Shape-Induced Separation of Nanospheres and Aligned Nanorods
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ABSTRACT: We studied the phase separation and spatial arrangement of gold nanorods and nanospheres after evaporative self-assembly from aqueous suspension. Depending on the position relative to the contact line of the drying droplet, spheres and rods separate into various liquid-crystalline phases. Nanorods exhibit a strong preference for side-by-side alignment, giving rise to smectic phases; spheres in solution are forced out of these regions and form close-packed arrays. We discuss this self-separation into nanorod- and sphere-rich phases in terms of various interactions, including electrostatic, van der Waals, and depletion interactions forces. The experimental results are compared to quantitative calculations of the colloidal interaction energies. We also describe and discuss the role of the surfactant on the different crystal facets of the nanorods on the assembly process.

INTRODUCTION

Phase separation of nanoparticles of different shapes and sizes has been and continues to be a topic of intense research. As an example, mixtures of rod-like and sphere-like particles have been shown to spontaneously phase-separate into rod-rich and sphere-rich phases. 1–4 The physical origin of this separation of different phases is generally considered in terms of competing translational entropy and entropy of mixing. Similar phase-separation mechanisms may also be relevant in protein crystallization, 5 the manufacture of nanocomposite materials, 6 and assembly of block copolymers 7 as well as in bioseparation and DNA partitioning methods. 8

Obtaining a detailed understanding of the phase separation and assembly of nanoparticles, and therewith to achieve ultimate control over these processes in mixtures of particles of various shapes and sizes, remains a major challenge. Since the middle of the 20th century, a considerable amount of theoretical work has been done on phase separation of various shapes and assemblies of nanoparticles. 8–12 More specifically pertaining to the phase separation of rod–sphere mixtures, the theoretical work focused on elucidating the formation of separate phases has been complemented by simulations as well as experimental work. 13–19

The formation of self-assembled superstructures of nanoparticles strongly depends on particle size, 20,21 shape distribution, 22–26 evaporation rate, 27,28 and, most importantly, a range of interparticle interactions. 12,20,21,27,29 The latter includes capillary forces, 30 depletion interaction, 31–33 electrostatic forces, 34 and surfactant-mediated interaction. 12 At sufficiently high concentrations, anisotropic particles such as rods and plates form various liquid-crystalline assemblies, referred to as nematic, smectic, and columnar phases. 3,11,35–41

All of the aforementioned interactions play a role in the self-assembly of nanoparticles. However, in the case of anisotropic micro- and nanoparticles, extensive research has been focused mainly on depletion interactions, and this was initially considered to be the dominant interaction responsible for the phase separation of rod–sphere mixtures. 42 The attractive interaction between spheres due to addition of rods was discussed by Auvray, 43 and the interaction induced by thin rods was investigated using the Derjaguin approximation by Mao et al. 44 Moreover, it was shown that polydispersity in rod length considerably affects the result. 32 In an experimental study, Koenderink et al. 33 concluded that at very low concentration of high-aspect-ratio rods, phase separation of rod–sphere mixtures is already found, demonstrating the high efficiency of rods as a depletion agent.

Although depletion interaction is important for phase separation in microcolloidal systems, when going down toward the nanoscale, DLVO forces also come into play and become more dominant. In particular, the balance between van der Waals forces and electrostatic interaction due to surface charge in nanoparticulate systems effectively competes with the entropic effects of depletion interaction. A number of studies have focused on quantifying these interactions for suspensions containing only a single component with a narrow size distribution, 12,29 examples include nanotriangles 25 and nanorods. 35–47

In this work, we focus on the frequently observed phase separation upon drop-casting and subsequent evaporative self-assembly of differently shaped nanoparticles (nanorods...
and nanospheres) in mixed suspensions. As far as we are aware, a quantitative description of DLVO interactions for binary systems comprising nanorods and nanospheres has not been reported. We present results on the phase separation of aligned nanorod phases and nanosphere-rich domains. The observations are analyzed in terms of relevant nanocolloidal interactions. The novelty of this work lies in the fact that we apply the well-established DLVO formalism to estimate the interactions between differently shaped nanoparticles in relation to those between identical particles. Although many open questions remain, our findings expand the toolbox for controlling nanoparticle interactions at the nanoscale and therewith their assembly and phase separation.

■ EXPERIMENTAL SECTION

Materials. Hydrogen tetrachloroaurate (HAuCl4·3H2O, 99.999%, Aldrich), silver nitrate (AgNO3, 99%, Acros), ascorbic acid (AA, 99%, Merck), cetlytrimethylammonium bromide (CTAB, Aldrich, 98%), sodium borohydrate (NaBH4, 99%, Aldrich), and hydrochloric acid (HCl, 37%, Merck) were all used as received without further purification. All water that was used in the synthesis was of Milli-Q quality (18.2 MΩ cm), produced in a Simplicity 185 system (Millipore).

Synthesis and Assembly. We adopted the two-step seed-mediated protocol, as described by Nikoobakht and El-Sayed,54 to synthesize the gold nanorods used for this study. First, CTAB-coated seed particles were prepared by mixing 25 μL of HAuCl4 (0.1 M) with 10 mL of CTAB (0.1 M). Then, 60 μL of ice-cold NaBH4 (0.1 M) was introduced while continuously stirring for 3 min. The resulting solution quickly turns light brown, which indicates the formation of gold seeds. The solution was kept at 25 °C for 1 h without stirring to achieve saturation of the seed growth.

To synthesize aspect ratio (AR) 4 gold nanorods, the growth solution was prepared by adding 50 μL of HAuCl4 (0.1 M) with 10 mL of CTAB (0.1 M). This solution was heated at 35 °C for 20 min while slowly stirring to dissolve CTAB and was then left to cool to 25 °C. While maintaining this temperature, 25 μL of AgNO3 (0.1 M) was added, followed by 70 μL of ascorbic acid (0.1 M) with gentle stirring; the resulting solution becomes colorless. Next, 150 μL of HCl (1 M) was introduced; the pH of the solution was maintained at 3. Finally, 24 μL of the seed particle suspension was added into the growth solution. The final solution was left undisturbed overnight at 25 °C.

Similarly, for the synthesis of AR6 nanorods, the growth solution was prepared by adding 50 μL of HAuCl4 (0.1 M) with 10 mL of CTAB (0.1 M). This solution was kept at 35 °C for half an hour to completely dissolve the CTAB. Thereafter, while maintaining the solution at 25 °C, 20 μL of AgNO3 (0.1 M) was added. Then, 70 μL of ascorbic acid (0.1 M) was added, followed by 100 μL of HCl (1 M). Finally, 24 μL of seed solution was added into the growth solution. This solution was left undisturbed overnight at 25 °C.

Before use, the nanorod suspensions were centrifuged at 15 000 rpm for 10 min to remove the excess CTAB. Also, the same growth solution was centrifuged again at 5600 rpm for 5 min to separate spherical nanoparticles from the nanorods. The supernatant containing primarily nanorods was carefully separated from the precipitate in the bottom of the centrifuge tube; the latter contains mostly spheres. The nanorod suspensions were stored in the refrigerator. The separation of nanorods and nanospheres is not perfectly selective. Different suspensions have varying amounts of spheres; as such, the spheres are byproducts.

For drop-casting experiments, SiO2 substrates were ultrasonically cleaned in distilled water for 5 min at room temperature. Then, the substrates were rinsed twice with distilled water and dried in a nitrogen flow. Droplets (10 μL) of each solution were placed on the clean SiO2 substrate and allowed to evaporate. During 2 h the solvent is completely evaporated, leaving a coffee stain-like ring on the substrate.

Characterization. Ultraviolet–visible (UV–vis) spectroscopy measurements were carried out using two different systems: (i) a Varian Cary 300 Scan spectrometer (this system enables measurement of spectra in the range of 200–900 nm) and (ii) an Ocean Optics HR2000+ spectrometer operated using the SpectraSuite software package in combination with a Mikropack UV–vis light source (model DH-2000-BAL) (for the measurement of spectra up to wavelengths of 1100 nm). We used standard semimicro UV cuvettes with outer dimensions of 12.5 mm × 12.5 mm × 45 mm for the optical analysis; the optical path through the liquid amounts to 10 mm. These cuvettes can hold up to 1.5 mL of liquid, enabling analysis of limited volumes of liquid.

High-resolution scanning electron microscopy (SEM; on a Merlin Zeiss 1550 system) was used for imaging of our samples; typical voltages in the range 0.1–30 kV are accessible. All images in this article were taken at an accelerating voltage of 2 kV.

■ RESULTS

When a droplet is deposited on the substrate, the solvent evaporates slowly, typically within 1 to 2 h. As soon as the droplet is in contact with the substrate, the contact line appears to be pinned. Because of convective processes, a typical coffee stain-like ring is formed,55–59 with nearly all nanoparticles assembled into dense arrays near the three-phase contact line.

A typical image near the edge of the ring is shown in Figure 1a. A UV–vis absorbance spectrum of the suspension used in these drop-casting experiments is presented in Figure 1b. At 520 nm, a characteristic peak is observed, which is partly due to the transverse resonance of the gold nanorods but also expresses the relatively large number of spheres in the suspension. The wide peak centered near 980 nm is due to only the longitudinal resonance of the nanorods with AR6; the average length and width of the nanorods amount to 60 ± 5 and 9 ± 1 nm, respectively.

The nanoparticle assemblies exhibit various phases consisting of spheres and/or rods at different positions within the coffee
stain ring. Clearly, the rods and spheres self-separate into rod- and sphere-rich phases. To explore these various phases formed within the entire width (9 to 10 μm) of the coffee stain ring as shown in Figure 2a, we identify three regions, which we refer to as the outer, middle, and inner areas.

Figure 2. SEM images at different positions of the coffee stain ring after drying a suspension of aspect ratio 6 nanorods: (a) Large-scale overview of the edge (the scale bar represents 20 μm), (b) outer edge, where alternating rows of spheres and rods are observed, (c) close-packed sphere arrays bounded by aligned layered superstructures of rods, and (d) various phases of rods and spheres further away from the edge. The scale bar in panels b–d corresponds to 200 nm.

At the very outer edge close to the three-phase contact line of the evaporating droplet, most of the rods are oriented parallel to this contact line. One to two nanorod lengths (approximately 100−200 nm) away from the edge, rods are oriented perpendicular to the contact line, as shown in Figure 2b. These perpendicularly oriented rows of nanorods are separated by a layer of spheres, effectively forming alternating rows of rods and spheres. These alternating rods/spheres superstructures were observed up to a distance of approximately 3 to 4 μm from the contact line. Moreover, such phase separation was observed around the entire circumference of the droplet.

At a distance of 4−6 μm from the contact line, the middle portion of the coffee stain ring consists of completely different arrangements of superstructures, as shown in Figure 2c. The nanorods form aligned mono- and multilayered blankets of side-by-side assemblies. These three-dimensional superstructured nanorod layers appear to be oriented in arbitrary directions. Moreover, they enclose the close-packed arrays of spherical particles.

Close to the inner edge of the ring, approximately 6−10 μm from the contact line, the phase separation of rods and spheres becomes very pronounced, as shown in Figure 2d. Large three-dimensional superstructures are observed, with the nanorods assembled into smectic phases, i.e., the nanorods are aligned in distinct layers, with their long axis nearly perpendicular to that plane. These smectic phases are completely free of spheres. On the other hand, the spherical entities also aggregate, but within the sphere-rich phases, some nanorods can still be discerned.

To investigate the effect of nanorod shape on their assembly and phase-separation behavior, we did a similar experiment using nanorods of AR4 (length 55 ± 5 nm, width 12 ± 3 nm). The result is shown in Figure 3a. From the UV−vis spectrum in Figure 3b, we conclude that the much lower peak near 520 nm represents the markedly lower concentration of spherical particles in these suspensions. Also, the longitudinal peak for these suspensions is now at 810 nm, owing to the lower aspect ratio of the thicker but equally long nanorods.

The SEM image in Figure 3a reveals that the thick AR4 nanorods also assemble into aligned smectic phases (top left and bottom of the image), where the few spheres assemble at the boundary between various phases. In the middle and toward the right of the image, close-packed arrays of particles are observed. Judging by the diameter, these are nanorods aligned with their long axis perpendicular to the image plane (referred to as the columnar phase in the literature); we cannot conclude whether this is a single layer or a multilayered structure. The results in Figures 1−3 suggest that during droplet evaporation the nanorods in suspension always assemble into highly ordered arrays with spheres forced out from these superstructures.

Finally, we also studied the behavior of mixed suspensions, containing both thick and thin nanorods, with AR4 and AR6. The result is shown in Figure 4. For this purpose 1000 μL of AR6 suspension was mixed with 300 μL of AR4 suspension; the resulting UV−vis spectrum of the mixture (Figure 4c) clearly shows three features. One peak near 520 nm arises mainly from the spheres in the suspension and contains a minor contribution from the transverse plasmon resonance. The broad peak is due to the longitudinal plasmon resonance and as such contains contributions from the AR6 nanorods (the maximum at 970 nm) and the AR4 nanorods (a shoulder around 900 nm).

Surprisingly, the SEM images in Figure 4 reveal that thick nanorods with AR4 are assembled into layers of perpendicularly aligned layers, similar to the aforementioned results. These layers of close-packed nanorods (approximately in the center of

Figure 3. (a) SEM image of aligned phases of aspect ratio 4 nanorods. The scale bar represents 100 nm. (b) UV−vis spectrum of a suspensions of aspect ratio 4 nanorods (solid red line) prior to deposition on the surface. As a reference, the spectrum of aspect ratio 6 nanorods from Figure 1b is included (dashed blue line).
the image) appear to be loosely stacked perpendicular to the contact line, most likely due to convective processes. The thin nanorods and the spheres do not appear to assemble into any notable structure. The agglomeration of the thick nanorods forces the thinner ones into more disordered structures further away from the contact line (on the left of Figure 4a). Moreover, we do not observe mixed phases comprising both thick and thin nanorods.

## DISCUSSION

Prior to a quantitative discussion of the results in terms of colloidal interactions, in Figure 5 we first summarize the various superstructured phases we observe at different positions with respect to the contact line of the evaporating droplet. As indicated in the previous section, we deposit a liquid droplet of nanoparticle suspension, which is left to dry. Initially, because of a finite contact angle and the relatively slow evaporation, convection is not very strong within the droplet in the first state of solvent evaporation. During this initial phase, the nanorod concentration gradually increases, giving rise to the formation of high-density phases that eventually develop into aligned phases due to steric limitations. After some time, the volume within the droplets decreases substantially, and the evaporation rate increases, which is most pronounced at the three-phase contact line. This will set up a flow profile that drives the liquid, where we assume assembled nanorod layers have already formed, toward the contact line where they assemble into superstructures.

Comparing the results in Figure 2b with those in Figure 4a reveals that the orientation of the layers of nanorods relative to the contact line differs in the two images. It is tempting to ascribe this to the different composition of the suspension, but close examination of many images indicates a more random process. In some images, even mixed situations occur, with layers partly oriented perpendicular and partly parallel to the contact line. An example is shown in Figure 6. These observations support our claim that the nanorods assemble in suspension prior to being driven toward the contact line by convective flow. Although many reports in the literature show similar layered ordering of the nanorods, to the best of our knowledge, in none of these is there a focus on the interaction between the nanorod assemblies and the three-phase contact line.

![Figure 4](image_url)  
**Figure 4.** (a) SEM image of nanorod assemblies after evaporative assembly of a mixture of thick (aspect ratio 4) and thin (aspect ratio 6) nanorods. The scale bar represents 200 nm. (b) UV–vis spectrum of the suspension containing thick and thin nanorods mixed in a ratio of 3:10.

![Figure 5](image_url)  
**Figure 5.** Schematic representation of the various phase separations of spheres and rods at different positions of the coffee stain ring, as observed in the experiments: (1) alternating layers of rods and spheres at the outer edge, (2) close-packed spheres fenced by aligned layers of rods, and (3) phase-separated regions of rods and spheres close to the inner edge.

![Figure 6](image_url)  
**Figure 6.** SEM image (aspect ratio 6 nanorods) revealing different orientations of the nanorod layers with respect to the three-phase contact line. In the lower left part, the layers are parallel to the contact line, whereas in the middle and top right, they are perpendicular.

**Colloidal Interactions in the Self-Assembly.** As opposed to numerous previous studies, our suspensions consist of nanoscale rods and spheres that clearly self-separate into nearly pure phases containing only nanorods or nanospheres (Figures 1 and 2).
The electron microscopy (SEM) images in the previous section reveal the close-packed structures with a relatively high degree of positional and rotational order, i.e., in smectic phases. Self-assembly in general arises from a balance of attractive and repulsive interactions between the nanoparticles in suspension, mediated by the solvent. To obtain a more quantitative understanding of the various interactions, below we briefly summarize the various interactions and compare their relative contributions to the overall nanoparticle interactions. Electrostatic, van der Waals, and depletion interactions are analyzed in line with previous work, specifically applied to our system of rods and spheres.

For the side-by-side electrostatic interaction for CTAB-coated gold nanorods, the interaction energy of curved particles is obtained using the Derjaguin approach; the curved nanorods surface is approximated as sets of infinitesimal parallel plates, which represent the nanorod cross-section. The exact expressions for a large range of particles and orientations have been summarized by Walker et al. The plate–plate electrostatic interaction energy per unit area at constant potential is given by

$$U_{es, plate}(h) = \epsilon_{water} \kappa \phi_0 [1 - \tanh(\kappa h/2)]$$  \hspace{1cm} (1)

with $h$ being the spacing between plates and $\epsilon_{water} = 81$ (the relative dielectric constant of water). For the effective screening length in our solution, taking into account the ionic strength, we assume $\lambda = 1/\kappa = 1.5 \text{ nm}$. The surface potential of the CTAB-coated particles in 50 mM CTAB solution is estimated to amount to $\phi_0 = 60 \text{ mV}$.

To estimate the rod–rod electrostatic interaction energy in the side-by-side configuration, we assume a cylindrical shape of the nanorods

$$U_{es, ss}(h) = L \cdot \frac{2 \pi r_2}{\sqrt{r_1 + r_2}} \int_h^{\infty} \frac{U_{es, plate}(x)}{\sqrt{x - h}} \text{d}x \tag{2}$$

where $L$ is the total length and $r_1$ and $r_2$ are the radii of the two interacting rods; for identical rods, $r_1 = r_2$. The distance of closest approach is given by $h$; this is the separation of the outer surfaces of the CTAB layer coating on the nanoparticles.

To quantitatively estimate the van der Waals interaction between two aligned nanorods spaced $h$ apart, we use

$$U_{vdW, ss}(h) = -\frac{A_{vdW}}{24 h^{3/2}} \left[ \frac{2 \pi r_2}{r_1 + r_2} \right] \tag{3}$$

where $A_{vdW} \approx 10^{-19} \text{ J}$ represents the Hamaker constant.

Finally, owing to the CTAB that remains in the solution, the nanorods will experience an attractive force due to depletion interaction. In principle, not only the CTAB micelles (diameter $d_{micelle} \approx 5.6 \text{ nm}$) but also the spherical particles in solution may give rise to an effective osmotic pressure. However, considering their very small number density ($\sim 10^{13} \text{ m}^{-3}$), as compared to the micelle concentration (estimated to amount to $2 \times 10^{23} \text{ m}^{-3}$), the CTAB micelle concentration will dominate the effective depletion force. The attractive potential between side-by-side aligned nanorods, arising from the osmotic pressure $P_0$ is given by

$$U_{depl, ss}(h) = -\frac{L}{2} P_0 [ -h \sqrt{2 r_{rod} + d_{micelle}}^2 - h^2 ]$$  

$$+ \left( 2 r_{rod} + d_{micelle} \right)^2 \tag{4}$$

with $r_{rod}$ being the radius of the nanorod.

With $r_{rod} = 10 \text{ nm}$, the electrostatic interaction is positive, i.e., repulsive, whereas the van der Waals interaction is attractive. The depletion interaction is also attractive but is much smaller than the other two contributions, typically on the order of $kT$. Combination of these gives rise to a primary minimum $U_{min} = -6.24 kT$ at an interparticle separation $h = 6.5 \text{ nm}$. The strong decrease of the overall interaction curve below $h = 2 \text{ nm}$ originates from the rapid drop of the van der Waals interaction (eq 3). In an actual colloid system, repulsive steric interaction will dominate at such short distances; we have not taken this into account here and focus only on the primary minimum.

The various interactions contributing to the overall interaction curve depend on the length and diameter of the nanorods. This enables a straightforward calculation of the minimum interaction energy for various sizes and aspect ratios of the nanorods. The results are summarized in the bottom panel of Figure 7. As expected, with increasing length $L$ of the nanorods, the mutual attractive interaction strength increases.

![Figure 7](image-url)

**Figure 7.** (top) Theoretical curves for the electrostatic (red), van der Waals (green), and depletion (blue) interactions for side-by-side aligned nanorods with length $L = 60 \text{ nm}$ and diameter $2 r_{rod} = 10 \text{ nm}$. The total interaction curve (black) is the sum of all individual contributions. (bottom) Minimum energy of the total interaction curve as a function of nanorod length $L$ and diameter $2 r_{rod}$.
due to a larger overlap of the neighboring particles. For larger diameter, i.e., a lower curvature, a similar effect occurs. For the largest nanorods ($L = 100$ nm and diameter $2r_{\text{rod}} = 26$ nm), the minimum drops to large negative values. This is in line with experimental results that exhibit limited stability of such nanorod suspensions. The agglomeration is energetically much more favorable than their Brownian motion.

Considering that the minimum of the interaction curve for nanorods with moderate dimensions is markedly more negative than $kT$ (the energy related to Brownian motion), this implies that the assembly of nanorods is indeed favorable. However, their relatively low concentration (i.e., the number density of nanorods) provides a reasonable separation, therewith providing a fair stability of the solutions. During the drying of the suspension droplets, the concentration gradually increases, giving rise to spontaneous assembly of the nanorods in suspension.

**Nanorod Alignment and Phase Separation.** The SEM images in Figures 1–3 clearly reveal that the nanorods have a strong preference to assemble into highly ordered arrays of side-by-side aligned nanorods. In addition, suspensions containing both nanorods and nanospheres exhibit a clear phase separation between the two types of particles. Similar phase separation has been observed previously in mixed suspension containing differently shaped particles.\(^1\),\(^2\),\(^3\),\(^7\)

As described in relation to Figure 2, the spheres seem to be surrounded by layers of perpendicularly aligned nanorods. This suggests that the nanorods first assemble in a side-by-side fashion, after which these layers move toward the edge of the drying droplet under the influence of convection. In that process, the remaining spheres are trapped, giving rise to separate phases of rods and spheres. To support the statement that nanorods have a (strong) preference to assemble side-by-side, as compared to their end-to-end alignment or in comparison to the sphere–sphere interaction, we compare the theoretically calculated overall interaction curves for the three cases in the top panel of Figure 8. Details on the calculations are provided in the Supporting Information. As is clear from this energy consideration, the side-by-side assembly of nanorods is the most preferential configuration. In comparison, the mutual interaction between nanospheres, which have a larger radius than that of the nanorods, is smaller but still amounts to $2kT$. As expected, the end-to-end configuration is negligible and will, under normal ambient conditions, not be stable in relation to Brownian motion. The fact that curvature has a pronounced effect on the particle–particle interaction is clearly reflected in the top panel of Figure 8.

As revealed in Figures 1–3, after evaporative assembly, the nanorod superstructures generally exhibit a smectic-like ordering. As opposed to a nematic ordering in which there is only orientation order, the nanorods also exhibit a strong positional ordering within the assemblies; layers of perpendicularly aligned prolate nanoparticles are stacked onto each other. Such smectic phases have been observed in a number of different micro- and nanocolloidal systems.\(^2\),\(^3\),\(^6\),\(^7\),\(^8\),\(^26\),\(^27\),\(^38\),\(^40\),\(^41\),\(^47\)

This observation is in line with our assumption that these densely packed layers form in solution due to the decreasing volume within the droplet (and thus increasing nanoparticle concentration). Because of convective processes within the evaporating droplet, the particulate layers are then stacked on top of each other.

To assess the favorable configuration of the side-by-side orientation, as observed in the layers of the smectic arrays, in the bottom panel of Figure 8 the overall interaction is plotted as a function of overlap distance $d$; when $d = L$, the nanorods are completely parallel, whereas for $d \approx 0$, the rods are effectively in an end-to-end configuration. For decreasing overlap of the $L = 60$ nm nanorods, the minimum interaction energy clearly decreases from $|U_{\text{mid}}| = 6.24kT$ for 100% overlap to $|U_{\text{mid}}| = 0$ for negligible overlap. As such, the sum of the colloidal interactions considered for our system confirms that the side-by-side configuration with nanorods “in registry” is favorable and in combination with the temporal sequence of assembly contributes to the smectic phases observed.

Up to now, we have considered only assemblies of identical nanorods as well as their combination with spheres. The theoretical expressions for electrostatic and van der Waals interactions in eqs 2 and 3 also enable us to evaluate the effect of mixtures of nanorods (Figure 4) with different diameters $r_1$ and $r_2$. In Figure 9, the effect of varying diameters (and therewith different aspect ratios) is shown. As discussed in relation to Figure 8, the curvature of the surface is relevant. Going back to the Derjaguin approximation, a relatively flat surface will give rise to larger overall interactions as compared to a surface with strong curvature. As such, we expect that the attractive interaction between nanorods with a larger radius will be stronger in comparison with thinner nanorods. The...
calculations in Figure 9 indeed support this, and the experimental result in Figure 4 confirms that thicker nanorods assemble into superstructures more effectively. Convection of the assembled thick rods is more pronounced, therewith pushing out the spheres and the thinner nanorods. For the latter, Brownian motion will be more pronounced owing to their smaller mass; this has not been taken into account in the calculation. A similar effect was reported by Ming and coworkers.9 In their study, they varied both the length and diameter of the nanorods, and they concluded that only nanorods with different widths self-separate to form their own smectic superstructures; for nanorods with different lengths but with equal diameter, such self-separation was not observed. Surprisingly, mismatched pairs of thick and thin rods have not been observed, and we have not found mixed phases comprising both types of nanorods, despite only a relatively small difference of $2kT$ between the energy minima in Figure 9. This may suggest that other processes may also be involved; in the next section, we discuss the possible effect of the stabilizing CTAB layer on the assembly process.

**Role of CTAB Surfactant Layer.** In the previous section, we have considered only long-range colloidal forces acting on the nanoparticles and also the approximately spherical ends of the nanorods, the CTAB molecules radiate outward. As a result, the angles of approach in flat-versus-sphere interactions are mismatched, effectively giving rise to a repulsion.

Now, we turn back to the interacting nanoparticles. Two nanorods with dense layers of aligned CTAB molecules will enable a certain extent of interpenetration of layers of neighboring particles (middle of Figure 10). In the case of two nanospheres (right of Figure 10), the outer region of the CTAB layers is relatively dilute, therewith allowing the surfactant molecules to interact to a certain extent. Finally, the overlap between CTAB layers of two surfaces with markedly different curvature (left of Figure 10) will be hindered by the fact that one surfactant layer is densely packed and the molecules on the two surfaces are not aligned.

Combining all of the long- and short-range forces in relation to the shape and size, a schematic summary is depicted in Figure 11. Depletion interaction was shown to be only a minor interaction, whereas van der Waals attraction and electrostatic interactions may also be involved. The surfactant molecules on the two surfaces are not aligned.

**Figure 9.** Theoretical curves depicting the effect of different nanorod diameters $r_1$ and $r_2$ on the overall interaction for nanorods (with length $L = 60$ nm). Interaction energies are given for two nanorods with radii $r_1 = r_2 = 5$ nm (black), with radii $r_1 = 8$ nm (red), and the mixed case for $r_1 = 5$ nm and $r_2 = 8$ nm (blue).

**Figure 10.** Schematic drawing of the surfactant configuration at differently curved nanorod surfaces. The interaction between a flat and a curved surface (left), two flat surfaces (middle), and two curved surfaces is shown.

**Figure 11.** Schematic summary of the assembly process in nanoparticle suspensions containing rods and spheres. Under the influence of long-range electrostatic and van der Waals forces, combined with short-range surfactant interactions, similar particles will self-separate into sphere- and nanorod-rich phases; side-by-side alignment in the latter case is preferred.
repulsion comprise the long-range interactions. We have shown that on the basis of the theoretical analysis the side-by-side oriented alignment of nanorods is strongly favored, with an even more pronounced energy minimum for larger nanorod diameters. Moreover, we discussed that the short-range interaction between surfactant layers on the nanoparticle surfaces also favor self-separation of the nanorods and -spheres into separated phases. Within the drying droplet, the nanoparticle concentration in the suspension increases. As a result, the various superstructures are driven toward the three-phase contact line, where they assemble into phase-separated superstructures, as shown in the experimental results in Figure 1–4.

**CONCLUSIONS**

In summary, we investigated the phase separation of aligned gold nanorods from nanospheres within the coffee stain ring formed during evaporative self-assembly using a combination of electron microscopy and theoretical analysis. The orientation and density of the various crystalline phases at different positions of the coffee stain ring is attributed to the convective flow, which changes as the environment within the droplet becomes more dense owing to the continuously decreasing height of the droplet during evaporation. In the theoretical analysis, which provides a benchmark for interpretation of experimental results, all major interactions between the nanoparticles were discussed for our specific system, which ultimately provides a net interaction energy depending on particle shape, size, and orientation. Both the experimental results and the theoretical analysis confirm that the side-by-side arrangement of the nanorods is the lowest energy state for our system. Furthermore, we also discuss variation of the energy minimum for different orientations, sizes, and shapes of the nanoparticles. Although the overall attractive interaction plays a major role in bringing the nanoparticles together in suspension, we also discuss the possibility that short-range steric interaction caused by the CTAB coating on the nanoparticle surface could play a role in the self-separation of spheres and rods.

**ASSOCIATED CONTENT**

Supporting Information

Theoretical analysis of the colloidal interactions (electrostatic, van der Waals, and depletion) for nanospheres and for nanorods in an end-to-end configuration. This material is available free of charge via the Internet at http://pubs.acs.org.

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