Experimental report

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Proposal: 9-12-480 **Council:** 4/2016

Title: Structure of the organic shell of mesomorphous dendronized gold nanoparticles

Research area: Materials

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Samples: Aux[CnHmOpFqS]y

Instrument	Requested days	Allocated days	From	To
D16	2	2	27/06/2016	29/06/2016

Abstract:

We are engaged in the bottom-up synthesis of metamaterials based on metal nanoparticles. Through grafting with specially designed ligands we drive gold nanoparticles to self-organize into mesophase-like states. The superlattices formed by nanoparticles were characterized by SAXS, but this technique fails to differentiate the segregation of incompatible segments at the periphery, which is at the origin of mesomorphism. On the contrary, neutron scattering renders possible to detect this differentiation and was already performed in the bulk, in solution, at room temperature and on heating, at q between 0.003 and 0.3 Å-1. The definitive proof of the mesomorphism and the assignment of the phase type however require exploring the q range between 0.5 and 2 Å-1, which contains the signature of the lateral organization of mesogens and of chains. We propose here to measure our best or two best materials on the line D16 between 0.15 and 2 Å-1. This experiment should complete the structural investigation of the hybrid materials and hopefully help to elucidate and to control the self-organization of nanoparticles and the connected unconventional magnetism and other properties.

Structure of the organic shell of mesomorphous hybridized gold nanoparticles

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With the idea to construct metamaterials i.e. materials based on the periodic arrangement of functional building blocks (artificial atoms) possessing simultaneously magnetic, electronic and optical properties unreachable with natural elements, we are currently developing the synthesis of complex architectures based on the self-organization of mesomorphous coated nanoparticles into single and binary superlattices. The organic shells include antagonistic segments able to nanosegregate into juxtaposed domains and to induce the formation of mesophases, with the precise control of the interparticle spacings and arrangements of NPs within the lattices, and ultimately the physical properties of the material, through the responsive mesomorphic structure. Systematic variations of the shell composition allowed us to circumscribe series of coated NPs that spontaneously arrange into various superlattices. The elucidation of the underlying mesomorphism needs however to resort to Neutron scattering at both small- and wide-angles, which was the purpose of this session on D16 beamline.

Planning of the experiment

The NP superlattices were previously investigated by TEM, SAXS and GISAXS, but the details of the nanosegregation process inside the shell are not accessible by these techniques, due to the low contrast between shell constituents, when compared to the high electron-density of the gold fraction. In SANS, the major contrast is on the contrary between the antagonistic organic segments and information on the lateral arrangements and on domain alternation is therefore expected in the 0.5 to 2 $Å^{-1}$ and 0.05 to 0.5 $Å^{-1}$ q ranges, respectively.

This 0.05 $Å^{-1}$ limit is actually known from previous measurements performed in the 0.003 to 0.3 $Å^{-1}$ q-range on another beamline (SANS-II at SINQ). These previous experiments showed in particular coincidence of the fundamental periodicity between SAXS and SANS curves and confirmed the absence of a lower-angle signal. Nothing conclusive could however be stated upon the higher-order reflections, due to the insufficient resolution and statistics.

The principal motivation of the choice of the D16 beamline for this proposal is the fact that it is to our knowledge the only SANS beamline with an acquisition window going from 0.03 to 2 $Å^{-1}$, that perfectly fits the scattering range of our samples. The line moreover benefits from a high-brilliance beam and from a setup providing high-resolution in q, which might be essential for the separation of higher-order reflections.

Progress of the experiment

The appropriate experimental conditions were determined by our local contact, in particular the wavelength of 4.5 Å, for which the region of interest covers scattering angles from 1.2 to 75° and requires nine linear detector configurations with a sample environment change between 0.5 and 0.8 $Å^{-1}$. Standard cells for liquids are indeed the more adequate at low scattering angles, as they ensure regular sample thicknesses over large beam sections, and thus accurate subtractions and

calibrations. A cylindrical sample shape is on the contrary mandatory at high angles, which implies to drastically limit the beamsize, and thus the beam intensity, to the median part of the sample cylinder.

For the whole series of coated NPs, the optimal sample thicknesses are of roughly 1 mm, as calculated from the composition and verified from the previous SANS session. Hence, the small-angle part of scattering curves was recorded using 1 mm Hellma cells filled with the crude powders. Lindemann glass capillaries of 1.5 mm diameter, normally devoted to X-ray diffraction, were the sample containers chosen for the wide-angle configurations. In this case, the calibration runs were also recorded with capillaries, thus an empty capillary and capillaries filled with B4C powder and with water. The small-angle runs reached sufficient statistics in relatively short time and the five samples and standards could be acquired within 7 hours. The remaining beamtime was dedicated to configuration changes and to the wide-angle runs of two samples and of the standards.

Results

Two sets of samples were investigated during this session.

The organic shell of the principal sample is composed of rod-like mesogens and several terminal aliphatic chains, which nano-segregate into juxtaposed domains with different possible lateral arrangements, distinguishable by their signature in the 0.5 to 2 $Å^{-1}$ range. In the end, the SANS curve exhibits a broad scattering maximum at about 1.4-1.5 $Å^{-1}$ (see figure 1), which demonstrates that the lateral packing inside each domain is liquid-like. On the other hand, the reflections in the small-angle region define a long-range correlated structure, and the pristine material state is therefore identified as a frozen mesophase.

The previously noticed superimposition of the fundamental SAXS and SANS periodicities is of course confirmed. With the improved resolution and statistics, a series of higher-order reflections is now clearly visible and show marked differences with respect to the SAXS curve. This finding comes obviously from the modified contrast ratios and provides additional information on the hybrid material structure.

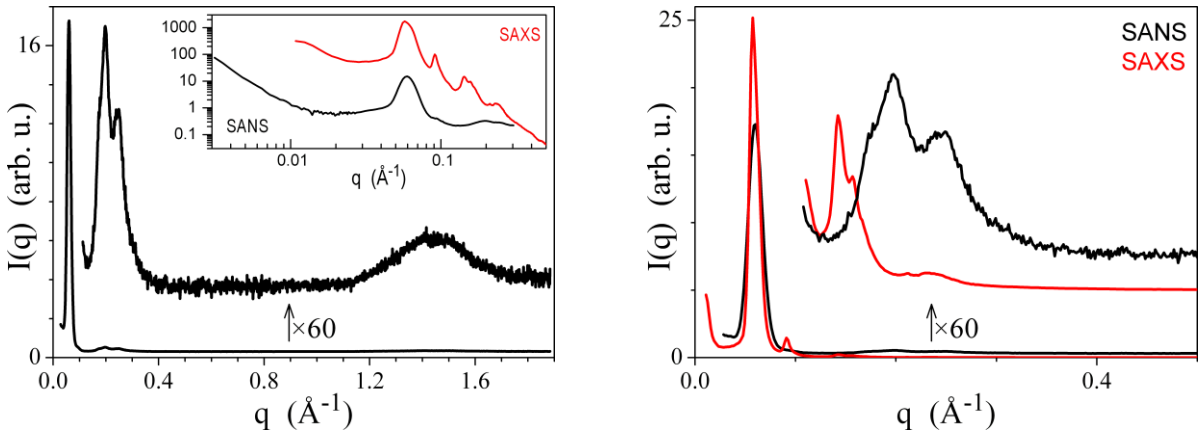

Figure 1, left: SANS curve of coated gold NPs in the pristine bulk state, from this D16 session; inset: SANS curve of the same bulk material from the previous session (SANS-II / SINQ) and superimposition with SAXS curve; left superimposition of SANS and SAXS curves.

The dendritic shells of the second set of compounds associate in their periphery various proportions of fluorinated segments (F) and of the hydrogenated analogues (H), with intent to take advantage of the fluorophobic effect to induce mesomorphism. The central questioning is therefore whether nano-segregated H/F domains are formed or not within the shell, which is directly probed in the wide-angle scattering region. Beamtime was sufficient to measure a single additional compound at wide-angles. The selected sample finally displayed a unique, broad wide-angle scattering maximum for lateral distances intermediate between neat F and H segments (see figure 2). The experiment therefore supports so far the formation of mixed F/H domains.

As shown by the broadened small-angle reflections, the coated NPs arrange in structures correlated over mesoscopic distances, ranging from 15 nm for the full fluorinated system, to 30-40 nm for the most hydrogenated F/H shell. A deeper structural analysis will follow the combination with SAXS data on the entire dendronized NP series and with SANS/SAXS experiments on coated NP solutions.

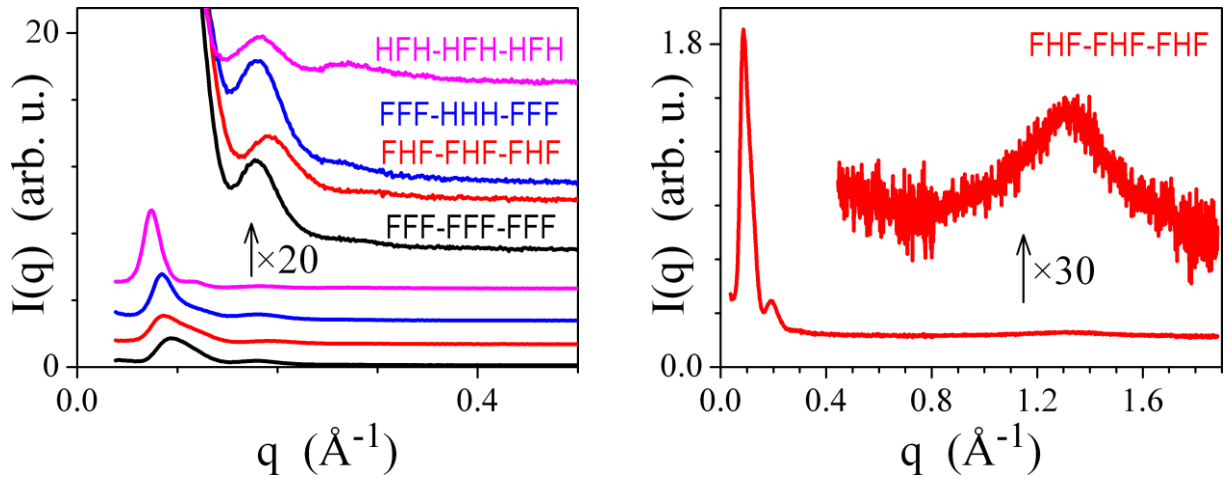

Figure 2, left: SANS curves of coated gold NPs with various proportions of fluorinated dendritic segments in the pristine bulk state, obtained at D16 during this session; right: scattering curve with wide-angle region for one selected compound.

Perspectives

The results of the D16 session confirmed our intuitions upon NP superlattices viewed by TEM, SAXS and GISAXS. After the compilation of the results from all techniques, a comprehensive publication will be elaborated in forthcoming months.

The results for the second coated NP series are also clear, but do not fit our expectations and the aim of the project, which will need further developments.

Acknowledgements

Nothing would have been possible without the kind and efficient help of Bruno Demé, our local contact, whom we also thank for the realization of the test measurement in 2015. We moreover thank people of the beamline for their permanent assistance.