ESRF	Experiment title: Hydrophilic AuNPs capped with thioglucose as innovative radiosensitizing agents for cancer diagnosis and treatment: molecular structure and local chemistry studied by	Experiment number: **CH- 4349**
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Report:

Introduction:

The development of new strategies for the chemical stabilization of metallic nanoparticles by means of capping metallic clusters with appropriate ligands (selected on the basis of the expected behaviour) is the general topic of our research. In this framework, the study and control of the interaction occurring between the capping molecular species and metal nanoparticles synthesized on purpose is of primary importance.

Hybrid systems obtained by chemically bonding properly functionalized molecules to nanometric metal clusters, own peculiar optical, photochemical, electrochemical, catalytic and magnetic properties [1], that can be modulated by appropriate choice of the metal, by changing the cluster dimensions and by modifying the molecular structure and/or chain length of the ligand. When properly stabilized by a shell of ligands such as thiols, amines, ammonium salts and polymers, MNPs display excellent stability toward aggregation, which enables attempts to achieve NPs with different sizes and shapes. In the midst of different materials, thiol stablized MNPs can exhibit desired reactivities due to the variety of functionalizations and the strong M-S bond formation [2].

In this context, the objective of this proposal was understanding the chemical and molecular structure of Gold Nanoparticles (AuNPs) stabilized by thioglucose-like ligands, that were synthesised on purpose to provide innovative radiosensitizing agents for cancer diagnosis and treatment. Chemical synthesis methods have proved to give rise to massive amounts of high quality, small and size controlled functionalized AuNPs; moreover, the possibility to opportunely select the capping agent gives rise to an additional degree of freedom to modify and tailor the NP properties, that are mandatory in the proposed field of application.

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 NPs, especially in view of innovative applications in the field of Nanobiotechnology.

Experiment:

We performed EXAFS measurements at Au L_{III}-edge to investigate three different nanosystems: AuNPs capped with the charged 3-MPS, ensuring water solubility; AuNPs functionalized by the organic TG, allowing for an improved NPs uptake by cells; the complex system obtained by stabilizing AuNPs with both 3-MPS and TG, i.e. AuNPs/3-MPS/TG, that gave the encouraging results in *in vitro* cells uptake and radiosensitising tests. NPs of different mean size, controlled by the synthesis procedure, were examined, as the NPs size is expected to influence the internalization by cells.

We probed the Au local structure in functionalized AuNPs capped with the single and mixed thiols. For each system 3 samples were studied having different AuNP core diameter: D= 3, 4, 6 nm. All the samples were previously characterized by TEM and XPS (laboratory).

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.

Preliminary results: The BM08 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 thiols interface. Moreover the multiple-shell XAFS data analysis may allow understanding the core size from an accurate next-neighbour coordination number analysis [3]. The analysis is in progress, here an example, the rough EXAFS spectrum of AuNPs/3MPS/TG sample hybrid obtained with Au/thiols stoichiometry = 1/4/6 is reported in Figure 1

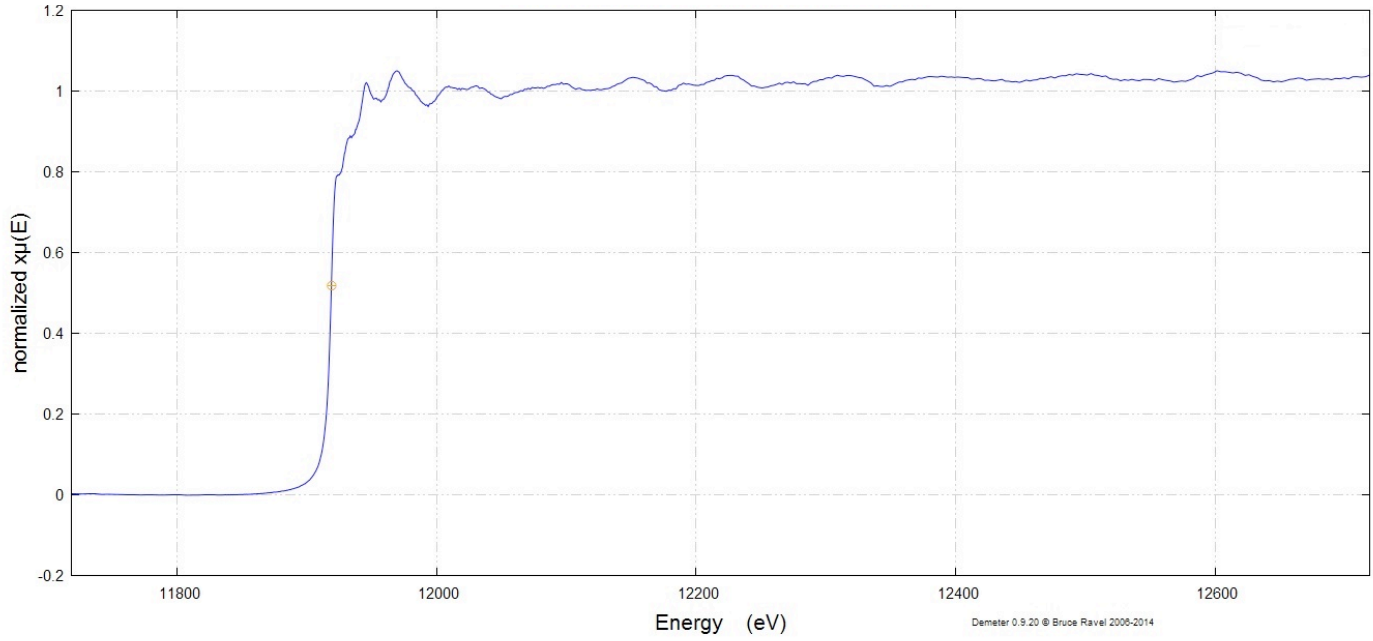

Figure 1: Raw EXAFS data for AuNPs/3MPS/TG sample (Au/thiols stoichiometry = 1/4/6).

Results:

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/thiols stoichiometry).
All these information will be compared with results from XPS preliminarily achieved on the same samples and biological tests [4] in order to have an accurate complete description of NP local atiomic structure, morphology and electronic nature, and the influence of these parameters on the NPs behaviour in biomedical applications.

References

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