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Visualizing and Analyzing Doped and Functionalized Nanoparticles with STEM-EELS Spectro-microscopy

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Inorganic nanoparticles can be functionalized by the introduction of dopants or the grafting of organic molecules. In both cases, the tailoring of the properties requires a comprehensive study of the main structural parameters of the functionalized nanoparticles. Among the various techniques offered by (S)TEM microscopes, electron energy-loss spectroscopy (EELS) presents obvious advantages for the characterization of such structures.

Indeed, light elements (C, N, O) of the organic part are easily probed by the excitation of the 1s electrons while the inorganic part or the dopants distribution is better evidenced by dark field imaging and/or by the EELS excitations of core-states (for example the 2p electrons of transition metal, the 3d electron of Rare Earth elements…). However, STEM-EELS techniques often see their potentiality reduced by the inherent low cross-sections of the involved EELS excitations so that the required electron doses are inadequate for the preservation of beam-sensitive nano-structures.

In this contribution, the main limitations of the EELS techniques and their sensitivity limits are considered. In particular, we discuss some recent instrumental developments such as the use of low-temperature electron multiplying CCD camera as final EELS detector (allowing the collection of up to 2500 spectra per second) and/or the reduction of the primary electron voltage (40-60 kV) to reduce the beam damage while preserving an atomic resolution.

As a first example, we will discuss the distribution of several dopants (Fe, Cr, Sm) into ceria nanoparticles and their influence on the magnetic properties. Positions of the dopants (surface, subsurface, substitutional, etc) have been determined by STEM-EELS while valence changes have been monitored either by EELS or by X-ray absorption spectroscopy. Figure 1 shows the case of a 3% Sm dopant distribution into ceria. The doping mechanism will be further discussed with respect of the ferromagnetism properties [1].

As a second example, we report the direct visualization, with nanometre resolution, of both organic and inorganic components of a lipid-coated silica particle containing quantum dots (QD@SiO_2@lipids) typical of multifunctional agents for biomedical applications [2]. The lipid coating is made of a dense paramagnetic (Gd) and poly(ethylene glycol) functionalized lipid monolayer (figure 2). The molecular signature, the relative amount, and the spatial extension of the carbon-containing layers are determined. In addition, the Gd-lipid position and the number of Gd atoms in lipid patches at the surface of the nanoparticles are revealed. Measurements performed under varying electron doses (at 150 K) give insight into the beam-damage effects, which do not however prevent the detailed characterization of these hybrid nanoparticles (fig. 2).

References
[1] Shih-Yun Chen, Ren-Jie Chen, Nan-Hong Chen, Chung-Li Dong, Alexandre Gloter, in preparation
[2] M. van Schooneveld et al., *Nature Nanotechnology* 5, (2010) 538.

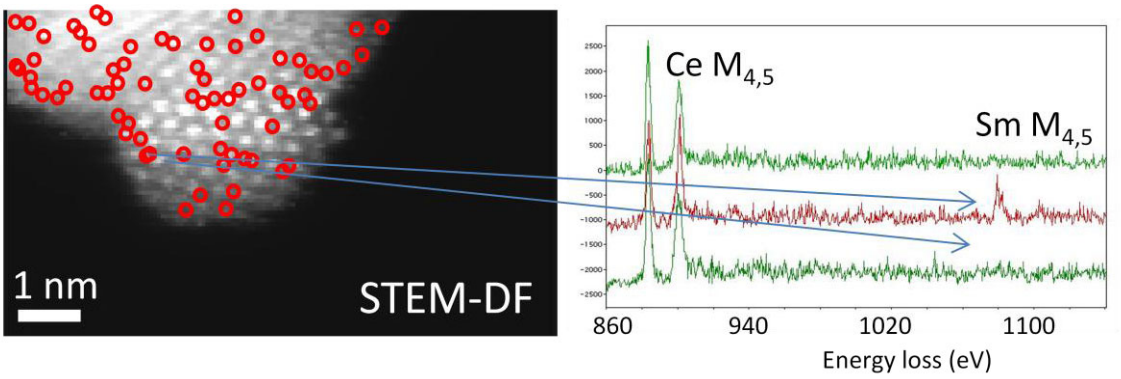

Figure 1. STEM-EELS on Sm doped CeO_2, 146*83 spectra have been acquired with a step of 0.06nm, an acquisition time of 3ms with 60 keV electrons. The STEM dark field image can be seen with superimposed red circles at the positions obtained for Sm dopants. EELS Sm $M_{4,5}$ and Ce $M_{4,5}$ can also be seen for three spectra that correspond to different atomic columns.

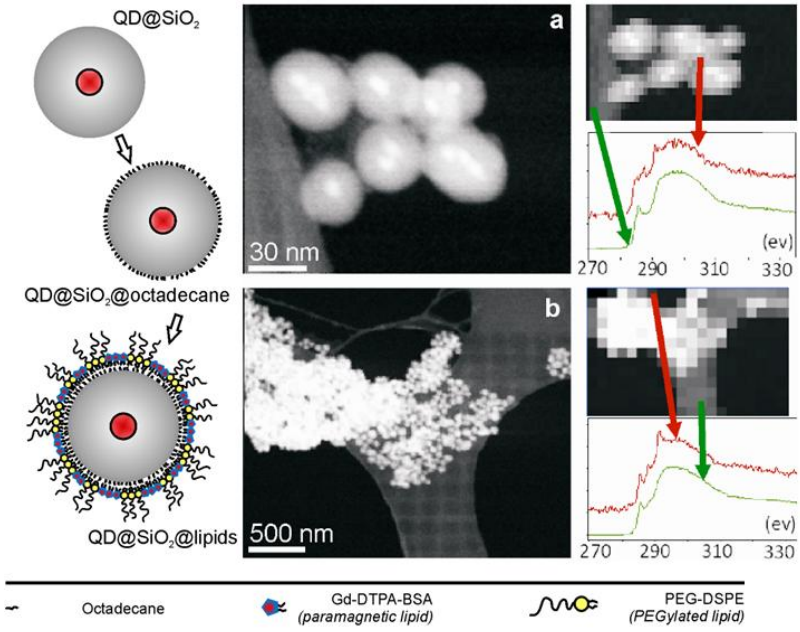

Figure 2. HAADF image and carbon K edge mapping of the QD@SiO_2@lipids nanoparticles acquired at different electron doses. (a) The spectrum image (spatial resolution of 4 nm) is measured with 2.10^4 e-.Å^{-2} dose. Differences between the carbon K EELS spectrum taken on the QD@SiO_2@lipids surface and the amorphous C from the electron microscopy grid can be seen (b) Spectrum image acquired with a spatial resolution of ca. 100 nm and an electron dose of 600 e-.Å^{-2} is shown next to the HAADF image.

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