

Electronic Supplementary Information.

Thiolate-Capped Silver Nanoparticles: Discerning Direct Grafting from Sulfidation at the Metal-Ligand Interface by Interrogating the Sulfur Atom

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Details of *ab initio* XANES calculations. *Ab initio* calculations of XANES spectra were performed with the FDMNES program, by making use of the finite difference method to solve the Schrödinger equation. The simulations parameters were tested over the spectra of reference compounds before being applied to thiolate functions grafted on Ag(111) surfaces.

We simulated the spectrum of protonated glutathione (GSH) and that of the same molecule deprotonated and bound to Ag(I) ions in the Ag-GSH complex, where the Cys moiety of GSH molecules bind to two Ag atoms to form -S-Ag-S-Ag- chains, as previously described.^{1,2} Considering that XAS is sensitive to the structure of a molecule in a radius of about 5 Å from the absorber, the tripeptide GSH (Glu-Cys-Gly) was represented through its Cys moiety that bears the thiol (R-SH) function. As further confirmation of the reliability of this choice, it can be observed that the S K-edge XANES spectra of reduced GSH and of Cys at pH 7.0 reported in literature are nearly identical.³

The input clusters for GSH (R-SH) and for the Ag-GSH complex are reported in Figure S1A, where the H atoms are omitted for clarity, except for the one of the SH group. The crystallographic structure of Cys from the CSD entry LCYSTN04 was used as input structure for this and all following calculations, without ever modifying its geometry.⁴

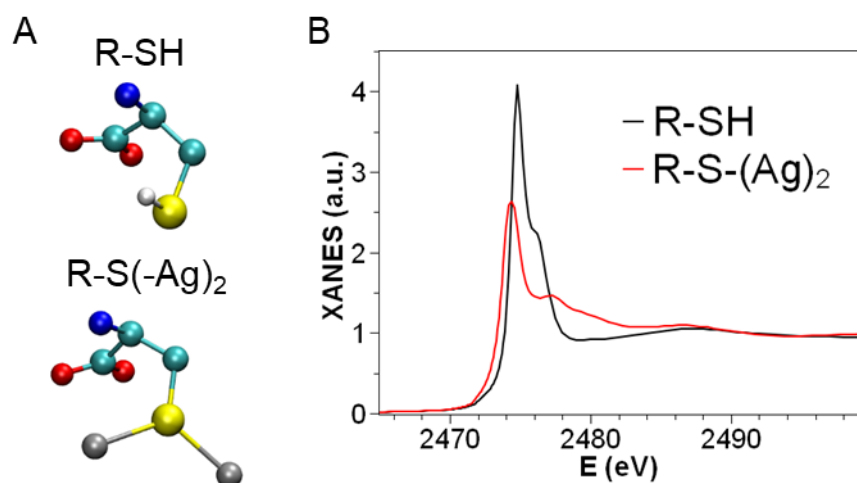


Figure S1. (A) Input geometries for *ab initio* simulations of XANES spectra of protonated Cys (R-SH) and of Cys bound to Ag(I) atoms (R-S-(Ag)₂), as in the Ag-GSH complex.

The spectra that provide the best agreement with the experimental data are simulated using the free shape potential Finite Difference Method (FDM), and with a self-consistent calculation of the electronic structure, in a 4.3 Å cluster radius around the absorber. Because the cluster is not an isolated molecule, one must eliminate the $1/r$ increasing potential when going away from the cluster. This is done thanks to a parameter empirically set to -6 eV. This way, we avoid for instance the Rydberg features observed in atoms and small molecules. Importantly, these parameters are optimized and kept constant for all the following calculations. The spectrum generated starting from the R-SH cluster is reported in Fig. S1B (black curve). It reproduces the main peak of the experimental spectrum of GSH (Main Text, Fig. 1A), with slightly more pronounced features and white line intensity. Two transitions are indeed expected in the main

peak of R-SH compounds, attributed to $1s \rightarrow \sigma^*(\text{S-C})$ and $1s \rightarrow \pi^*(\text{CH}_2)$, which are both visible in our simulated spectrum.⁵ When the H atom is removed and 2 Ag atoms are added in the S coordination sphere (R-S(-Ag)₂ cluster in Fig. S1A), the simulated spectrum (red curve in Fig. S1B) shows a decrease in the WL intensity and a clear change in spectral features with respect to R-SH, with a steep increase at the edge followed by a smoother post-edge decrease. This trend corresponds to the one observed in experimental spectra (Main Text, Fig. 1A). Overall, the spectral features of the reference compounds are reproduced, which allows us to extend the method to the study of the adsorption of R-SH molecules on AgNPs surfaces.

However, the non-relativistic calculations used so far for molecular complexes failed to reproduce the spectral features observed in Ag-surface-bound thiolate, i.e. in the spectra of AgNPs assemblies (Main Text, Fig. 1), regardless of the geometry. Relativistic calculations with spin-orbit were then tested and were found to have a dramatic effect on the calculated spectra of R-S-Ag(111) systems. An example is shown in Figure S2: three different calculations for the same input cluster where Cys binds on-top of a surface Ag atom were performed, changing only the calculation parameters. The FDM was always used, as well as self-consistent calculations. Non-relativistic (blue curve) and Time-Dependent DFT (TDDFT, red curve) calculations yielded similar spectra, whereas relativistic calculations with spin-orbit coupling (black curve) gave a completely different result. Remarkably, only the latter reproduces the features of the experimental spectrum of AgNPs assemblies (Main Text, Fig. 1A, black curves). When applied to the reference compounds R-SH and R-S(-Ag)₂, the spin-orbit coupling yields no difference with respect to non-relativistic calculations, demonstrating that the more heavy Ag atoms are present in the cluster, the more it is necessary to take this phenomenon into account in *ab initio* calculations. Therefore, all spectra of R-S-Ag(111) systems were generated through relativistic calculations.

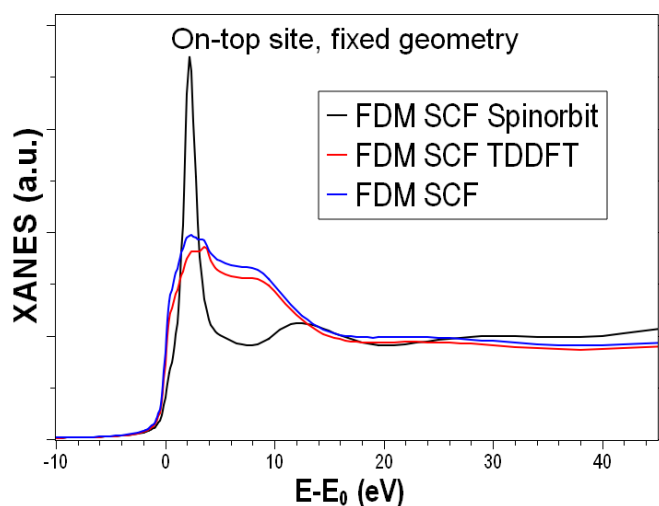


Figure S2. Effect of the simulation parameters on the spectral features of R-S-Ag(111) systems. Simulated S K-edge XANES spectra for Cys grafted on Ag(111) in the on-top geometry by making use of the Self Consistent Field (SCF) and relativistic (black curve), time-dependent DFT (red), or non-relativistic (blue) calculations.

References

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