ESRF	**EXAFS investigation of gold nanoparticles chemically stabilized by organic thiols for optoelectronics applications**	**Experiment number**: **CH-3940**
Beamline: BM23	**Date of experiment**: from: 05/12/2013 to: 10/12/2013	**Date of report**:
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Report:

Applicative perspectives of nanomaterials are widely addressed in the literature due to their nanostructure dependent properties and surface functionalities, which makes metal nanoparticles (MNPs) promising candidates for applications, as examples, in nanoelectronics, biomedicine, and catalysis [1]. In particular Gold NPs have been found to improve the performance of DSSC (dye sensitized solar cells)[2] and, when embedded into proton-conducting membranes of polymer electrolytes, to open new perspectives in fuel cell applications [3]. As a matter of fact the properties of MNPs are crucially determined by the finest structural, morphological and compositional details, therefore the accurate characterization of MNPs down to the atomic scale is a foundamental issue.

The objective of this research was the understanding of the chemical and molecular structure of functionalized metallic nanoparticles (NPs), obtained stabilizing noble metal particles with organic thiols. Chemical synthesis methods have proved to give rise to massive amounts of high quality, small and size controlled NPs; moreover, the possibility to opportunely select the capping agent gives rise to an additional degree of freedom to modify and tailor the NP properties. The nature and stability of the chemical interactions between metal and capping thiol and the local structure modifications induced by the chemical interaction at the metal/thiol interface are key information to understand the physical properties of capped NP, specially in view of innovative technological applications.

In this framework, the main aim of our experiment was to study the interaction between specific ligands, selected on purpose with the aim to modulate the MNPs optical properties (i.e. 9,9- didodecyl-2,7-ditioacilfluorene- **SFL**; 9,9- didodecyl-2,7-diphenylditioacilfluorene–**SFLPA**; 9,9- didodecyl-2,7-ditioacilfluorene-Pt(II) bis trybutyl phosphine – **SFLPt**), and gold NPs (AuNPs), synthesized following well assessed literature methods [9].

Experiment: We probed the Au local structure in functionalized AuNPs capped with thiols: AuNPs/SFL, AuNPs/ SFLPA and AuNPs/SFLPt. For each system 4 samples were studied having different AuNP core diameter: D= 1.5, 3, 4, 6 nm. All the samples were previously characterized by TEM, XPS (laboratory) and high resolution SR-XPS (ELETTRA).

XAFS measurements were carried out at the Au L_{III} edge (11.919 keV) at liquid nitrogen temperature, in fluorescence geometry (transmission geometry measurements were also attempted, ensuring better quality of the data in the most concentrated samples). The stability against radiation damage was preliminary successfully checked repeatedly measuring the XANES region of a test sample. In the AuNPs/SFLPt samples the close Pt L_{III} absorption edge (11.564 keV) made difficult the EXAFS data analysis, as expected. In these samples, we focused the analysis on the near edge region.

Preliminary results: The BM23 set-up provided high quality, reproducible XAS spectra; in particular, high quality data were required to distinguish the contribution coming from the Au atoms located at the NP-capping interface. Moreover the multiple-shell XAFS data analysis may allow understanding the core size from an accurate next-neighbour coordination number analysis (see ref. 10 for details about the analysis). The analysis is in progress, here an example, the rough EXAFS spectrum of AuNps/SFL hybrid obtained with Au/S atomic ratio = 1/1 is reported in Figure 1.

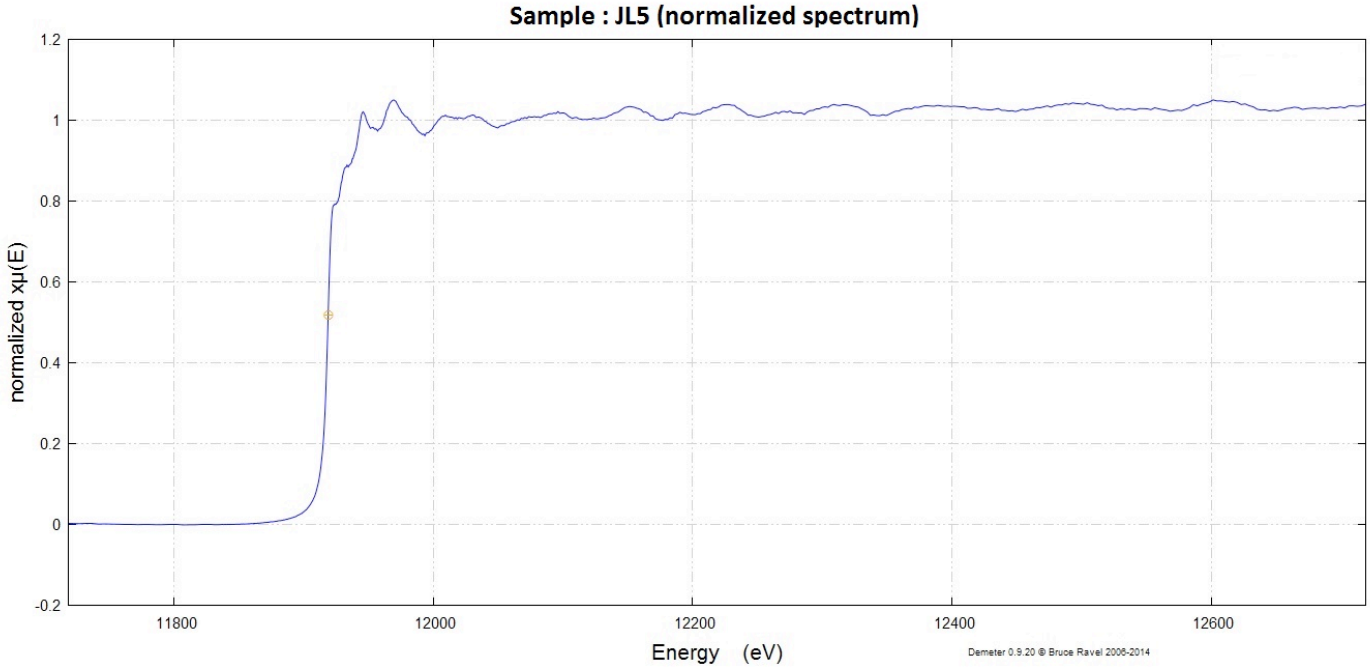

Figure 1: Raw EXAFS data for AuNPs/SFL sample (Au/thiol stoichiometry = 1/1).

Preliminary data refinement test have been attempted and demonstrate:
1. the core-shell nature of NP with the possibility to individuate the Au-S signal from surface layer atoms,
2. the possibility to extract information about NP size (spherical NP model)
these information will be related to the nature of the organic ligands as well as synthesis parameters (metal/thiol stoichiometry).
All these informatio will be compared with results from HR-TEM and HP-XPS preliminarily achieved on the same samples [10] in order to have an accurate complete description of NP local atiomic structure, morphology and electronic nature.

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