



	Experiment title: Synthesis of nanoparticles at the oil/water interface	Experiment number: SC2565
Beamline:	Date of experiment: from: 11 February 09 to: 17 February 09	Date of report: 26/02/09
Shifts:	Local contact(s): O. Konovalov	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Daillant* Jean, Carrière* David, Blot* Christian, LIONS, CEA Saclay Sanyal* Milan / Surface Physics Division, Saha Institute of Nuclear Physics, Kolkata, India		

Report:

The experiment took place from February 10th to 17th. Therefore, this report does not contain a full analysis of the results.

The aim of the experiment was to investigate chemical reactions leading to the formation of nanoparticles at the oil-water interface. Two systems were mainly investigated:

1. Formation of CuS nanoparticles at the water – toluene interface. Na₂S in water was brought in contact with toluene and copper cupferronate was added to the toluene phase at the beginning of the reaction.
2. Formation of Manganese oxide at the water - 2-ethyl hexanoic acid interface. manganese 2-ethyl hexanoate in 2- ethyl hexanoic acid is brought in contact with a 0.1M NaOH solution in water.

The experiment was performed at ID10B using and energy of 22keV. A home made cell consisting of a glass trough partially coated with teflon inserted in a teflon coated stainless steel container with thin teflon windows was specially designed for this experiment and worked perfectly well. A delicate point is to obtain a very flat meniscus for grazing incidence studies with a grazing angle of incidence as small as 0.02deg. This is achieved by adjusting the water level (using a very precise syringe pump) between two very thin silicon wafers mounted close to the cell windows.

As time resolution is an important issue when studying chemical reactions, a first aim of the experiment was to test the possibility of using a 2D detector in order to record the scattered intensity in a GISAXS like geometry. We initially planned to reexamine the first stages of synthesis of gold nanoparticles using this setup [1]. The background was however too high with this kind of geometry. We therefore mainly used a point detector with narrow collimating slits to record reflectivity curves giving access to the normal distribution of matter during the reaction and diffuse scattering in the plane of incidence which will give access to in-plane correlations and interfacial tension.

The concentrations were adjusted in order to obtain characteristic reaction times of approximately 2 hours which could be followed by x-ray scattering. Two examples of reflectivity curves are given in Fig. 1.

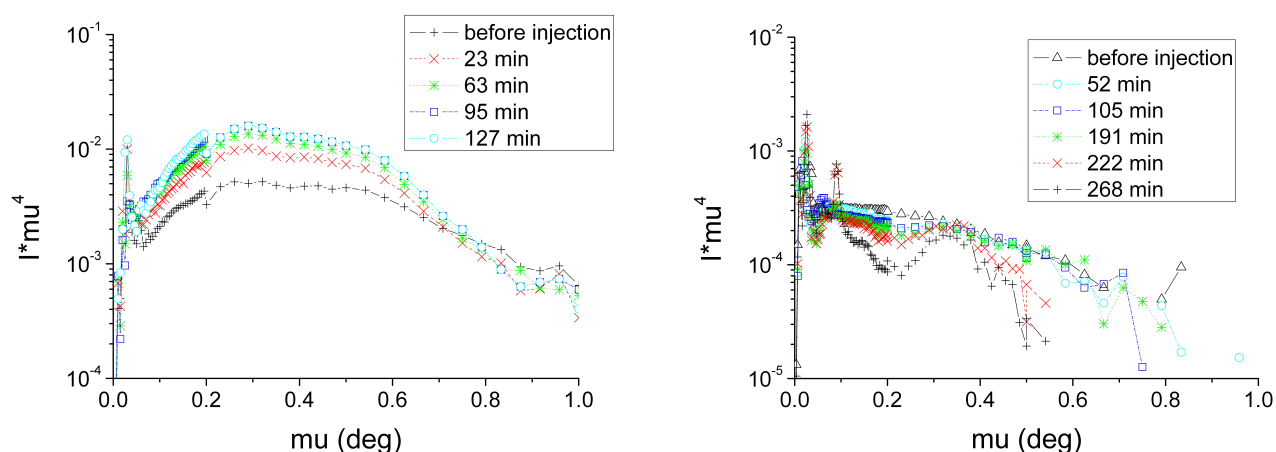


Fig. 1: Left, growth of CuS nanoparticles upon reaction of Na_2S in water with copper cupferrate in toluene. Right, growth of MnO nanoparticles upon reaction of NaOH in water with manganese 2-ethyl hexanoate in hexanoic acid.

In both systems, a systematic evolution of the reflectivity curve is observed as the reaction takes place. A full analysis of the data will now be performed, but it can already be concluded that the sizes and growth mechanisms of the CuS and MnO nanoparticles are clearly different. As a first approach, the CuS reflectivity curves are consistent with nanoscale bilayers at the interface, with little roughness: oil ($0.29 \text{ e}^-/\text{\AA}^3$), a first layer of 50 \AA with higher electron density ($0.31 \text{ e}^-/\text{\AA}^3$), a particle rich layer of 60 \AA ($0.41 \text{ e}^-/\text{\AA}^3$), water ($0.33 \text{ e}^-/\text{\AA}^3$). The MnO system shows a higher induction time before reaction, and is essentially described by a 200 \AA thick monolayer ($0.35 \text{ e}^-/\text{\AA}^3$) with higher roughness (12 \AA).

An unexpected feature has also been observed: in the case of MnO, an evolution of the reflectivity curve is observed at small angles even prior to injection of the metal cation, i.e. for the simple NaOH in water / oil interface. It is interpreted as a structuration of the oil/water interface due to partial conversion of oil into surfactant (sodium 2-ethyl hexanoate).

The success of this experiment already encourages application for the next semester to examine other challenging issues.

For MnO, in particular, we have designed chemical conditions that allow growth of nanoparticles that either remain adsorbed at the interface, or are transferred into either solvent (oil or water). In the first case, we will search for any correlation between the spontaneous structuration of the oil/water interface prior to reaction, and the size and assembly of the particles at the end of the reaction. In the latter case, probing the interface will provide a “snapshot” of the nucleation and early growth of the particles.