SUPPORTING INFORMATION

Speciation of Gold Nanoparticles by ex-situ EXAFS†

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Table S1. Atomic first shell distance, coordination number (CN) and corresponding EXAFS Debye-Waller factor of the Au(III) reference materials: KAuCl4 and a 5mM $HAuCl_4$ aqueous solution.

Sample	$HAuCl_4$ 5 mM	KAuCl4 solid
Au-Cl /Å	2.29(1)	2.286(4)
σ^2/Å^2	0.0025(10)	0.0022(5)
CN	4	4
θ_1 Cl-Au-Cl /degree	180 FIX	180 FIX
σ^2_θ / degree^2	41(10)	40(10)
$E_{0\,/}$ eV	11929(1)	11929(1)
S_0^2	0.91	0.91

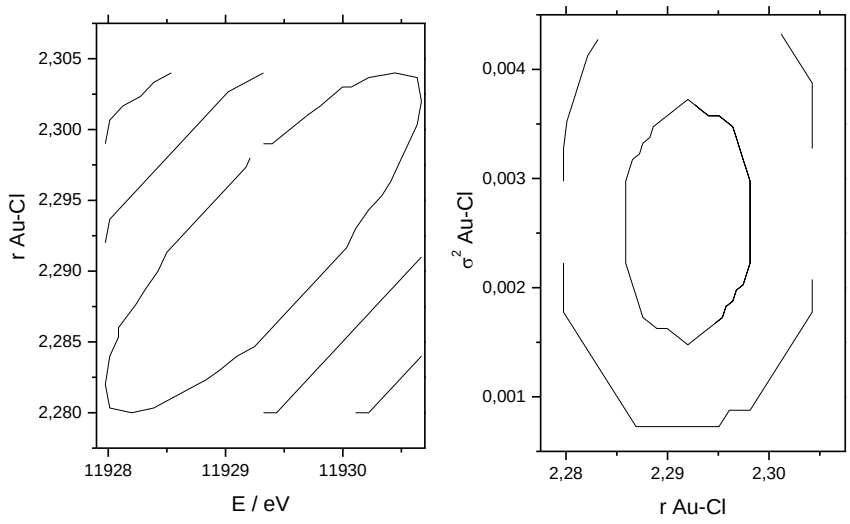

Fig. S1. Examples of CONTOUR plot for $HAuCl_4$ for the error parameters determination. These plots were selected among the parameters having strongest correlation to reflect the highest error. The estimated statistical error is associated with the 95% confidence interval.

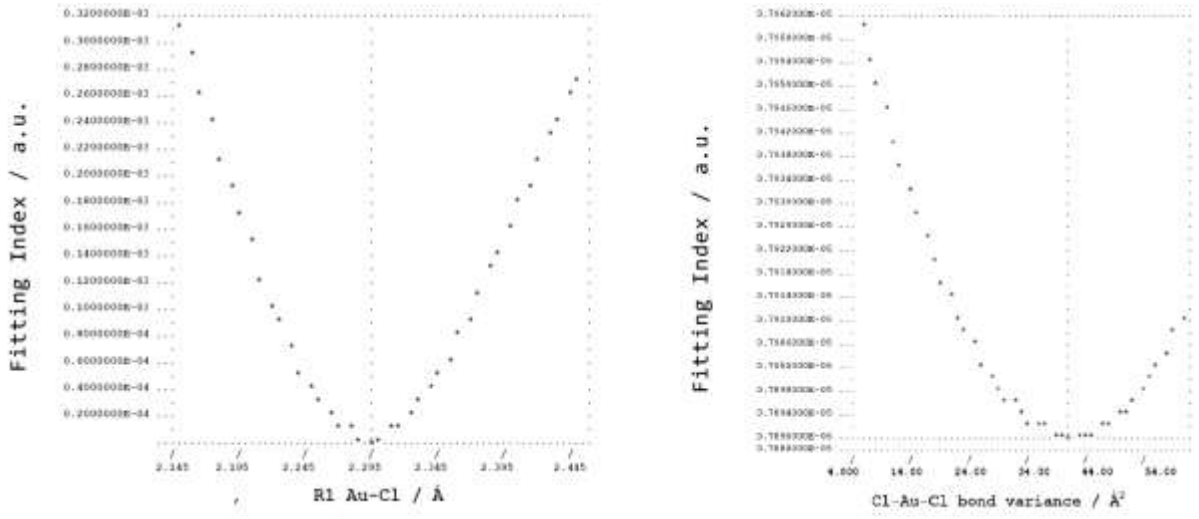

Fig. S2. Tests of the EXAFS fitting data for $HAuCl_4$. The figure displays the fitting index values (to be minimized during the fitting procedure) as a function of the Au-Cl distance (left) and of Cl-Au-Cl bond variance (right). The test have been obtained during a scan where all the other parameters were kept fixed to their optimized values. It is evident, for instance, the region of minima which identify the Au-Cl interactions 2.29 Å

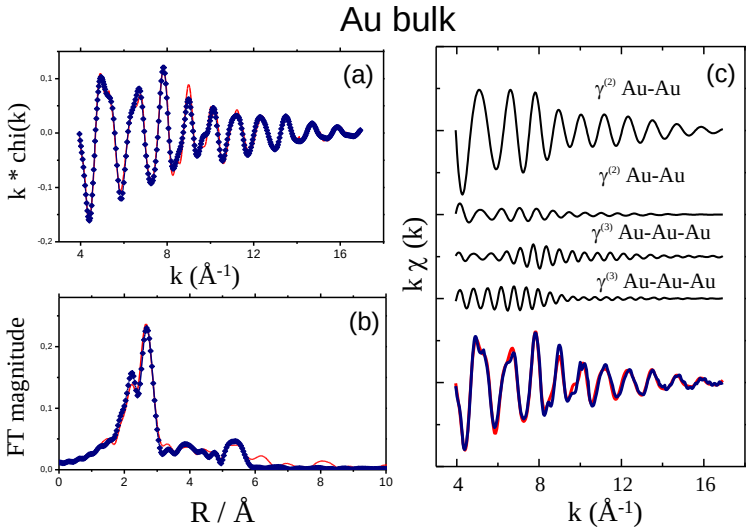

Fig. S3 Best fit of the Au L_{III}-edge EXAFS signals of Au foil (panel a) and the corresponding Fourier Transform (panel b). The figure shows the comparison of the experimental (-) and theoretical (…) k-extracted EXAFS signals. In the panel c, the details of the EXAFS analysis are shown, displaying the individual EXAFS contributions, in terms of two-body and three-body signals, to the total theoretical signal.

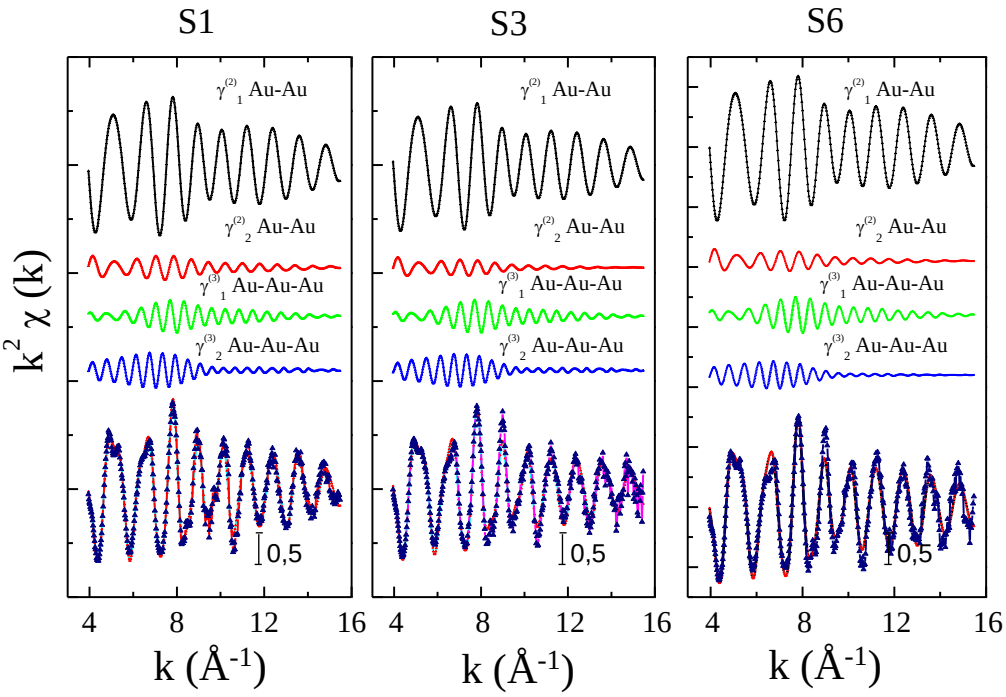

Fig. S4. Details of the EXAFS analysis of the Au LIII-edge of fully reduced samples S1, S3 and S6. The figure shows the individual EXAFS contributions, in terms of two-body and three-body signals, to the total theoretical signal. The comparison of the total theoretical signal (…) with the experimental one (-) is also reported.

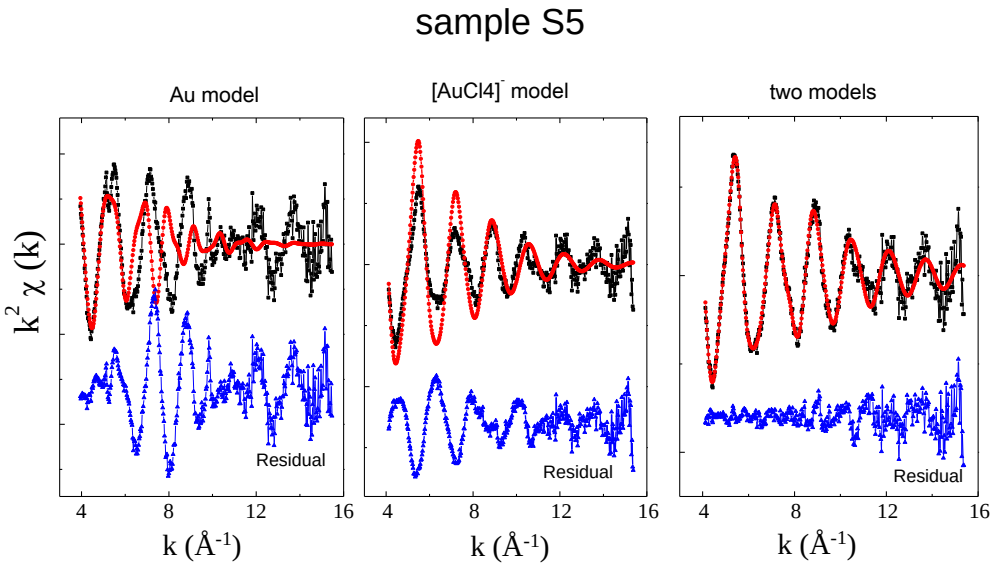

Fig. S5 Test of the EXAFS fitting procedure for sample S5 using the two selected (precursor and Au) structural models, and the combination of the two, as suggested by the LCF XANES analysis. Each panel of the Figure shows the comparison of the experimental (black curve) and theoretical (bred) and the residual (blue) at the bottom of each panel. The residual curve is rather large while the analysis has been conduved using exclusively one model (Au or AuCl4-).On the contrary, the residual curve is characterized by statistical noise in the "two models" fit (the progressive increase of the residual curve as a function of K its due to the K^2 weighted function)

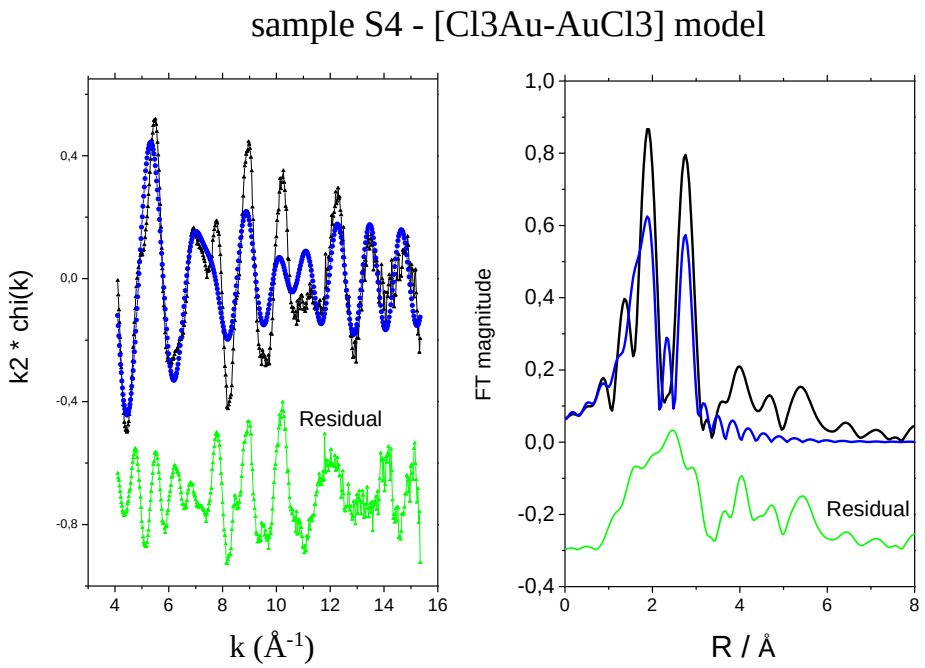

Fig. S6 Test of the EXAFS fitting procedure for sample S4 using the dimer structural model (left) and the corresponding Fourier Transform (right). The figure shows the comparison of the experimental (black curve) and theoretical (blu) and the residual (green) at the bottom of each panel. The residual curve of EXAFS is most likely due to a multiple scattering contribution (triplet of Au atoms) which is not present in the dimer model.