Thiol-functionalized gold and silver nanoparticles using mixed ligands: a close look at the atomic structure and chemico-physical properties by SR-XPS and SERS

L. Carlini[1*], G. Testa[2], C. Fasolato[3], I. Venditti[2], F. Sciubba[2], I. Fratoddi[2], P. Postorino[3], C. Battocchio[1].

[1]*Department of Science, Roma Tre University, Rome, Italy*
[2]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[3]*Department of Physics, Sapienza University of Rome, Rome, Italy*

[*]*laura.carlini@uniroma3.it*

In recent years, thiol-functionalized noble metal nanoparticles (MNP-s) have been synthesized, characterized and developed to be used in many different fields such as optoelectronics, sensors, catalysis, and biomedicine [1]. Gold and silver nanoparticles, composed of a metallic core and a ligand shell show a peculiar optical behavior and provide a very powerful tool for biotechnological applications. Mixtures of ligand molecules can be used to coat the nanoparticles, controlling the toxicity, the stability and the surface charge density of the system. Typically, this is done so that each of the ligand shell components provides a different property to the nanoparticles. In this work we present gold and silver nanoparticles functionalized by sodium 3-mercapto-1-propansulfonate (3MPS) and 2-diethylaminoethanethiol hydrochloride (DEA), chosen on purpose for the biomedical applications [2,3]. The MNP-s were synthesized with different thiols molar ratios with the aim to investigate the properties of the functionalized nanoparticles.
The characterization of the nano-systems was carried out investigating the chemical and electronic structures at the MNP-organic ligand interface by means of Synchrotron Radiation induced X-ray Photoelectron Spectroscopy (SR-XPS). SR-XPS provides information on the local bonding environment of a given species and it has been demonstrated to be a unique tool for investigating the nature of the interaction at the capping agent/metal nanoparticle interface, as well as the chemical structure of MNPs surface [4,5]. FESEM measurements showed dimensions from few nanometers up to 10 nm. The localized surface plasmon resonance (LSPR) of the MNP-s allow the use of another useful technique, Surface Enhanced Raman Spectroscopy (SERS). In SERS, the Raman intensity diffused by molecules close to a nano-curved metallic surface is highly enhanced by the LSPR, allowing the spectroscopical investigation of molecular monolayers [6]. Moreover, structural information on the nanosystem has been gathered by means of Nuclear Magnetic Resonance (NMR) and Dynamic Light Scattering (DLS). In this work we compared the semi-quantitative SR-XPS and SERS analysis to obtain a better understanding of the system. The reported results show a possible correlation between the molar ratio and the thiol affinity for the metal. In conclusion, the present study explores the potential synergy between different techniques in order to give new insights in the field of nanomaterials.

[1] F. Porcaro, C. Battocchio, A. Antoccia, I. Fratoddi, I. Venditti, A. Fracassi, S. Moreno, I. Luisetto, M. V. Russo and G. Polzonetti, Colloids and Surfaces B 2016, **142**, 408-416.
[2] I. Venditti, L. Fontana, I. Fratoddi, C. Battocchio, C. Cametti, S. Sennato, F. Mura, F. Sciubba, M. Delfini and M. V. Russo, Journal of Colloid and Interface Science 2014, **418**, 52-60.
[3] I. Venditti, C. Palocci, L. Chronopoulou, I. Fratoddi, L. Fontana, M. Diociaiuti and M. V. Russo, Colloids and Surfaces B: Biointerfaces 2015, **131**, 96-101.
[4] C. Battocchio, C. Meneghini, I. Fratoddi, I. Venditti, M. V. Russo, G. Aquilanti, C. Maurizio, F. Bondino, R. Matassa, M. Rossi, S. Mobilio and G. Polzonetti, J. Phys. Chem. C 2012, **116**, 19571−19578.
[5] C. Battocchio, F. Porcaro, S. Mukherjee, E. Magnano, S. Nappini, I. Fratoddi, M. Quintiliani, M. V. Russo and G. Polzonetti, J. Phys. Chem. C 2014, **118**, 8159−8168.
[6] C. Fasolato, F. Domenici, S. Sennato, F. Mura, L. De Angelis, F. Luongo, F. Costantini, F. Bordi and P. Postorino, Appl. Phys. Lett. 2014, **105**, 073105.