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|  | Experiment title: Self-organization of CdSe/CdS nanorod membranes at the toluene/air interface | Experiment number: SC-3537 |
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| Names and affiliations of applicants (* indicates experimentalists): F.T. Rabouw* [1], F. Pietra* [1], J.L. Peters* [1], J.G.M. Ligthart* [1], A.V. Petukhov* [2], D.A.M. Vanmaekelbergh [1] [1] Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Princetonplein 1, 3584 CC Utrecht, The Netherlands [2] Physical and Colloid Chemistry, Debye Institute for Nanomaterials Science, Padualaan 8, 3584 CH Utrecht, The Netherlands | | |

Report:

We performed GISAXS measurements on the self-organization of colloidal CdSe/CdS nanorods (NRs; diameter ~5 nm; length 15-50 nm) at the toluene/air interface. For the self-organization experiments we used a large area teflon cell in which 23 mL of immiscible liquid diethylene glycol (DEG) was loaded. On top we deposited 4 mL of NR dispersion in toluene. Self-organization was induced by toluene evaporation at 50°C and under gentle N₂-flow. Complete evaporation of the toluene took about 60 minutes per sample. The toluene/air interface drops during toluene evaporation. To keep it well-aligned with the X-ray beam at grazing incidence, we compensated for solvent evaporation (~25 µm/min) by injecting additional DEG in the immiscible liquid substrate layer using a computer-driven syringe (injection speed controlled through manual feedback from outside the hutch). With this method we were able to follow NR self-organization at the toluene/air interface until complete evaporation the toluene solvent.

The goal of our experiments was to test and further investigate the NR self-organization model that we have proposed based on earlier experiments (session SC-3300, Oct 2011) [1,2]. In brief, we had observed that the orientation under which the NRs self-assemble can be tuned to upright (longer NRs, higher concentration) or lying flat (shorter NRs, lower concentration). We have attributed the upright orientation to clustering of NRs in the bulk solution (which is more prominent for long NR and at high concentrations) prior to adsorption at the liquid/air interface, whereas the single non-clustered NRs (short or low concentration) adsorb in lying orientation.

During this set of experiments the brighter and narrower X-ray beam of the upgraded ID-10 beamline has allowed us to follow the self-organization process at a higher time resolution and with less domain averaging. Our new results seem to confirm the model that we had proposed previously and to discover new details of the assembly and the (re)orientation process. In particular, we have seen the formation dynamics of the lying structure for a low concentration of NRs to occur in a layer-by-layer fashion [see the example described below (Fig. 1)], and the presence of preformed clusters in the bulk solution for a higher concentration of NRs. Furthermore, we have now been able to follow the contraction of the NR superstructure during the solvent evaporation. Finally, we have seen double diffraction peaks that may indicate the occurrence of fractionated

crystallisation [3] in which a polydisperse sample of NRs phase separates into an ordered array of thin NRs and one of thicker NRs. We are currently working on the data analysis.

To illustrate the results, in Figure 1a we show the GISAXS pattern recorded at 1 min 50 s after the beginning of the self-organization process (initiated by depositing the NR dispersion on top of the pre-heated liquid DEG substrate). We clearly observe two “Bragg rods” at $q = 0.71 \text{ nm}^{-1}$ evidencing in-plane structures with a periodicity of $a = 8.9 \text{ nm}$. We attribute these to monolayers of NRs lying flat on the interface side-to-side (Fig. 1c). Indeed, the periodicity of $a = 8.9 \text{ nm}$ is consistent with NRs of 4.3 nm diameter separated by two layers of organic capping ligands. Upon closer inspection of the pattern (Fig. 1a) we see two additional weaker Bragg rods at $q = 0.15 \text{ nm}^{-1}$. We attribute these features to head-to-tail ordering of the lying NRs (periodicity $b = 41 \text{ nm}$, corresponding well to the NR length of 37 nm + two layers of ligands).

The pattern evolves into the one shown in Figure 1b. Here we see that the prominent Bragg rods from Fig. 1a ($q = 0.71 \text{ nm}^{-1}$) have narrowed to a pair of intense peaks at an angle of 27° from the horizon. The distance from the origin of the reflected beam to these peaks corresponds to $q = 0.83 \text{ nm}^{-1}$. In addition, there is a third intense peak at a scattering vector of $q = 0.83 \text{ nm}^{-1}$ normal to the horizon. This pattern is characteristic of hexagonal order in the direction normal to the liquid/air interface. Specifically, the three intense peaks are (10) reflections on a hexagonally ordered structure with lattice constant $a = 8.7 \text{ nm}$, a value very close to the $a = 8.9 \text{ nm}$ found for the monolayer structure in Fig. 1a,c. We conclude that with the evolution of pattern a into pattern b we observe in real-time the formation of a multilayer of lying NRs (Fig. 1d) by addition of additional NRs to the initial monolayer (Fig. 1c).

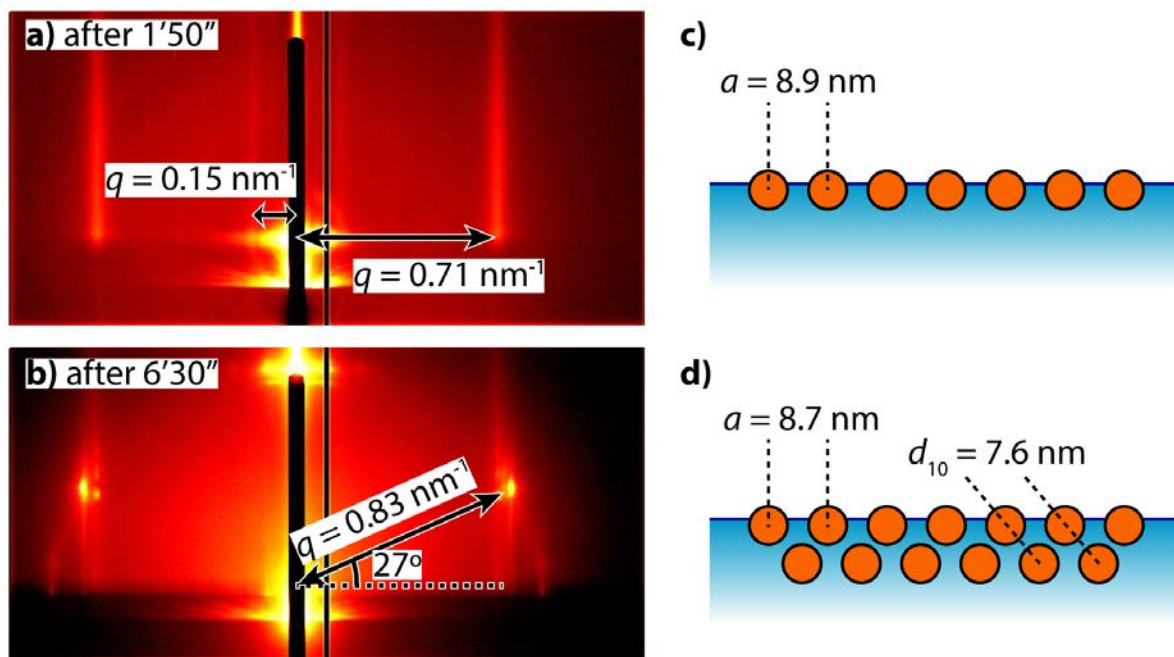


Figure 1 | GISAXS patterns (a,b) and cartoons (c,d) representing the dynamics of the self-organization of CdSe/CdS nanorods at the liquid/air interface. See text for description.

Note the fine splitting of the three intense peaks in Fig. 1b, which was not possible to resolve in our previous experimental session. We currently attribute the splitting to fractionated crystallisation [3]. As shown in this example above, new insights into the self-assembly process can be gained from the results of the present experiment, which are currently being analyzed in more detail. A publication based on these data is targeted.

Finally, we would like to thank Dr. Oleg Konovalov and Dr. Federico Zontone for their support.

[1] Experimental report SC-3300 (Oct 2011)

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[3] D.V. Byelov et al., *Langmuir* **2010**, 26, 6898-6901