

Technical Report:

Combined real-time in-situ X-ray reflectivity (XRR) and Grazing incidence small angle x-ray scattering (GISAXS) measurements at the liquid-air interface during the self-assembly of coupled organic-inorganic nanostructures (COIN) have been carried out at beamline ID10 at ESRF, Grenoble, France at room temperature. The XRR and GISAXS patterns were collected using a linear Mythen and a two-dimensional (2D) Pilatus 300K detector, respectively. The energy of the monochromatic beam was set to 10 KeV ($\lambda = 0.124$ nm) during all the measurements. The size of the beam was focused to $14 \times 200 \mu\text{m}^2$ for our experiment to illuminate x-ray photons at the middle of the flat air-liquid meniscus inside a home-made sample cell (30 mm along the beam) with kapton windows ($40 \times 20 \text{mm}^2$) at two opposite walls. The Mythen detector was kept closer to the cell for liquid surface alignment and to collect specular reflectivity data. The 300K Pilatus was placed at 990 mm away from the sample/goniometer center along the beam in order to get the highest resolution within the q-range of interest for nanoscopic superlattice information.

We have spread $\sim 150 \mu\text{l}$ of native oleic acid (OA) coated PbS nanoparticles onto the liquid (acetonitrile) surface and waited for half an hour to stabilize the NPs. Then we have injected the small organic semiconductor molecules (OSC) dissolved in hexane/DMSO at the bottom of the liquid cell by a syringe pump, controlled by SPEC commands from the outside of the hutch and monitored the ligand exchange procedure over three hours. We repeated the in-situ formation procedure of several COIN samples (PbS+TTFDA/CuTAPc) with varying size and concentration of NPs and of ligands at the air-liquid interface.

We have collected the scattering data before and after ligand exchange and also from the very beginning of the chemical reaction during ligand exchange. The in-situ real-time GISAXS patterns of these films were taken at incident angles of 0.15, 0.19 and 0.23 degree (just below, at and above the critical angle of the sample) after aligning with the liquid interface by the Mythen detector at the half-cut position. We have observed nice in-plane and out-of-plane scattering patterns in GISAXS images and their relative positional shift during the reaction. (Fig 1). The ordered correlation peaks along in- and out-of-plane directions of the momentum vector transform in GISAXS/XRR are due to constructive interference among the COIN network which confirms nanoparticle superlattice formation. With the carried-out experiments we will determine the structural changes of the samples before and after ligand exchange and confirm the counter ligand exchange procedure to form COINs. We are presently in the process of analyzing in depth the structural changes and the associated kinetics. Due to the complexity of the system this will take some time, but based on what we could do so far, the experiment has been successful, and is very likely going to lead to a publishable result. Finally, we would like to emphasize the professional support provided by the local contact (Oleg Kononov).

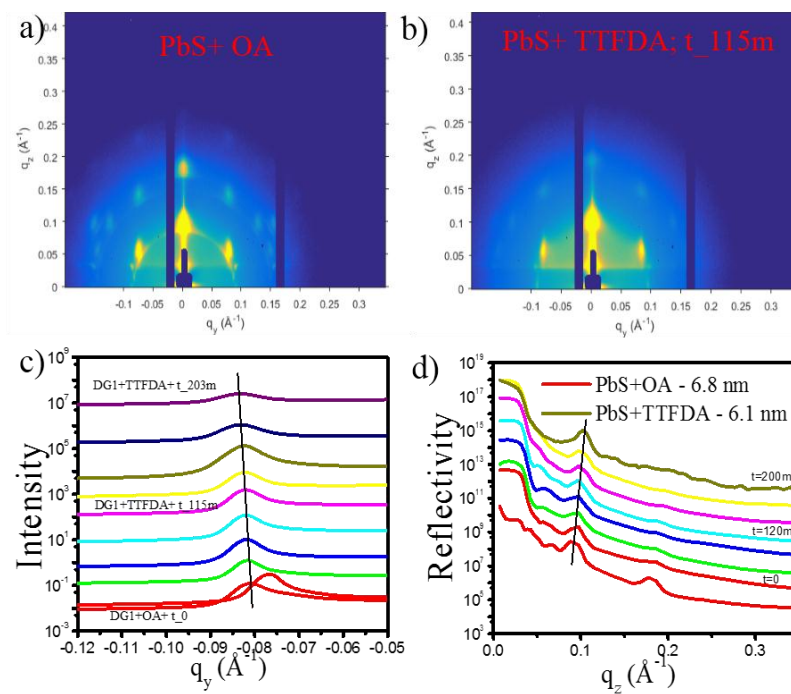


Fig. GISAXS pattern of a) OA coated PbS NPs and b) PbS-TTFDA COIN after 115 minute of Ligand exchange reaction. c) Scattering Intensity profile along q_y at $q_z = 0.055 \text{\AA}^{-1}$ at different time interval. c) XRR data at different time of the reaction.