



	<b>Experiment title:</b> Structure of Ag nanoparticles on cerium oxide ultrathin films	<b>Experiment number:</b> HC-758
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**Report:**

In this experiment we investigated the structure of Ag nanoparticles of controlled size supported on cerium oxide single crystalline films by means of Ag K-edge x-ray absorption measurements in the near edge and in the extended energy ranges, also exploiting polarization dependence of the X-ray absorption cross section. The experiment was based on a previous study by the proposers in which Ag nanoparticles on ceria films were investigated by means of STM and x-ray photoemission spectroscopy and the experimental results were interpreted with the help of DFT calculations [1]. The deposition of different amounts of Ag on cerium oxide films was shown to result in the self assembly of nanoparticles of different size [1]. The atomic scale structure of such particles represents an interesting aspect, which is important to fully understand the catalytic properties of the Ag/CeO<sub>2</sub> system.

The samples for the present experiment were grown with the procedures exposed in [1] and brought to the ESRF in non-reactive atmosphere. We measured four samples differing in the amount of Ag grown on a 10 ML thick CeO<sub>2</sub> film, in turn epitaxially grown on a Pt(111) single crystal. The nominal Ag amount of the measured samples was 0.1 Å, 0.2 Å, 0.7 Å, 1.5 Å. The measurements were performed at the Ag K edge and measured in fluorescence yield mode using a solid state detector. Three different geometries were used to selectively probe in-plane and out-of plane atomic coordinations. The geometry giving the best signal to noise ratio was with the sample in horizontal position, the photon beam at a few degrees from the sample surface and the electric field vector in the surface plane. In this configuration, highly sensitive to the surface layers, it was possible to measure the four samples, even the most diluted 0.1 Å Ag one. With the samples in vertical position the grazing angle which allowed to reliably align the beam on the sample surface was 10°. In this configuration we measured the 1.5 Å Ag sample only. In an intermediate configuration i.e. at 50° incidence we measured the 0.7 Å and 1.5 Å Ag samples. Two reference samples, namely a metallic Ag foil and an Ag<sub>2</sub>O sample in powdered form, were also measured in transmission mode for comparison.

Fig.1 reports the XANES spectra for the four different samples with Ag nanoparticles and for the Ag and Ag<sub>2</sub>O reference samples. A comparison of the lineshapes shows that the 1.5 Å Ag sample has a shape very

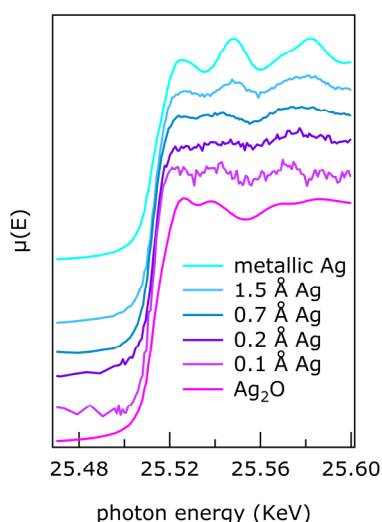
similar to the metallic Ag one. At decreasing Ag coverage the absorption structures start to evolve towards a configuration similar to the Ag<sub>2</sub>O one, however even the 0.1 Å Ag sample does not show a fully oxidized character.

Fig.2 shows a comparison of the k-weighted  $\chi(k)$  spectra of the nanoparticle samples and of the reference samples measured with the electric field vector parallel to the sample surface and at grazing incidence in horizontal geometry. Again the shape of the 1.5 Å Ag sample spectrum is very similar to the metallic one. Also the 0.7 Å and 0.2 Å Ag sample spectra have features similar to those of metallic Ag, although with a worse signal-to-noise ratio. The 0.1 Å Ag sample spectrum is reliable only up to  $k=5 \text{ \AA}^{-1}$  and, in spite of the low signal-to-noise ratio, it shows some peaks in intermediate positions compared to the spectra of the metallic and oxidized reference samples, which could possibly reflect a different Ag atomic environment ascribed to reduced dimensionality.

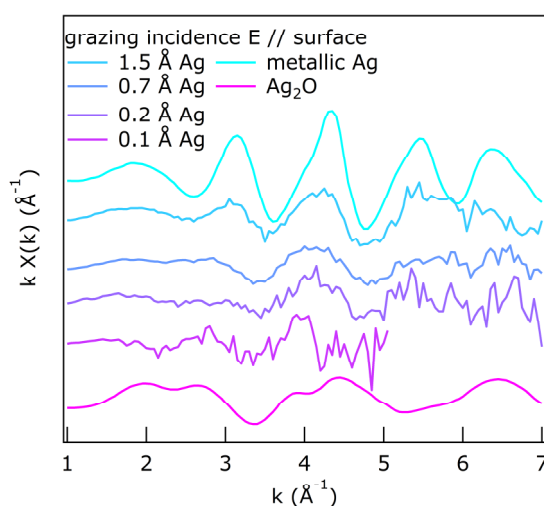
The k-weighted  $\chi(k)$  spectra of the 1.5 Å Ag sample measured in three different geometries, namely with the electric field vector parallel, perpendicular and at 50° from the surface plane, are shown in Fig.3. The slight differences in the positions and relative weight of the peaks in the low k region may reflect a slight anisotropy of Ag atomic environment in the nanoparticles grown on CeO<sub>2</sub>.

To corroborate all these qualitative considerations, a quantitative analysis is required. A fitting of the spectra in the extended energy range using the theoretical scattering amplitudes and phase shifts generated by the FEFF code is in progress. Its results are expected to clarify the evolution of the Ag atomic environment as a function of particle size and the presence of possible structural anisotropies.

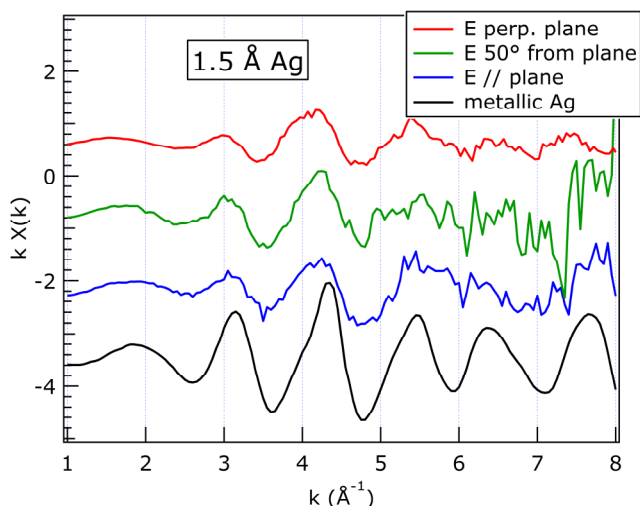
[1] P. Luches et al., J. Phys. Chem. C 116, 1122 (2012).



**Fig.1:** XANES spectra of the Ag nanoparticle samples and of the Ag and Ag<sub>2</sub>O reference samples.



**Fig.2:** k-weighted  $\chi(k)$  spectra of the Ag nanoparticle samples and of the Ag and Ag<sub>2</sub>O reference samples measured in horizontal geometry at grazing incidence with the electric field vector parallel to the sample plane.



**Fig.3:** k-weighted  $\chi(k)$  spectra of the 1.5 Å Ag nanoparticle sample measured in three different geometries. The spectrum of the metallic Ag sample is also shown for comparison.