Monte Carlo (MC) methods. Zhang et al. studied the correlation between vdW/CI interactions and the OA orientations through molecular static calculation.[25] Alimohamadi et al. employed a classical MD simulation to study the preferential aggregation of TiO2 NPs with both Wulff and asymmetric shapes by assuming TiO2 NPs are rigid in the vacuum.[26] Qin et al. employed MD simulations to resolve the forces between two NPs in a Lennard–Jones (L–J) liquid.[27] Using MD simulations, Sathiyanarayanan et al. found that solvent plays a dominant role in the anisotropic growth of colloidal nanostructures,[28] which is consistent with the experimental results obtained by Giersig et al.[29] Schapotschnikow et al. computed the potential of mean force, a sum of CI, vdW, DI, and other inter-particle forces, for two gold NCs through atomistic simulations and investigated the effects of temperature, capping molecule length, and the presence of solvent on these interac-

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tions.[30] In particular, the authors have recently studied the CI and vdW between NPs and NRs by constructing a geometrically spherical NP and a cylindrical NR in the derivations of these inter-particle interactions.[31–34]

Despite theoretical studies on the OA assembly of isotropic NCs, investigations into the inter-particle interactions associated with the OA assembly of 1D NCs are still lacking. In this study, we employ molecular simulations to study the vdW interactions associated with the assembly of Ag NRs. The correlation between vdW and various parameters including the size, AR, and inter-particle separation of Ag NRs is evaluated in detail. The work facilitates the fundamental understanding of vdW interactions in 1D and 2D OA assemblies of 1D NCs and the attachment mechanism of OA-growth systems in general.

Models and Methods

In our study, we employ an uncapped NR–NR assembly model, as shown in Figure 1. Ag NCs are used as the material platform because Ag has a large Hamaker constant, typically resulting in a strong vdW attraction between attaching NCs.[35] In our model, the precursor NR has a few (100) layers stacked in a cubic configuration with a cross-section $a \times a$. The growing NR is also constructed by (100) layers, with a length $L$ and a square cross-section $a \times a$. The aspect ratio of the growing NR can then be defined as $L/a$, and $d$ is the surface-to-surface inter-particle separation between the two NRs. In particular, side-by-side growth forms 2D or 3D structures whereas end-to-end growth results in anisotropic nanorods. The vdW attraction is then calculated by molecular static simulations. The universal force field is employed[36] and vdW can be described by the Lennard–Jones potential expressed in Equation (1):[37]

$$E = D_0 \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6$$  

(1)

where $r_0$ is the equilibrium bond distance, $r$ is the distance between two atoms, and $D_0$ is the equilibrium potential well depth. The summation method is atom-based with no truncation, meaning that vdW between any two atoms is summed. The zero separation ($d = 0$) between two NRs is defined as the position where atoms on the two surfaces form chemical bonds. The total vdW for the configuration of the NR assembly with a separation of $d$ is noted as $E_{vdw}(d)$. vdW with an infinite inter-particle separation is noted as $E_{vdw}(\infty)$. $E_{vdw}(d)$ varies little at adequately large $d$ and can thus be used to substitute $E_{vdw}(\infty)$. Then, the vdW energy between the two NRs with a separation can be determined by the difference between $E_{vdw}(d)$ and $E_{vdw}(\infty)$, as given in Equation (2):

$$\Delta E_{vdw}(d) = E_{vdw}(d) - E_{vdw}(\infty)$$  

(2)

Results and Discussion

The size and aspect ratio largely impact the properties of Ag nanorods. For instance, the wavelength of the local surface plasmon resonance can be tuned from the visible-light range by varying the diameter and length of the Ag NRs.[38] Therefore, the synthesis of one-dimensional Ag crystals with controlled size and AR is highly desirable in the nanoscience field. Based on our calculations, where the length of all NRs is fixed at 20 nm, the effect of the diameter of the NRs on the vdW interactions in side-by-side and end-to-end assemblies is investigated, as shown in Figure 2. The vdW attraction rapidly decreases upon increasing the NR–NR separation due its short-distance characteristics. There is a critical point at which the vdW drop becomes gradual. The critical point is similar for NRs with the same diameters in both assemblies and varies from 0.2 to 0.8 nm as the diameter of the NRs increases from 0.4 to 4 nm. Thus, a large concentration of NR precursors and high synthetic temperatures should be employed to promote both OA assemblies. In both assemblies, the vdW interactions increase as the diameters of the NRs increase. In addition, at a certain precursor concentration, precursor NRs with larger diameters experience faster kinetics as vdW governs the growth. Nevertheless, the effects of the changes in the separation and diameter on the vdW of the...
two types of OA assemblies largely differ. For instance, as \(d\) decreases in the range of 0–0.2 nm, vdW increases much faster in the end-to-end assembly compared to the vdW increase in the side-by-side assembly. Such a difference appears to be even more obvious at NR diameters above 1.2 nm. Thus, the end-to-end assembly is more sensitive to the concentration of NR precursor and synthetic temperature compared to the side-by-side assembly.

To investigate the detailed effects of the size of the precursor NRs on the two assemblies, plots of the vdW interactions versus the diameter at fixed separations are given in Figure 3. At a fixed \(d\), the vdW interaction increases linearly with increasing diameter of the NRs in the side-by-side assembly, whereas it increases quadratically in the end-to-end growth. At a zero separation, vdW increases by over ten times in the end-to-end assembly as the diameter increases from 1.2 to 4 nm, whereas in the side-by-side assembly, the vdW only increases threefold. This suggests that increasing the size of the precursor NRs can facilitate the end-to-end OA assembly more efficiently compared to the side-by-side OA assembly because vdW dominates the OA growth. This result is supported by Sau and Murphy’s work. They found that Au NRs with a diameter of 14–15 nm followed a side-by-side growth, whereas NRs with a diameter of 29 nm followed an end-to-end growth.\(^{39}\)

In addition to the diameter of the NR and the separation between two NRs, the aspect ratio is also an important factor in a typical OA assembly. In our calculations, AR is varied to evaluate the effects of vdW in the side-by-side and end-to-end assemblies, as shown in Figure 4. The vdW increases dramatically as AR increases in the side-by-side assembly. At a zero separation, vdW increases from 9.2 to 205 kT and the critical point increases from 0.1 to 0.8 nm as the AR increases from 1 to 20. Thus, in the side-by-side growth, NR precursors with larger ARs experience a faster kinetics because of the significantly increased vdW. With increasing reaction time, the side-by-side NR assembly is more thermodynamically favorable due to the increased ARs, which is consistent with the experimental work of Sau et al. and Li et al.\(^{39,40}\) In contrast, the vdW interaction varies only slightly with increasing AR of the precursor NRs in the end-to-end growth, as confirmed by the overlapping plots of vdW versus \(d\) in Figure 4b. This indicates that the end-to-end growth kinetics is insensitive to the increase in the growth time as vdW is the dominant inter-particle interaction. By compensating the increasing counteracting effects of other interactions, increasing the synthetic temperature or injecting more precursor NRs in the assembly system can help maintain stable growth kinetics in the end-to-end OA growth. A recent example of the experimental end-to-end assembly of NRs into ultra-long nanorods was achieved by imposing geometric confinement via supramolecular assembly.\(^{41}\)

In this study, we employ Ag as a material platform to study the vdW interactions associated with the assembly of 1D NCs through molecular simulations. Surface ligands, crystalline directions, and the specific shapes of the NRs, inadequately investigated in this work, can also influence the inter-particle interaction and the growth kinetics in the side-by-side and end-to-end OA assemblies.\(^{3,20,31}\) In particular, the shape of the attaching NRs largely impacts the vdW interaction in the side-by-side assembly. This is because the attaching surface area substantially varies for nanorods with different shapes in such an attachment; the number of interacting atoms with the nearest separation greatly varies with varying NR shape, which then greatly influences the vdW force due to its short-distance nature. More complex material platforms along with additional interactions are subject to future research.
Conclusions

In summary, the vdW interactions associated with the side-by-side and end-to-end assemblies of one-dimensional nanorods are investigated via molecular static calculations. Our results show that parameters including the size, AR, and separation of the NRs differently influence the two types of assemblies. Our study improves the analytical understanding of the OA assembly mechanism of 1D NCs from an energy point of view and also facilitates the design of the synthetic parameters before an experiment is conducted.

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Molecular static calculations are carried out to evaluate the van der Waals interactions associated with different oriented-attachment growth systems based on one-dimensional nanorods.

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