Experimental report

17/02/2017

Proposal:	**8-03-876**	**Council:**	4/2016
Title:	Effect of nanoscale structure on interfacial energy		
Research area:	Materials		

This proposal is a new proposal

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Samples: Gold nanoparticle

Instrument	Requested days	Allocated days	From	To
D22	3	2	06/11/2016	08/11/2016

Abstract:

A bird's eye view of any folded protein shows a complex surface composed of hydrophobic and hydrophilic patches closely packed. To date little is known on the fundamental properties that such packing determines. Self-assembled monolayers (SAMs) provide a unique opportunity to generate model biological interfaces. When mixed SAMs formed on gold nanoparticle surfaces, nanoscele phase separation domains will form with sizes comparable to that of proteins. At this length scale, it has been found that the interfacial energy shows a non-monotonic dependence on composition. The sizes of hydrophobic and hydrophilic domains play an important role. We are able to tune the ligand shell organization on nanoparticle surfaces with suitable thermal processes like annealing while keeping the composition and sizes unchanged. Here we propose to use this model system to study the effect of mixed ligand gold nanoparticle surface structure on its interfacial energy. SANS is a inevitable tool since it can provide us information on organic shell around heavy gold cores, thus it can help better establish the structure-property relationship of nanoscale interfaces.

Mixed ligand nanoparticles with special morphology

Core-shell gold nanoparticles have been widely employed in numerous research fields like catalysis, electronics and biology. The easily tunable surface properties of AuNPs provide a versatile platform to investigate and control the surface properties of NPs. Our group has discovered that when a mixture of different thiolated ligands self-assembles at the surface of gold nanoparticles, nanometer-sized domains can form, which determine a large fraction of the nanoparticles' properties. Through simulation and experimental studies, we have established that the different morphologies result from the balance of the enthalpy and entropy of ligand packing and ligand chain conformational entropy. Nano-scale phase separation is thus determined by the sizes of nanoparticles, ligand chain length mismatches and ligand tail properties.

Synthesis and Characterization of Janus nanoparticles

To make Janus type mixed ligand nanoparticles, we synthesized nanoparticle coated with a mixture of 11-mercaptoundecanoic acid (MUA) and dodecanethiol (DDT). The ligand ratio was found to be MUA: DDT=1.8: 1 and the average diameter 4.0 ± 0.4 nm. Small angle neutron scattering (SANS) data of dMUA-DDT (red curve) and MUA-dDDT (blue curve) were collected using deuterated tetrahydrofuran (THF) as solvent, Figure 2. Coarse-grained simulations (Figure 2) suggest a Janus-like arrangement of the ligands after equilibration in solvent medium. From the SANS pattern of MUA-DDT particles, one could immediately find that MUA-DDT particles give less sharp oscillations. This is due to the fact that Janus particles have overall a lower symmetry deviating from a concentric distribution. This is especially true in the dMUA-DDT case, when the MUA phase is matched to solvent, and the shape of the nanoparticles is no longer close to spherical. The P(r) of the two SANS data gave the same D_{max} value, confirming that MUA and DDT have substantially the same chain length. We fitted the SANS data with an *ab initio* Monte Carlo modeling method and the resulting morphology from SANS fitting agrees well with simulation.

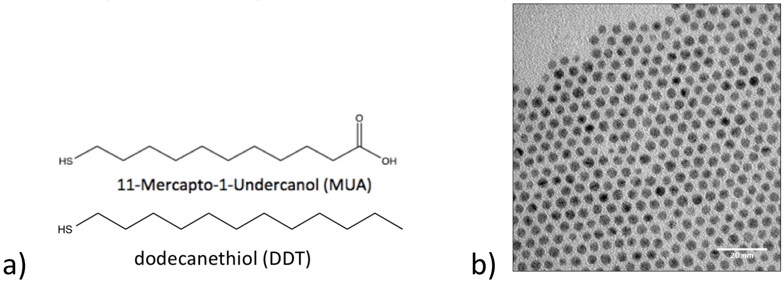


Figure 1 Chemical structure (a) and TEM image (b) of MUA-DDT nanoparticles.

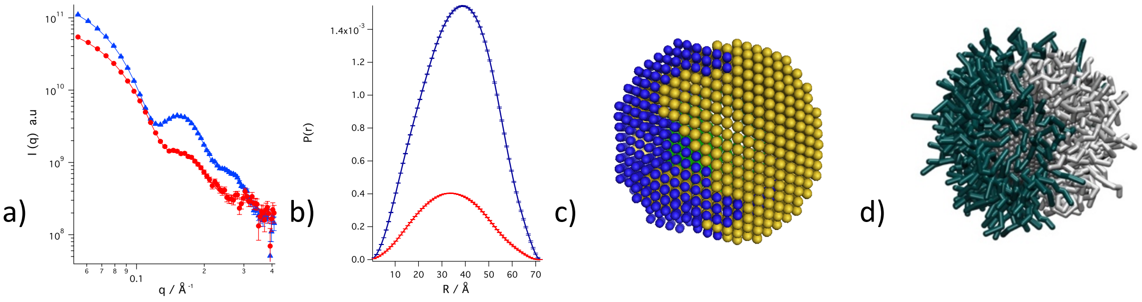


Figure 2. SANS data and fits (a) and P(r) function (b) of MUA-dDDT (blue) and dMUA-DDT (red) nanoparticles. Low-resolution three phase model (c) of MUA (yellow)-DDT (blue)

nanoparticles. (d) Mesoscale morphology (front and side view) from DPD simulation of MUA (forest green)-DDT (grey) nanoparticles. Solvent not shown for clarity.

Unlike any other Janus nanoparticles reported in the literatures, this mixed ligand nanoparticles is the first non-alkanethiol protected nanoparticles. With its carboxylic functional group on one side of the nanoparticles surfaces, the nanoparticle presents a permanent dipole. The nanoparticles with such permanent dipoles show Amphiphilic properties. Therefore, it is sensitive to external stimuli in several different ways.

1. Spontaneous alignment of dipoles at liquid-liquid interfaces.

Amphiphilic nanoparticles tend to self-assemble at liquid interfaces to minimize the interfacial energy. Therefore, once the solvent environment of the nanoparticles are changed, we are able to create a film of nanoparticles with well-aligned dipoles. Such films would present different surface properties on different sides. Currently we are studying the conductivity of such films.

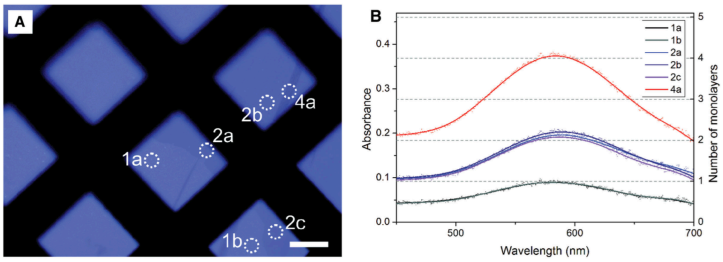
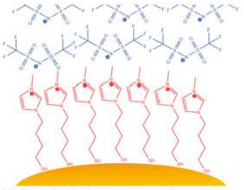


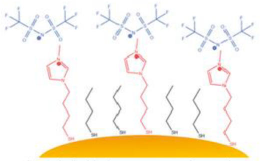
Figure 3. Free standing films formed by the alignment of Janus nanoparticles at the liquid liquid interfaces.

2. Counter-ion directed aggregation of nanoparticles

Since all the negative charge are all on one side of the nanoparticles surfaces, the arrangement of counter-ions near the surfaces would be different compared to more-mixed morphologies. The most obvious difference would be that the two surfaces would show a clear difference in the steric hindrance for counter-ions. We have tested that by using different sized counter-ions, one can control the colloidal stability of nanoparticles in water. For example, when bulkier counter-ions are used, the nanoparticles become more stable since the thickness of stern layer is increased.



High steric hindrance upon anion exchange
Low colloidal stability



Low steric hindrance upon anion exchange
Colloidal stability is maintained

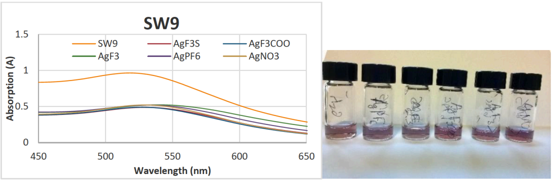


***Figure 12.** UV-Vis and photos of sample SW9. 2:1 mixed ligand with different anions. Notice the lower peak broadening compared to all-C$_{11}$TMA NPs in presence of bulky anions.*