

An optical fiber sensor for Hg^{2+} detection based on the LSPR of silver and gold nanoparticles embedded in a polymeric matrix as an effective sensing material.

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Abstract: In this work, an optical fiber sensor based on the Localized Surface Plasmon Resonance (LSPR) phenomenon is presented as a powerful tool for the detection of heavy metals (Hg^{2+}). The resultant sensing film has been fabricated using a nanofabrication process, known as Layer-by-Layer Embedding (LbL-E) deposition technique. In this sense, both silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) have been synthesized using a synthetic chemical protocol as a function of a strict control of three main parameters such as polyelectrolyte concentration, loading agent and reducing agent, respectively. The use of metallic nanostructures as sensing materials is of great interest because well-located absorption peaks associated to their LSPR are obtained at 420 nm (AgNPs) and 530 nm (AuNPs), respectively. Both plasmonic peaks provide a stable real-time reference that can be extracted from the spectral response of the optical fiber sensor, giving a reliable monitoring of the Hg^{2+} concentration.

Keywords: optical fiber sensor; gold nanoparticles; silver nanoparticles; localized surface plasmon resonance; mercury

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1. Introduction

The presence of heavy metals in human's daily life has become a concern due to their adverse health effects. Among all them, the mercury is showing a major focus of attention because its presence is associated to serious problems such as lung or nervous system damage, heart diseases or even neurological and psychological symptoms [1]. Due to this, a wide variety of detection methods can be found in the bibliography, ranging from electrochemical sensors [2]-[4], colorimetric sensors [5]-[7] or optical sensors [8]-[10]. In this work, it is focused on the optical fiber sensors based on the Localized Surface Plasmon Resonance (LSPR) phenomenon. It is well-known that LSPR is an optical phenomenon which is generated thanks to the interaction between the incident light and the electrons in the conduction band of the metal surface [11]. It has been demonstrated that the resultant amplitude and the plasmonic resonance energy can vary as a function of the geometry and the distance between the nanoparticles. Until now, LSPR optical fiber sensors for mercury ions detection mostly contain gold nanoparticles (AuNPs) as the main plasmonic sensing material, showing the interaction between gold and mercury a change in the physical and chemical properties of the metallic nanoparticles [12]-[13]. The novelty of this work is the possibility of introducing two different metallic nanoparticles such as

AgNPs and AuNPs into LbL films with the aim to obtain two different LSPR sensing signals for the detection of mercury ions. This deposition technique makes possible to obtain thin films with a good control in the resultant thickness in the nanometric range as a function of operational parameters such as pH, ionic strength or number of bilayer deposited [14]-[16]. An initial study is performed onto glass slides in order to optimize the nanofabrication technique, and secondly, the sensing coating is implemented onto optical fiber. Finally, a change in the wavelength position of the LSPR band can be observed as a function of the concentration of the analyte. To sum up, this is the first time that an optical fiber sensor with a dual reference state is presented for mercury ions detection.

2. Methods

2.1 Materials

The polymeric matrix is composed by poly(allylamine hydrochloride) (PAH) ($M_w \sim 15,000$) which is acting as a polycation, and poly (acrylic acid) (PAA) 35 wt% solution in water which is acting as a polyanion. In order to obtain AuNPs and AgNPs, gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and silver nitrate (AgNO_3) have been used as loading agents for the synthesis of metallic nanoparticles. Finally, dimethylamine borane complex (DMAB) has been used as reducing agent.

2.2 Chemical process for the synthesis of the metallic nanoparticles

2.2.1 Gold nanoparticles (AuNPs) synthesis

Firstly, aqueous solutions of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (20 mL, 5 mM) and PAA (120 mL, 10 mM) which acts as an stabilizing agent have been mixed and stirred for a period time of 2 h. After that, an aqueous solution of the reducing agent DMAB (1 mL, 100 mM) has been added to the previous solution, and the mixture has been stirred for 24 h at room temperature. Finally, a color change from yellow to violet has been obtained, indicating the synthesis of AuNPs. The combination of PAA and AuNPs will be denoted as PAA-AuNPs.

2.2.2 Silver nanoparticles (AgNPs) synthesis

For the synthesis of AgNPs, firstly, aqueous solutions of AgNO_3 (2 mL, 10 mM) and PAH (120 mL, 10 mM) which acts as stabilizing agent have been mixed and stirred for a period time of 2 h. After that, an aqueous solution of the reducing agent DMAB (1 mL, 100 mM) has been added to the initial solution, and the mixture has been stirred for 24 h at room temperature. Finally, a color change from transparent to orange has been obtained, indicating the synthesis of AgNPs. The combination of PAH and AgNPs will be denoted as PAH-AgNPs.

2.3 Optical characterization

The optical properties of the synthesized metallic nanoparticles have been determined by using a Jasco V-630 spectrometer. Two different and well-separated absorption bands have been obtained.

2.4 Layer-By-Layer Nano-Assembly

The Layer-by-Layer nano-assembly technique have been used for the fabrication of the thin films. In this work, the presence of PAH and PAA are used as the positive and negative charged polyelectrolytes for the build-up of the polyelectrolyte structure film. In addition, as it has been demonstrated in the previous section, these charged structures also play a key role as stabilizing of the synthesized nanoparticles. More specifically, the polycationic solution PAH-capped AgNPs (PAH-AgNPs) and the polyanion PAA-capped AuNPs (PAA-AuNPs) have been used for the fabrication of the thin-films. A scheme of the deposition process is presented in Figure 1.

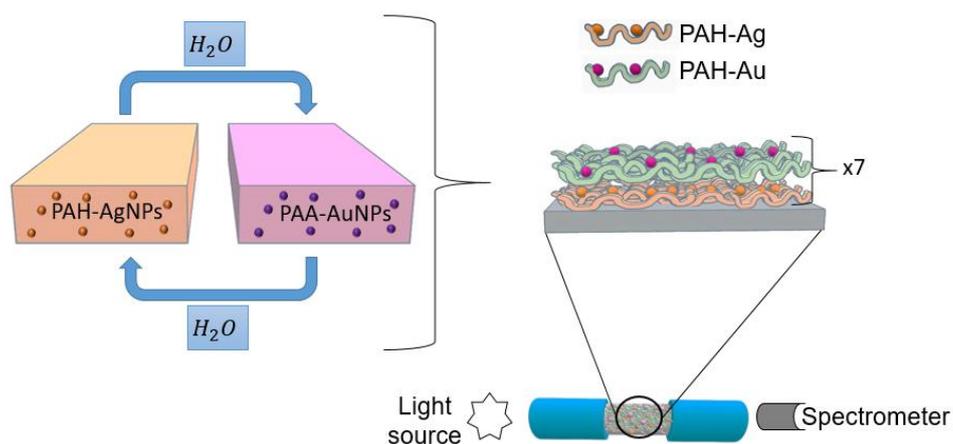


Figure 1. Schematic representation for the fabrication of the LbL films by using PAH-AgNPs as a polycation and PAA-AuNPs as a polyanion.

2.5 Mercury samples preparation

The mercury samples were prepared using Mercury (II) chloride (HgCl₂). Every concentration of mercury were prepared with Phosphate buffer (PB) solution for achieving a constant pH=7.6. The Hg concentrations were varied from 50, 1 and 0.1 ppm, respectively. An important aspect is that for each measurement, the fiber optical sensor is immersed in PB + DMAB buffer solution with the aim to obtain a stable baseline for a further mercury detection.

3. Results and Discussion

As an initial step, the nanofabrication process has been performed onto glass substrates and then, this same procedure is extrapolated to the optical fiber for a further chemical sensing. The selected pH for the fabrication of the whole process is 7.0 in the dipping polyelectrolytes. As it can be observed in Figure 2, the sample for a thickness coating with 10 bilayers has shown a clear predominance of the LSPR related to AgNPs (plasmonic peak centered at 450 nm), without being able to identify the peak related to AuNPs. However, when the thickness coating is gradually increased up to a total thickness of 30 bilayers, both LSPR peaks can be clearly observed which are centered at 420 nm (AgNPs) and 540 nm (AuNPs), although transparent films are still obtained which is observed by the naked eye.

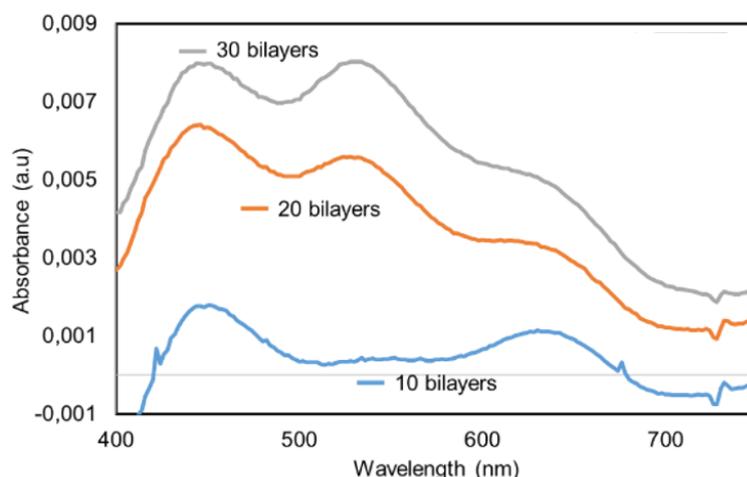


Figure 2. UV-Vis spectra of the LbL coatings based on PAH/AgNPs and PAA/AuNPs deposited onto glass slides as a function of the thickness coating (10, 20 and 30 bilayers) for pH 7.0, respectively.

Once it has been demonstrated the presence of both LSPR peaks onto glass slides, the next step is based on the deposition of this same thin-film onto optical fiber at the same pH value 87.0) in order to appreciate both absorption bands in the UV-Vis spectra. In Figure 3, it has been demonstrated that by only a final thickness of 7 bilayers, it is possible to appreciate the LSPR of the AgNPs (centered at 420 nm) and AuNPs (centered at 540 nm), being this sensing thin-film for the mercury ion detection.

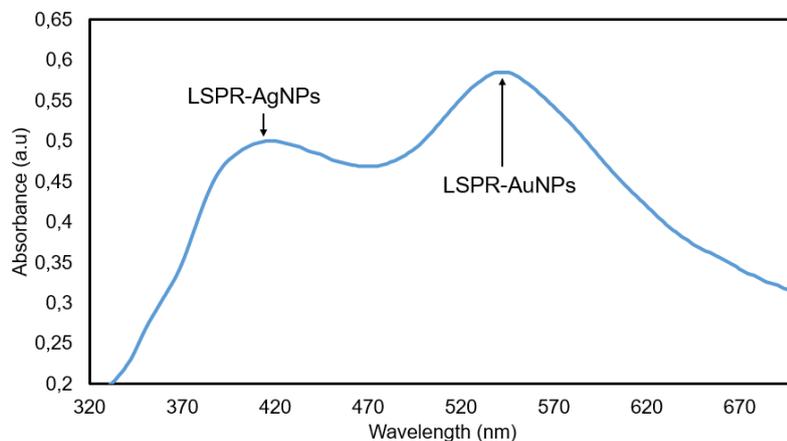


Figure 3. UV-Vis spectrum of the LbL coatings based on PAH/AgNPs and PAA/AuNPs deposited onto optical fiber for a thickness coating of 7 bilayers.

3.2 Detection of Mercury Ions with Fiber Optic Sensor.

Once the thin film has been fabricated, the optical fiber has been immersed in the Buffer PB + DMAB solution for 1 h in order to have a stable baseline for the mercury detection stage. After that, the sensing film has been immersed in a fixed mercury concentration of 50 ppm, and as a very interesting result is that, a clear wavelength shift of 23 nm has been observed for LSPR (AuNPs), whereas the LSPR (AgNPs) has been also displaced 10 nm, respectively.

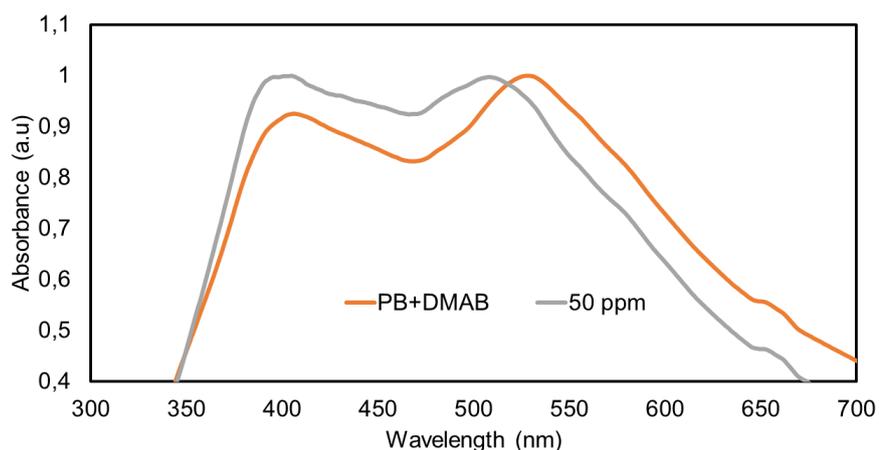


Figure 4. Wavelength shift of the LSPR absorption bands for 50 ppm of mercury concentration.

Different sensors have been fabricated with the same sensing materials in order to detect a particular mercury concentration. Although both LSPRs bands experimented changes in the presence of mercury ions, it is clearly visible that the LSPR band corresponding to AuNPs has shown a greater blue-shift in comparison with the LSPR of AgNPs. Finally, the dynamic response of the LSPR band inherent to AuNPs is presented in Figure 5 for different mercury concentrations (0.1, 1 and 50 ppm).

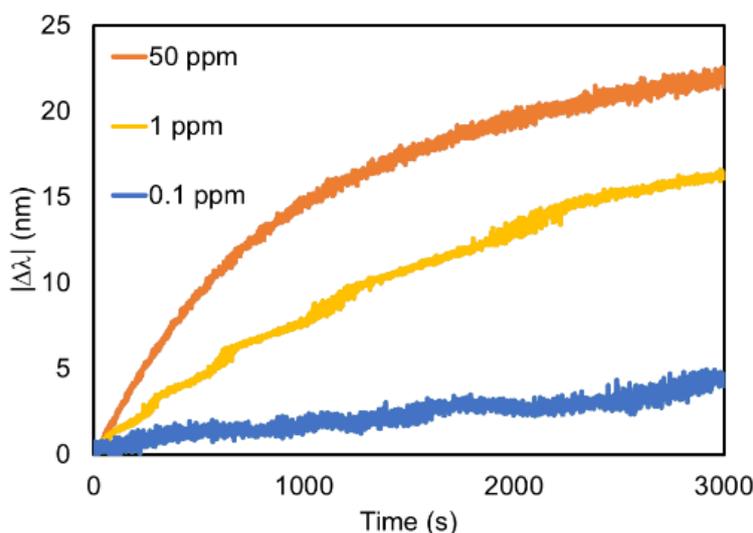


Figure 5. Dynamic response of the optical fiber sensors for the LSPR (AuNPs) to different Hg concentration, ranging from 50 ppm to 0.1 ppm, respectively.

4. Conclusions

In this work, a fiber optic sensor based on two different LSPR sensing signals for the detection of Hg^{2+} has been presented. The metallic nanoparticles have been incorporated into the sensing films by using the Layer-by-Layer nano-assembly technique. The sensors have been exposed to different Hg^{2+} concentrations, being the wavelength response of the LSPR (AuNPs) greater than LSPR (AgNPs). Finally, this resultant sensing material can be extrapolated to the detection of different heavy metals in environmental applications.

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Conflicts of Interest: The authors declare no conflict of interest.

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