Experimental Report

24/09/2013

Proposal: **9-10-1274** **Council:** 4/2012

Title: Striped Gold Nanoparticles

This proposal is resubmission of: 9-10-1227

Researh Area: Soft condensed matter

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Samples: gold nanoparticles

Instrument	Req. Days	All. Days	From	To
D16	4	4	29/10/2012	02/11/2012

Abstract:

The Stellacci group has studied in depth the structure of the self-assembled thiolated shell of nanoparticles. It has been established that when a mixture of distinct thiolated molecules is assembled at an interface, it spontaneously separates in domains, typically several nanometers wide.
Up to now Scanning Tunneling Microscopy (STM) has been the main technique to characterize the formation of the striped domains on the nanoparticles surfaces. However STM is limited to the characterization of few particles and has the disadvantage of poor statistics. There is a strong need to characterize these nanoparticles by using scattering techniques. With this proposal, we aim to investigate the stripes on the nanoparticles surface by using Small Momentum Transfer Diffractometer, D16 and the method of contrast variation.

Nanoparticles (NPs) are novel materials that find applications in fields ranging from electronics to medicine. Here, we focus on monolayer protected noble-metal NPs. These are supramolecular assemblies composed of a noble metal core surrounded by a self-assembled monolayer (SAM) of organic molecules, typically bound to the metal through a thiol-metal bond. They can be readily synthesized and have unique optical and electronic properties depending on their size and shape.[1] The protecting monolayer, i.e. the ligand shell, plays a crucial role, providing the particles with a series of great properties.

A true strength of gold NPs coated with a SAM of thiolated molecules is the ease with which a wide variety of different thiolated molecules can be placed in the ligand shell[1,2]. The SAMs that these molecules form on the intrinsically tridimensional (3D) metallic core of a NP resemble their two-dimensional (2D) counterpart formed on flat surfaces,[3] with whom they share an exquisitely complex structure,[4] and the many possible applications in biology[3] because of their resemblance with folded proteins.[5]

The Stellacci group has studied in depth the structure of the self-assembled thiolated shell of nanoparticles. It has been established that when a mixture of distinct thiolated molecules is assembled at an interface, it spontaneously separates in domains, typically several nanometers wide.[6] This form of separation occurs due to the balance between the enthalpy of phase-separation (that would lead to the formation to two large domains) and the conformational entropy that long molecules gain when at the interface with shorter molecules.

Up to now Scanning Tunneling Microscopy (STM) has been the main technique to characterize the formation of the striped domains on the nanoparticles surfaces (Fig.1). However STM is limited to the characterization of few particles and has the disadvantage of poor statistics. There is a strong need to characterize these nanoparticles by using scattering techniques.

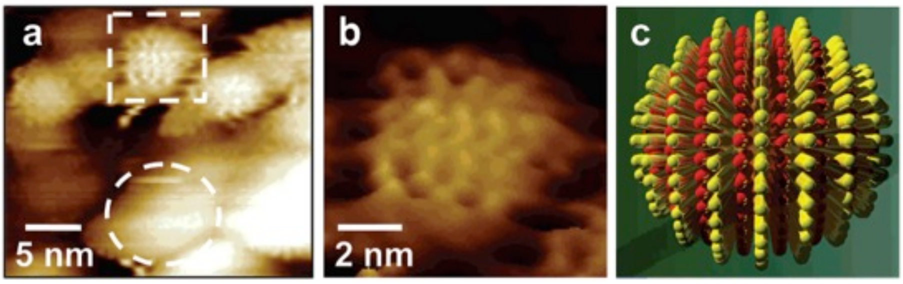

Figure 1. STM height images (*a* and *b*) of gold nanoparticles coated with OT: MPA with a 2:1 molar ratio, showing ribbon-like stripes due to phase separation of the two ligands. The cartoon in *c* is meant to schematically exemplify the arrangement of the ligands on the nanoparticles

We tried to investigate the stripes on the nanoparticles surface by using Small Momentum Transfer Diffractometer, D16. We attempted to do this by using the method of contrast variation, which employs a mixture of deuterated toluene ($5.7\ 10^{10}$cm^{-2}) and h-toluene ($9.4\ 10^{9}$cm^{-2}), to contrast match the gold core ($4.5\ 10^{10}$cm^{-2}) and the deuterated thiols ($5.3\ 10^{10}$cm^{-2}), thus highlighting the presence of hydrogenous thiolated stripes wrapping the particles. On the other hand, the use of hydrogenous solvent will give a full characterization of the gold core and the surrounding deuterated thiols that wrap the particles like ribbons.

Powder diffraction has also been performed in order to fully characterize the nanoparticles samples obtaining information about the interparticles distance, the interdigitation between nanoparticle ligands and the semi-crystalline state of striped domains on nanoparticles.

The experiment has been performed on a series of nanoparticles (core diameter equal to 4 nanometer, measured by transmission electron microscopy) coated with different thiols that form a shell of around 1 nanometer thickness. Contrast variation has been used by coating the nanoparticles with a mixture of a fully deuterated thiol ligand together with a fully hydrogenous one.

We have studied this series of nanoparticles coated by deuterated octanethiol (d-OT): 4-methylbenzenethiol (MBT) in the molar ratio 1:2, 1:1, 2:1 and also mercaptopropionic acid (MPA) and dOT in the ratio 1:1 and 1:2. Also d-OT and MPA homoligand nanoparticles were also investigated. Branched MBT were also used. The diameter of the gold core is around 4 nm, surrounded by 1 nm shell of thiolated molecules. The formation of stripes in the molar ratio 1:2, 1:1 and 2:1 has been proved by STM and the width of the stripes has been found to be in the range of 1-2 nm.[7]

The experiment has been performed both on nanoparticles solutions (Fig. 2) and on powder (Fig. 3).

The Q range required to fulfill a full characterization of the NPs ranges from 0.05 Å^{-1} to 1.5 Å^{-1} and will be covered on D16 with three detector angles.

The experiments were not successful as the scattering signal obtained from the amount of gold nanoparticles used was really low and we were not able to obtain suitable information.

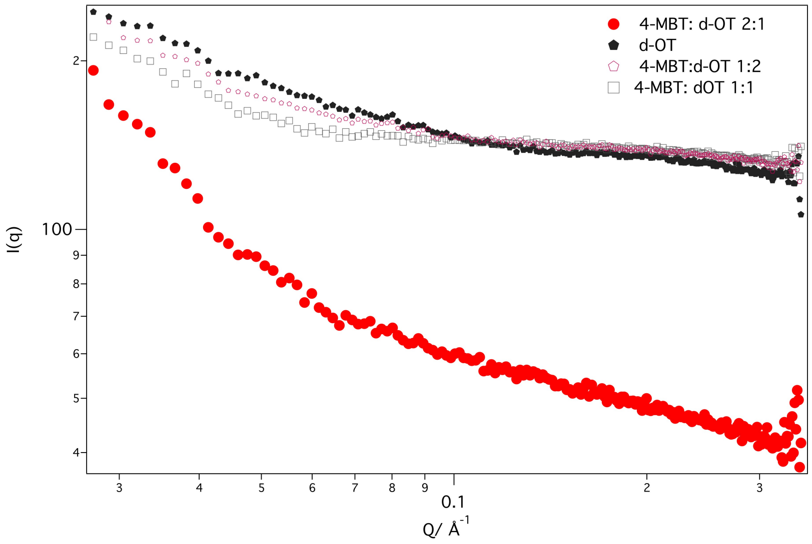

Fig.2 SANS data collected from nanoparticles solution .

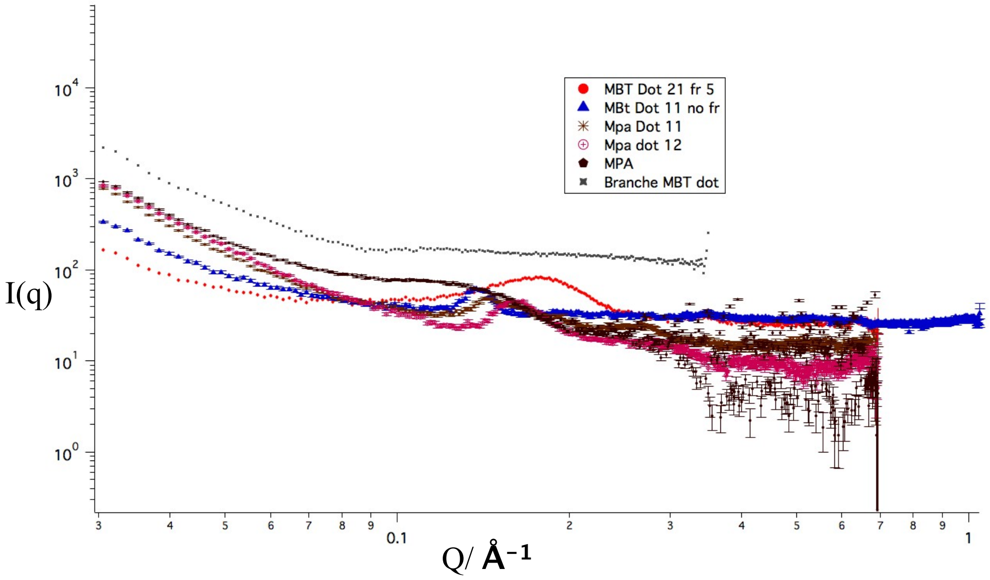

Figure 3. SANS data collected on nanoparticles powders.

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