Lead (II) ions induce the transformation of a collection of Citrate-Capped Gold Spherical Nanoparticles into large Nanotriangles

A. Ansín¹, S. Botasini², E. Méndez*²

¹Laboratorio de Biomateriales, Instituto de Química Biológica, Facultad de Ciencias, Universidad de la República, 11400 Montevideo, Uruguay.

*Corresponding Author, E-mail: emendez@fcien.edu.uy, phone/Fax: +598-25250749.

ABSTRACT
Spectral changes associated to physicochemical alterations in a colloidal system are key in nanosensor design for decentralized analyses. Citrate-capped spherical gold nanoparticles in basic medium interact with lead (II) ions to give rise to different products depending on the molar concentration ratio nanoparticles/lead (II). For low values of this ratio, lead (II) ions act as charge shield forming ionic associations. For intermediate values, lead (II) ions coordinate to carboxylate moieties from citrate, inducing aggregation of the nanosystem. Finally, for the higher values, a redox reaction is favoured leading to the deposition of PbO₂ on the nanoparticle surface, thus causing changes in the UV/VIS/NIR spectra compatible with the formation of nanotriangles. Transmission Electron Microscopy confirms this shape change and the incidence of the incident rays in the vacuum chamber on the sample confirm the selective melting of the formed PbO₂ layer.

Keywords: Nanoparticles; gold; aggregation; lead; adsorption.

INTRODUCTION
Plasmonic nanoparticles are nanosized materials, which exhibit novel optic and physical properties. Among them, the localized surface plasmon resonance (LSPR) bands observed in UV/VIS/NIR spectra provide important information related to the size, shape and properties of the nanomaterial surroundings [1,2,3]. In the limited space constituted by the nanomaterials and their surroundings, different chemical processes take place, including ligand exchange, molecular recognition, and corrosion phenomena [4].

These characteristics are advantageously used in the development of specific optical sensors [5], which can be used in decentralized analysis [6]. The determination of lead ions [Pb(II)] is of particular interest, because the deleterious impact it has on the children health and development [7].

Citrate-capped gold nanoparticles (AuNP-cit) are widely used in the development of optical sensors, mainly due to
the ease that adsorbed citrate molecules are replaced by ligand exchange [8]. However, when they are used as synthesized, specifically interacts with lead(II) ions to induce nanoparticle aggregation through surface coordination [9].

In this work, we discuss our observations derived from the systematic change of the molar ratio AuNP-cit/Pb(II), followed by UV/VIS/NIR, that include ion association, surface coordination formation, and surface corrosion and shape transformation, the latter confirmed by Transmission Electron Microscopy (TEM).

MATERIALS AND METHODS
Reagent-grade commercial products were used without further purification, and MilliQ water was used throughout this work. Citrate-capped gold nanoparticles were synthesised according to Liu and Lu [10]. A molar extinction coefficient of 2.4 x 10^8 M^-1 cm^-1 [11] was considered for quantitation. An aliquot of the colloidal gold in the concentration range 1.1 – 2.7 nM, and Pb(NO_3)_2 solutions in the concentration range 2 – 50 μM, were diluted in NaOH to a final pH of 9. Colloidal solutions were characterized by UV/VIS/NIR spectroscopy (Analytika Spelec 200), Transmission Electron Microscopy (JEOL, model JEM 1010), Dynamic Light Scattering and ζ-Potential (Brookhaven model ZetaPlus 90 and SZP-Surface Zeta Potential electrode), and Fourier-transformed infrared spectroscopy (Shimadzu model IR-Prestige 21).

RESULTS AND DISCUSSION
The colloidal solution of the freshly synthesized AuNP-cit show a well dispersed population of spherical particles (figure 1a) with a mean diameter of 16 nm (Fig. 1b). The pH of the solution was 5.5, and the measured ζ-potential was -39.4 mV. An ionic strength as low as 5 mM induce the aggregation of the colloidal system.

If the pH of the solution is increased to 8.5 with NaOH, AuNP-cit aggregation is impeded up to an ionic strength of 60 mM, and the colloidal system has a ζ-potential of -51.84 mV. This increase in the ζ-potential is ascribed to a higher degree of ionization of adsorbed citrate, exposing carboxylate groups rather than carboxylic moieties to the solution.

FTIR analysis confirms such assumption, with intense absorption bands centred at 1581 cm^-1 and 1405 cm^-1 assigned to the asymmetric and symmetric vibrations of the carboxylate group, respectively (figure 2).

Fig. 1. a) TEM image of freshly synthesized AuNP-cit and b) The size distribution of the population, (red bars) and the Gaussian distribution of the sizes (blue line).

Fig. 2. FTIR spectra of citrate-capped AuNPs.
An initial insight into the behaviour of the nanoparticulate system including Pb(II) ions is provided by UV/VIS/NIR analysis, which allows for the detection of the shape of the nanoparticles, and its physical state, namely, isolated, aggregated or coalesced. For Pb(II) concentrations of 2, 10 and 50 μM, the spectral profiles for increasing AuNP-cit concentrations markedly differ. As the ratio AuNP-cit/Pb(II) increase, the behaviour induced by Pb(II) ions changes from a red-shifted signal. A new absorption band centred at 650 nm, and the development of a wide absorption band which maximum is within the NIR region is observed.

The features related to the induced aggregation of citrate-capped nanoparticles is well documented [12,13]. However, the development of the wide NIR spectral band induced by the presence of Pb(II) ions, up to our knowledge, was not reported. These spectral characteristics are consistent with the formation of triangular gold nanoparticles. To probe this hypothesis, we carried out TEM measurements. As expected, large gold nanotriangles were observed, with sides between 400 nm and 1000 nm that give rise an absorption above 850 nm. In addition to these nanotriangles, several aggregates are also observed. A closer inspection is depicted in figure 5, where it can be seen that these aggregates are indeed nanowires, and are responsible of the UV/VIS absorption at 650 nm.

The mechanism of formation of these large nanostructures is directly related to the molar concentration ratio AuNP/Pb(II), in particular, they are observed for the higher values of this ratio. In order to understand the formation of these large nanotriangles, we recall first the attention to the large nanowires formed.
The physicochemical conditions for these nanowires to form are derived from a balance between the van der Waals forces that induce the aggregation, and the electrostatic potential that prevent such aggregation. In the presence of divalent ions, their large Debye lengths also prevent the attachment of the nanoparticles onto any part of the aggregates but on the end of a growing chain [6]. Depending on how much each nanoparticle can approach to each other, there is a chance for sintering of the nanoparticles in the chain, which is clearly seen in figure 5.

As a second point to understand the formation of the large nanotriangles, it is necessary to understand how the concentration of AuNPs and Pb(II) affects the formation of aggregates or nanotriangles, as followed by the colloidal solution absorbance at 650 nm and 850 nm, respectively (figure 6).

As detailed in ¡Error! No se encuentra el origen de la referencia., aggregate formation is observed for all AuNPs concentrations assayed, and the more concentrated the AuNP solutions, the larger the amount of aggregates. However, in the case of the formation of nanotriangles, these are clearly favoured for the more concentrated AuNP solutions, that is, for the larger ratio AuNP/Pb(II), which is in agreement with a higher electrostatic repulsion between nanoparticles that favours the attachment of the isolated nanoparticles to the growing chain ends.

Finally, to understand the formation of the nanotriangles, we should consider the process of adsorption of Pb on the AuNP. At high pH, Au(I) ions present on the nanoparticle surface are in the Au(OH) state, while Pb(II) ions in solution are complexed as Pb(OH)$_3^-$.

The following reaction may take place:

$$2\text{Au(OH)} + \text{Pb(OH)}_3^- \rightarrow 2\text{Au} + \text{PbO}_2 + 2\text{H}_2\text{O} + \text{OH}^- \quad (1)$$

Au(I) are formed on the surface on the more unstable crystallographic faces, namely (100) and/or (110) [14]. As the electrochemical reaction takes place, the (111) facets are still protected by citrate ions, and progressively, the growing nanoparticle is reshaped. According to this, the triangle structure emerges from this reaction, leaving the
new Au adsorbed atoms (Au\(_{ad}\)) and the PbO\(_2\) on the outer side of the structure.

Strong evidence of this was obtained by letting the nanotriangle for some time under the flux of electrons in the TEM chamber. The local increase of the temperature produce the melting of adsorbed PbO\(_2\), letting by the small spherical nanoparticles inside the border of the nanotriangle (Fig. 7).

**CONCLUSIONS**

Through careful regulation of the AuNP/Pb(II) ratio in alkaline media, it is possible to obtain different kind of responses derived from the interaction of lead ions and the gold nanoparticles. For the lower values of the ratio, Pb(II) induced the aggregation of AuNPs, while for the larger values of the ratio, Pb(II) induced the formation of large nanotriangles, surrounded by a layer of PbO\(_2\). The spectral features of these two nanosystems provide different approaches for the design of specific nanosensor for Pb(II) ions after an alkaline digestion, as that employed in the pre-treatment of leaded-paints [15].

**ACKNOWLEDGEMENT**

We acknowledge the financial support of Universidad de la República through CSIC-Inclusión Social program. S. Botasini and E. Méndez are ANII-SNI and PEDECIBA researchers.

**REFERENCES**


