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|  | Experiment title: Core-shell nanoparticle self-assembly at liquid-liquid interfaces: a structural study by high-energy X-ray reflectivity | Experiment number: SI-2359 |
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Report:

We have demonstrated the application of high-energy X-ray reflectivity (HE-XR), already recently used to characterize the adsorption of silica NP monolayers at buried liquid-liquid interfaces by the staff of ID15A, as a unique tool to investigate in-situ the vertical positioning and the inter-particle spacing of composite NPs with an iron oxide core whose surface is covered by a soft repulsive poly(ethylene glycol) (PEG) shell.

We have designed a custom-built polyacetate liquid sample cell which allowed the creation of a macroscopically flat interface ($2 \times 8 \text{ cm}^2$) between purified n-decane and aqueous suspensions of the core-shell nanoparticles. The interface was pinned at the edge of a trough and its level could be accurately controlled by a precision syringe pump connected to the container. The liquid cell had two 1mm thick entry and exit windows for the x-ray beam in reflectivity mode (see Figure 1 for a schematic representation). Roughly 8mL of nanoparticle suspension and 50mL of decane were necessary for each experiment.

We devoted particular attention to the investigation of the in-situ, time-resolved adsorption studies of nanoparticles with several core size and polymer molecular weight and architecture.

After formation of an air-water interface, decane was carefully poured on top of the water interface to create a buried liquid-liquid interface. Due to diffusion, the nanoparticles moved towards the interface where they adsorbed as a monolayer whose properties were probed by HE-XR performed with a beam of energy 70 keV and using a scintillator-based point detector.

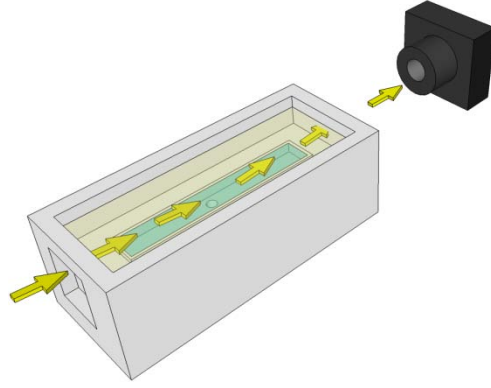


Figure 1. Schematic representation of the sample cell and experimental geometry.

We initially investigated the adsorption of particles with a core diameter of 6.5 ± 0.8 nm stabilized by linear PEG with 5000 D molecular weight. Reflectivity curves were taken every 20 minutes. As the nanoparticles adsorb, the intensity of the reflected beam increases and oscillations in the reflectivity curve develop which are characteristic of the particle size, of their vertical position relative to the interface and of the inter-particle separation at the interface. Fig. 2 shows the measured Reflectivity R normalized by the Fresnel Reflectivity R_f at different stages of the experiment (curves scaled for clarity). (\circ) 12h after interface formation; (\triangle) 10h ($\times 10^{-1}$); (∇) 6h ($\times 10^{-2}$); (\diamond) 3h ($\times 10^{-3}$); (\triangleright) 2h ($\times 10^{-4}$); (\square) bare water/decane interface ($\times 10^{-5}$). The symbols are the experimental data, while the solid lines are fits obtained by using a physical model which takes into account the spherical shape of the particles. The fitting was done in collaboration with Davide Calzolari who was previously part of the ID15A team.

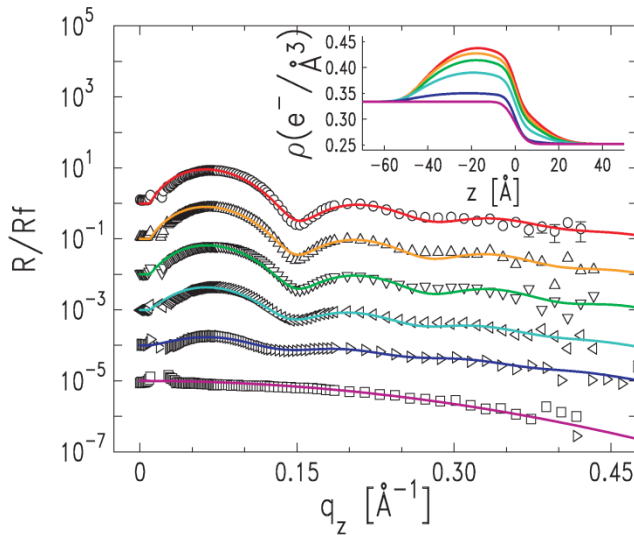


Figure 2. Normalized reflectivity curves for the 6.5 nm iron oxide particles. The inset shows the corresponding electron density profiles across the water/decane interface. From the maximum of these curves, the

We observe that the oscillations and the strength of the signal increase with time and thus with the number of particles residing at the interface. In the inset of the figure we report the electron density profiles $\rho(z)$ corresponding to the reflectivity model fits presented in the main figure. The increase of the $\rho(z)$ peak amplitude with time is a signature of the increasing number of nanoparticles adsorbed at the interface, while the peak location indicates the average particle position relative to the water/hexane interface, from which an effective contact angle can be calculated. From these curves we deduce that the particles, hydrophilic in nature, are mainly residing on the water side of the interface, with a contact angle of approximately 60° after saturation of the interface (12h).

We subsequently moved to the study of particles with 8.2 ± 1.2 nm cores and PEG of different molecular weight and architecture. We measured particles with linear PEG and molecular weight 5500 Da (type A), with linear PEG and molecular weight 2700 Da (type B) and with dendritic PEG with 2500 Da molecular weight (type C). The normalized reflectivity curves, scaled for clarity) after several hours of adsorption of the three different samples are reported in Figure 3. (\circ) type A 3h after interface formation; (\square) type B 5h after interface formation ($\times 10^{-1}$); (\triangle) type C 3 h after interface formation ($\times 10^{-2}$). In the inset the corresponding electron density profiles are reported. From these data we can observe that the polymer architecture has only a limited effect on the average water immersion and interfacial contact angle of the particles, since in all cases we deduce contact angles around 30° , but that the presence of residual charge not screened by the short dendritic PEG can be responsible for a much slower particle adsorption and a lower particle density at the interface, as highlighted by the lower signal intensity for type C particles.

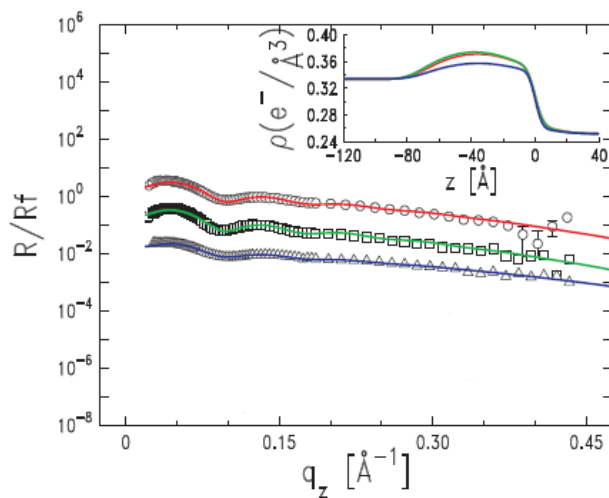


Figure 1. Normalized reflectivity curves for the 8.2 nm iron oxide particles stabilized by different polymers. The inset shows the corresponding electron density profiles across the water/decane interface.

From these data sets, we could also infer the inter-particle separation, and thus, by knowing the particle size, the coverage of the interface. Surprisingly we found that the inter-particle distance approaching interface saturation is significantly larger than the particle size in bulk, which is a strong indication of a deformation of the polymer shell surrounding the particles at the interface. This result can only be obtained by the HE-XR experiments and constitutes a novel finding which sheds new light on the behavior of complex, core-shell nanoparticles at buried liquid-liquid interfaces.