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Langmuir−Blodgett Nanorod Assembly

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Techniques for directing the assembly of metal or semiconductor quantum dots into novel superstructures have been extensively pursued over the past decades.[1−3] Recent interest has been drawn toward 1-dimensional nanoscale building blocks such as nanotubes, nanowires, and nanorods.[4−14] If these one-dimensional nanoscale building blocks can be ordered and rationally assembled into appropriate 2-dimensional architectures, they will offer fundamental scientific opportunities for investigating the influence of size and dimensionality with respect to their collective optical, magnetic, and electronic properties, as well as many other technologically important applications. Currently, efforts have been focused on the development of new synthetic methodologies for making nanorods with uniform sizes and aspect ratios.[4−14] Few studies addressed the organization of these anisotropic building blocks except the 3-dimensional spontaneous superlattice formation of $BaCrO_4$,[7] FeOOH,[13] CdSe,[4] Ag,[6] and Au[12] nanorods. Herein, we report 2-dimensional nanorod monolayer assembly using the Langmuir−Blodgett technique. Pressure-induced isotropic−nematic−smectic phase transitions as well as transformation from monolayer to multilayer nanorod assembly were observed.

Uniform $BaCrO_4$ nanorods were prepared by using published procedures.[7] Briefly, Barium bis(2-ethylhexyl)sulfosuccinate ($Ba(AOT)_2$) reverse micelles were added to sodium chromate (Na_2CrO_4)-containing NaAOT microemulsion droplets, to give final molar ratios of $[Ba^{2+}]:[CrO_4^{2-}] = 1$ and water content $[H_2O]:[NaAOT] = 10$. The as-made yellow precipitate consists of ribbonlike and rectangular superstructures made of uniform nanorods. The nanorods were uniform in length (~20 nm) and diameter (~5 nm). Energy-dispersive X-ray analysis and electron diffraction patterns indicated that the nanorods were single crystalline $BaCrO_4$ with an orthorhombic unit cell ($a = 0.91$ nm, $b = 0.55$ nm, $c = 0.73$ nm). These as-made nanorods generally are stabilized with AOT surfactant molecules. They were diluted and redispersed into isooctane to make a stable nanorod colloidal suspension, which is used as stock solution for subsequent Langmuir−Blodgett studies.

The nanorod colloidal suspension was spread dropwise (typically 1 mL of 2.5 mg/mL concentration) on the water surface of a Langmuir−Blodgett trough (Nima Technology, M611). The nanorod surface layer was then compressed slowly while the surface pressure was monitored with a Wilhelmy plate. Due to the presence of noncovalently bonded surfactant molecules, the compression starts with a nonzero surface pressure. In addition, since AOT is partially soluble in subphase water, the surface pressure decays with the time. In general, it was observed that the surface pressure increases during the compression. At different stages of compression, the nanorod assemblies at the water−air interface were transferred carefully onto transmission electron microscope (TEM) grids covered with continuous carbon thin film using the Langmuir−Schäffer horizontal liftoff procedure.

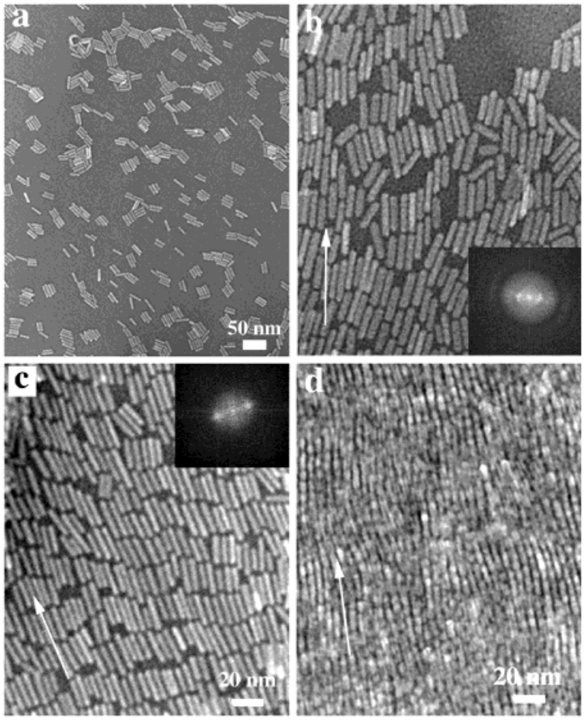

Figure 1. Transmission electron microscopy images of the nanorod assemblies at the water/air interface at different stages of compression: (a) isotropic distribution at low pressure; (b) monolayer with partial nematic arrangement; (c) monolayer with smectic arrangement; and (d) nanorod multilayer with nematic configuration. Insets in panels b and c are the Fourier transform of the corresponding image.

Nanorod assemblies were examined systematically by using TEM. Initially, at low surface pressure, individual nanorods (generally 3 to 5 rods) form raft-like aggregates. These aggregates disperse on the subphase surface in a mostly isotropic state (Figure 1a). The surface pressure remains unchanged until the nanorods start forming a monolayer and when the monolayer was compressed to a surface pressure of ~30 mN/m.[15] During this process, monolayer of nanorods in a nematic arrangement are first obtained where the directors of these nanorods (or nanorod rafts) are qualitatively aligned presumably dictated by the barrier of the trough. Figure 1b shows such a partial nematic region with an orientational order parameter S of 0.83. The regularity of side-by-side inter-rod distance is reflected in the Fourier transform of the region (Figure 1b, inset). This nematic ordering, however, only occurs within a quite narrow pressure range. With further compression (surface pressure about ~35 mN/m), nanorod

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(15) The free surfactants in the system can form Langmuir films themselves and may interfere with the formation of the nanorod monolayers. Consequently, the actual surface pressure during the compression may differ from the observed value.

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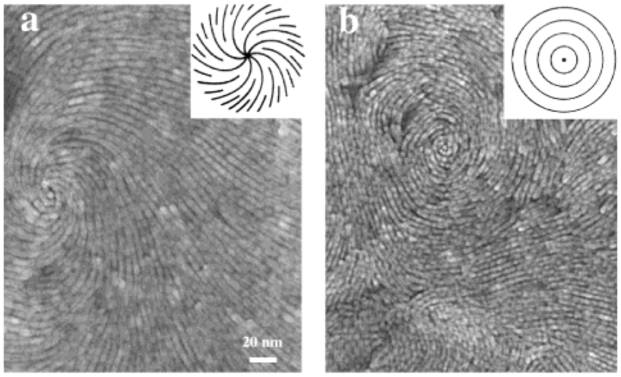

Figure 2. TEM images for textural defects within the multilayer nanorods. Both defects have strength of +1. Insets show the nanorod director orientation in the vicinity of disclinations.

assemblies with smectic arrangement are obtained, which is characterized by layer-by-layer stacking of ribbon-like nanorod superstructures (Figure 1c). The Fourier transform of the configuration (Figure 1c, inset) also shows the regularity of the inter-rod distances parallel and normal to the rod axis. When the surface pressure reaches above 38 mN/m, a transition from monolayer to multilayer was observed. The 2-dimensional (2D) smectic nanorod ordering disappears and the system eventually resumes a disordered 3-dimensional (3D) nematic configuration (Figure 1d).

Furthermore, we observed that the overall nematic arrangement in multilayer nanorod superstructures is frequently disrupted by singularities such as disclinations. Figure 2 shows two typical examples with strength *s* of the disclination being +1, where the director of individual nanorods changes continuously about the disclinations. In liquid crystal literature, these *Schlieren* textural defects are commonly observed under polarized optical microscope as microscopic manifestation of molecular director rotation.[16,17] It is noticed that this type of singularity does not occur in the monolayer nanorod system, presumably because it is energetically unfavorable.

It should be mentioned that the organization of the nanorods here differs significantly from that of the spherical nanoparticles where the hexagonal close-packed lattice is generally preferred due to the isotropic interparticle interactions.[1−3] The 2-dimensional assembly reported here also differs from the 3-dimensional spontaneous assembly of the nanorods where ribbonlike and vertical rectangular/hexagonal superstructures are favored.[4,7,12] In the current experiments, a nanorod includes an inorganic core surrounded by the surfactants. The nanorod suspension can be treated within hard-rod approximation with the consideration of directional attraction between these rods.[18−23] At sufficient low densities (i.e. low surface pressure) the rods form raft-like aggregates by aligning side-by-side due to the directional capillary force and van der Waals attraction. The raft aggregates assume all possible orientations and the fluid will be isotropic (Figure 1a). As the density increases, it becomes increasingly difficult for the rods/rafts to point in random directions and intuitively one may expect the fluid to undergo a transition to a more ordered anisotropic phase having uniaxial symmetry, whether it is nematic or smectic (Figure 1b−d and Figure 3). This ordering occurs to maximize the entropy of the self-assembled structure by minimizing the excluded volume per particle in the array as first proved by Onsager.[22] In fact, Frenkel et al.[23] have carried out Monte Carlo simulation on the phase behavior of two-dimensional hard-rod fluids and found the isotropic-2D nematic-2D smectic phase transitions for rods with an aspect ratio above 7, while only isotropic-2D smectic transition is possible for shorter rods. This simulation, however, does not account for the rod-rod directional interactions such as capillary force and van der Waals attraction. The observation of transient (maybe metastable) nematic ordering in our nanorod system (with an aspect ratio of 4−5) indicates the importance of both entropy and energetic consideration for the nonideal hard-rod system.

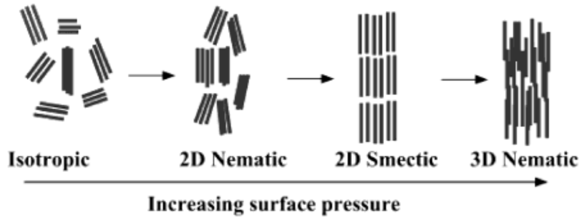

Figure 3. Schematic illustration of the pressure-induced phase transition when the nanorods are compressed at the water−air interface.

In addition, at a critical buckling surface pressure, the 2D smectic phase transforms into a 3D nematic phase with high orientational order. On the basis of our TEM studies, no monolayer smectic ordering is maintained upon the phase transition, neither is there any observable lattice registry between layers. Exactly how this phase transition proceeds remains unknown at this stage and warrants further investigation.

In summary, we have explored the organization of inorganic nanorods at the water−air interface using Langmuir−Blodgett technique. The pressure-induced isotropic-2D nematic-2D smectic-3D nematic phase transition as well as common textural defects in 3D nematics have been directly examined using TEM. Providing suitable surface passivation chemistry, this technique should be generally applicable to other nanorod systems such as CdSe, Fe, Au, and Cu, which promise interesting, tunable collective physical properties and functional 2-dimensional nanodevices.

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