

Outstanding chemical inertness of sub-nanometric Au₂ and Au₃ clusters

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Abstract

Subnanometric clusters of a few number of atoms are of large interest due to totally different properties than nanoparticles and bulk materials. In these subnanometric range exceptional catalytic activities have been reported. However, cluster properties change dramatically with only a few atoms difference, and not always following a trend. For example, one can extrapolate that the smaller is the cluster, the better would be the catalytic activity. Using monodisperse Au cluster samples containing only Au₂ and Au₃, we show here that this is far from being the case. These smallest clusters, due to their huge bandgap, show outstanding inertness, demonstrating that clusters larger than 3 atoms have to be used for application in catalysis.

Keywords: Gold cluster, subnanometric, chemical inertness, bandgap

Introduction

It is well known that when the size of materials is reduced the catalytic activity increases due to the increase of the surface/volume ratio. However, different behaviors appear at the lower limit of particles sizes (below ≈ 10 nm). For example, the catalytic activity of Pt nanoparticles (NPs) for the CO oxidation decreases almost 2 orders of magnitude from 10 to 1.5 nm. On the contrary, the catalytic activity of Au NPs increases 20 times in the same range of sizes (Shimada et al., 2010).

Moreover, when the size is below ≈ 2 nanometers (called *metal clusters of atoms*) new properties appear. Metal clusters can be considered as transition materials between NPs and atoms. They show significant features totally different from NPs, due to the appearance of a band gap (more precisely a HOMO-LUMO gap), such as luminescence, magnetism, circular dichroism, catalytic activities, etc. (D. Buceta et al., 2014; X. Huang et al., 2019; Jena & Sun, 2018; Jin et al., 2016; Kang & Zhu, 2019; Liu & Corma, 2018). For the case of gold, the transition from a metallic to an emissive behavior occurs at ≈ 1.5 nm, which corresponds to around 200 atoms (Jin et al., 2016). Au clusters also show excellent catalytic properties (see e.g. (Liu & Corma, 2018)).

Although many studies have been reported about their catalytic activities there is no general agreement about how the catalytic activity depends on the number of atoms. For example, Lee et al. (Lee et al., 2009) reported that Au₆-Au₁₀ clusters can catalyze the epoxidation of propylene with a selectivity of 90% towards propylene oxide; however, using larger clusters with sizes < 2nm, the group of Haruta (J. Huang et al., 2009) found a lower selectivity of 53%, indicating that smaller sizes display higher activities. For thiol oxidation Corma et al. found that only Au clusters in the range Au₅-Au₁₀ show outstanding catalytic activities, whereas neither isolated atoms nor clusters above 15-25 atoms show any catalytic activity (Corma et al., 2013). The question now arises what the minimum number of atoms are needed in the cluster to display catalytic activities. We previously show that, for electrocatalytic activities, only clusters in the medium range of sizes $\approx >10$ atoms could display catalytic activities for the HOR, whereas small clusters with 2-5 atoms do not display any activity for this reaction (D Buceta et al., 2014).

However, the conclusions showed above were taken with polydisperse cluster samples, so that more specific studies must be done to arrive to the right conclusions.

Using a modification of a previous electrochemical method (Corma et al., 2013) we could synthesize Au clusters in water, without any capping agent, containing only 2 and 3 atoms. With these samples we could demonstrate that such small clusters do not display any appreciable electrocatalytic activity, contrary to what happens with larger clusters.

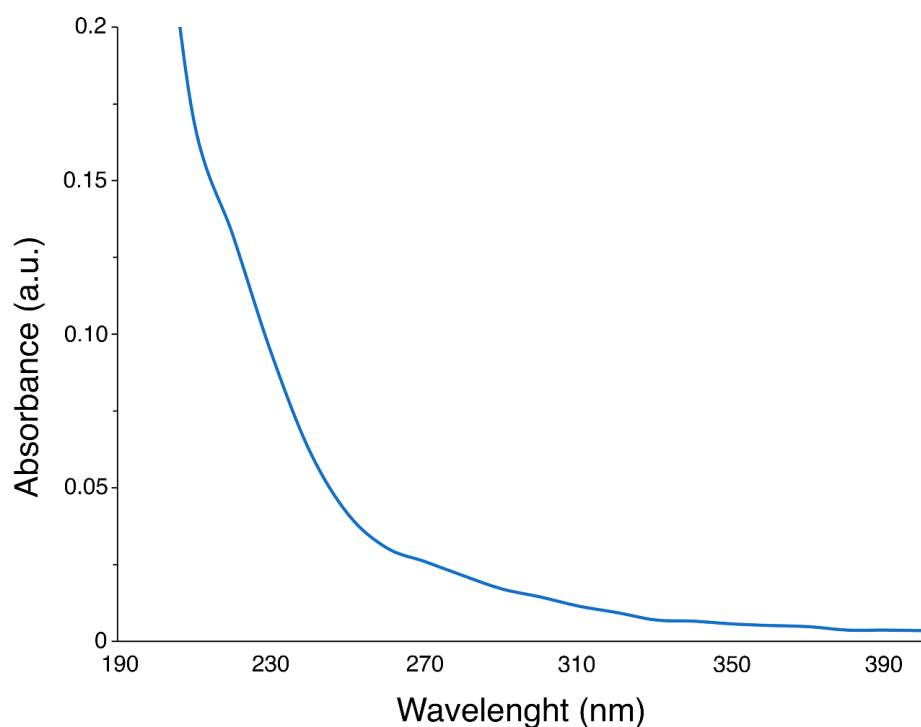
Results and Discussion

Cluster synthesis and characterization

Our group reported before the synthesis of small Au clusters by an electrochemical technique. In the first report in 2008 we used a galvanostatic procedure (with a gold sheet as counter electrode and a platinum sheet as working electrode) in acetonitrile, using tertbutyl ammonium bromide (TBA) and applying a current density of 5 mA/cm² during 300s.

The samples contained a broad distribution of sizes in the range Au_3 - Au_{11} , being Au_3 the major species in the samples. A large improvement was made a couple of years later (Gonzalez et al., 2010) in which a much monodisperse sample of Au_2 and Au_3 could be synthesized using again a galvanostatic procedure (with a gold sheet as counter electrode and a copper sheet as working electrode) in acetonitrile, using PVP as protecting agent and applying a current density of $10\text{mA}/\text{cm}^2$ during 300 s. Both described methods used a capping agent, which it is recognized that can change the physicochemical properties of clusters. For this reason, in 2013 we reported for the first time a procedure to prepare similar small clusters in water without using any capping agent (Corma et al., 2013). For this purpose, we applied a fixed potential (8V) between a gold foil and a platinum foil at 35°C fixing the potential at -8V during 6200 s. Although the main cluster size obtained with such procedure was Au_3 , the samples contained a not negligible number of larger clusters (Ag_4 - Au_{10}), as it can be observed by the broad emission peak of the reported luminescence spectrum. In this work we could reduce further the polydispersity of cluster sizes employing similar conditions (i.e. water as solvent without any protecting agent) but just reducing the temperature to 25°C .

Figure (1) shows the UV-Vis spectrum of the synthesized samples. It can be seen that there is an increase of the absorption at low wavelengths ($\approx 350\text{nm}$, i.e. 3.5eV) with some small bumps, characteristic of very small cluster samples.



Figure(1): Absorbance spectrum of the Au cluster samples in water

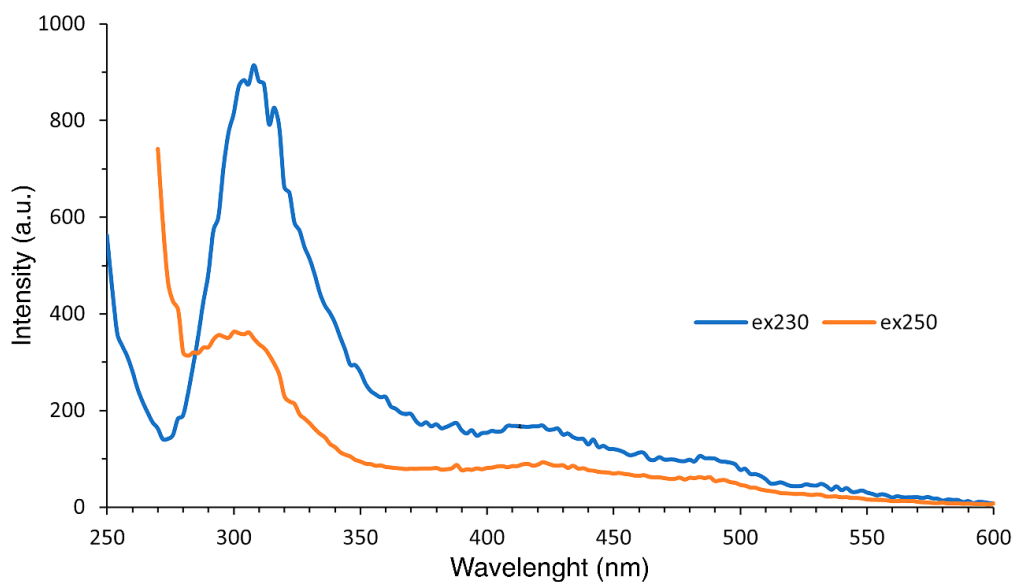


Figure (2): Emission spectra (with excitations at 230 nm and 250 nm) of the Au cluster samples in water

The emission spectra (Figure (2)) show the presence of a main broad peak at 306 nm (with additional small peaks at 410nm and 480nm).

The main peak can be fitted to three main Lorentzians (Figure (3)) centered at 306nm, 330nm and 350nm (4.05eV, 3.76eV and 3.54eV, respectively). The position of the emission peaks can be used to estimate the cluster size using the Jellium model (Piñeiro et al., 2018; Zheng et al., 2007). According to this model, the number (N) of atoms in the cluster can be deduced by the formula, $N = [E_F / E_g]^3$, where E_F is the Fermi level of the metal and E_g is the bandgap (or HOMO-LUMO gap), which can be approximated by the emission peak. Then, from the emission peaks one can conclude the presence of clusters with 2 and 3 atoms ($N = 2.3$; 2.8 and 3.3). It has to be noticed that three bands at similar wavelengths (315nm, 335nm and 350 nm) were also found for a mixture of Au_2 and Au_3 clusters synthesized by an electrochemical procedure using PVP as a protecting ligand. Also, a much broader and non-resolved emission band, centered at 337nm, was attributed before to Au_3 clusters (Corma et al., 2013), clearly indicating the much more monodispersity of the samples obtained by the new electrochemical procedure.

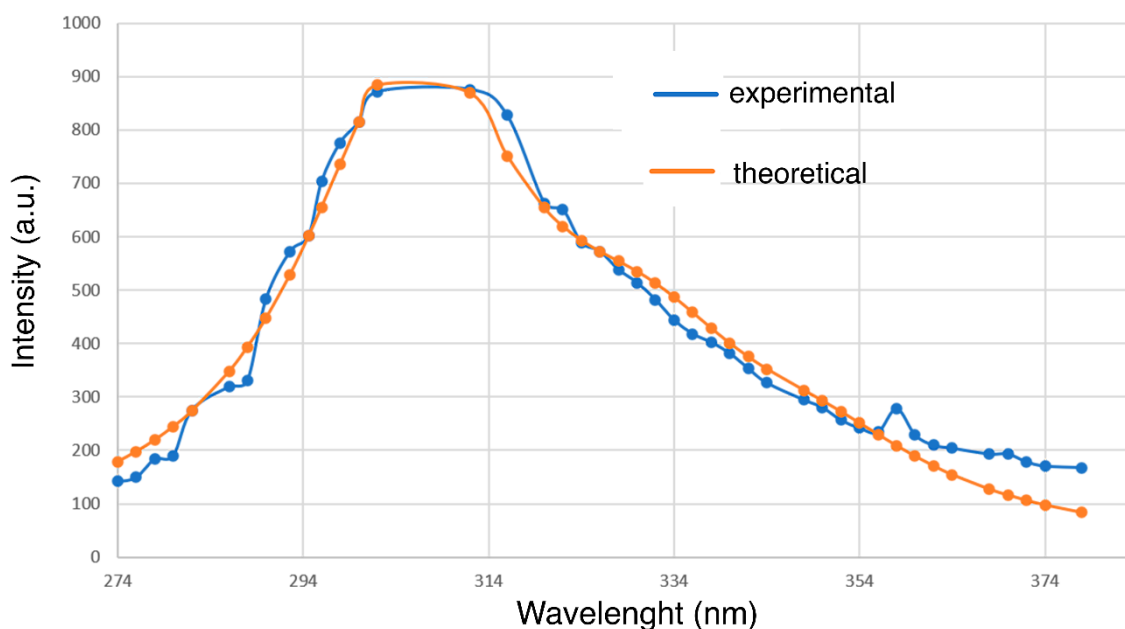


Figure (3): Lorentian fitting of the emission spectrum of Au clusters

To identify further the Au cluster samples we carried out an analysis by atomic force microscopy in non-contact mode (NC-AFM). For this purpose, samples were deposited onto planar mica, with a mean roughness of 150pm (Figure (4)).

Figure (5) shows a typical topographic image of the synthesized samples indicating that clusters are sub-nanometric in size ($\approx 750\text{pm}$). The histogram of the images (Figure (6)) gives an average cluster size of 0.56 nm , which is very similar to the sizes ($\approx 0.3\text{nm}$ and 0.5nm for Au_2 and Au_3) derived from HAADF-STEM images previously obtained (Corma et al., 2013). It has to be noticed that some larger spots observed in the AFM images can be due to unavoidable clustering of clusters, during the sample deposition.

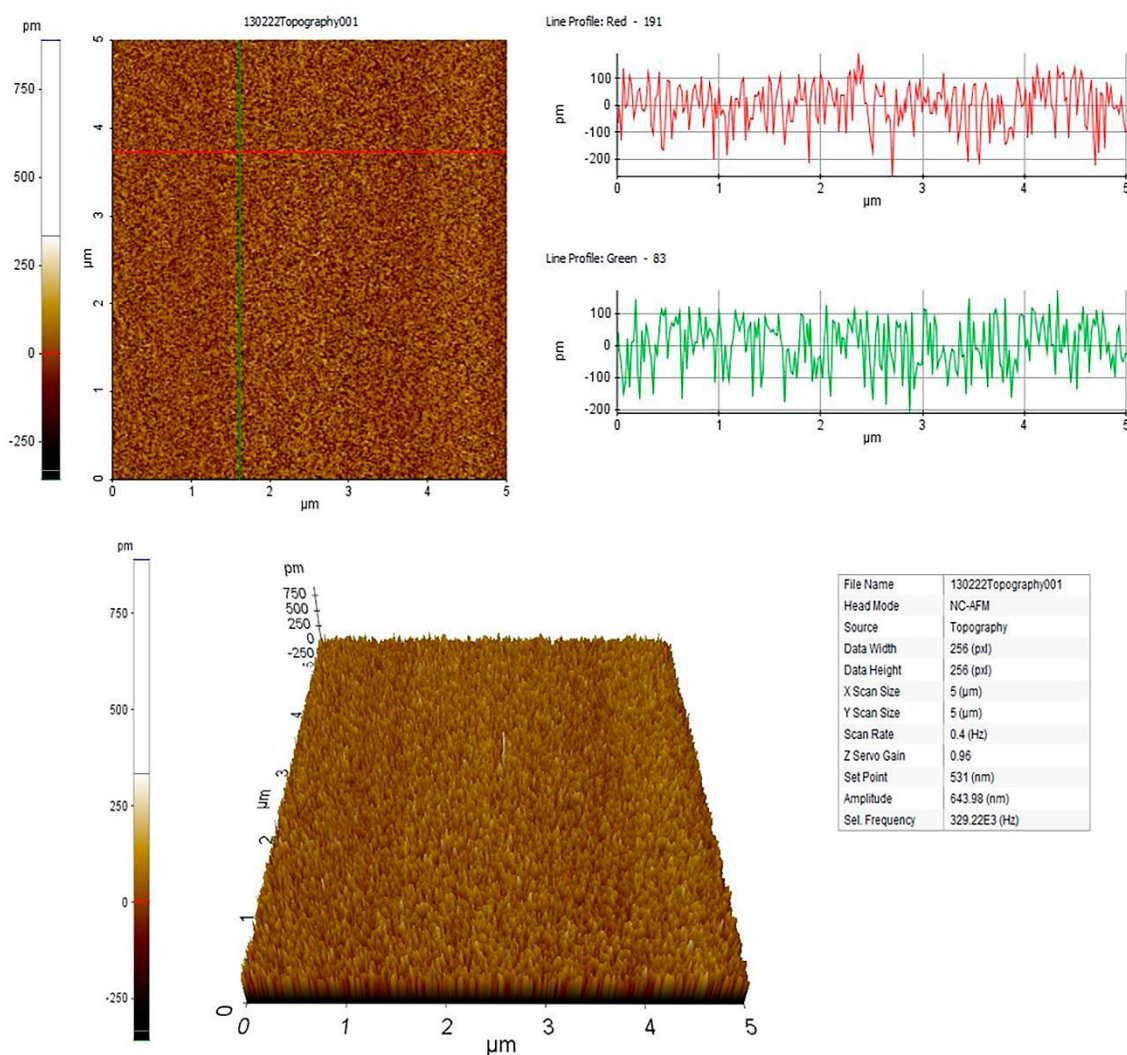


Figure (4): NC-AFM topographical images of bared mica.

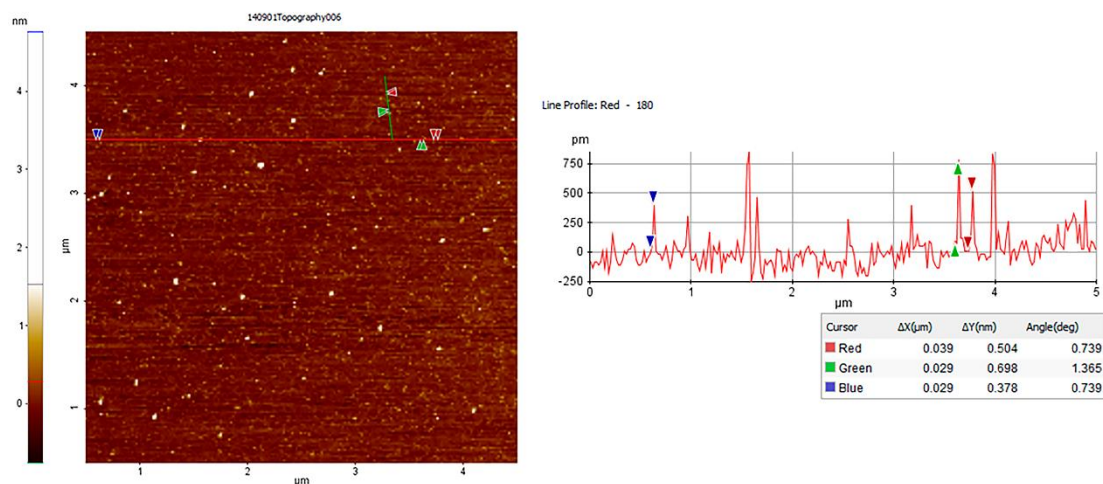


Figure (5): NC-AFM topographical images of cluster samples deposited on mica.

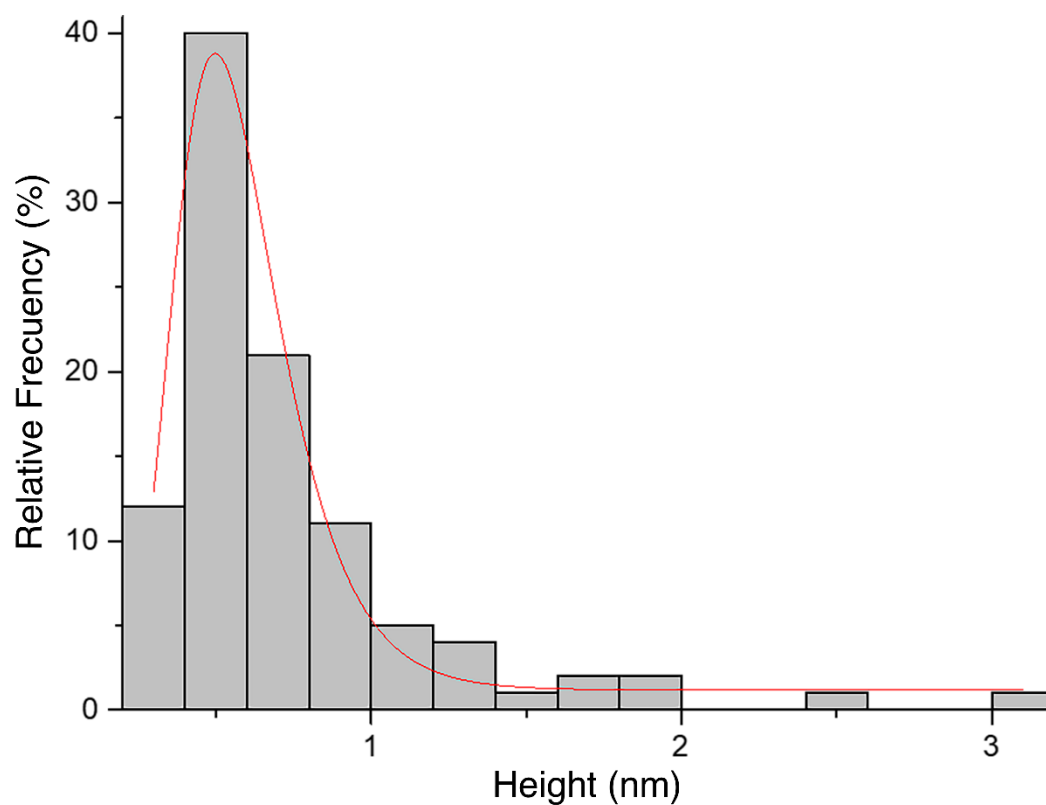


Figure (6): Histogram of the cluster size distribution obtained by NC-AFM.

Electrochemical behavior

Figure (7) shows a cyclic voltammogram (CV) of the Au cluster samples deposited on glassy carbon (GC) in HClO_4 0.1M (N_2 atmosphere). The corresponding voltammogram of GC is also shown for comparison. It can be observed that clusters are very stable in the entire spanned window (-0.3V, +1V). Also, the observed capacitance cycle is squeezed indicating that the presence of clusters at the solid-liquid interface diminish the electrical double layer.

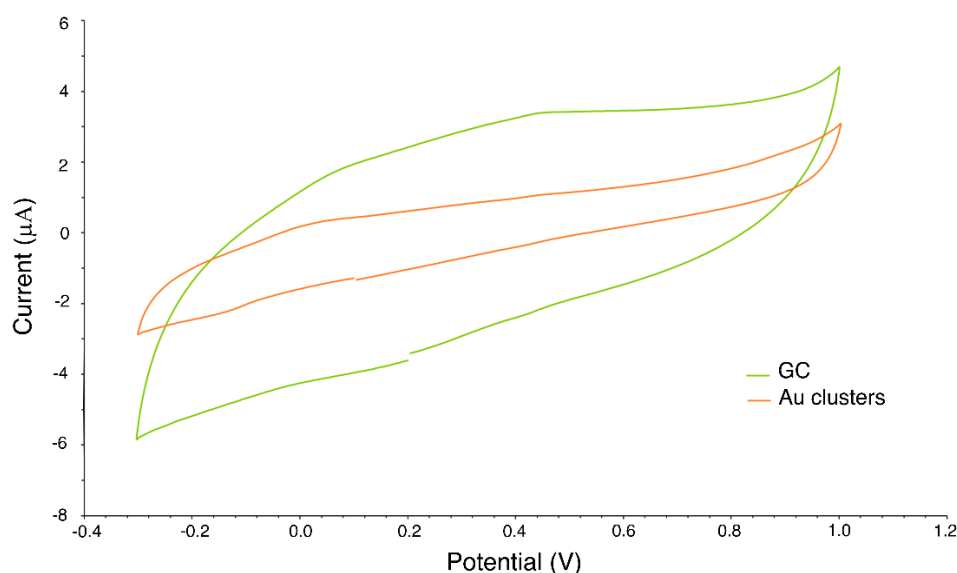


Figure (7): Cyclic voltammogram at 20mV/s scan rate in the range (-0.3V; +1V)

Figure (8) shows the CV of the Au cluster samples in a larger spanned window (-1V; +1V) indicating that also clusters prevent the hydrogen evolution observed at negative potentials in the blank of GC. This result again confirms that clusters are very inactive and that are very stable in terms of their oxidation or reduction, which agrees with their huge HOMO-LUMO gap ($\approx 3.5\text{-}4$ eV), and the position of the frontier orbitals, in comparison with the electrochemical spanned window, as it can be shown schematically in Figure (9).

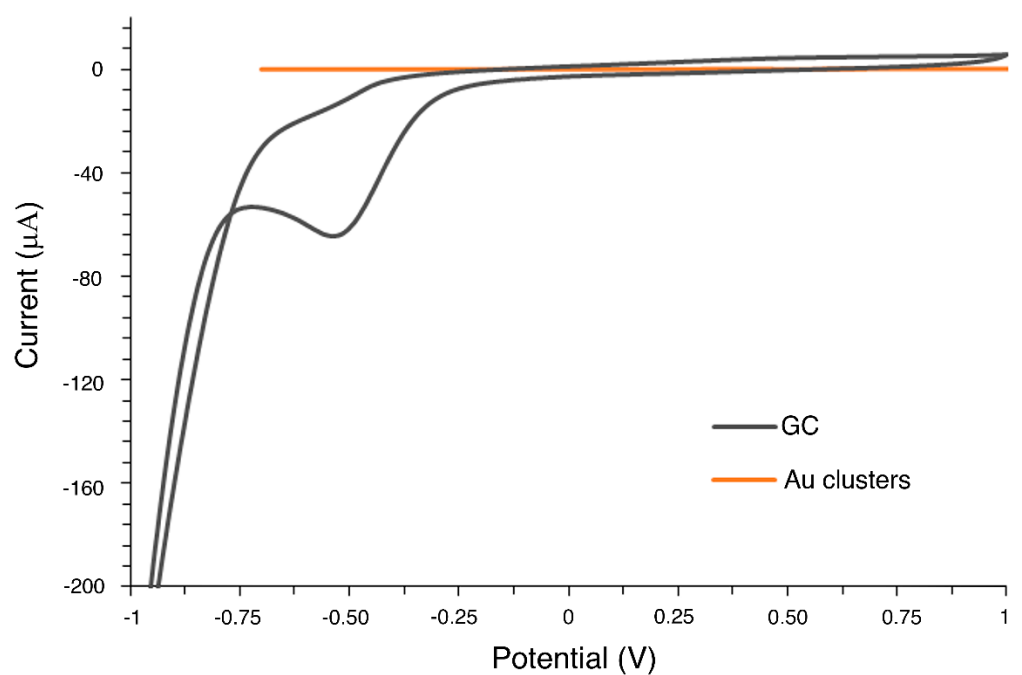


Figure (8): Cyclic voltammogram at 20 mV/s in the range (-0.3V; +1V)

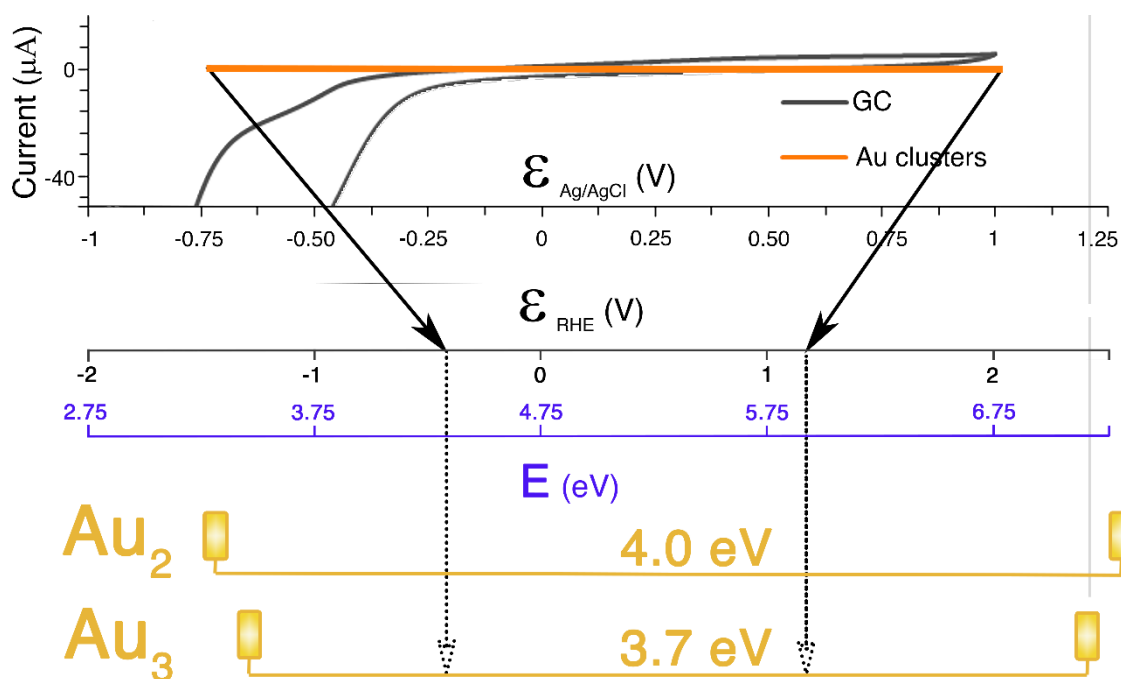


Figure (9): Schematic picture of the HOMO-LUMO gaps in Au_3 and Au_2 clusters showing their outstanding electrochemical stability.

Conclusions

We demonstrate here the inertness of Au_2 and Au_3 clusters. These results are in line with previous reports for other metals. For example, Buceta et al. (ref) reported that Ag_2 seems to be totally inactive whereas Ag_3 displays only hydrophobic interactions with aromatic rings, such as pyrenes, and DNA into which intercalates. By comparison with our results one can conclude that such small clusters, with only 2 or 3 atoms are very inactive due to the huge HOMO-LUMO gap they have, implying a large stability against their reduction or oxidation. Although more data with other metals are needed, the current results indicate that clusters must have more than ≈ 3 atoms to display catalytic activities.

Materials and Methods

Unless otherwise specified, all reagents were purchased from Sigma Aldrich, Co., Spain. Gold and Platinum sheets (99%) were purchased from Goodfellow Cambridge Ltd., Huntingdon, UK. Aluminum nanoparticles (average size $\approx 50\text{ nm}$) and cloth pads were purchased from Buehler, Düsseldorf, Germany. Sandpaper (1,000 grit) was supplied by Wolfcraft España S.L., Madrid, Spain. All aqueous solutions were prepared with MilliQ-grade water using Direct-Q8UV system from Millipore (Milli pore Ibérica S.A., Madrid, Spain).

Synthesis of Au_2 and Au_3 clusters:

The synthesis of small Au_2 and Au_3 clusters with no surfactant or stabilizing agent was performed with an adaptation of a previously reported method (Corma et al., 2013) which is based on kinetic control for cluster formation (Piñeiro et al., 2015). A 50 ml three-electrode chemical cell was used with two foil electrodes (2.5 cm^2 surface area) of Pt (as working electrode) and Au (as counter electrode) and a Ag/AgCl (3 M KCl) reference electrode.

A -8V constant voltage was applied for 6200s in N_2 deaerated MilliQ water at 25°C . Prior to the synthesis, gold electrode was polished with sand paper (600 grid, Wolf craft) followed by alumina ($\approx 50\text{ nm}$, Buehler), washed thoroughly with MilliQ

water and sonicated. Platinum electrode was electrochemically cleaned by cyclic voltammetry in 1M MeOH/1M NaOH solution followed by cyclic voltammetry in 1M H₂SO₄.

Sample characterization

UV-vis spectra were recorded with a Thermo Evolution300 UV-Visible spectrophotometer using 1 cm path-length Hellma quartz cuvettes.

Fluorescence spectra were recorded with a Cary Eclipse Varian fluorometer using 1 cm path-length Hellma quartz cuvettes.

Atomic force microscopy (AFM) measurements were conducted under normal ambient conditions using a XE-100 instrument (Park Systems) in non-contact mode. The AFM tips were aluminum-coated silicon ACTA from Park Systems with a resonance frequency of 325 kHz. For AFM imaging, a drop of a diluted sample of Ag-AQCs was deposited onto a freshly cleaved mica sheet (SPI Supplies, Grade V-1 Muscovite), which was thoroughly washed with milli-Q water and dried under nitrogen flow.

Cyclic Voltamograms were recorded with an Autolab PGSTAT 20 Potentiostat, with a constant temperature of 25 °C. 100 µl of Au-AQCs sample were pipetted on polished glassy carbon (GC) with geometric area of 0.196 cm² (Pine Instruments, Grove City, PA) with a loading of 5% of total surface covered by gold clusters, and dried for 90 min under Ar at room temperature. Before Au-AQCs deposition, the GC electrode was electrochemically characterized by cycling in 0.1 M HClO₄ between -1000 and +1000 mV versus Ag/AgCl.

All the experiments were carried out in 0.1 M HClO₄ at room temperature in a conventional electrochemical glass cell. A platinum flag was used as counter electrode. A leak-free Ag/AgCl (3 M KCl) reference electrode was used with a double-junction reference chamber.

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