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Surface plasmon resonance sensor based on golden nanoparticles and cold vapour generation technique for the detection of mercury in aqueous samples

Jimmy Castillo *, José Chirinos, Héctor Gutiérrez, Marie La Cruz

Universidad Central de Venezuela, Facultad de Ciencias, Escuela de Química, Caracas, Venezuela

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ABSTRACT

In this work, a surface plasmon resonance sensor for determination of Hg based on golden nanoparticles was developed. The sensor follows the change of the signal from solutions in contact with atomic mercury previously generated by the reaction with sodium borohydride. Mie theory predicts that Hg film, as low as 5 nm, induced a significant reduction of the surface plasmon resonance signal of 40 nm golden nanoparticles. This property was used for quantification purposes in the sensor. The device provide limits of detection of 172 ng/L that can compared with the 91 ng/L obtained with atomic fluorescence, a common technique used for Hg quantification in drinking water. This result was relevant, considering that it was not necessary to functionalize the nanoparticles or use nanoparticles deposited in a substrate. Also, thanks that Hg is released from the matrix, the surface plasmon resonance signal was not affected by concomitant elements in the sample.

1. Introduction

Mercury is a heavy metal element present in the environment and it is a hazardous substance due its toxicity, mobility, and long residence time. Toxic effects of this element are well documented. It produce damages in the brain, kidney, nervous system and endocrine system in humans and animals [1–4]. Hg release in the environment comes from natural sources like volcanic emissions or antropogenic origin such as combustion of fossil fuels and illegal mining [5].

Currently, the highest level of a contaminant that is allowed in drinking water is 2 μg/kg according to EPA 2016. This low concentration level of the element justify any effort to develop new sensitive and selective technologies for its detection and quantification [6–8].

Atomic vapour generation using absorption or fluorescence spectroscopy are common analytical techniques used determination of Hg in environmental samples [9,10]. These instruments exhibit limit of detection as low as few ng/L and good selectivity but are expensive and difficult to use in the fieldwork. New Hg detection systems have been developed based on bio, chemi, and nanosensors. These are attractive for quantification purposes because they are simple, sensitive and compact systems [11–22,20,23,24].

The uses of nanoparticles (NPs) of noble metals have been considered for development of sensors because they absorb and scatter the electromagnetic radiation resonantly due to a phenomenon known as surface plasmon resonance (SPR). The latter can be defined as the excitations of the conduction electrons of the metallic surface coupled to the incident electromagnetic field [25]. The SPR signal is extremely sensitive to the bulk properties of the metal and is strongly influenced by the size, shape, and composition, degree of aggregation of the NPS. In addition, the signal can be affected by local dielectric environment of the surrounding medium. These unique optical properties of noble metal nanoparticles open up novel applications in chemical sensors for the quantification of Hg(II) [27–31] Today, Ag and Au sensors generate great interest because of their strong SPR sensitivity. In the case Au-NPs, this resonance lays in the visible region of the electromagnetic spectrum, although the exact value of the light's wavelength where the resonance occurs depends on the particle radius and the optical properties of the surrounding medium. Literature reports some Au-NPs systems for Hg determination. These instruments provide good sensitivity but required the funtionalization of the NPs [32,33] or the deposition of the Hg in a substrate [21,20,19] that is an arduous process to make the nanoparticles selective to Hg, taking out the interferences from concomitants elements [35–36]. For all above mentioned, this work evaluates the

* Corresponding author.
E-mail address: jimmy.castillo@ciens.ucv.ve (J. Castillo).

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possibility to use SPR signal from Au-NPs for the determination of Hg using the cold vapor generation (CVG) technique. The main goal was to optimize a method to generate Au-NPs with laser ablation and design an inexpensive and sensitive sensor to be used for a fast determination of Hg sensor in aqueous samples without any functionalization procedure or deposition of the NPs in a subtrate. The CVG produces atomic Hg in the vapor phase so the analyte can be easily transferred to the NP solution and the SPR signal obtained without any effects of concomitants of the sample. In addition, the CVG improved the sensitivity due a better interaction with Au-NPs with the atomic Hg.

2. Theory

2.1. Effect of Hg on the SPR signal of AuNPs

The Mie theory [37] describes exactly the SPR on metallic particles of any size. For particles with diameters of 100 nm or smaller the interaction of the NPs with the electromagnetic field can be analyzed with the simpler quasi-static approximation [25]. The main result of this approximation is that the polarizability of the NPs has the form:

$$\alpha = 4\pi a^3 \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m} \tag{1}$$

where a is the NP radius, $\epsilon(\omega)$ is the dielectric constant of the metal and ϵ_m the dielectric constant of the surrounding medium.

It is evident that the polarizability experiences a resonant enhancement when $|\epsilon(\omega) + 2\epsilon_m|$ is minimum. This condition occur when

$$Re[\epsilon(\omega)] = -2\epsilon_m; \qquad \mathrm{Im}[\epsilon(\omega)] \simeq 0$$

This is precisely the surface plasmon resonance. The optical consequence of the enhancement of the polarizability of the NP, is an enhancement in the efficiency of absorption and scattering of light by the metallic nanoparticle. The corresponding efficiencies for absorption and scattering Q_{abs} and Q_{sca}, calculated from the Poynting vector [37], are:

$$Q_{sca} = \frac{k^2}{6\pi^2 a^2}|\alpha|^2 = \frac{8}{3}k^4 a^4 \left|\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}\right|^2 \tag{2}$$

$$Q_{abs} = \frac{k}{\pi a^2}\mathrm{Im}[\alpha] = 4\pi k a \mathrm{Im}\left[\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}\right] \tag{3}$$

Scattering and absorption efficiencies depends on the nanoparticle size, and indirectly through the dielectric constant of the metal, on the wavelength of the incident light.

For NP's coated with a thin layer of a different material the magnitude of the plasmon resonance depends also on the thickness of the coating. In this case the nanoparticle's polarizability, α, also obtained from the quasi-static approximation, has the form:

$$\alpha = 4\pi b^3 \left[\frac{\epsilon_b - \epsilon_m + (a/b)^3(1 - \epsilon_a/\epsilon_b)(\epsilon_m - 2\epsilon_b)}{2\epsilon_m + \epsilon_b + 2(a/b)^3(1 - \epsilon_a/\epsilon_b)(\epsilon_m - \epsilon_b)}\right] \tag{4}$$

where a is the core's radius, b the external radius (core plus coating), ϵ_a and ϵ_b are de dielectric constants of the core and the coating respectively.

3. Modeled results

The effect of Hg films on Au-NPs was simulated using the above theory, the idea was to test the viability to use no-functionalized Au-NPs to modify the SPR signal for quantification purposes. Using Eq. 3 the extinction efficiency is calculated for 40 nm gold NPs, Fig. 1 shows the extinction efficiency ($(Q_{ext} = Q_{abs} + Q_{sca})$) as a function of the wavelength. The plot show a typical maximum at 520 nm correspondent to well-known surface Plasmon resonance of Au-NPs of 40 nm in size.

For the nanoparticle covered with a thin layer of different material, the extinction efficiency was calculated using the polarizability of Eq. 4 where the parameters dieletric constant and layer thickness of the Hg were also considered. Fig. 2 shows the effect on the SPR of a thin layer of Hg coating on Au nanoparticle having a diameter 40 nm. For Hg cover of less than 1 nm thick the effect is a diminishing in the SPR band of AuNPs. Indeed, it can be appreciated that absorption signal of 5 nm thickness layer was completely supressed. In addition,it can be appreciated that Hg induced the blue shift of the Au-NPs band. Modeled results demonstrate that it is possible to develop a Hg nanosensor without functionalization of the NPS, taking advantage of the strong reduction effect of analyte on the SPR signal of Au-NPS.

4. Experimental

Fig. 3 A shows a schematic diagram of the experimental setup used in this work. The Laser used to obtain the nanoparticles by ablation of a golden foil was a Nd: YAG nanosecond pulse laser model Surelite, Continuum, San Jose, California, USA. The system has a fundamental wavelength of 1064 nm and was operated in the second harmonic at 532 nm. The beam was focused by means of a dichroic mirrors to the Au foil immersed in a vial having sodium dodecyl sulfate solution (SDS). Fig. 3B presents the system used for both to generate the cold vapor (Hg atomic gas) and capture the element with the Au-NPs (amalgamation process). It consists of two glass vials: The first one contains the solution of Hg^{+2} in acid media that react with the excess of sodium borohydride to generate the cold vapor that is transferred, thanks to the generated hydrogen, to the second vial having the Au-Nps in a SDS solution. The SPR signal from NPs were acquired by using a UV–Visible spectrometer (model LS-I, Ocean Optic, Dunedin, Florida, USA).

4.1. Reagents

Solutions of sodium dodecyl sulfate (SDS) used to stabilize Au-NPs were prepared from the reactive provided by Sigma-Aldrich (seelze, Germany) and passed through 0.45 μm Millipore filter. Hg (II) standard were obtained from Fluka (Seelze, Germany), Sodium borohydride, hydrocloric acid, tin (II) chloride were used to generate the cold vapor were provided by Riedel-de-Haen (Seelze, Germany). The gold foil used to obtain nano particles was obtained from Sigma-Aldrich.

4.2. Metodology

4.2.1. Generation and stability of the Au_{Nps}

Au-NPs were generated by laser ablation that is a fast and efficient method to obtain the particles. Optical properties of the SPR signal strongly depends on the quality of the NPs so it was necessary to optimize the experimental conditions of the laser to obtain the lowest possible particle size diameter. It was study the effects of the energy, pulse duration, frequency and time of the ablation on the size distribution. Homemade dynamic light dispersion system was used for monitoring the particles and details of the system can be found elsewhere [37]. It was considered the effect of the SDS solution concentration on the stabilization of the NPs, avoiding the aggregation process and providing the highest SPR signal. Long-term stability was monitored during one week considering the importance that any sensor device should be reproducible in long period of time.