



A COMPARATIVE STUDY IN THE SENSITIVITY OF OPTICAL FIBER REFRACTOMETERS BASED ON THE INCORPORATION OF GOLD NANOPARTICLES INTO LAYER-BY-LAYER FILMS

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Abstract- In this work, optical fiber refractometers based on the successive incorporation of gold nanoparticles have been fabricated by means of the Layer-by-Layer Embedding (LbL-E) deposition technique. This enables the apparition of two different optical phenomena, Localized Surface Plasmon Resonance (LSPR) and Lossy Mode Resonance (LMR). The absorption peaks related to both phenomena were captured during the fabrication process, showing a different evolution as a function of the resultant thickness coating. Initially, LSPR band is observed for thinner coatings, whereas multi-LMR bands are observed as the thickness coating is increased. In addition, the response of both phenomena to variations of the surrounding medium refractive index (SMRI) was monitored, studying their different sensitivities. LSPR band only shows intensity variation with negligible wavelength displacement whereas LMR bands present a strong wavelength response. The combination of both resonances opens the door in the design of self-referenced optical devices for sensing applications.

Index terms: Optical fiber sensors, gold nanoparticles, optical phenomena.

I. INTRODUCTION

Refractometers are extensively used in fields as diverse as chemistry, biochemistry, food and beverage industry or medicine to measure the surrounding medium refractive index (SMRI). They can be also combined with sensing coatings whose refractive index depends on the specific parameter under study [1-3]. Several technologies take advantage of this aspect. Among them, optical fiber has attracted the attention of many research groups in the last decades due to its intrinsic advantages such as light weight, small size, portability, remote sensing, and immunity to electromagnetic interferences or possibility of multiplexing several signals [4]. Different optical geometries such as single-mode fiber, multi-mode fiber, long-period fiber gratings (LPGs) or fiber Bragg gratings (FBGs) have been studied with the aim of increasing the sensitivity of the devices [5-10]. However, recent works have demonstrated that the use of nanodeposition techniques for the design of optical fiber sensors is becoming a hot topic in the fabrication of thin-film coated devices [11-17].

Very recently, an electromagnetic resonance known as Lossy Mode Resonance (LMR) has been observed in optical fiber devices, being used to develop different kind of sensors and refractometers [18-21]. The LMR-based devices typically consist of an optical fiber topology (stripped fibers, tapers, polished fibers, etc.) coated by a LMR-supporting thin-film. LMR occurs when the real part of the thin film permittivity is positive and higher in magnitude than both its own imaginary part (also positive) and the real part of the optical fiber core permittivity. When this happens, there is a resonant coupling from light guided in the core to modes guided in the external coating, the LMRs. This phenomenon can be clearly observed because several attenuation bands appear in the optical transmission spectrum of the devices [20]. This technology can be of high interest in optical fiber sensing because it allows the generation of multiple resonance bands, the tuning of the operation wavelengths as a function of the coating thickness or the use of different types of materials (polymers, ceramics, metal oxides, etc.) to fabricate the coatings. In addition, it avoids the necessity of using complex optical devices, such as polarizers or lasers [21].

Another widely-known optical phenomenon is the Surface Plasmon Resonance (SPR) [22-25], which occurs when the real part of the thin film permittivity is negative and higher in magnitude than both its own imaginary part and the real part of the permittivity of the material

surrounding the thin film (i.e., the optical waveguide and the surrounding medium in contact with the thin film). In order to obtain this SPR phenomenon, it is necessary a metallic thin film, typically gold or silver, which is sandwiched between two dielectrics such as the optical fiber core and the liquid of the sample to be measured. However, this phenomenon can be monitored only for TM (transverse magnetic) or p-polarized light. According to this, the two main limitations of the SPR-phenomenon are the use of expensive materials (noble metals) and the need of optical polarizers to observe the optical phenomenon.

The physical phenomenon of the SPR changes when the metallic material is distributed into nanoparticles instead of a continuous thin-film onto the optical waveguide. For this specific case, the phenomenon is called Localized Surface Plasmon Resonance (LSPR). According to the scope of this work, which is devoted to the synthesis of metal gold nanoparticles (AuNPs) and their further incorporation into thin films for sensing applications as refractometers, the initial focus consists of the fabrication and design of LSPR-devices instead of SPR-devices. It is well-known that the use of metal nanoparticles for optical sensors is of great interest because the phenomenon of LSPR can be used as a sensing signal [26-29]. The location of this resonant peak in the visible or infrared region depends on multiple factors such as shape, size, aggregation state, distribution or interaction of the nanoparticles [30-34].

In this work, the Layer-by-Layer (LbL) Embedding (LbL-E) deposition technique has been selected to deposit different multilayer coatings made of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid)-capped gold nanoparticles (PAA-AuNPs) onto the optical fiber core to observe both LSPR and LMR optical phenomena. The LbL-E deposition technique can be used to fulfill the technological conditions required to observe these two optical phenomena [35, 36]. Although a previous work has demonstrated that it is possible to combine both phenomena in the same device using silver nanoparticles [37], the use of gold nanoparticles presents several advantages such as biocompatibility, non-reactive, great chemical stability and easy to functionalize. Both phenomena have been simultaneously observed during the fabrication of the thin film, studying the variation of the different peaks as far as the thickness is increased. In addition, their responses to variations of the SMRI have been monitored, studying their different sensitivities that they present.

II. EXPERIMENTAL PROCESS

a. Materials

The polymers poly(allylamine hydrochloride) (PAH) and poly(acrylic acid, sodium salt) (PAA) as well as gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and dimethylamineborane complex (DMAB) were purchased from Sigma–Aldrich without any further purification. Plastic-clad silica fiber of 200/225 μm core/cladding diameter (FT200EMT) were provided by Thorlabs.

b. Fabrication of the multilayer films

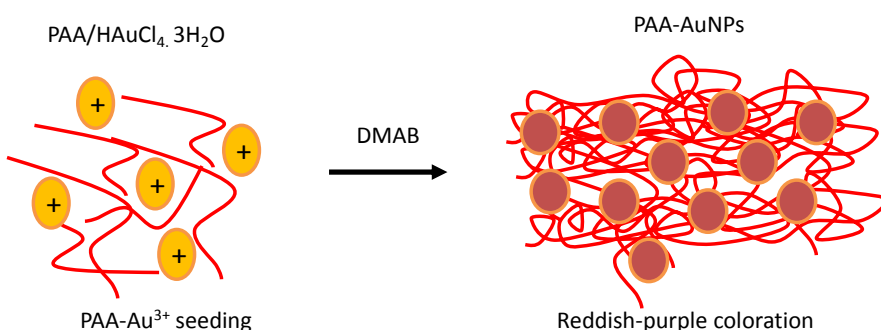
The incorporation of the gold nanoparticles (AuNPs) with a specific coloration into multilayer thin films is presented using the Layer-by-Layer Embedding (LbL-E) deposition technique. This technique is based on a first step of synthesis of AuNPs with a desired shape using PAA as a protective agent (PAA-AuNPs) and then, a second step, where the Layer-by-Layer Embedding (LbL-E) deposition technique of the previously synthesized AuNPs into a thin film is performed.

The AuNPs have been synthesized at room temperature via chemical reduction process of an aqueous solution of gold precursor ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) with an aqueous solution of dimethylamineborane complex (DMAB) which acts as a reducing agent. In this synthetic process, the reduction of gold ions (Au^{3+}) to gold nanoparticles (Au^0) is possible thanks to the use of a protective agent, poly(acrylic acid, sodium salt) (PAA) which can control the shape and size of the resultant nanoparticles, preventing their agglomeration or precipitation in the colloidal solution. A change of coloration from yellowish to reddish-purple indicates that AuNPs have been successfully synthesized.

In this synthetic route for preparing the AuNPs, the protective agent used (PAA) is of vital importance for a further incorporation of the nanoparticles into thin films using the Layer-by-Layer Embedding (LbL-E) deposition technique. This is due to the presence of free carboxylate groups at a suitable pH which are used to build the sequentially multilayer film in the LbL assembly. To perform this deposition technique, the electrostatic attraction between monolayers of opposite charge such as the cationic polyelectrolytes (PAH) and the anionic polyelectrolytes with the nanoparticles embedded (PAA-AuNPs), makes possible to obtain a thin multilayer film with a structure homogeneous, resistant and compact. The combination of a cationic monolayer

and an anionic monolayer is called bilayer henceforward. All solutions were prepared with a 10 mM concentration using ultrapure deionized water. In Figure 1, a schematic representation of the LbL-E deposition technique is shown. The cycle of [PAH/PAA-Au-NPs] was repeated up to 6, 15 and 22 times in order to fabricate 6, 15 and 22 bilayers coating with the aim of monitoring and evaluating in a separated way a LSPR sensor (7 bilayers coating), LSPR-LMR sensor (16 bilayers) and multi-LMR sensor (22 bilayers coating) to refractive index variations. The nanocoatings were carried out using a 3-axis robot from Nadetech Innovations.

1) Synthesis of gold nanoparticles (PAA-AuNPs)



2) Incorporation of PAA-AuNPs into multilayer thin films

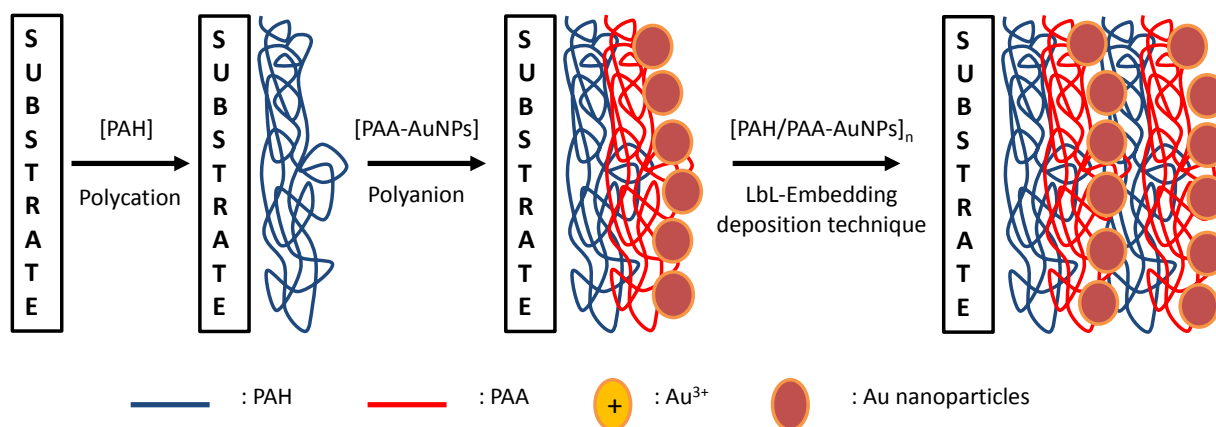


Figure 1. A schematic representation of the PAA-AuNPs synthesis (reddish-purple color) and a further progressive incorporation into thin films using the Layer-by-Layer Embedding (LbL-E) deposition technique.

c. Device fabrication and characterization

In order to monitor the evolution of the different absorption bands (LSPR and LMR, respectively) as a function of the resultant thickness during the LbL-E deposition technique, the transmission spectra were collected after each bilayer as it is schematically represented in Figure 2. This setup basically consists of a white halogen lamp connected to one end of the optical fiber and a CCD-based UV-Vis spectrometer (OceanOptics HR4000) connected to the other end of the fiber. This allows the observation of a wavelength range from 400 to 1000 nm. Light passes through the sensitive region, which is located between the white light source and the spectrometer.

In addition, in order to characterize the response of the device as refractometer, the transmission spectra were recorded when the sensitive zone was immersed in different water solutions of glycerin with refractive index values of 1.33, 1.3627, 1.3923 and 1.4204. The measurements were performed at 25 °C.

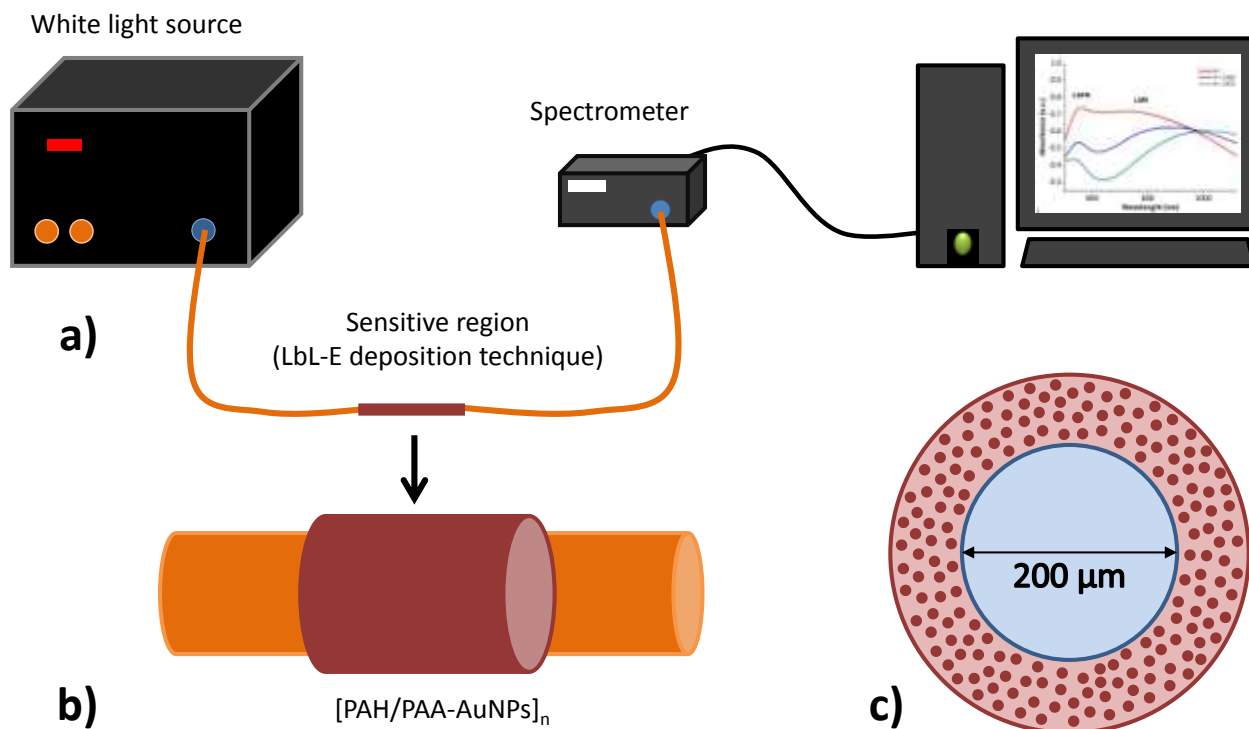


Figure 2. a) Schematic representation of the experimental setup used to capture the spectra during the fabrication process; b) Detail of the sensitive region after the LbL-E deposition technique; c) Detail of transversal section of the device with the gold nanoparticles incorporated (not to scale).

d. Characterization of the gold nanoparticles (PAA-AuNPs)

Transmission electron microscopy (TEM) was used to characterize the size and distribution of the metallic nanoparticles. Samples for TEM were prepared by drop-casting the AuNPs dispersion onto a collodion-coated copper grid. TEM micrographs were carried out with a Carl Zeiss Libra 120.

UV-visible (UV-Vis) spectroscopy was used to characterize the optical properties of the gold nanoparticles suspension (PAA-AuNPs). Measurements were carried out with a Jasco V-630 spectrophotometer.

III. RESULTS AND DISCUSSION

First of all, gold nanoparticles have been synthesized (PAA-AuNPs) as it was explained in the Experimental process. A change of coloration from yellowish (source of gold ions, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) to reddish-purple (PAA-AuNPs) is indicative that metal nanoparticles have been successfully synthesized prior to the LbL-E deposition technique. In addition, this aspect is also corroborated by UV-Vis spectroscopy (see Figure 3) because it is possible to appreciate the existence of a plasmon resonance band, known as Localized Surface Plasmon Resonance (LSPR). This phenomenon occurs when the conduction electrons in metal nanostructures collectively oscillate, as a result of their interaction with an incident electromagnetic radiation. A specific wavelength position of the LSPR displays a high dependence on the resultant shape and size of the nanoparticles. In this case, the wavelength location of the LSPR band at 530 nm indicates that PAA-AuNPs with mostly a spherical shape have been synthesized and this aspect is corroborated by TEM micrograph. Gold nanoparticles with a quasi-spherical or spherical shape are obtained with a size less than 50 nm.

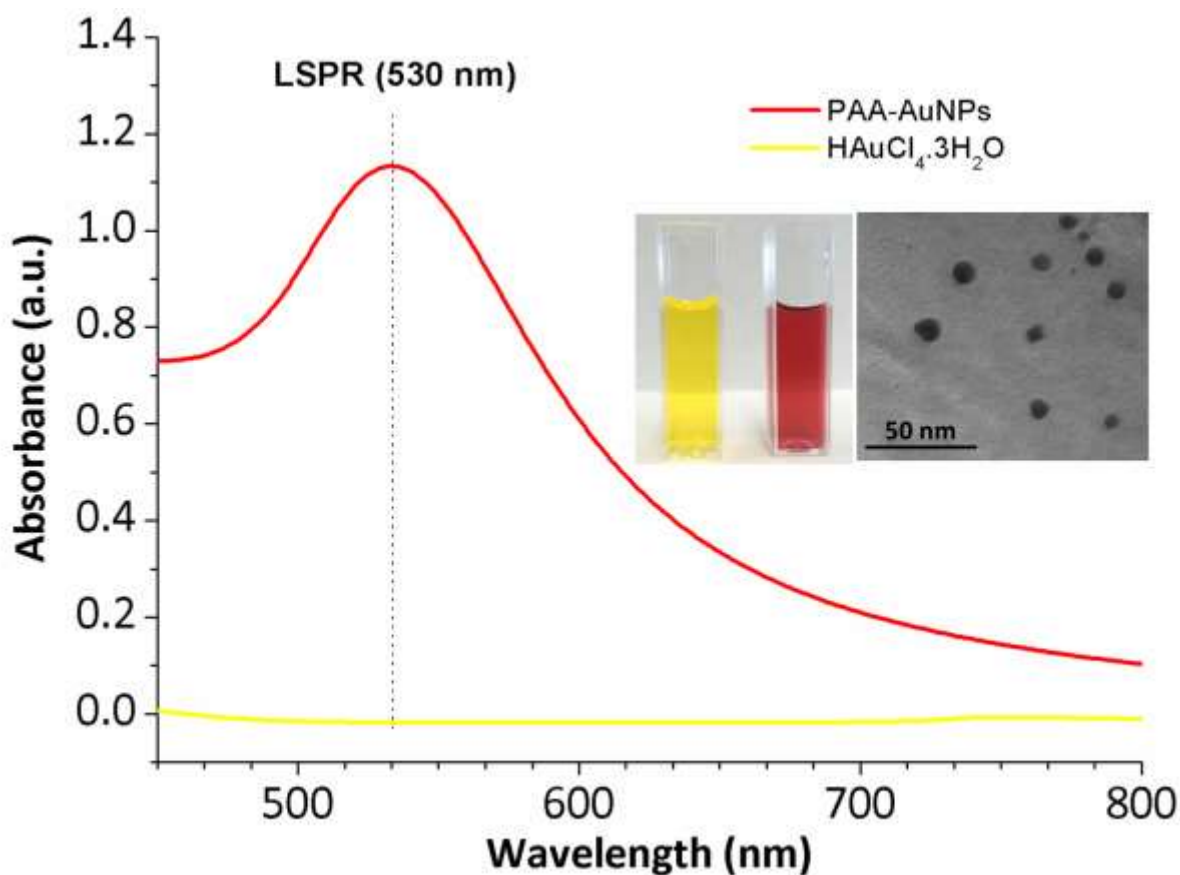


Figure 3. UV-Vis spectra of the gold ions source ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, yellowish color) and the synthesized gold nanoparticles (PAA-AuNPs, reddish-purple color) after chemical reduction process with their corresponding spherical shape (TEM image).

Once PAA-AuNPs have been synthesized with their characteristic reddish-purple coloration, the next step is to incorporate these nanoparticles into thin-films using the Layer-by-Layer Embedding (LbL-E) deposition technique. The use of PAA as an encapsulating agent of the nanoparticles plays a dual role. Firstly, it prevents the agglomeration or aggregation of the nanoparticles during the synthesis process. And secondly, this weak polyelectrolyte can be manipulated as a function of the pH in order to obtain ionized groups which are used to perform the multilayer assembly by the electrostatic attraction of oppositely charged polyelectrolytes. In this work, a pH 9.0 has been selected in order to fabricate the nanocoatings because it has been demonstrated that both polyelectrolytes at this pH value are totally ionized.

In Figure 4, the evolution of the transmitted spectra corresponding to $[\text{PAH}(9.0)/\text{PAA-AuNPs}(9.0)]_n$ at different number of bilayers is shown. The optical signal of the bare optical fiber was taken as reference for the absorption measurements during the fabrication process.

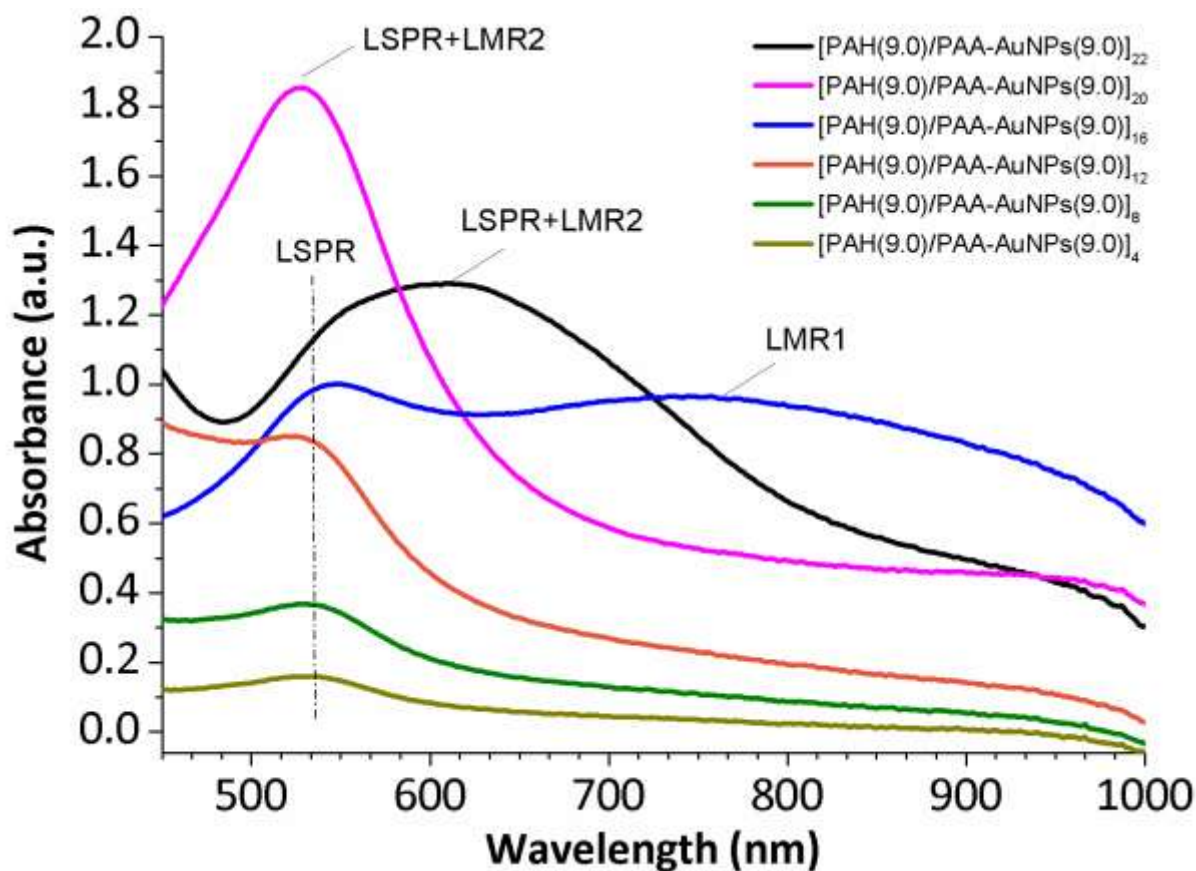


Figure 4. Transmitted absorption spectra during the deposition process from 1th to 22th bilayers. The curves plotted are 4, 8, 10, 12, 16, 20 and 22 bilayers.

Initially, when the thickness coatings is increased from 1 to 12 bilayers, only an absorption band centered at 530 nm is observed. This peak related to the LSPR phenomenon becomes higher as far the number of bilayers is increased, although it remains at the same wavelength position. Nevertheless, when the number of bilayers is increased up to 16 bilayers, two different resonant phenomena, LSPR and LMR1, are observed simultaneously in the visible spectra. The new LMR peak (LMR1) appears at low wavelengths and shifts to the right during the fabrication process. And finally, when thickness coating is increased up to 22 bilayers, the LMR1 peak exceeds the visible range and a new LMR band (LMR 2) is observed in the visible spectrum which is shifted

from shorter wavelengths to longer wavelengths as a function of the resultant thickness. This LMR2 peak can mask the LSPR peak when they are centered near it as it happens after 20 bilayers coating.

In order to characterize separately the response of the different resonances (LSPR, LMR1 and LMR2) to variations in the surrounding medium refractive index (SMRI), three different nanocoatings with different number of bilayers have been fabricated and characterized.

a. LSPR sensor (7-bilayers device)

The first device consisted of a coating with just 7 bilayers of [PAH(9.0)/PAA-AuNPs(9.0)] in which only the LSPR peak can be observed without any perturbations from LMR phenomena that could mask the signal. In Figure 5, it is shown the response of the LSPR band generated in this device when the sensitive coating is immersed into glycerin solutions with different SMRI.

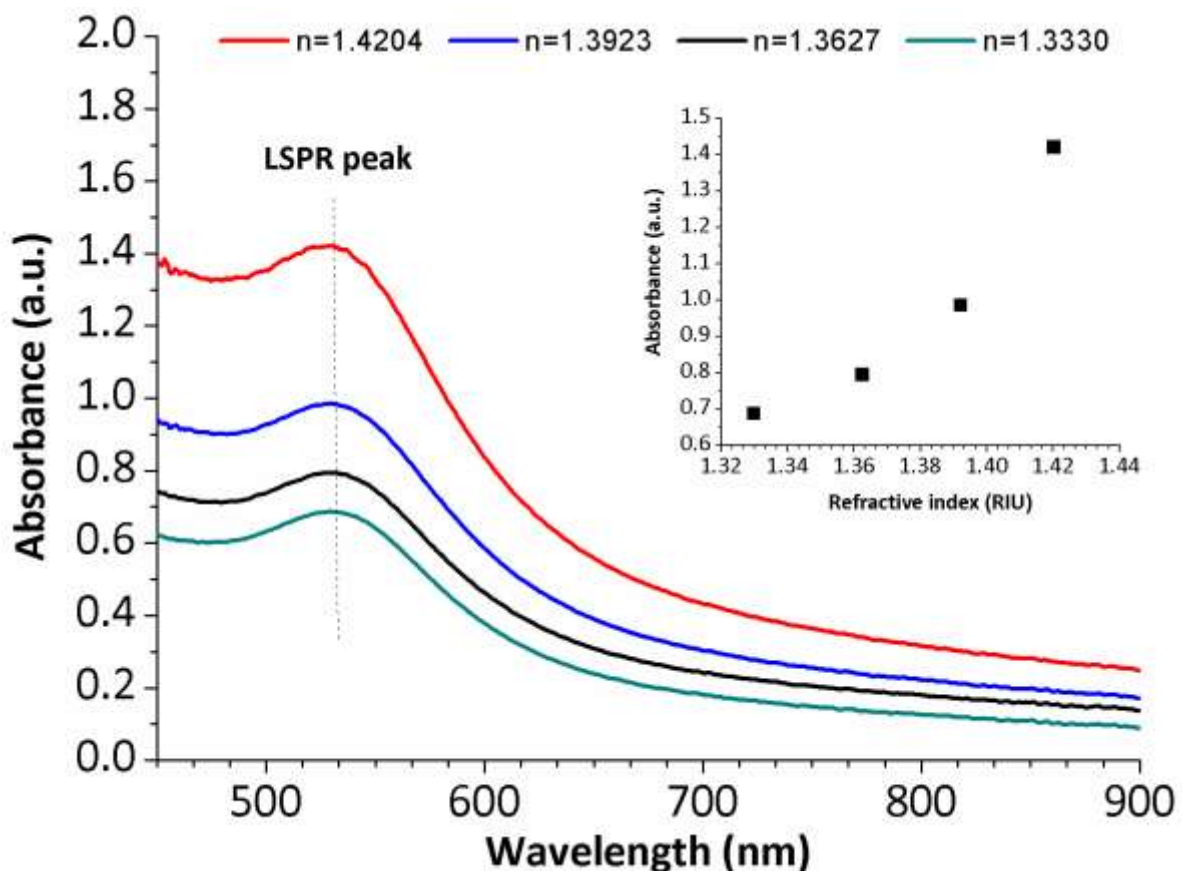


Figure 5. Spectral response of the LSPR absorption peak (7-bilayers device) and the evolution of the maximum absorbance of the LSPR band (inset) when the sensitive coating is immersed in different surrounding medium refractive indices (SMRI).

The results displayed in this Figure indicate that only a change in intensity of the LSPR absorption band is observed as SMRI is varied. As it can be clearly observed, the intensity of the LSPR absorption band increases as far as the SMRI becomes higher. In addition, no significant changes are observed in the wavelength position of the LSPR peak which it is perfectly centered at 530 nm after immersing the sensitive coating to different SMRI. In the inset of the Figure 5, the evolution of maxima absorbance of the LSPR absorption band is represented as a function of variable refractive index values from 1.33 to 1.4204.

b. LSPR-LMR sensor (16-bilayers device)

The second device was fabricated by depositing 16 bilayers of [PAH(9.0)/PAA-AuNPs(9.0)] in order to show clearly both LSPR and LMR1 absorption bands in the spectral range. As it was observed in Figure 4, the LSPR absorption band is centered at 550 nm, whereas the LMR1 band is located around 750 nm.

In Figure 6, it is shown the red-shift of the LMR1 absorption band as SMRI is increased. In this same graph, it is possible to appreciate how the LSPR band shows no significant wavelength dependence with variable refractive index values because it is located between 540-550 nm and this aspect had been previously corroborated in the Figure 5. However, the LMR1 band shows a shift of 265 nm when the sensitive region is immersed in water solutions of glycerin with refractive index values from 1.3330 to 1.3627. In addition, a higher value of the refractive index ($n > 1.3627$) makes the LMR1 band to be already out of the scope for this wavelength visible range. The LMR1 absorption band shows a very broad absorption peak with a high sensitivity of 8922 nm/RIU. This aspect has been experimentally proved in previous works [20] where it can be observed for polymeric films that the first LMR (LMR 1) shows a higher spectral width than the higher order LMRs. Due to this a study in higher order LMR has been performed in this work and it is shown in the following section.

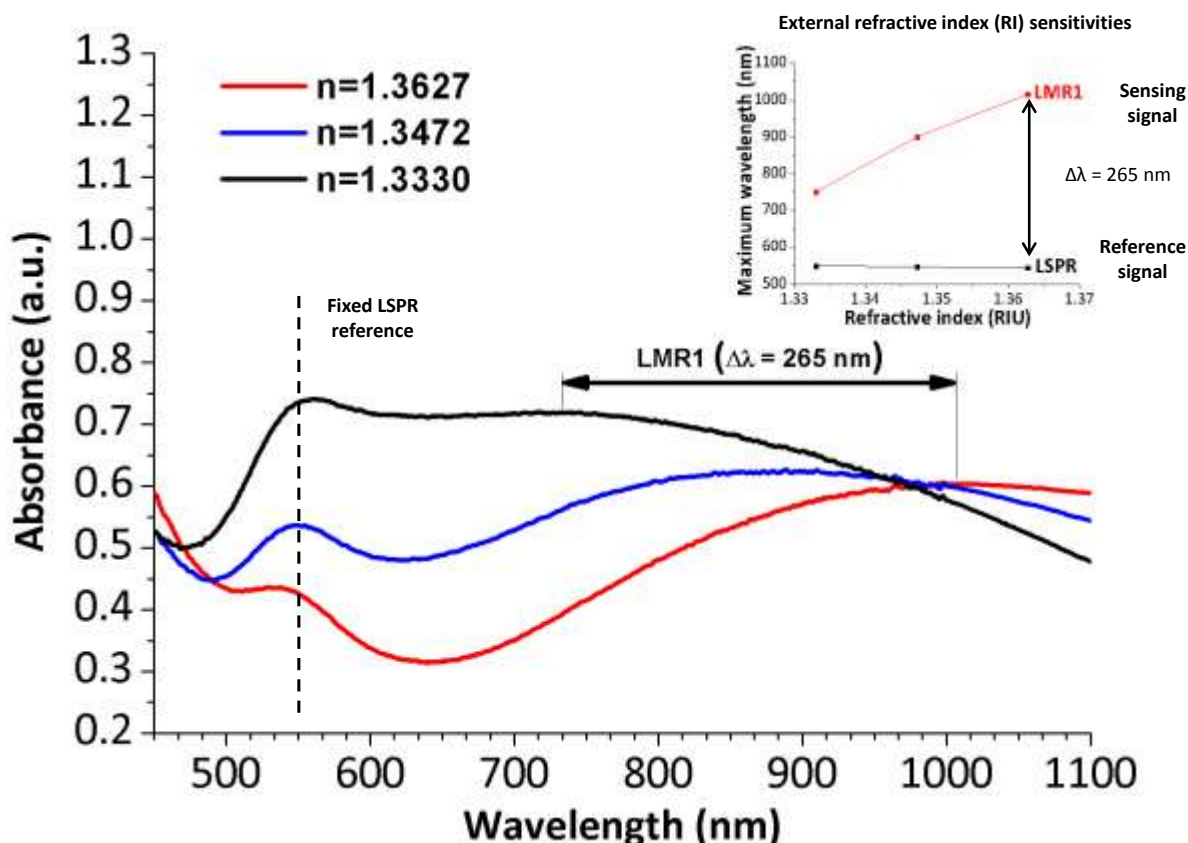


Figure 6. Spectral response of the LSPR (wavelength fixed reference) and LMR 1 (wavelength variation) absorption bands for 16-bilayers device when the sensitive region is immersed in different refractive indices from 1.3330 to 1.3627. The inset of the figure shows the great difference in sensitivities of both absorption bands to the external refractive index.

One of the main advantages of the design of this dual LSPR-LMR device is the possibility of fabricating self-referenced sensors. As we can see in the inset of the Figure 6, the LSPR band can be used as a reference signal (no variation in the wavelength position), whereas the LMR1 band can be used as a sensing signal to variations of the external refractive index.

c. Multi-LMR sensor (22-bilayers device)

The third device was fabricated by depositing 22 bilayers of [PAH(9.0)/PAA-AuNPs(9.0)] in order to make new LMR bands observable in the spectral range. For this specific number of bilayers, LMR1 is already out of the scope for this wavelength range, whereas LMR2 band remains in the visible range.

In Figure 7, it is possible to appreciate two new LMR absorption bands (LMR3 and LMR4) when the sensitive region is immersed in the water solution of glycerin with a refractive index value of 1.3627 and 1.4204, respectively. In addition, a red-shift of LMR peaks is observed, LMR2 and LMR3 respectively, as SMRI is increased. LMR2 is centered at 570 nm when the SMRI is 1.33 and is shifted to 935 nm when the SMRI is 1.4204. In a similar way, the LMR3 is shifted from 430 nm when the SMRI is 1.3627 to 540 nm when the SMRI is 1.4204. Attending to these results, the LMR2 shows a sensitivity of 4037 nm/RIU, whereas the LMR3 shows a sensitivity of 1906 nm/RIU. As we can see in Figure 7, the aspect of the LMR 2 and LMR 3 absorption bands are narrower than the LMR 1 absorption band (see Fig. 6).

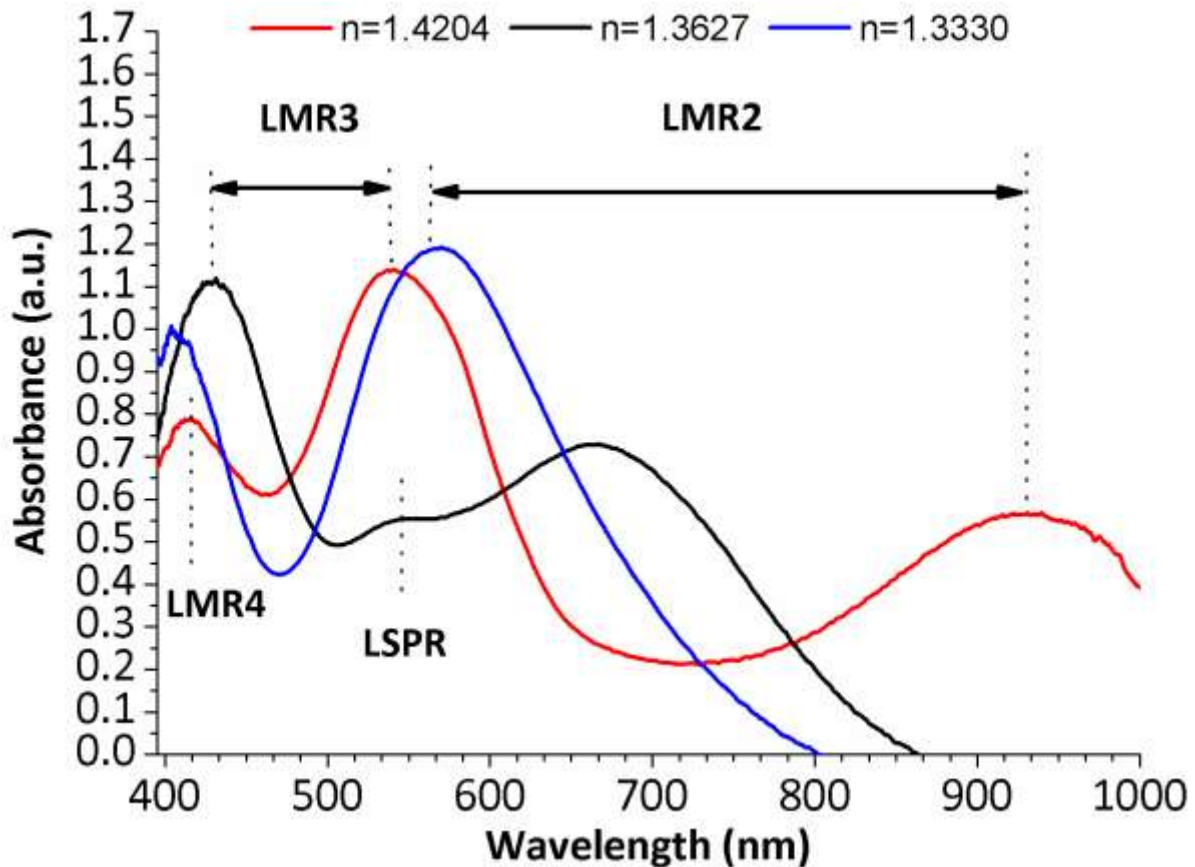


Figure 7. Spectral response of the LMR absorption bands (LMR2 y LMR3) for the 22-bilayers device when the sensitive region is immersed in different surrounding refractive indices.

In order to have a more precise idea of the different behavior in sensitivity related to the 22-bilayers device, Figure 8 shows the wavelength shift versus refractive index values of both

LMR2 and LMR3 bands. According to these results, the LMR2 shows more than two-fold increase in sensitivity than LMR3. The presence of this dual peak in a same device (22 bilayers) presents the additional advantage of more accurate measurements of the refractive index, showing a wavelength-based detection. Due to this, it is possible to estimate the SMRI as a function of the wavelength displacement of the both LMRs, and not only with the intensity shift of the LSPR. In Table 1, the main differences between the three fabricated devices are presented with their corresponding sensitivities.

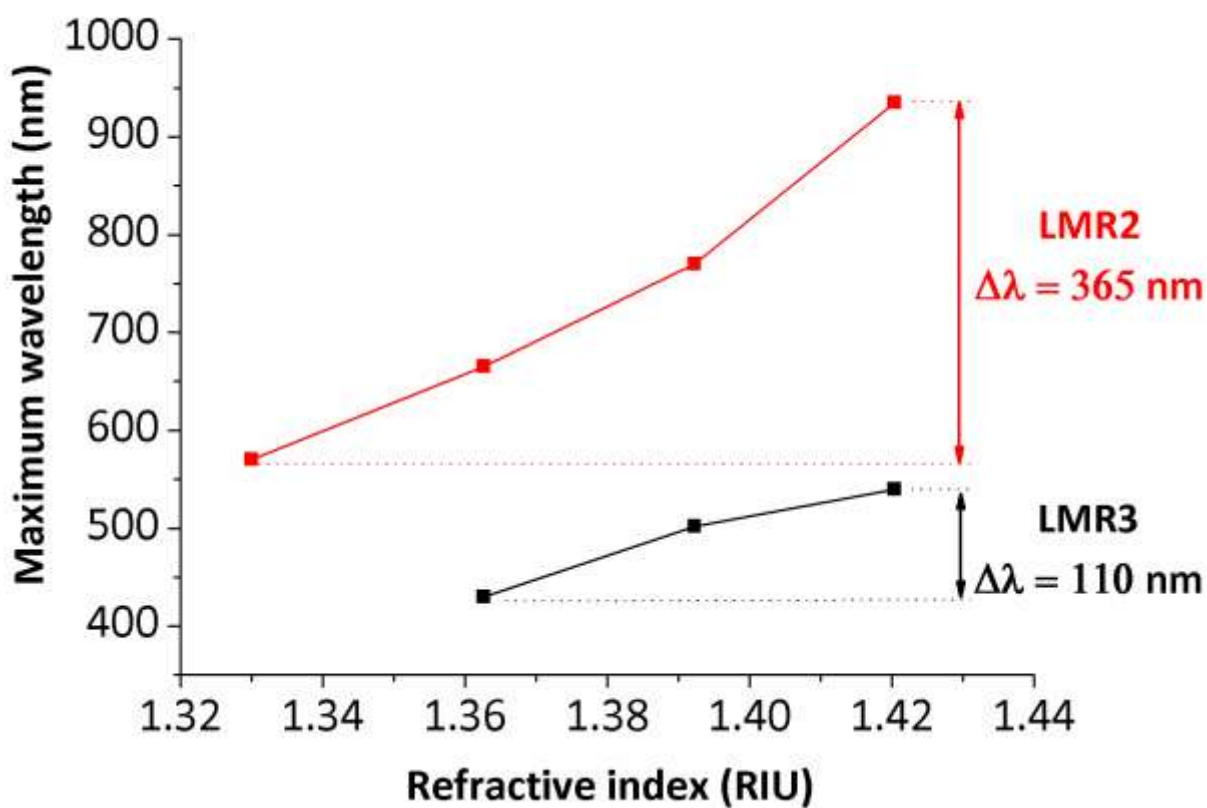


Figure 8. Experimental wavelength shift evolution of both LMR2 and LMR3 absorption bands to different surrounding refractive indices of the 22-bilayers device.

Table 1. A comparative table of the sensitivities (wavelength shift in nanometers versus refractive index unit) for the three devices analyzed.

Optical fiber device	Optical phenomenon	Sensitivity (nm/refractive index unit)
7-bilayers device	LSPR	Negligible
16-bilayers device	LSPR	Negligible
	LMR1	8922 nm/RIU
	LMR2	4037 nm/RIU
22-bilayers device	LMR3	1906 nm/RIU

Finally, and according to the experimental results, one of the most important advantages of using the LbL-E deposition technique is that the optical response of the sensors can be monitored during the fabrication process and it can be stopped at the moment when the LSPR, LSPR-LMR or multi-LMR bands are tuned to the desired wavelength position with their characteristic sensitivities.

IV. CONCLUSIONS

In this work, three optical fiber devices based on different optical phenomena, LSPR, LSPR-LMR and multi-LMR absorption bands, have been fabricated and characterized for measuring the refractive index. The LbL-E deposition technique has been selected to fabricate the nanocoatings based on the successive incorporation of gold nanoparticles onto the uncladded core of a multimode optical fiber fragment. The transmitted spectra monitored during the deposition allow the study of the apparition and evolution of different absorption peaks as a function of the thickness coating.

The first device consists of a 7-bilayers coating and only the LSPR peak is observed which is centered at 530 nm, inherent to the gold nanoparticles. This peak remains at the same wavelength position during the whole fabrication process, showing only intensity variation without any wavelength dependence to the SMRI. The second device consists of 16-bilayers coating and two optical phenomena (LSPR and LMR1) at different wavelength positions are observed in the spectral range, showing a different behavior to the SMRI. The LSPR shows no significant wavelength dependence whereas LMR1 shows a strong wavelength response with a sensitivity of 8922 nm/RIU. And the third device consists of a 22-bilayers coating and multiple LMR peaks (LMR2, LMR3, LMR4) are observed when the sensitive coating is immersed in glycerin solutions with a variable refractive index value. The LMR2 and LMR3 peaks showed a sensitivity of 4037 and 1906 nm/RIU respectively. These results indicate that LMR2 improves the sensitivity in more than two times than LMR3. Finally, the presence of the LSPR peak in a same optical device can be used as a wavelength fixed reference, while LMR peaks can be used to measure the refractive index. To our knowledge, this is the first time that LSPR generated by gold nanoparticles and LMR peaks are simultaneously observed in a same device.

V. ACKNOWLEDGMENTS

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