ESRF	**Experiment title:** Nucleation and growth of binary nanocrystal superlattices at solvent-vapour and solvent-solid interfaces	**Experiment number**: SC-3300
Beamline: ID-10B	**Date of experiment**: from: 28-09-2011 to: 04-10-2011	**Date of report**: 28-02-2012
Shifts: 18	**Local contact(s)**: Oleg Konovalov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

W.H. Evers*, F. Pietra*, F.T. Rabouw*, D. Byelov*, A.V. Petukhov, D.A.M. Vanmaekelbergh

Debye Institute for Nanomaterials Science,

Utrecht University

Report:

We performed GISAXS measurements on the self-organization of colloidal nanocrystals (NCs) at the liquid/air interface. A large area teflon cell is used, in which 8 mL of immiscible liquid diethylene glycol (DEG) was loaded. On top we deposited 4 mL of NC dispersion in toluene. Self-organization was induced by toluene evaporation at 50°C and under gentle N_2-flow. Complete evaporation of the toluene took about 30 minutes per sample. The liquid/air interface drops during toluene evaporation. To keep it well-aligned with the X-ray beam, we compensated for solvent evaporation (~40 μm/min) by mechanically rising the sample stage. However, we found that the X-ray beam (incident under grazing incidence) hit the wall of the sample cell within a few minutes, after which we could no longer follow the dynamics of self-organization. Therefore we had to change the measurement protocol to keep the liquid/air interface aligned with the X-ray beam during solvent evaporation. After a number of trial-and-error attempts, a new method is developed. Using a computer-driven syringe we were injecting additional DEG in the immiscible liquid layer on the bottom. In this way we were able to follow NC self-organization at the liquid/air interface until complete evaporation the toluene solvent.

One of the systems investigated consisted of CdS nanorods (NRs; 5 nm thick, 15 – 50 nm long) with a small CdSe seed. Under the right conditions these NRs are known to self-organize into stacks of membranes, with each membrane consisting of aligned NRs with 2-dimensional hexagonal order. Using a combination of in-situ GISAXS and ex-situ transmission electron microscopy (TEM) we were able to prove that the structures observed in TEM form at the liquid/air interface. Furthermore we found that the orientation in which NRs adsorb to the liquid/air interface depends on the NR length: short NRs adsorb parallel to the interface, whereas long NRs adsorb with their long axis perpendicular to the interface. This length dependence of NR orientation was observed both in the GISAXS patterns and in the TEM images, as shown in Figure 1.

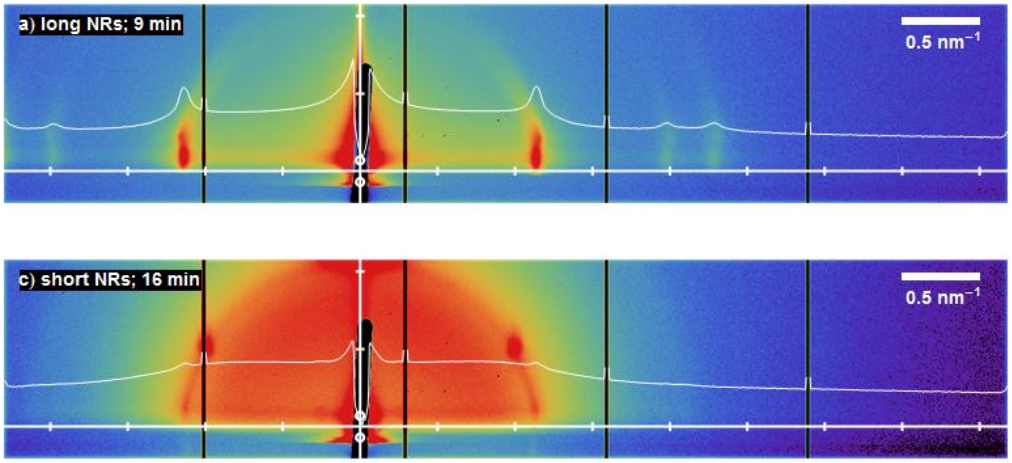

Figure 1 | GISAXS pattern (a) and TEM image (b) of the final structure formed by self-organization of long (50 nm long) NRs. GISAXS pattern (c) and TEM image (d) of the final structure formed by self-organization of short (15 nm long) NRs.

We were also able to partly follow the dynamics of the self-organization process. Figure 2 shows GISAXS patterns recorded on a sample with medium-length NRs (21 nm long), at different stages of the self-organization process: (a) 6 min, (b) 7 min, and (c) 8 min after the beginning of solvent evaporation. We see a clear proof that the NRs initially adsorb with their long axis parallel to the liquid/air interface. Between 6 min and 8 min after the beginning of solvent evaporation they reorient into an upstanding structure, with the long NR axis perpendicular to the interface.

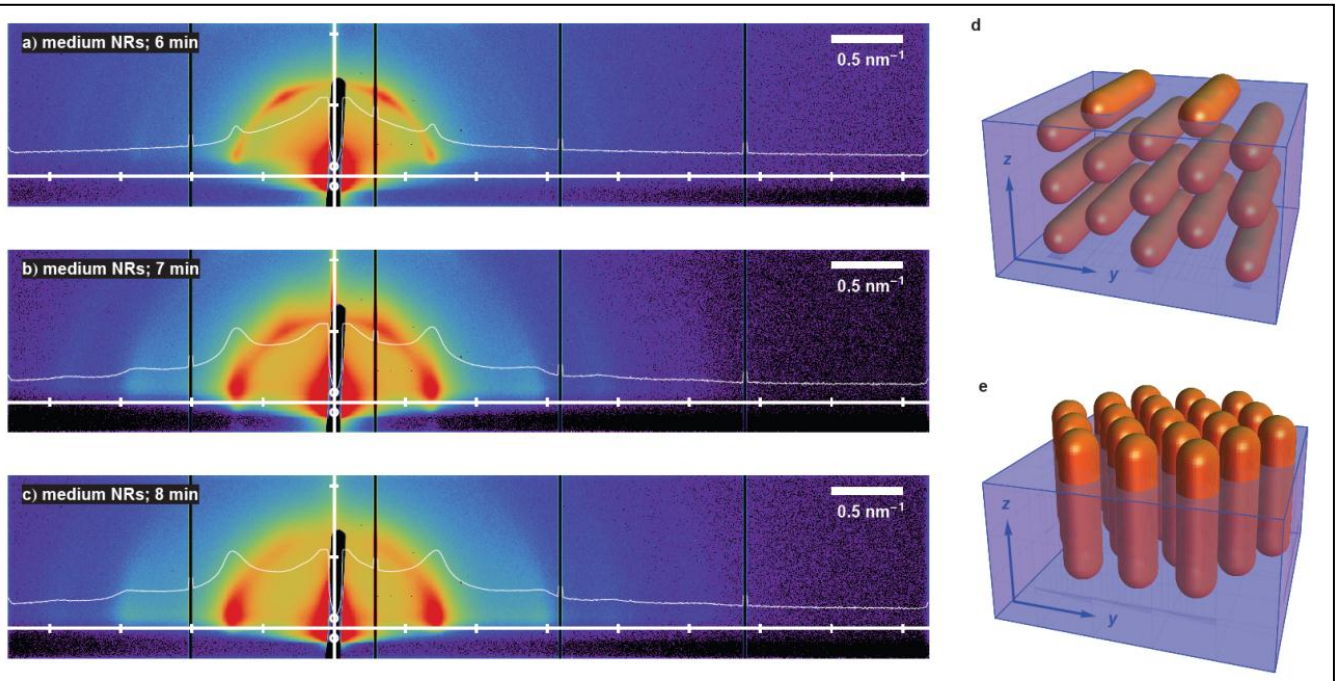

Figure 2 | GISAXS patterns of the NR superstructures at the liquid/air interface (a) 6 min, (b) 7 min, and (c) 8 min after the beginning of solvent evaporation. Pattern (a) corresponds to NRs lying down as in schematic (d). Pattern (c) corresponds to the final structure of NRs standing up as in schematic (e). Pattern (b) is an intermediate, originating from a combination of structure (d) and structure (e).

We are now preparing a manuscript on the self-organization of CdSe/CdS NRs at the liquid/air interface. In addition to reporting the results summarized above, we propose a mechanism for NR self-organization at the liquid/air interface. Our mechanism can explain the NR length dependence of the structures observed.