ESRF	**Experiment title:** Nanoparticles at liquid-liquid interfaces: organization and synthesis	**Experiment number**: SC2224
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Report:

Experiment SC2224 consisted of two parts. In the first part we investigated the organization of gold nanoparticles at the water/tetradecane interface in the context of emulsion stabilization by nanoparticles. In the second part, we investigated the synthesis of metal nanoparticles at the water/toluene interface.

For the X-ray studies at the liquid-liquid interface a specially designed LB-trough was mounted on an active anti-vibration system. The energy of the monochromatic beam was set to 21.9 keV (wavelength λ=0.057nm) to allow the x-ray beam to pass through the upper liquid (toluene here). Both reflectivity and in-plane scattering data were collected from the oil-water interface. Two thin silicon wafers of equal heights were used near the entry and exit X-ray windows of the Langmuir trough to anchor the oil-water interface. In this setup, the X-ray intensity reduces by a factor of 0.14 as the 21.9 keV beam passes through 7 cm of oil. All of the measurements were performed at room temperature with the incident beam size of 0.015 x 0.5 mm2 (V x H) defined using conventional slits. The position of the liquid-liquid interface was adjusted in order to minimize the meniscus by controlling the amount of water in the trough and monitoring the peak shape of the reflected beam at small grazing angle of incidence. Reflectivity data were recorded using a point detector and scattering data using a linear position sensitive detector (PSD).

Nanoparticles have the ability to stabilize emulsions (Pickering emulsions) and foams. In the present study we investigated the structure and properties of gold nanoparticles at the oil/water interface on a specially designed LB-trough using X-ray reflectivity and diffraction. Both reflectivity (XRR) curves and in-plane scattering data (GIXD, Figure 1) were recorded as a function of surface pressure at ID10B. From the XRR measurements one can see that the particles form a monolayer at the oil/water interface and below a pressure of 25mN/m the reflectivity curves are almost identical as the thickness of the layer stays constant. At higher surface pressures, the particle layer is buckled, which leads to an apparent higher layer thickness. GIXD measurements indicate that the interparticle distance decreases with increasing surface pressure and the in-plane order disappears as soon as the nanoparticle layer buckles. The buckling of the interfacial layer is fully reversible and the expansion of the compressed layer leads again to a well ordered monolayer. In order to verify the experimental results and to precisely determine the interface-particle and particle-particle interaction potentials we have done model calculations by Monte-Carlo simulation using a hard sphere with a soft shell as model particles and a classical surface-particle interaction potential based on wetting energies. The Monte-Carlo simulations (Figure 1b) perfectly agree with the experimental measurements and this work will be submitted for publication in March 2008.

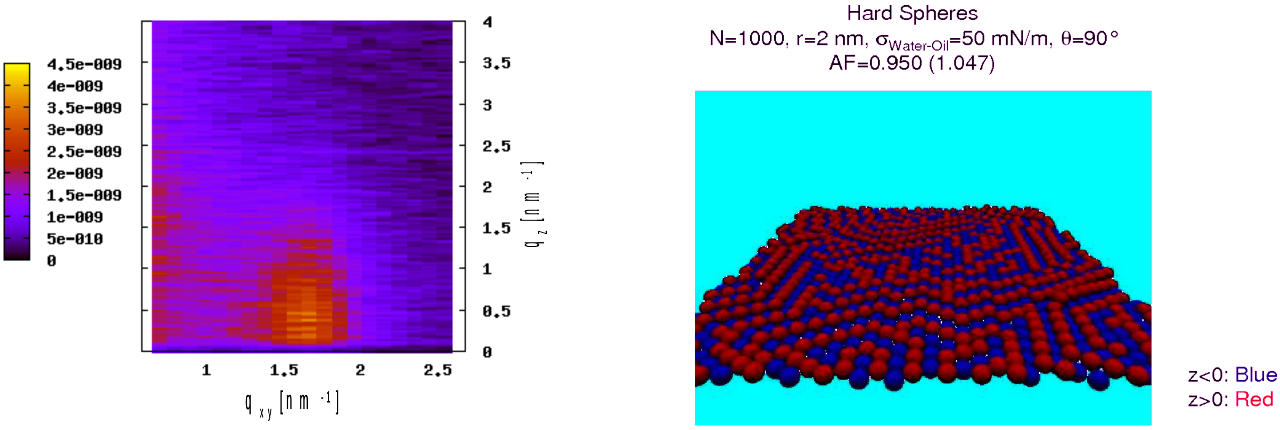


Figure 1. Grazing incidence scattering data from gold nanoparticles at the water/tetradecane interface (left). Monte-Carlo simulation results at a high surface coverage consistent with the data (right).

Microscopic measurements that provide direct information in nanometer length scales are essential to obtain a proper understanding of the interfacial reactions that form nanostructured materials. The synthesis of gold nanoparticles through a reduction reaction has been followed by x-ray reflectivity and grazing-incidence scattering. The analysis of the x-ray reflectivity and scattering data reveals a complex organization. The nanoparticles have a diameter of about 12 Å, similar to Au-55 nanoparticles, with about an 11 Å organic layer. They are organized in "clusters" at the water-toluene interface. Each cluster consists of 13 nanoparticles with an in-plane cluster-cluster separation of 180 Å. The electron density profile of the monolayer of these clusters exhibits three layers of nanoparticles as a function of depth that evolves with time.

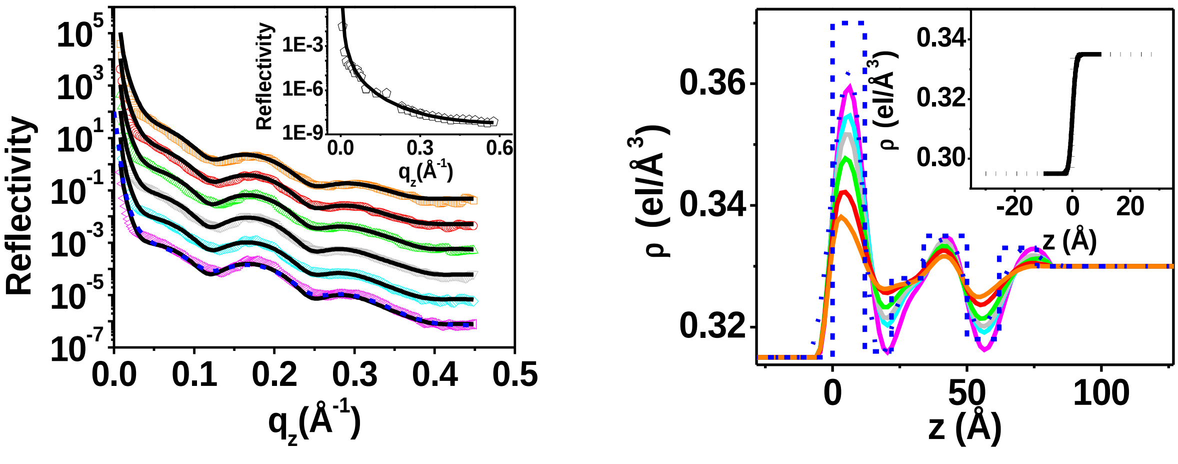
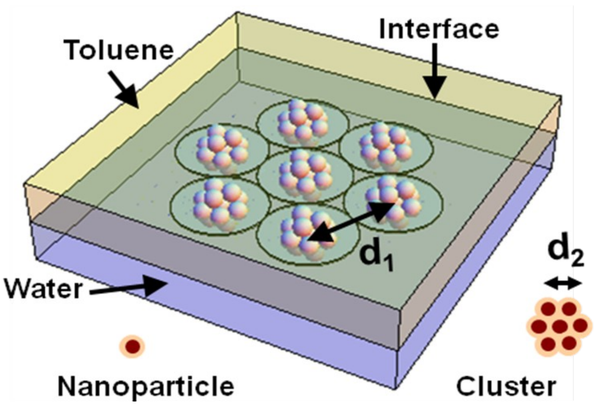


Figure 2. (a) Variation of reflectivity and fits as function of qz after initiation of reaction (Pink-194 min, Light Blue-224 min, Grey-253 min, Green-283 min, Red-312 min, Orange-364 min)and the fits (Solid lines). The reflectivity (Dashed line) generated from the simple box model is also shown. Inset: The reflectivity data (Symbol) from Toluene-water interface and its fit (Solid line). (b) The Electron Density Profiles (EDPs) (colours same as (a)) as function of depth obtained from fitting. Positions of the two upper peaks as measured from water interface (dashed line) 70 Å and 40 Å are marked. A simple model without (Dashed line) and with roughness convolution (Solid line, Blue) are also shown.

Reflectivity measurements (shown in Figure 2a) confirm the presence of three layers in the electron density profiles (shown in Figure 2b) with the lower two layers showing slightly less than the calculated values probably due to partial coverage. The presence of low electron densities in between these peak values confirms the monodispersity of these aligned clusters. The higher electron density of the top peak indicates the presence of individual gold nanoparticles with these clusters. As the reaction progresses, the number of individual Au nanoparticles reduces. The presence of an organic layer at the water toluene interface lowers the interfacial tension as seen in diffuse scattering measurements. It seems that the presence of the clusters and the associated organic layer hinders the progress of the reaction unless the interface is disturbed by surface pressure and/or vibrations. The information about the formation and ordering of gold nanoparticles formed at the interface, which comes out from reflectivity and diffuse scattering measurement is shown schematically in Figure 3.



our model that involve 13 member cluster of organic capped gold nanoparticles at toluene-water interface are shown along with the two dimensional schematics of individual nanoparticle and the cluster.

Reference Details:

"Formation and Ordering of Gold Nanoparticles at the Toluene-Water Interface." Milan K. Sanyal, Ved V. Agrawal, Mrinal K. Bera, K. P. Kalyanikutty, Jean Daillant, Christian Blot, S. Kubowicz, Oleg Konovalov and C. N. R. Rao, J. Phys. Chem. C **112**, 1739 (2008).

"Gold nanoparticles at the liquid-liquid interface" S. Kubowicz, M. A. Hartmann, J. Daillant, M. K. Sanyal, V. V. Agrawal, C. Blot, O. Konovalov, H. Möhwald, to be submitted (March 2008).