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

Yasser A. Attia,^{a,b,c} David Buceta,^a Félix G. Requejo,^d Lisandro J. Giovanetti^d and M. Arturo López-Quintela^{*a}

Anisotropic gold nanostructures prepared by the seed method in the presence of Ag ions have been used to study their photostability to low-power UV irradiation (254 nm) at room temperature. It has been observed that, whereas spheres are very stable to photo-irradiation, 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 direct evidence of the presence of Ag clusters in Au nanorods by XANES. These results confirm a 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 (≈ 1.7 nm in size).¹ The behavior of such clusters is different from nanoparticles of larger sizes because their sizes are comparable to the Fermi wavelength of the electrons (approx. 2 nm in Au or Ag).¹ Many examples have been reported for the synthesis of clusters of different metals and their applications.² One of the main features of metal clusters is that the surface plasmon resonance (SPR) – typical of metallic particles – disappears since all cluster electrons are covalently bonded.³

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 clusters.⁴ Due to the presence of such band gaps, 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 gaps.⁵ 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 practitioners.⁸ One of the desired objectives of nanoscale science is the challenge to control the morphology of the nanoparticles. For this reason, systematic efforts have been made to find different parameters that directly affect the substantial properties of materials on this length scale.⁹ Large developments in shape control nowadays enable the synthesis of nanoparticles of non-spherical shapes, such as rods, prisms, cubes, cuboctahedra, octahedra, decahedra, icosahedra, truncated octahedra, *etc.* having different physical properties.^{10–19} Synthesis of anisotropic structures such as gold nanorods and nanowires has been widely studied since Murphy's²⁰ and El-Sayed's^{21–23} 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 on the stability under photo-irradiation of gold nanoparticles have also been reported.^{37–44} 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 have shown that small Ag clusters can not only catalyze the formation of gold nanorods,⁶ but also promote the photocorrosion of Au nanowires by low intensity UV irradiation. However, direct proof of the pres-

^aLaboratorio de Magnetismo y Nanotecnología, Technological Research Institute, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain. E-mail: malopez.quintela@usc.es

^bNational Institute of Laser Enhanced Sciences, Cairo University, 12631, Egypt

^cDepartment of Chemistry, Faculty of Sciences, Taif University, 21974, Saudi Arabia

^dInstituto de Investigaciones Físicoquímicas Teóricas y Aplicadas – INIFTA (CONICET, UNLP) – Diagonal 113 y calle 64, 1900 La Plata, Argentina

ence 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 also show the Au oxidation by Ag clusters, confirming the high stability of clusters. We further show that the photocorrosion of Au prisms begins – similar 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 shown previously.⁶ Anisotropic gold nanoparticles with different shapes were synthesized using different concentrations of silver ions and seed solutions. Fig. 1 shows the UV-Vis spectra of different anisotropic gold nanoparticles synthesized in the present study.

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

For comparison purposes we show here the evolution of the absorbance intensity for gold nanorods under UV light irradiation (Fig. 3). Both longitudinal SP_L and transverse SP_T plasmon bands decrease when the irradiation time increases and the absorption maximum is gradually shifted to shorter wavelengths until the total disappearance of the plasmon bands and the increase of the band at ≈ 400 nm corresponding

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

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

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

to the Au(III) salt. This shows the total dissolution of the gold nanorods in agreement with previously reported results.⁶

Fig. 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 first disappears very fast (after approx. 5 hours of irradiation), and then the two remaining plasmon bands also disappear gradually, similarly to the evolution observed previously for the gold nanorods. Finally, a complete dissolution of the Au prisms occurs, as 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 irradiation times. A comparison of the nanoparticles evolution by TEM is summarized in Fig. 5 for

Fig. 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) ion band at 398 nm.

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

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 first evolve to form snapped prisms, which are then transformed into peanut-shape nanostructures, and finally dissolve almost completely after 30 hours of irradiation.

The exposure of Au nanorods and Au nanoprisms to low-power UV-irradiation (254 nm) 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 shown in Fig. 3 and 4. This band is similar to the absorption spectrum of the Au(III)-CTAB complex solution indicating the complete photocorrosion of Au, as was pre-

Fig. 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 lines indicate the resonance associated with the metallic state of Ag.

viously reported for Au nanorods.⁶ 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 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 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 Fig. 6.

The feature of the XANES spectrum of Ag at the L_3 -edge corresponding to the Ag clusters present in nanorods shown in Fig. 6 clearly does not fit to any reported reference compound. Even then 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 Fig. 6, are in the same position as 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 the Ag

atoms at distances similar to that of the Ag bulk. The smooth feature of the XANES spectrum in this region corresponding to Ag-clusters is consistent with their extreme nano/sub-nano-size characteristic. The region just after the edge gives information of the LUMO orbital of the Ag atoms and in the particular case of Ag L_3 it is assigned to the transition from $2p$ to $5s$ enhanced by the s - d hybridization.⁴⁵ Comparing the spectra of the Ag cluster over Au rods with that of the AgCl, it is evident that the density of the 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 with Ag atoms in the cluster configuration.

Additional insights about the Ag clusters' electronic structure and their interaction with Au atoms in nanorods can also be obtained from XANES. In Fig. 7 we show the comparison between the Ag L_3 -XANES spectra corresponding to the isolated Ag clusters (Ag clusters dispersed in water) and those present in Au-nanorods. A visible difference between both

Fig. 7 Upper figure shows 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 with the $2p_{3/2} \rightarrow 4d^*$ electronic transition in relation to the metallic Ag. Differences of Ag $4d$ electron density of unoccupied states in relation to metallic Ag are shown in the lower figure.

XANES spectra, in both shape and intensity, is clearly observed indicating that the electronic structure of Ag clusters is modified due to the interaction with Au. More specifically, the higher intensity of the spectrum corresponding to the Ag atoms in isolated clusters, in relation to those on the Au rods, indicates the higher density of the unoccupied states at the s - d hybrid orbitals in the isolated clusters. This result suggests the interaction between Ag clusters and 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 of the Ag bulk for both samples (shown in the lower part of Fig. 7) it is clear that the multiple scattering region is preserved between the samples. This last result shows that, even though there is an interaction between the Ag clusters and the Au rods, the geometrical structure of Ag clusters is almost preserved.

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 of (1) their atom-scale size and (2) the fact that they are directly attached to the Au nanorods without any intermediate region, such properties being 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 is observed by the appearance of their absorption bands (see Scheme 1). Such a mechanism also explains that, in the absence of Ag clusters, no photodissolution occurs, which is the case for the growth

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).

of gold nanospheres, these clusters' absence being the main reason for their stability under UV-irradiation.

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 an 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 in the absence of Ag clusters, are photostable. These results confirm a 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 tetrachloroauratetrihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 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 of 2 to 4 atoms in size. Before use, cluster sizes were checked by us using Mass Spectrometry and Fluorescence Spectroscopy.

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

Seed solution. 2.5 mL of 0.2 M CTAB solution was mixed with 2.5 mL of 0.5 mM HAuCl_4 . To the stirred solution, 30 μL of ice-cold 0.1 M NaBH_4 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 (0–0.25 mL) of 4 mM AgNO_3 solution were added to 2.5 mL of 0.2 M CTAB solution. Then, 2.5 mL of 1 mM HAuCl_4 was added and after gentle mixing of the solution, 35 μL of 0.1 M ascorbic acid was added. Ascorbic acid changes the growth solution from dark yellow to colorless within 10 minutes.

Then the seed 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, 254 nm, USA). Photostability of gold nanoparticles

was 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 Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, Brazil. XANES spectra were obtained at the Ag L_3 -edge (3351 eV). In order to perform the XANES experiments at the Ag L_3 -edge, the 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 was used that allowed to achieve a resolution of about 0.5 eV. Details of the experimental setup of the SXS beam line have been published elsewhere.⁵⁸ 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 L_3 -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 by following the usual procedure.

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