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Polymer and Colloid Highlights

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Adsorption and Microstructure of Core-Shell Nanoparticles at Liquid-Liquid Interfaces: An X-ray Reflectivity Study

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Self-assembly of nanoparticles (NPs) is becoming a common strategy to fabricate functional materials. In particular, NPs assembled at liquid-liquid interfaces retain the lateral mobility required to yield uniform monolayers, which can be cross-linked *in situ*[1] or deposited later onto solid substrates.[2] NPs with a solid core stabilized by polymer shells are particularly suited as building blocks because control on core size, polymer molecular weight and architecture gives ample flexibility to design the structure of the final assembly. We recently demonstrated that NPs comprising iron oxide cores, coated by an irreversibly bound shell of poly(ethylene-glycol) (PEG), adsorb strongly at water/*n*-decane interfaces and form full monolayers with a kinetics depending on bulk concentration and PEG molecular weight.[3] We have also recently carried out X-ray reflectivity experiments at buried, planar water/*n*-decane interfaces at the ID15A beamline of the ESRF in Grenoble which shed new light on core-shell NPs monolayers at interfaces. In particular, we have followed in real time the adsorption of iron oxide particles stabilized by linear PEG of 5kDa (L5) and 2.5kDa (L2.5) and by dendritic PEG of 2.5kDa (D2.5).[4] In accordance with macroscopic interfacial tension measurements, particles with linear PEG adsorbed faster compared to the dendritic ones. The position of the maximum of the electron density profiles coming from the NP cores allowed to resolve the particle position relative to the interface ('effective contact angle') and indicated that all particles are hydrophilic (mostly on the water side). The intensity of the peak is directly related to the number of adsorbed NPs, from which an inter-particle distance can be calculated assuming uniform hexagonal packing. Surprisingly, we found that core separation in a saturated linear PEG NP interfacial monolayer greatly exceeded twice the thickness of the PEG shell in bulk water. This implies strong deformation of the shell and the creation of a stretched 'quasi-2D' brush at the interface driven by the PEG surface activity, with a thickness matching our simple model. Dendritic PEG particles instead showed continuous densification as expected for NPs stabilized by rigid shells.

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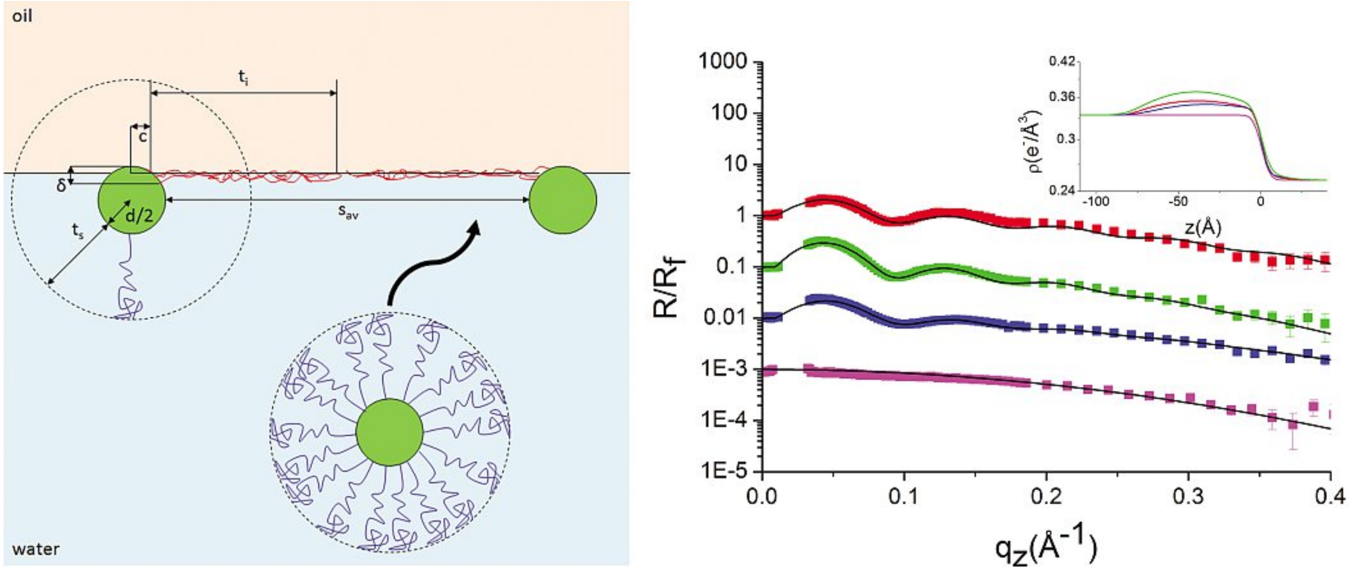

Fig. 1. (Left) Schematics of core-shell nanoparticles adsorbing at an oil/water interface. The particles have a solvated shell in bulk water, which deforms and flattens out upon adsorption. The thickness of such 'quasi-2D' shell determines the inter-particle separation in a full monolayer. The balance between shell solvation in the two fluids and its surface activity also determines the position of each particle relative to the interface (effective contact angle). (Right) Measured X-ray reflectivity profiles normalized by the theoretical Fresnel reflectivity for L5 (red), L2.5 (green) and D2.5 (blue) after 3h adsorption with corresponding fits (solid lines). Magenta: pure water/*n*-decane interface (curves are shifted for clarity). Inset: corresponding electron density profiles ρ(z). The peak of ρ(z) indicates the average position of the particle core centers.

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