

Ag Nanoparticles Functionalized with Amines and Thiols: Structural and Magnetic Characterization

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Size confinement to a nanometer scale has induced permanent magnetism in gold nanoparticles when capped with thiols [1]. The combination of particle size and the surface environment induces a strong charge transfer from the Au surface atoms to the S atoms, generating unoccupied densities of *d* states located at the Au surface atoms. These gold atoms present an intrinsic magnetic behaviour, which has been corroborated by element selective techniques such as x-ray magnetic circular dichroism (XMCD) and ¹⁹⁷Au Mössbauer spectroscopy [2]. In spite of the investigation performed with gold nanoparticles, silver ones remain to be studied. In this way we are dealing with the preparation and characterization of silver nanoparticles surrounded by different type of ligands in order to know the influence of the metal concentration and functional groups on the magnetic behaviour of the nanoparticles.

Silver nanoparticles were synthesized following the Brust method [3], which is based on the transfer of AgNO₃ from an aqueous solution to toluene using tetraoctylammonium bromide (TOAB) as the phase-transfer reagent. The reduction of the solution with aqueous sodium borohydride in the presence of dodecanethiol, octadecanethiol, dodecylamine and 1-dodecanol yields Ag-SR, Ag-oSR, Ag-NR and Ag-OR colloidal solutions, respectively. By the addition of ethanol to the suspension, only Ag-SR and Ag-oSR samples precipitate.

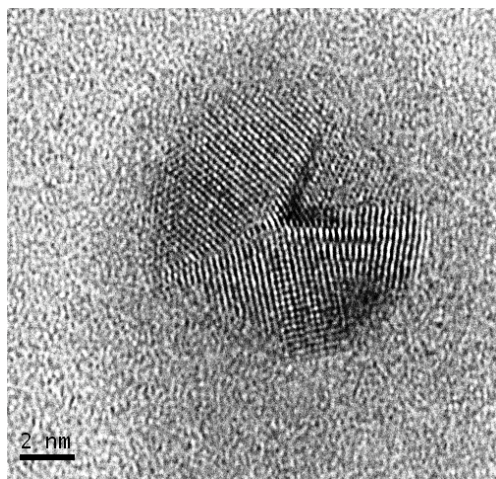


Figure 1. HRTEM image of Ag-NR nanoparticles.

Colloidal solutions were studied by means of TEM and HRTEM microscopy and UV-visible microscopy. Nanoparticles present high crystalline nature and a mean size of 2.3 nm. In some cases icosahedral and Marks shapes have been observed in the samples (Fig. 1).

In UV-vis spectra, a band centered at 415-445 nm appears for Ag-oSR, Ag-NR and Ag-OR samples and is associated to a plasmonic resonance characteristic of non-localized electrons. The lack or attenuation of this band in the case of Ag-SR NPs, evidences the Ag-thiol interaction.

In the cases of the solid samples, thermogravimetric measurements were performed and a content of organic matter of 22% was observed for Ag-SR NPs. Magnetic measurements of the NPs with dodecanethiol (-SR) and octadecanethiol (-oSR) were performed at 5 and 300 K, and only dodecanethiol capped NPs showed magnetic behaviour with a maximum value of 6.8 emu/g_{Ag} at 5 K.

In this way, and in order to note the influence of the length of the ligand on the interaction Ag-S in the nanoparticles XAS measurements (X-ray absorption spectroscopy) have been performed in transmission mode in Ag K-edge 25514 keV edge at BL01B1 beamline at SPring8. Figure 2 shows the XAS spectra of the measured samples. The absorption spectra of three thiol-capped samples, Ag-oSR, Ag-SR(1) and Ag-SR(2) (these last two last samples differ in the initial concentration of the metallic salt) revealed all the main features of bulk Ag. Nevertheless, owing to the reduce particle size, an overall attenuation and broadening is observed over the whole XAS spectra.

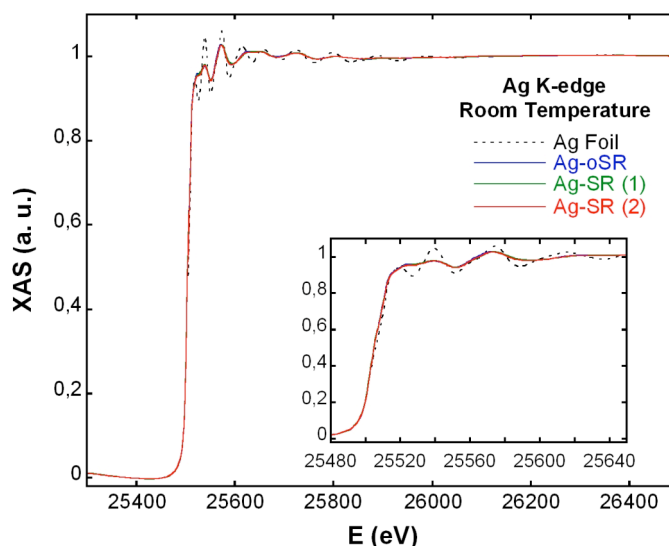


Figure 2. Ag K-edge XAS spectra for three thiol-capped Ag nanoparticle samples: Ag-oSR, Ag-SR (1) and Ag-SR (2). In the inset the attenuation of the oscillations can be better distinguished.

References:

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