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ARTICLE

Photostability of gold nanoparticles with different shapes: role of Ag clusters

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Anisotropic gold nanostructures prepared by the seeds method in the presence of Ag ions have been used to study their photostability to low-power UV irradiation (254nm) at room temperature. It has been observed that, whereas spheres are very stable to photoirradiation, rods and prisms suffer from photocorrosion and finally dissolve completely with the production of Au (III) ions. Interpretation of these differences is based on the presence of semiconductor-like Ag clusters, adsorbed onto rods and prisms, able to photocorrode the Au nanoparticles, which are absent in the case of Au spheres. We further show a direct evidence of the presence of Ag clusters in Au nanorods by XANES. These results confirm previous hypothesis (J. Am. Chem. Soc. 2014, 136, 1182–1185) about the major influence of very stable, small Ag clusters, not only on the anisotropic formation of nanostructures, but also on their photostability.

Introduction

Clusters are particles with well-defined structures and composition having a low number of atoms, below approximately 150 ($< \approx 1.7$ nm in size)¹. The behavior of such clusters is different from nanoparticles of higher sizes because their sizes become comparable to the Fermi wavelength of the electron (approx. 2 nm in Au or Ag)¹. Many examples have been reported for the synthesis of clusters of different metals and their applications². One of the main features of metal clusters is that the surface Plasmon resonance (SPR) -typical for metallic particles- disappears since all cluster electrons are covalently bonded³. Secondly, a band gap appears giving rise to semiconductor-like (or molecular-like) properties, such as photoluminescence, which is one of the most studied properties in metal clusters⁴. Due to the presence of such band gap, clusters are very stable, mostly those with a small number of atoms, which are very difficult to reduce or oxidize due to their huge band gaps⁵. From such studies photocatalytic activities of clusters could be expected, and indeed, some of us recently reported large photocatalytic activities for Ag and Cu clusters^{6,7}.

Unlike bulk or clusters, gold nanoparticles can exhibit bright colors and different properties, which have made them hugely popular objects of study for chemists, physicists, and biomedical practitioners⁸. One of the desired objectives of nanoscale science is the challenge to control the morphology of the nanoparticles. For that reason, systematic efforts have been made to find different parameters that directly affect the substantial properties of materials

at this length scale⁹. Large developments of shape control enable nowadays to synthesize nanoparticles of non-spherical shapes, such as rods, prisms, cubes, cuboctahedrons, octahedrons, decahedrons, icosahedrons, truncated octahedrons, etc. having different physical properties¹⁰⁻¹⁹. Synthesis of anisotropic structures such as gold nanorods and nanowires were widely studied since Murphy's²⁰ and El-Sayed's²¹⁻²³ pioneering works, and has attracted much attention due to the fine-tuning of light absorption from visible to near infrared just by changing the aspect ratios (length/diameter). These unique optical properties of gold nanostructures have been exploited in sensing, imaging, biomedicine, biodiagnostics, catalysis, optoelectronics, film growth seeding, and other potential applications^{8, 24-36}. Several studies about the stability under photoirradiation of gold nanoparticles have also been reported³⁷⁻⁴⁴. For example, Al-Sherbini *et al.*³⁷ studied the effect of UV-light on gold nanorods with different aspect ratios in water/ glycerol mixtures. Recently, we show that small Ag clusters can, not only catalyze the formation of gold nanorods⁶, but also promote the photocorrosion of Au nanowires by low intensity UV irradiation. However, a direct proof of the presence of such semiconductor-like Ag clusters at the surface of the Au nanorods and their possible influence on the photostability of other gold shapes, like spheres, prisms, etc. is still lacking.

In this work we show the presence of small Ag clusters in Au nanorods by XANES. Such experiments show also the Au oxidation by Ag clusters, confirming the high stability of clusters. We further show that the photocorrosion of Au prisms begins -similarly to Au nanorods- at the prism tips indicating the preferential adsorption of Ag clusters on the tips crystal planes. On the contrary, Au

nanospheres (in which Ag clusters are absent because no Ag is added in their synthesis) do not photocorrode. These results confirm the major influence that small Ag clusters have on the photostability of anisotropic Au nanostructures.

Results and discussion

We successfully modified the seed method in order to get a more precise control of the shape of the gold nanoparticles using the results showed before⁶. Anisotropic gold nanoparticles with different shapes were synthesized using different concentrations of silver ions and seeds solutions. Figure 1 shows the UV-Vis spectra of different anisotropic gold nanoparticles synthesized in the present study.

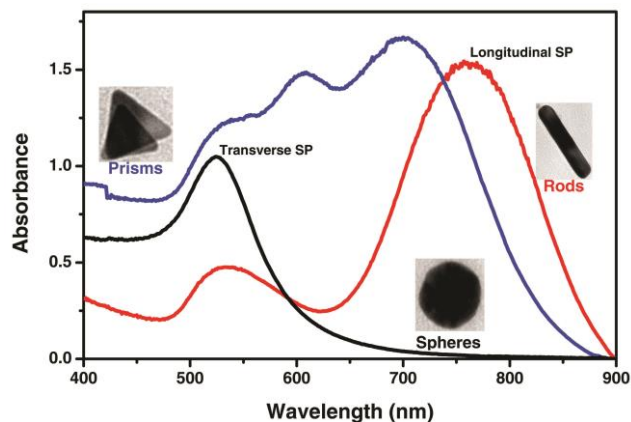


Figure 1. Typical absorption spectra of gold nanoparticles with different shapes.

Spherical gold nanoparticles show high stability against low-power UV-irradiation (254nm), as it can be seen from their optical UV-Vis spectra, showing only very small changes after 25 hours of irradiation (see Figure 2).

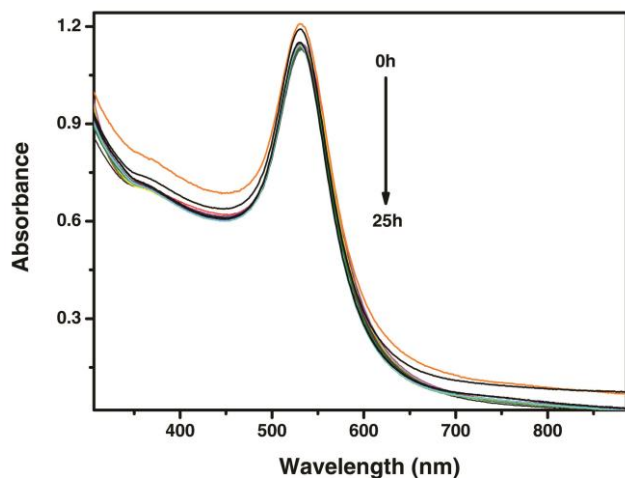


Figure 2. Absorption spectra of gold nanospheres showing almost no remarkable change after 25 hours of low-power UV-irradiation.

For comparison purposes we show here the evolution of the absorbance intensity for gold nanorods under UV light irradiation (Figure 3). Both longitudinal SP_L and transverse plasmon SP_T bands decrease when irradiation time increases and the absorption maximum is gradually shifted to shorter wavelengths until total disappearance of the plasmon bands and the increase of the band at ≈ 400 nm corresponding to the Au (III) salt. This shows the total dissolution of the gold nanorods in agreement with previously reported results⁶.

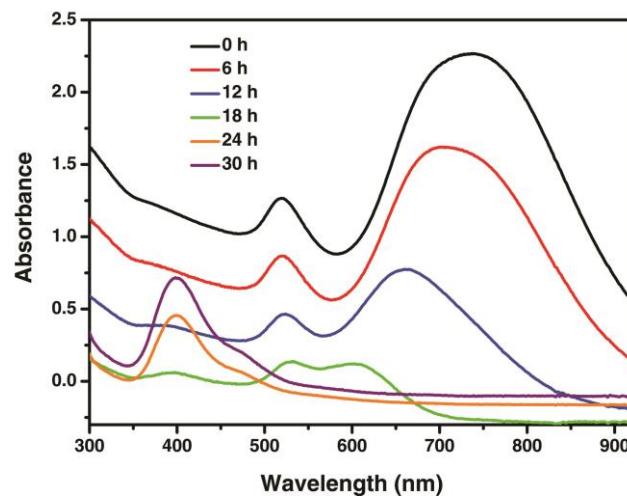


Figure 3. Absorption spectra showing the exposure of gold nanorods to low-power UV-light at different times until their complete dissolution, and the growing of the corresponding Au (III) ions band at 398nm.

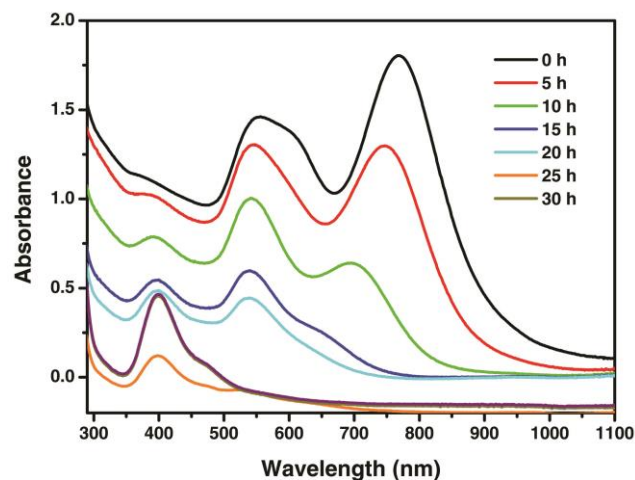


Figure 4. Absorption spectra showing the effect of low-power UV-light on gold nanoprisms at different times indicating their complete dissolution, and the appearance of the Au (III) ions band at 398nm.

Figure 4 shows the evolution of the UV-Vis absorption spectra of gold nanoprisms with the irradiation time. It can be observed that the third intermediate band firstly disappears very fast (after approx. 5 hours of irradiation), and then the two remaining

Plasmon bands also disappear gradually, similarly to the evolution observed before for the gold nanorods. Finally, a complete dissolution of the Au prisms occurs, as it is observed by the increase of the band at ≈ 400 nm corresponding to the Au (III) salt.

In order to check the evolution of the gold nanostructures during UV-irradiation we carried out a TEM analysis of the samples at different times of irradiation. A comparison of the nanoparticles evolution by TEM is summarized in Figure 5 for nanorods and nanoprisms. It can be seen that nanorods firstly evolve through the formation of peanut-shaped nanostructures, giving rise to spherical particles, which shrink and finally almost disappear after 25 hours. Nanoprisms firstly evolve to the formation of snapped prisms, which are then transformed into peanut-shape nanostructures, and finally dissolve almost completely after 30 hours of irradiation.

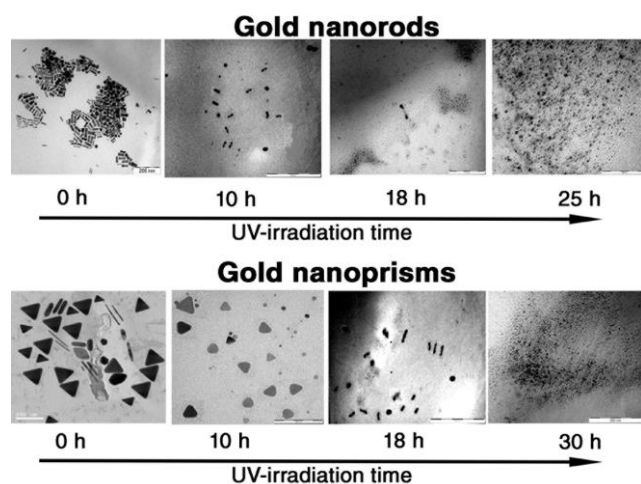


Figure 5. TEM images showing the effect of the low-power UV-irradiation on gold nanorods and nanoprisms at different irradiation times.

The exposure of Au nanorods and Au nanoprisms to low-power UV-irradiation (254nm) leads to complete photodecomposition of these particles after approx. 30 h. In both cases, at the end, a new band at 398 nm with a small shoulder at 478 nm started to grow at 16 and 10 hours of irradiation, respectively, as it is shown in Figures 3 and 4. This band is similar to the absorption spectrum of Au(III)-CTAB complex solution indicating the complete photocorrosion of Au, as it was previously reported for Au nanorods⁶. It can be seen that both, Au nanoprisms and Au nanorods display a similar behavior, forming firstly peanut-shape particles, which are finally photo-etched to produce spherical particles and finally dissolve completely. Attia *et. al.*⁶ explained this behavior assuming the presence of Ag clusters, with semiconducting-like properties, adsorbed preferentially at the tips of the nanorods, although a direct proof for the presence of such clusters is still lacking. For this purpose we used XANES methods to clarify this important aspect. The results are shown in Figure 6.

The feature of the XANES spectrum of Ag at the L_3 -edge corresponding to Ag clusters present in nanorods shown in Figure 6 clearly does not fit to any reported reference compound. Even this it is possible to analyze qualitatively the shape of the spectra in order to elucidate the state of Ag atoms in this system. The most remarkable feature is that the resonances in the XANES spectrum for Ag-clusters present in gold nanorods, indicated with vertical lines in Figure 6, are in the same position than that of the metallic

Ag spectra. These resonances are related to the multiple scattering contribution of the atoms around Ag and its similarity to the Ag bulk reveals that the main contribution to the XANES spectra in this region is due to Ag atoms at distances similar to that of the Ag bulk. The smoothed feature of XANES spectrum in this region corresponding to Ag-clusters is consistent with their extreme nano/sub-nano-sized characteristic. The region just after the edge give information of the LUMO orbital of the Ag atoms and in the particular case of Ag L_3 are assigned to the transition from 2p to 5s enhanced by the *s-d* hybridization⁴⁵. Comparing the spectra of Ag cluster over Au rods with that of the AgCl it is evident that the density of unoccupied electronic states clearly decreases (Fig. 6), evidenced by the disappearance of the peak in the AgCl spectra. This indicates that Ag *s-d* hybrid orbitals near the Fermi level are filled in Ag atoms in the cluster configuration.

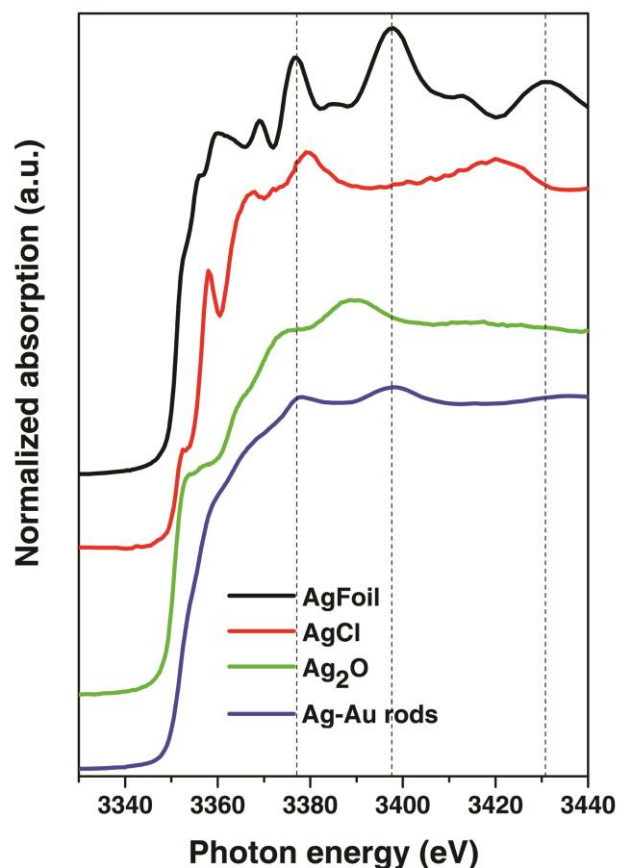


Figure 6. Normalized Ag L_3 -XANES spectra of metallic Ag (black), AgCl precursor (red), Ag_2O (green) and Ag clusters present in Au nanorods (blue). Vertical dotted line indicates the resonance associated with metallic state of Ag.

Additional insights about the Ag clusters' electronic structure and their interaction with Au atoms in nanorods can be also obtained from XANES. In Figure 7 we show the comparison between the Ag L_3 -XANES spectra corresponding to isolated Ag clusters (Ag clusters dispersed in water) and those present in Au-nanorods. A visible difference between both XANES spectra, in both shape and intensity, is clearly observed indicating that electronic structure of Ag clusters is modified due to the interaction with Au. More specifically, the higher intensity of the spectrum corresponding to

Ag atoms in isolated clusters, in relation to that on the ones in Au rods, indicates the higher density of unoccupied states at the *s-d* hybrid orbitals in the isolated clusters. This result suggests the interaction between Ag clusters with Au nanorods by transferring electrons from Au to Ag atoms supporting the hypothesis about the Au photooxidation by Ag clusters. Looking at the difference between Ag clusters spectra and that one of the Ag bulk for both samples (showed in the lower part of Figure 7) it is clear that the multiple scattering region is preserved between samples. This last result shows that, even there is an interaction between Ag clusters and the Au rods, the geometrical structure of Ag clusters is almost preserved.

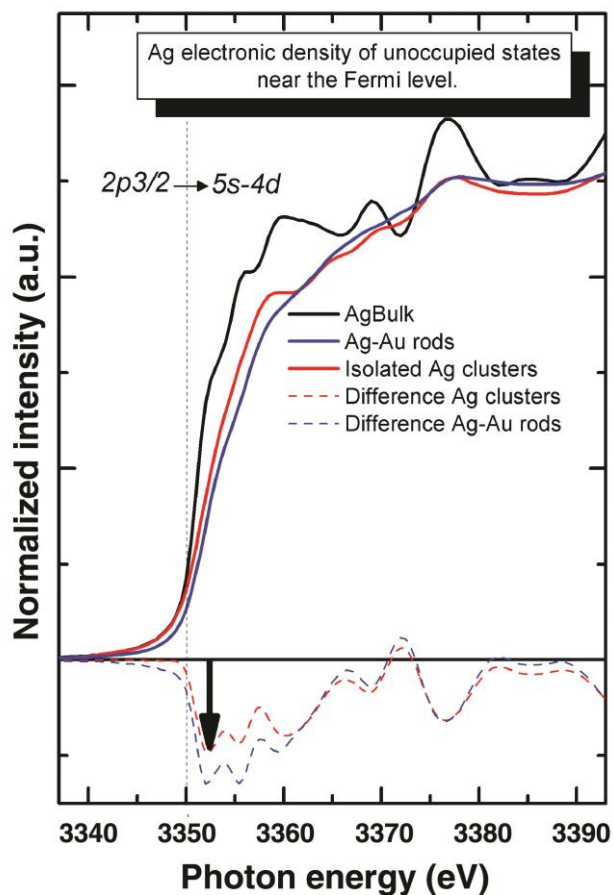
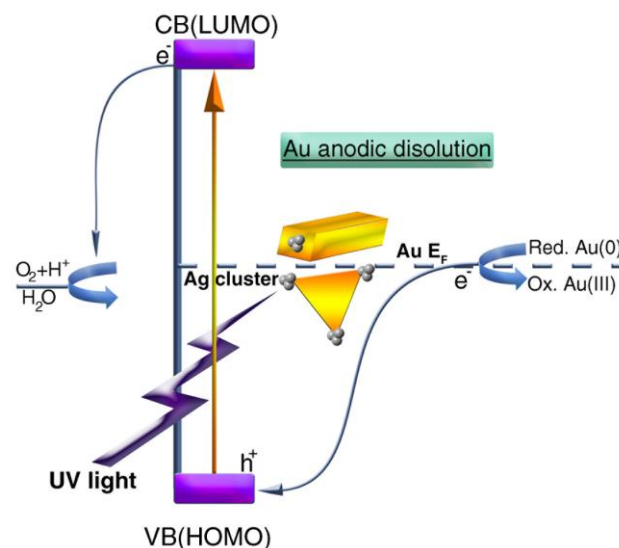


Figure 7. Upper figure show the near edge region for isolated Ag clusters (red) and Ag clusters in Au rods (blue). In both cases Ag clusters exhibit lower density of unoccupied electronic states, associated to the $2p_{3/2} \rightarrow 4d^*$ electronic transition in relation to the metallic Ag. Difference of Ag 4d electronic density of unoccupied states in relation to metallic Ag are showed in the lower figure.

All the results presented above allow us to argue that the presence of Ag clusters is responsible for the observed photodissolution of the rods and prisms. As we mentioned in the Introduction, clusters have molecular or semiconductor-like properties^{3,4, 46-57}, and in the particular case of the small silver clusters considered here, they also show absorption bands in the UV region^{5,6}. When irradiated with UV light, the photoproduced electrons and holes are easily separated because 1) their atom-scale size and 2) the fact that they are directly attached to the Au nanorods without any intermediate

region, being such properties very different from typical semiconductors. The dissolved oxygen easily scavenges photoelectrons and the highly oxidant photoproduced holes oxidize the Au nanoparticles producing Au(III) ions as it is observed by the appearance of their absorption bands (see Scheme1). Such mechanism also explains that, in the absence of Ag clusters, no photodissolution occurs, which is the case of the growth of gold nanospheres, being this clusters' absence the main reason for their stability under UV- irradiation.



Scheme 1. Illustration of the involvement of semiconductor-like Ag clusters in the photodissolution of gold nanorods and nanoprisms by low-power UV irradiation (Au E_F = Gold Fermi level).

Conclusions

It has been observed that gold nanorods/nanoprisms are photodissolved under low-power-UV irradiation at room temperature, indicating that Au (0) is totally oxidized to Au (III) yielding a Au (III)-CTAB complex. Using XANES we could confirm the presence of very stable, small Ag-clusters attached to gold, which allows us to explain the observed Au photodissolution by their semiconductor-like properties. On the contrary, Au nanospheres, which grow without the presence of Ag clusters, are photostable. These results confirm previous hypothesis about the major influence of Ag clusters, not only on the anisotropic formation of nanostructures, but also on their photostability, which is an important parameter for the application of Au nanostructures, previously overlooked.

Experimental Section

Materials and Methods

Cetyltrimethylammonium bromide (CTAB) (98%), Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99%), Sodium borohydride (NaBH_4 , 99%), Silver nitrate (AgNO_3), Polyvinyl pyrrolidone (PVP-K30), and L-ascorbic acid were purchased

from Sigma-Aldrich. Ag clusters (NGAP AQC Ag-1104W) dispersed in water were purchased from Nanogap. According to the supplier Ag clusters are in the range 2 to 4 atoms in size. Before using, cluster sizes were checked by us using Mass Spectrometry and Fluorescence Spectroscopy.

For the preparation of different shapes of gold nanoparticles, seeds and growth solutions were made as described below.

Seeds solution: 2.5 ml of 0.2 M CTAB solution was mixed with 2.5 ml of 0.5mM HAuCl₄. To the stirred solution, 30 μ l of ice-cold 0.1M NaBH₄ was added, which results in the formation of a brownish yellow solution. Vigorous stirring of the seeds solution was continued for 2 minutes.

Growth solution: Different amounts (0 - 0.25ml) of 4mM AgNO₃ solution were added to 2.5 ml of 0.2 M CTAB solution. Then, 2.5 ml of 1mM HAuCl₄ was added and after gentle mixing of the solution, 35 μ l of 0.1 M ascorbic acid was added. Ascorbic acid changes the growth solution from dark yellow to colorless within 10 minutes.

Then the seeds solution was added to the growth solution. The color of the solution gradually changed within 10-20 minutes.

Photostability of gold nanoparticles:

To study the photostability of gold nanoparticles, 3 ml of the colloidal gold solution was put in a thermostated quartz cuvette (25°C) and irradiated with a UV source (Analamp mod. 81-105-7-01, 254nm, USA). Photostability of gold nanoparticles has been followed by measuring the changes in absorption spectra as a function of time using a Perkin-Elmer Lambda 40 spectrometer. The particles were characterized by Transmission Electron Microscopy (TEM) with a Philips CM20 microscope, operating at an accelerating voltage of 200 KV.

X-ray absorption near edge structure (XANES) experiments:

X-ray absorption fine structure measurements with soft X-rays were obtained at the SXS beamline of the Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. XANES spectra were obtained at the Ag L₃-edge (3351 eV). In order to perform the XANES experiments at the Ag L₃-edge samples were carefully mounted in a liquid sample holder designed ad-hoc for this experiment. A Si(111) double-crystal monochromator with a slit aperture of 1 mm that allow to achieve a resolution of about 0.5 eV. Details of the experimental setup of the SXS beam line have been published elsewhere⁵⁸. The X-ray absorption spectra were recorded in fluorescence mode, collecting the emitted X ray from the Ag L $\alpha_{1,2}$ emission lines. Experiments were performed in a vacuum of 10⁻⁸ mbar at room temperature. The energy scale was calibrated setting the Ag L₃-edge, defined by the first inflection point, of the X-ray absorption spectrum of the Ag metallic foil sample to 3351 eV. The final XANES spectra were obtained after background subtraction and normalization to the post edge intensity following usual procedure.

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Notes and references

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