

Attenuated total reflection infrared (ATR-IR) spectroscopy *in-situ* monitoring of the synthesis of bare gold nanoparticles.

A.I. López-Lorente^{1,2}, M. Sieger², M. Valcárcel¹, B. Mizaikoff²

¹Department of Analytical Chemistry, University of Córdoba, E-14071 Córdoba, Spain. Phone/Fax +34 957 218616; E-mail: qa1meobj@uco.es

²Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Ulm, Germany.

Abstract

Gold nanoparticles (AuNPs) possess exceptional properties which have promoted their use in many fields, such as biomedical imaging and diagnostic tests, biological applications, catalysts and for uses based on their enhanced optical properties such as absorption, enhanced Rayleigh scattering or surface-enhanced Raman scattering of adsorbed molecules [1]. Infrared spectroscopy has been usually employed until now for the characterization of functionalized gold nanoparticles, due to the vibration features of ligands attached to the nanoparticles. Hartstein et al. [2] reported for the first time the so-called surface-enhanced infrared absorption (SEIRA) effect. Two enhancement mechanisms – electromagnetic and chemical – are thought to mainly contribute to the total enhancement in SEIRA spectroscopy. Electromagnetic mechanism increases the local electric field at the surface and the chemical one assumes an increase of the absorption thanks to chemical interactions between molecules and gold nanoparticles.

In this work, photoenhanced adsorption of water on gold nanoparticles has been employed for the *in-situ* monitoring of the synthesis of bare gold nanoparticles by surface-enhanced attenuated total reflection (ATR) infrared spectroscopy.

Gold nanoparticles are synthesized directly inside the ATR unit by means of the stainless steel ring forming the walls. While synthesizing, AuNPs adsorb in the SiO₂ ATR surface (Figure 1). When increasing the number of gold nanoparticles at surface coverage, Coulomb repulsion from the already adsorbed AuNP film increases and leads to saturation. Despite the IR inactivity of gold nanoparticles, their formation can be monitored by measuring the increase in water absorption bands during the synthesis process, arising from the so-called surface-enhanced infrared absorption (SEIRA) effect. The deposition of gold nanoparticles on the SiO₂ ATR surface enhances the absorption signal from water.

According to literature [3], the vibrational modes of water in the infrared region are the H₂O bending mode at 1644 cm⁻¹, the combination of H₂O bending and libration at 2128 cm⁻¹, and one around 3404 cm⁻¹. This one is composed by the overtone of bending mode at 3250 cm⁻¹, symmetric OH stretch at 3450 cm⁻¹ and the antisymmetric OH stretch at 3600 cm⁻¹ [4]. As gold nanoparticles are formed and deposited on the ATR surface an increase in the H₂O bending (see Figure 2) and the OH stretching bands is observed, despite a decrease in the amount of water molecules present in the evanescent field during the deposition and exchange of water molecules by gold nanoparticles. This increase can be attributed to the so-called SEIRA effect of water molecules in the enhanced field created by formed nanoparticles. This enhanced near-field decays when increasing the distance from the particle surface and it compensates the loss of water molecules replaced by nanoparticles.

The influence of gold(III) precursor concentration as well as ATR unit temperature has been investigated. A similar effect has been observed in the case of gold nanoparticles synthesized in deuterium oxide media, the band of deuterium being enhanced during the formation of AuNPs. Moreover, the suitability of infrared (IR) spectroscopy for the investigation of gold solutions has been proved by studying the effect of salts and pH on the aggregation state of gold nanoparticles in solution. Finally, it has been shown that IR spectroscopy can be used to evaluate the sedimentation process of gold nanoparticles on the surface.

References

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Figures

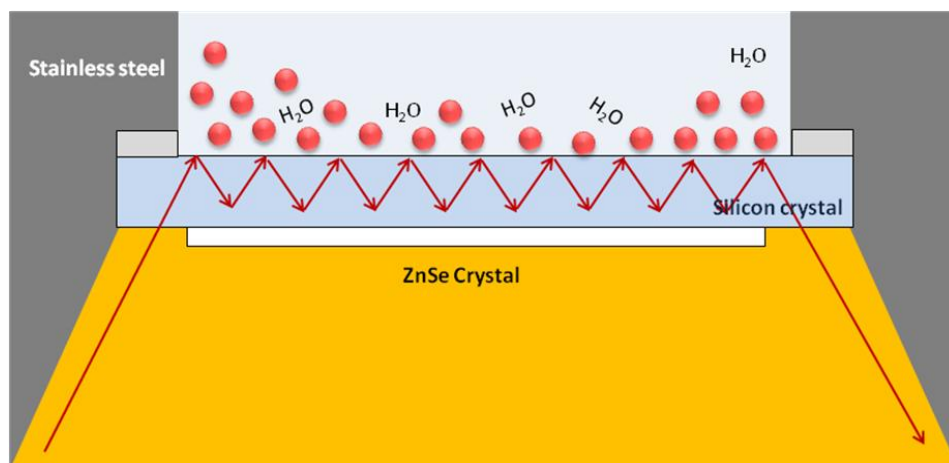


Figure 1. Scheme of the ATR unit employed in this work. As it can be seen the walls of the cell are composed of stainless steel, which acts as reducing agent leading to the in-situ formation of gold nanoparticles from tetrachloroauric acid solution.

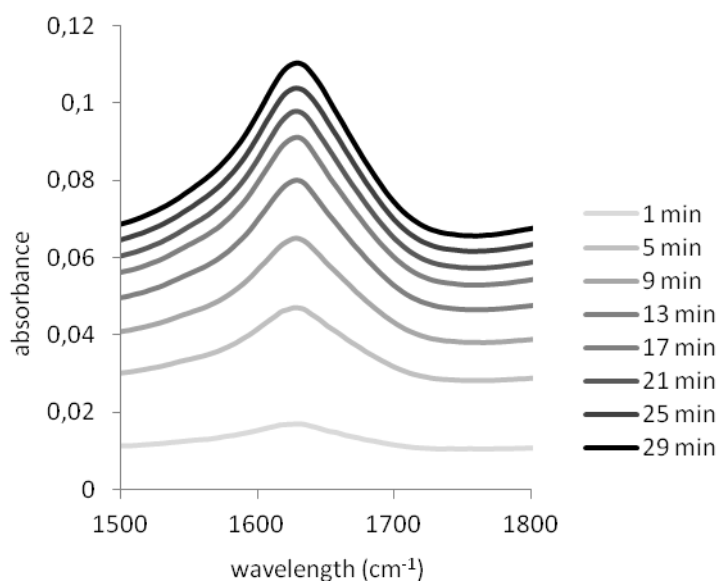


Figure 2. *In situ* ATR-SEIRA H₂O bending mode spectra during the synthesis of gold nanoparticles inside the ATR unit in a water environment (from a 200 mg dL⁻¹ HAuCl₄ solution). To see the SEIRA effect of gold nanoparticles over water bands, a spectrum of tetrachloroauric acid solution in water just before the synthesis starts was used as background reference. Thus, the water features shown in the spectra are directly the enhancement produced as gold nanoparticles are obtained.