

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

A. Ansín^a, S. Botasini^a, E. Méndez^{a*}

^aLaboratorio 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.

Los iones Plomo(II) inducen la transformación de un conjunto de Nanopartículas de Oro Esféricas estabilizadas con Citrato en grandes Nanotriángulos

RESUMEN

Los cambios espectrales, asociados a las alteraciones fisicoquímicos en un sistema coloidal, son claves a la hora del diseño de nanosensores descentralizables selectivos. Las nanopartículas de oro esféricas protegidas con citrato en medio básico interactúan con los iones plomo (II) para dar diferentes productos dependiendo del cociente de concentraciones nanopartículas/plomo(II). Para bajos valores de este cociente, los iones plomo (II) actúan apantallando la carga neta de las nanopartículas, dando lugar a agregados iónicos. Para valores intermedios, los iones plomo (II) coordinan con los grupos carboxilato del citrato, induciendo la agregación del nanosistema. Finalmente, para altos valores, se favorece una reacción redox que conduce a la deposición de PbO₂ sobre la superficie, produciendo cambios en los espectros UV/VIS/NIR que coinciden con la formación de nanotriángulos. Las micrografías obtenidas por microscopía de transmisión electrónica confirman el cambio de forma, a la vez que la acción de los rayos incidentes sobre la muestra en la cámara a vacío confirma la fusión selectiva de la capa de PbO₂ formada.

Palabras claves: Nanopartículas, oro, agregación, plomo, adsorción.

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 $2.4 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ [11] was considered for quantitation. An aliquot of the colloidal gold in the concentration range 1.1 – 2.7 nM, and $\text{Pb}(\text{NO}_3)_2$ 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.

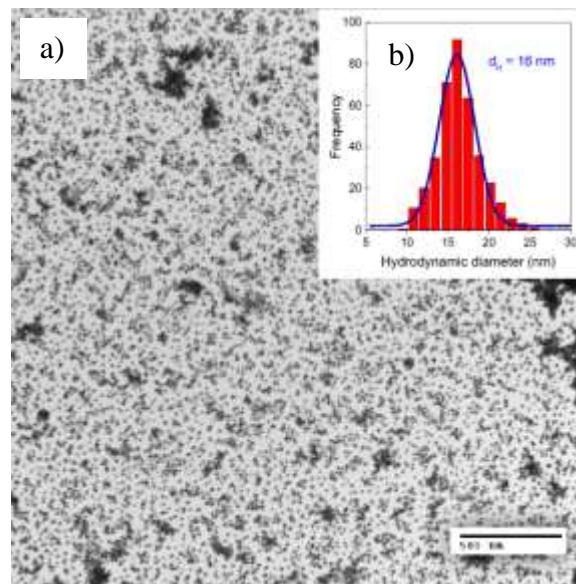


Fig. 1. a) TEM image of freshly synthesized AuNP-cit and b) The size distribution of the population, (red bars) and the Gaussian distribution of the sizes (blue line).

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).

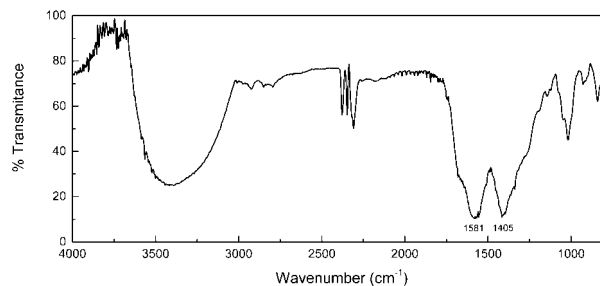


Fig. 2. FTIR spectra of citrate-capped AuNPs.

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 (**¡Error! No se encuentra el origen de la referencia.**). 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 in **¡Error! No se encuentra el origen de la referencia.**

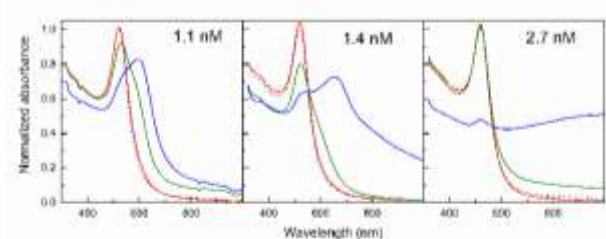


Fig. 3. UV/VIS/NIR spectra for the nanosystem composed by AuNP-cit at 1.1, 1.4 and 2.7 nM concentrations, and Pb(II) concentrations of 2 μM (red), 10 μM (green) and 50 μM (blue) in basic media. Dotted lines corresponds to the absence of Pb(II).

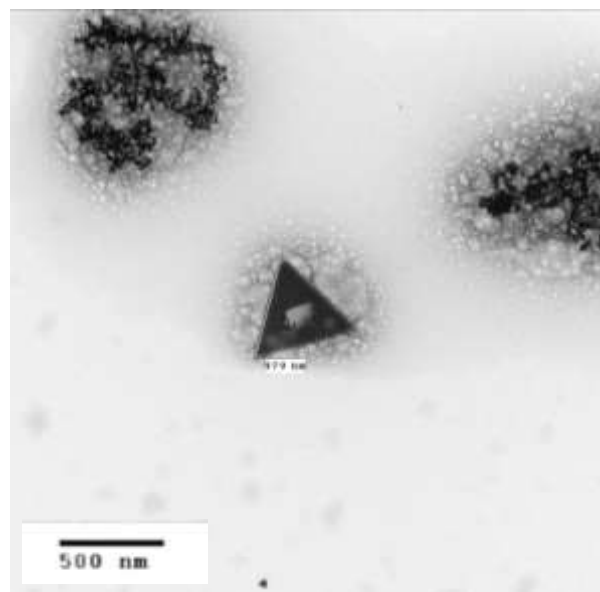


Fig. 4. TEM micrograph of a large nanotriangle along with large aggregates.

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 (**¡Error! No se encuentra el origen de la referencia.**), 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).

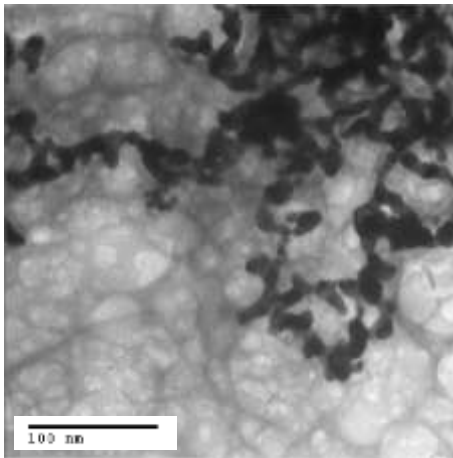


Fig. 5. TEM closer inspection of the large aggregates.

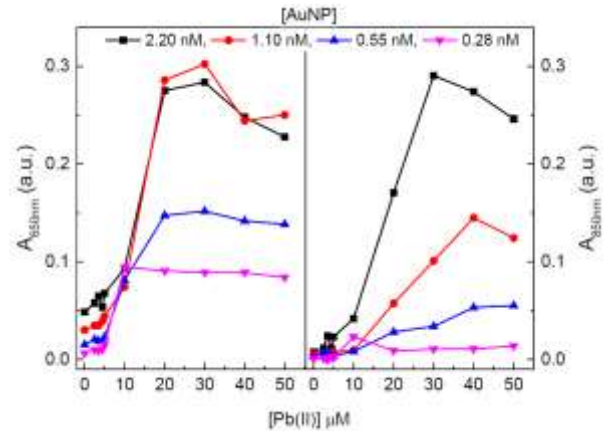
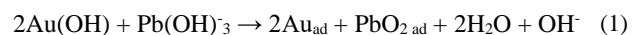


Fig. 6. Incidence of the concentration of AuNP and Pb(II) in the formation of aggregates (absorbance @650 nm) or nanotriangles (absorbance @850 nm).

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:



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).

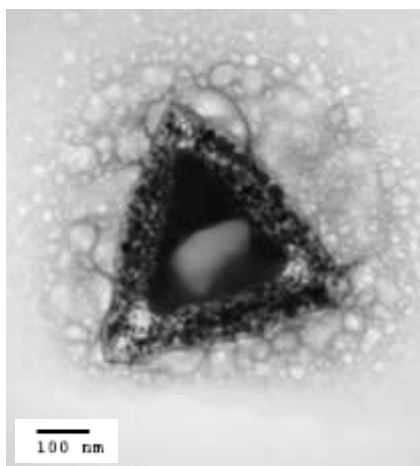


Fig. 7. TEM image of a large nanotriangle after few minutes under focus in the TEM chamber.

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

- [1] Alaqad, K., & Saleh, T.A. (2016) "Gold and Silver Nanoparticles: Synthesis Methods, Characterization Routes and Applications towards Drugs" *Journal of Environmental & Analytical Toxicology* 6.
- [2] Benetti, F., Fedel, M., Minati, L., Speranza, G., & Migliaresi, C. (2013) "Gold nanoparticles: role of size and surface chemistry on blood protein adsorption" *J Nanopart Res* 15.
- [3] Saha, K., Agasti, S.S., Kim, C., Li, X., & Rotello, V.M. (2012) "Gold nanoparticles in chemical and biological sensing" *Chem Rev* 112: 2739-2779.
- [4] Balasubramanian, S.K., Yang, L., Yung, L.Y., Ong, C.N., Ong, W.Y., & Yu, L.E. (2010) "Characterization, purification, and stability of gold nanoparticles" *Biomaterials* 31: 9023-9030.
- [5] Polavarapu, L., Pérez-Juste, J., Xu, Q.-H., & Liz-Marzán, L.M. (2014) "Optical sensing of biological, chemical and ionic species through aggregation of plasmonic nanoparticles" *J Mater Chem C* 2: 7460-7476.
- [6] Botasini, S., Heijo, G., & Méndez, E. (2013) "Toward decentralized analysis of mercury (II) in real samples. A critical review on nanotechnology-based methodologies" *Anal Chim Acta* 800: 1-11.
- [7] Singh, N., Kumar, A., Gupta, V.K., & Sharma, B. (2018) "Biochemical and Molecular Bases of Lead-Induced Toxicity in Mammalian Systems and Possible Mitigations" *Chem Res Toxicol* 31: 1009-1021.
- [8] Stobiecka, M., Deeb, J., & Hepel, M. (2010) "Ligand exchange effects in gold nanoparticle assembly induced by oxidative stress biomarkers: homocysteine and cysteine" *Biophys Chem* 146: 98-107.

- [9] Guan, J., Jiang, L., Zhao, L., Li, J., & Yang, W. (2008) "pH-dependent response of citrate capped Au nanoparticle to Pb²⁺ ion" *Colloids Surf, A* 325: 194-197.
- [10] Liu, J., & Lu, Y. (2006) "Preparation of aptamer-linked gold nanoparticle purple aggregates for colorimetric sensing of analytes" *Nat Protoc* 1: 246-252.
- [11] Haiss, W., Thanh, N.T.K., Aveyard, J., & Fernig, D.G. (2007) "Determination of Size and Concentration of Gold Nanoparticles from UV–Vis Spectra" *Anal Chem* 79: 4215-4221.
- [12] Miao, X.M., Ling, L.S., & Shuai, X.T. (2012) "Detection of Pb(2)(+) at attomole levels by using dynamic light scattering and unmodified gold nanoparticles" *Anal Biochem* 421: 582-586.
- [13] Ngamchuea, K., Batchelor-McAuley, C., Sokolov, S.V., & Compton, R.G. (2017) "Dynamics of Silver Nanoparticles in Aqueous Solution in the Presence of Metal Ions" *Anal Chem* 89: 10208-10215.
- [14] Liu, P., Qin, R., Fu, G., & Zheng, N. (2017) "Surface Coordination Chemistry of Metal Nanomaterials" *J Am Chem Soc* 139: 2122-2131.
- [15] Ansín, A., Galiotta, G., Botasini, S., & Méndez, E. (2019) "Lead analysis in paints for high impact control in homes" *Anal Methods* 11: 4254-4259.