XMCD measurements on organically capped magnetic copper nanoparticles

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We report first results on the magnetic behavior of various ~2 nm size Cu nanoparticles (NPs). These particles have been capped with thiol and amine type organic ligands and studied by means of magnetic circular dichroism at BL25SU under proposal number 2007B1743. The special feature of this work resides in the ability to induce different magnetic behavior on Cu NPs only varying the surrounding media. Besides, these differences in magnetism are clearly distinguishable in the XANES spectra and further corroborated by XMCD measurements. Here, the results obtained for thiol-caped ferromagnetic-like NPs are compared with diamagnetic counterparts as well as amine-capped superparamagnetic NPs.

The research towards the discovery of new properties in the field of nanoscience and nanotechnology has attracted much attention since the last decade. Initially, it was seen that particle-size reduction could induce unusual optical, magnetic, electronic and chemical properties when working in the nanometre scale. However, not only size, but also the surrounding media as well as particle shape and morphology play an important role in the definition of physical and chemical properties. In this sense, the ability of synthesizing particles with controlled size and capped with different compounds, that is, organic ligands, polymers or inorganic compounds is an step forward to the comprehension of the factors responsible of inducing such properties. Talking about metals, up to now Au and Ag NPs have been the most studied ones, mainly, due to their high chemical stability and unique plasmon resonance. However, and reinforced by the publication of a wet-synthetic method by Brust *et al.* in 1994, the study of the influence and importance of the bonding between surface atoms from the NP and the organic ligand has been extended to more metals and oxides such as ZnO.

Here, we report the results obtained for four different types of Cu nanoparticles all synthesised by a modification of the so-known Brust method. When capping with thiols, Cu NPs have happened to be ferromagnetic-like or diamagnetic depending on the metal-ligand interaction. On the other hand, when using an amine group, the resulting NPs present superparamagnetic behavior. The different samples have been measured by SQUID magnetometer, but XMCD measurements along with the study of XANES spectra not only have corroborate macroscopic measurements, but also have demonstrated that the difference in magnetism occurs as a result of the electron redistribution induced when NPs are capped.

Measurements were performed at the Cu $L_{2,3}$-edges using the highly sensitive spectrometer installed at BL25SU of SPring-8 Synchrotron in the 920-980 eV energy range. Detection of XMCD spectra was done in the electron yield mode under an applied magnetic field of ~ 2 T and, samples were spread on to a carbon tape and sticked on the sample holder.

The initial aim was to perform the experiment at room temperature, but this condition had to be modified because the exposure to radiation made

samples change irreversibly. In order to reduce the effect of the radiation the temperature was cooled to 20 K and the photon density was also diminished. In figure 1 it can be seen how even if the measurements were performed at low temperature the XANES spectra changes dramatically and, so, it becomes necessary to have a less intense radiation source.

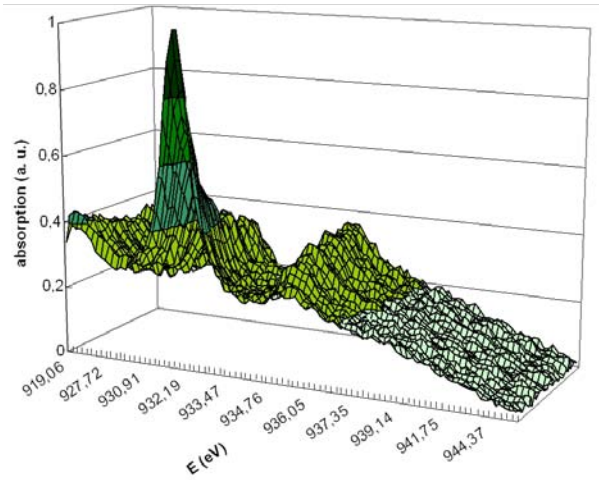

Figure 1. Variation of the XANES signal of ferromagnetic-like thiol capped Cu NPs measured at the Cu L_3-edge at 20 K.

Once optimum conditions were established, XMCD measurements could start. Four samples were measured: two different ferromagnetic-like (FM), a superparamagnetic (SPM) and a diamagnetic (DM) sample. Figure 2 shows L-edge XANES spectra for all Cu NPs along with the Cu foil.

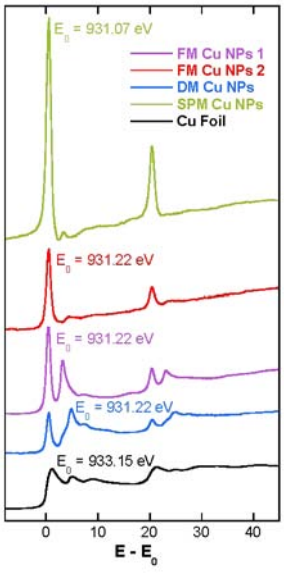

Figure 2. XANES spectra of all the samples measured.

At first sight, from figure 2 it can be seen how some XANES features seem to be related to magnetic behavior. In fact, it looks like the first intense whiteline it is characteristic of magnetic samples, as well as the lack of a second line just after the previous. This has been further corroborated with the XMCD study. In figure 3 XMCD measurements of FM and SPM Cu NPs are shown. Comparing the results it seems that an electron distribution without any second line, somehow, gives samples with higher magnetization value. These results are also in good agreement with SQUID values which are not shown in this report but we planned to publish them shortly.

Moreover, in the case of samples FM Cu NPs 1 and SPM Cu NPs 2 we were even able to measure de M vs H curve.

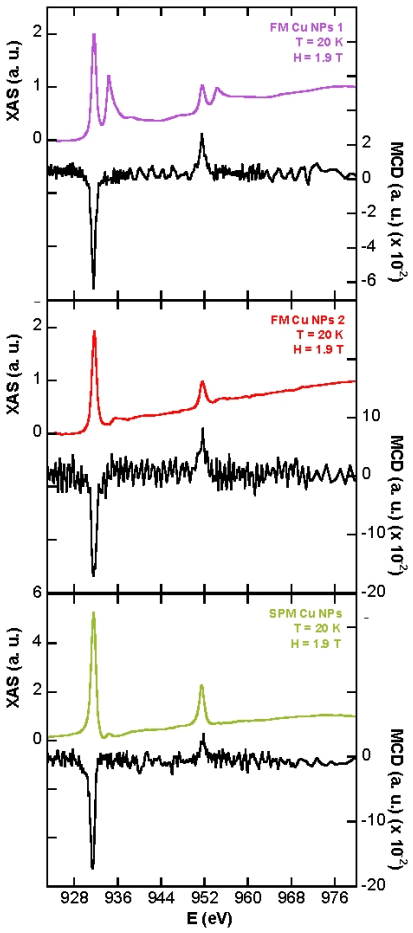

Figure 3. XMCD and XAS spectra at the Cu $L_{2,3}$-edges with an applied magnetic field of ~2 T. The XMCD and XAS spectra include the same scale factor so that the height of the edge jumps of the XAS spectra (colour lines) are unity.