	Experiment title: Structure and Kinetics of Nanoparticle Self-Assembly at Liquid Interfaces	**Experiment number:** **SI-1596**
Beamline: ID10B	**Date of experiment:** from: September 26, 2007 to: October 01, 2007	**Date of report:** 01.03.2008
Shifts: 12	**Local contact(s):** **Dr. Oleg KONOVALOV**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
Sergej Kutuzov *, Kerstin Schindler *, Adriana Mihut *, Jiri Novak*, Oleg Konovalov *.

Report:

Adsorption of certain micrometer-and nanometer-sized particles at the liquid interfaces leads to the reduction of the interfacial energy and, thus, is thermodynamically favorable for the liquid interfaces with originally high tensions. Self-organization of different types of nanoparticles at the oil-water or at the air-water interfaces was studied *in-situ* using time-resolved GISAXS. We used the home-synthesized CdSe/TOPO nanoparticles of the different core (CdSe) sizes ranging from 2 to 6 nm with organic ligands (TOPO: tri n-octyl phosphine oxide). The size dependent kinetics of the assembly process and the formation of the interfacial aggregates were followed.

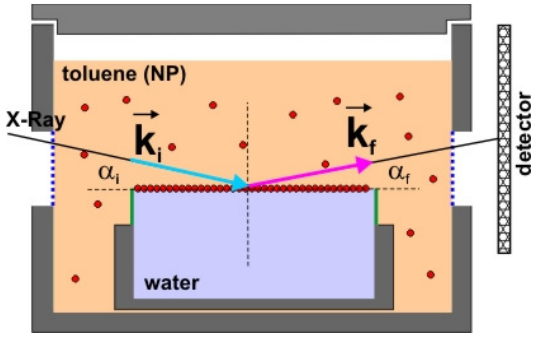

Figure 1. Schematic view of the GISAXS experimental setup.

<u>CdSe/TOPO nanoparticles at liquid interfaces</u>

A flat toluene-water interface was realized in a home-built chamber (Figure 1), consisting of two coaxial rectangular troughs. The inner trough was filled with the toluene-saturated ultrapure water, the outer trough with the colloidal solutions of the CdSe/TOPO nanoparticles in toluene. The GISAXS patterns were collected every 15-20 min. With time the particle array becomes denser and the interparticle spacing more regular. In Figure 2 dominated the scattering intensity arising from the spatial distribution of the particles at the

interface. The position of the Bragg-Peak at $q_y = 0.146$ Å^{-1} corresponds to an interparticle spacing of d = 4.3 nm. This is in good agreement with the size distribution of the nanoparticles used. In the case of the 2.3 nm nanoparticles, we only found diffuse scattering from the particles at the interface. Any ordered assembly of the 2.3 nm particles however was not observed (Fig. 3). This may be explained by the fact that the small particles undergo desorption from the interface more often than the larger particles. Due to this has a monolayer array from the 2.3 nm particles no long-range order.

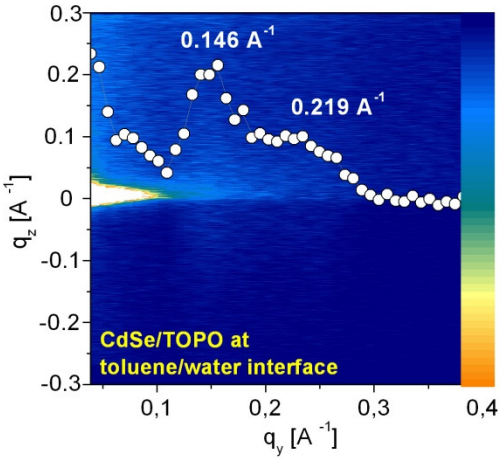

Figure 2. GISAXS pattern from 4.6 nm CdSe assembly at a planar toluene-water interface after 145 min. from beginning of the experiment.

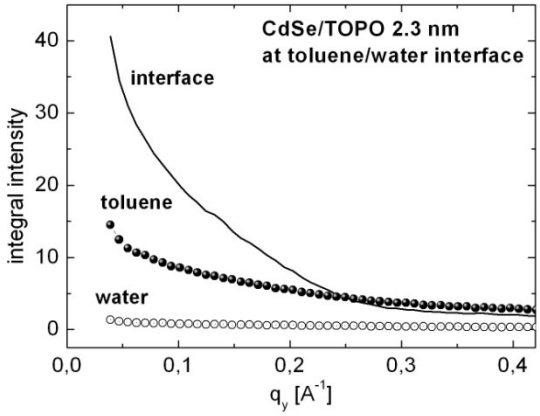

Figure 3. GISAXS scans along of q_y on the 2.3 nm CdSe/TOPO nanoparticles at the toluene-water interface.

Langmuir-Blodgett (LB) manipulation and *in-situ* GISAXS

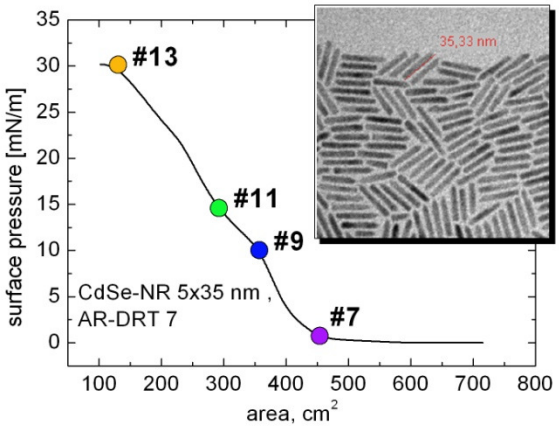

Figure 4. π-A-Isotherm (T=25°C) of the 5x35 nm CdSe/TOPO NRs at air-water interface.

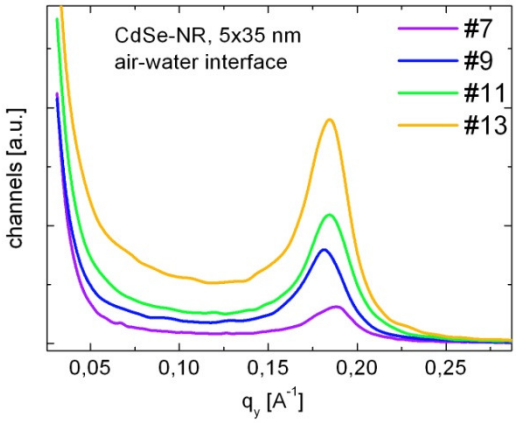

Figure 5. In-situ GISAXS data on the CdSe/TOPO NRs 5x35 nm at air-water interface (see Fig. 4).

Using of the Langmuir film balance it is possible to produce different states of close packed interfacial arrays by continuous compression of the nanoparticles at the air-water interface. The best results were found with the rod-shaped (NR) CdSe/TOPO nanoparticles. Figure 4 shows the two dimensional π-A phase diagram of the 5x35 nm CdSe/TOPO nanorods, recorded at room temperature. The π-A phase diagram of the CdSe nanorods shows gas-, liquid- and solid-like phases. This is similar to the phase diagrams of amphiphilic molecules. The GISAXS patterns, collected simultaneous with the compression of the arrays of the nanoparticles, are presented in Figure 5. With decreasing area of the 2D-film, the area under the Bragg-peak

increases. This points to the fact, that the number of the coherently scattering clusters in the beam increases. TEM measurements confirm the ordered structure of the densely packed ultrathin monolayer of the nanorods (inset in Fig. 4). The position of the Bragg-peak at q_y = 0.17 $Å^{-1}$ corresponds to the interparticle spacing of around 4 nm.

In Fig. 6 and Fig. 7 are the LB and related GISAXS experiments with the 4 x 30 nm CdSe/TOPO nanorods show. The previous conclusions are relevant for this type of particles, too.

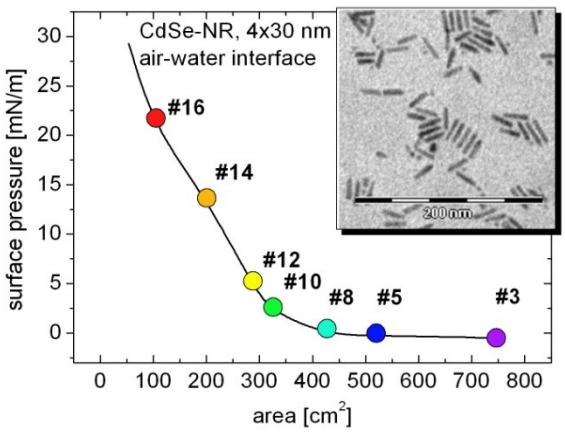

Figure 6. π-A-Isotherm (T=25°C) of the 4x30 nm CdSe/TOPO NRs at air-water interface.

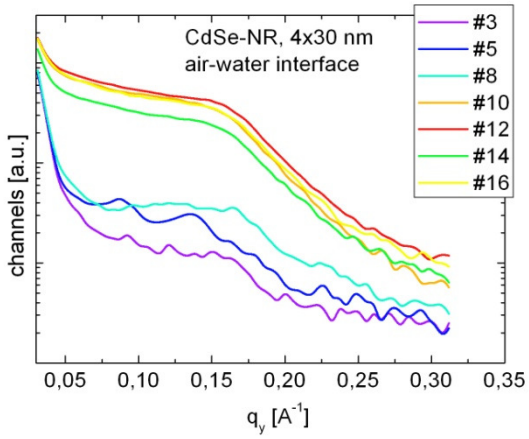

Figure 7. In-situ GISAXS data on the CdSe/TOPO NRs 4x30 nm at air-water interface (see Fig. 6).