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Humidity sensor based on silver nanoparticles embedded in a polymeric coating

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Abstract- In this work, it is presented a novel optical fiber humidity sensor based on silver nanoparticle-loaded polymeric coatings built onto an optical fiber core. The polymeric film was fabricated using the Layer-by-Layer assembly technique. The silver nanoparticles (Ag NPs) were characterized using transmission electron microscopy (TEM and UV-VIS spectroscopy. A Localized Surface Plasmon Resonance (LSPR) attenuation band is observed when the thickness of the coating increases, and showed a very good sensitivity to Relative Humidity (RH) variations, suitable for high performance applications such as human breathing monitoring.

Index terms*:* Optical fiber, humidity sensor, surface Plasmon resonance (SPR), synthesis of silver nanoparticles, polymeric coating.

I. INTRODUCTION

Nowadays, the design of optimal Relative Humidity (RH) sensing devices is a big concern among scientific sensor community. This kind of devices has a great interest in several fields such as food quality preservation, gas purification, textile production, medical facilities or air conditioning regulation. Due to this high number of applications in general industry, the design and development of sensing devices for monitoring RH has been increasing in industrial processing and environmental control [1].

Conventional electronic RH devices are the most used in the sensor market due to its low cost but the use of optical fiber sensors has grown significantly due to their fast response, small size and simple geometry. Moreover, there are a lot of applications in which the advantages of the optical sensors overcome those of common electronic ones, like electromagnetic immunity, or safety in explosive or unstable environments. In this particular field, one of the key points of the fabrication of a fiber optical sensor is the reproducibility for sensing devices. [2-5].

One of the most used techniques at nanoscale level in order to obtain self-ordered nanostructures with precise thickness control is the Layer-by-Layer (LbL) process [6]. This technique has been applied to a wide range of polymers and nanomaterials, such as polyelectrolytes, nanoparticles or nanotubes. [7-10]. Moreover, the use of LbL process provides the ability to place different kind of nanoparticles throughout the multilayer polymeric films.

The LbL technique has the advantage of being a simple method, versatile, systematic and ready for scaling-up whereas control over the assembly conditions (immersion time, solution pH, temperature, ionic strength and concentration of the polyelectrolytes) [11, 12]. In addition, room temperature processing and low cost fabrication makes it to be a popular technique for thin film fabrication. The combination of thin films with sensing devices has been studied in the field of optical fiber sensors so that the LbL assembly has potential applications in electronics and sensing devices. [13-15].

The use of silver nanoparticles (Ag NPs) inside the polymeric coating plays a key role because it is considered a very good antibacterial agent and silver ions show a notorious broad spectrum biocide effect [16-18]. Moreover, silver is particularly attractive because it combines a high toxicity for bacteria with a low toxicity for humans so that it could be used in sensing devices in order to prevent the growth of microorganisms onto the sensor coating in high RH environments. The introduction of Ag NPs into the LbL assembly is of special interest in materials science in order to prepare hybrid inorganic-organic nanostructures [19].

Besides, the utilization of Ag NPs makes possible the fabrication of optical sensors based on Localized Surface Plasmon Resonance (LSPR), which is perhaps one of the most well-known sensing mechanisms. This phenomenon 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. These optical properties of the silver nanoparticles makes possible the apparition of a strong absorption band in the visible spectrum which it is attributed to the collective oscillation of the conduction electrons of the nanoparticles by the electromagnetic field of the incident light. This resonant peak (LSPR) depends of multiple factors such as nanoparticle size, shape and interparticle interactions [20-22].

In this work, it is presented the fabrication and characterization of an optical fiber humidity sensor (OFHS) which has been built up by the LbL assembly with silver nanoparticles inside the polymeric coating. The device performance has been tested experimentally for Relative Humidity (RH) changes from 20% to 80% at room temperature.

II. EXPERIMENTAL PROCESS

a. Fabrication of the multilayer film

All chemicals used were obtained from Sigma–Aldrich and used without further purification. Plastic-clad silica fibers of 200/225 µm core/cladding diameter (FT200EMT) were provided by Thorlabs Inc.

Firstly, it has been developed a water-based chemical route of synthesis of silver nanoparticles similar to those reported by Liz-Marzan and co-workers [23]. Then, the Layer-by-Layer (LbL) technique was used for the fabrication of thin films. This method based on the sequential depositions of oppositely charged species followed by a rinse step in ultrapure water between each deposition in order to remove the excess of charge added to the substrate is represented schematically in Figure 1.

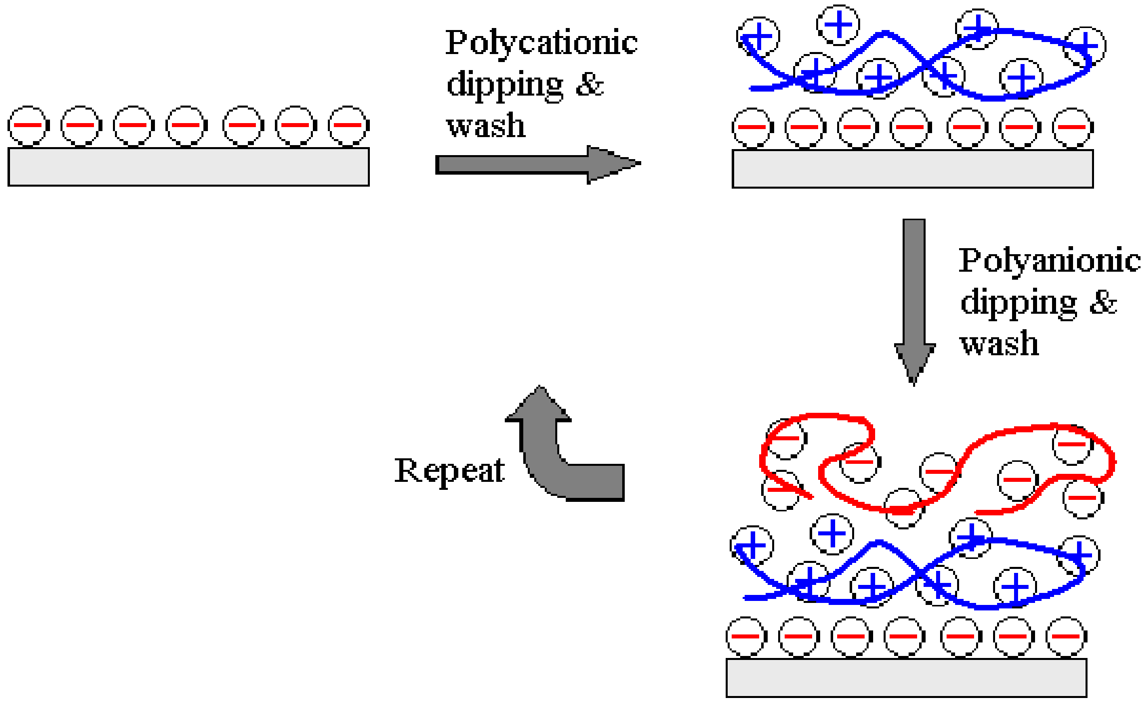

Figure 1. Detail of the LbL process.

The LbL assembly was performed by sequentially exposing the substrates to the cationic polyelectrolyte Poly(allylamine hydrochloride) (PAH) and the anionic polyelectrolyte Poly(acrylic acid sodium salt) loaded with silver nanoparticles (PAA-Ag NPs). The combination of a cationic monolayer and an anionic monolayer is called bilayer henceforward. All solutions were prepared with a 10mM concentration using ultrapure deionized water. The molecular structures of the chemicals used are shown in Figure 2.

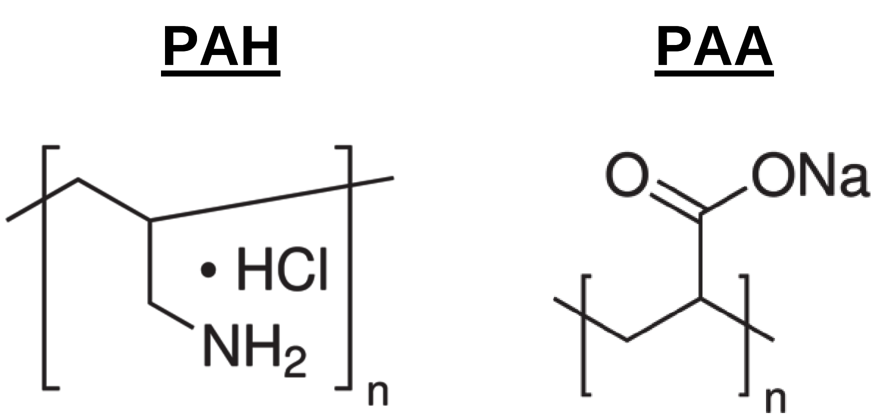

Figure 2. Molecular structure of polycation (PAH) and polyanion (PAA).

The LbL (PAH/PAA+Ag-NPs) cycle was repeated up to 10 times to fabricate 10 bilayers coating and was carried out using a 3-axis robot from Nadetech Innovations (see figure 3).

Figure 3. A 3-axis robot to the LbL process.

The polymeric coating with embedded silver nanoparticles was fabricated onto a fragment of 5 cm of a 200µm optical fiber core. This sensitive region is schematically shown in Figure 4.

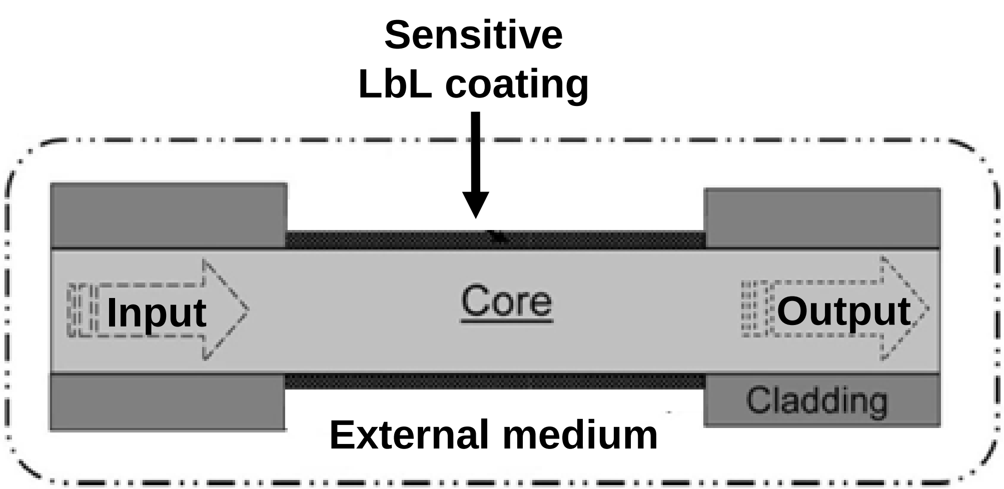

Figure 4. Detail of the sensitive region where LbL is deposited.

b. Characterization of the silver nanoparticles and coating

The morphology and size of the silver nanoparticles were characterized by transmission electron microscopy (TEM) using a Carl Zeiss Libra 120. Samples for TEM were prepared by dropping and evaporating the suspensions onto a collodion-coated copper grid.

The evolution of the optical absorption of the Ag NPs loaded polymeric film was monitored by UV-visible spectroscopy as the multilayer structure was built up by LbL.

c. Device characterization

Absorbance spectra were monitored using a typical optical transmission setup, as represented in Figure 5. This configuration basically consisted 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 1000nm.

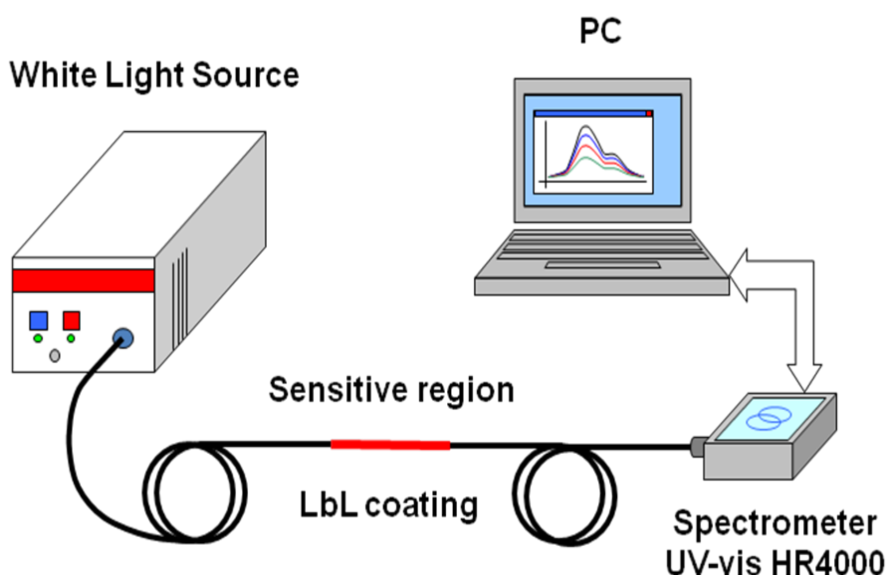

Figure 5. Schematic representation of the measuring setup.

Light passes through the sensitive region, which is located between the light source and the detector. Transmitted light is affected by the new boundary conditions created by the polymeric coating. Then, an environmental chamber (Angelantoni Inc.) was used to control both the Relativity Humidity (RH) and the temperature of the sensor surrounding medium. The sensor was exposed to humidity changes from 20%RH to 80%RH and the temperature was kept constant at 25ºC during the whole RH cycle. The complete process was repeated a number of 3 times.

III. RESULTS AND DISCUSSION

Firstly, a TEM image of the synthesized silver nanoparticles is shown in Figure 6. The size of the silver nanoparticles is 30 nm approximately and a well-dispersed distribution without any aggregation has been obtained.

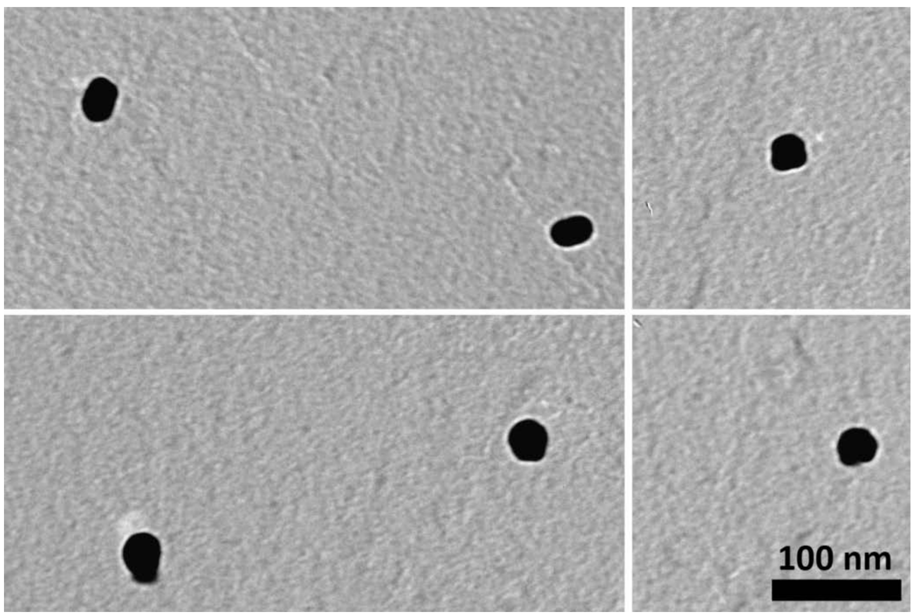

Figure 6. TEM micrograph of silver nanoparticles synthesized.

As it has been previously commented, TEM analysis proved the synthesis of quasi-spherical shaped silver nanoparticles. Due to this, the synthesized colloidal silver nanoparticles in aqueous PAA solution (PAA-Ag NPs) are stable in water without particle aggregation at room temperature and were deposited by LbL assembly onto the sensitive region.

The alteration of the visible absorption spectrum of the samples change is directly related with the Surface Plasmon Resonance (SPR) phenomenon typical of metal nanoparticles, such as silver nanoparticles. In fact, the UV/VIS absorbance was used to monitor the multilayer buildup LbL assembly in order to confirm the existence of this absorption peak of the SPR.

Figure 7 shows the UV-VIS absorbance spectrum of the coating when the LbL was built up. This spectrum shows the direct relation between the number of bilayers and the increasing absorbance of the SPR absorption bands, at 410 nm, proportional to the amount of silver nanoparticles within the coating.

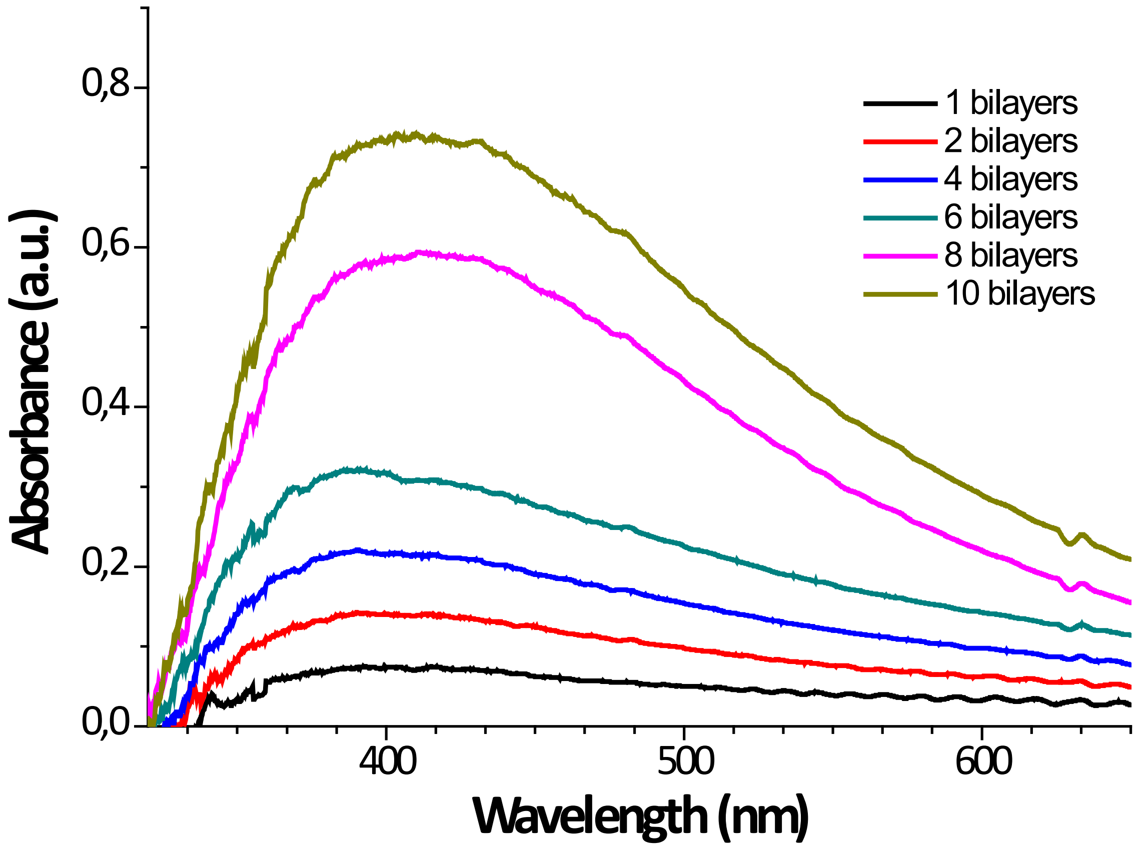

Figure 7. UV-VIS spectroscopy of the sensor as a function of the number of bilayers. The main absorption component is the SPR absorption band of silver NPs embedded into the polymeric fillm. The curves plotted are for 1, 2, 4, 6, 8 and 10 bilayers.

In other words, the results confirm that the optical absorbance of the coating increases directly with the number of bilayers and also corroborate that the amount of silver nanoparticles within the coating is higher as the number of bilayers grows. This opens the door to the monitoring of diverse parameters because the LSPR of Ag NPs depends on a wide number of factors (size, shape or dielectric environment of the nanoparticle) [20, 21]. It is very important to remark the use of PAA as a capping agent because well-dispersed and stable Ag nanoparticles in aqueous medium without any additional dispersants have been synthesized.

In addition, as it has been demonstrated in previous works, some weak polyelectrolyte-based coatings modify their thickness and refractive index with RH variations due to the swelling/deswelling phenomenon [24,25]. Therefore the polymeric film built up onto the sensitive region of the sensor will vary its optical resonance properties as the external RH is varied.

The resonance spectra for different RH variations are represented in Figure 8. The sensor was placed into a climatic chamber and was tested for RH ramps between 20% and 80%. The climatic chamber used in this experiment has a limited RH range from 20% to 80%. In addition, response of the sensor at the wavelength of the resonant peak (LSPR) is shown in Figure 9, when the RH inside the climatic chamber changes is plotted.

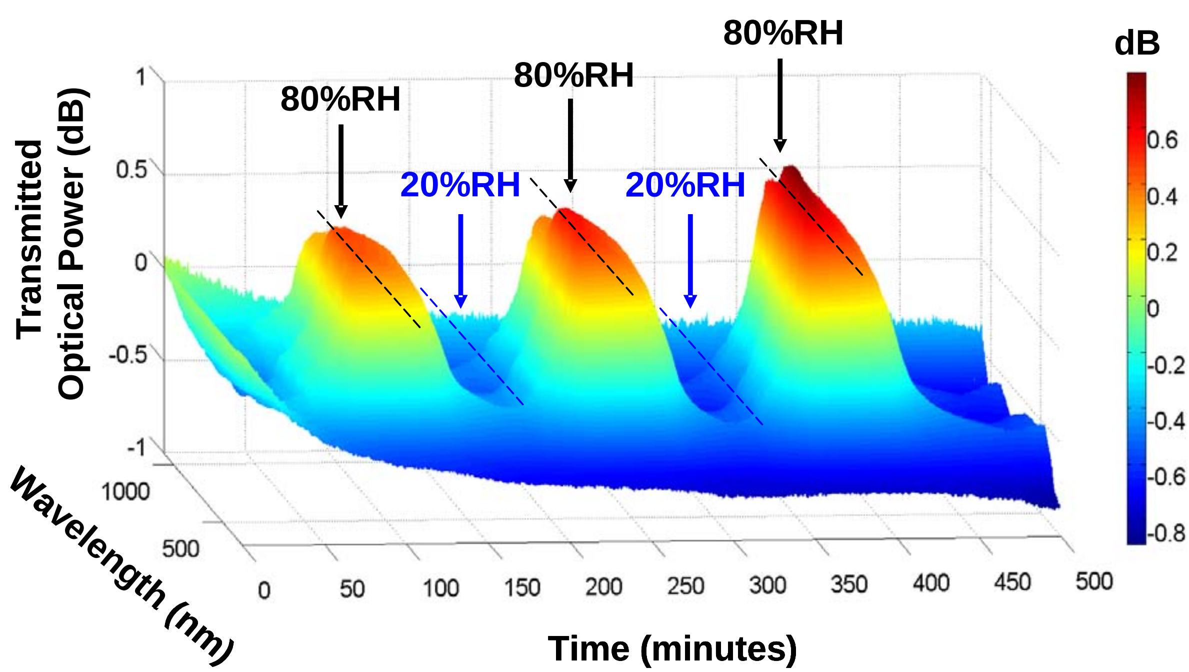

Figure 8. Spectral response of the sensor to changes in the RH (black arrow: 80% HR; blue arrow: 20% RH.

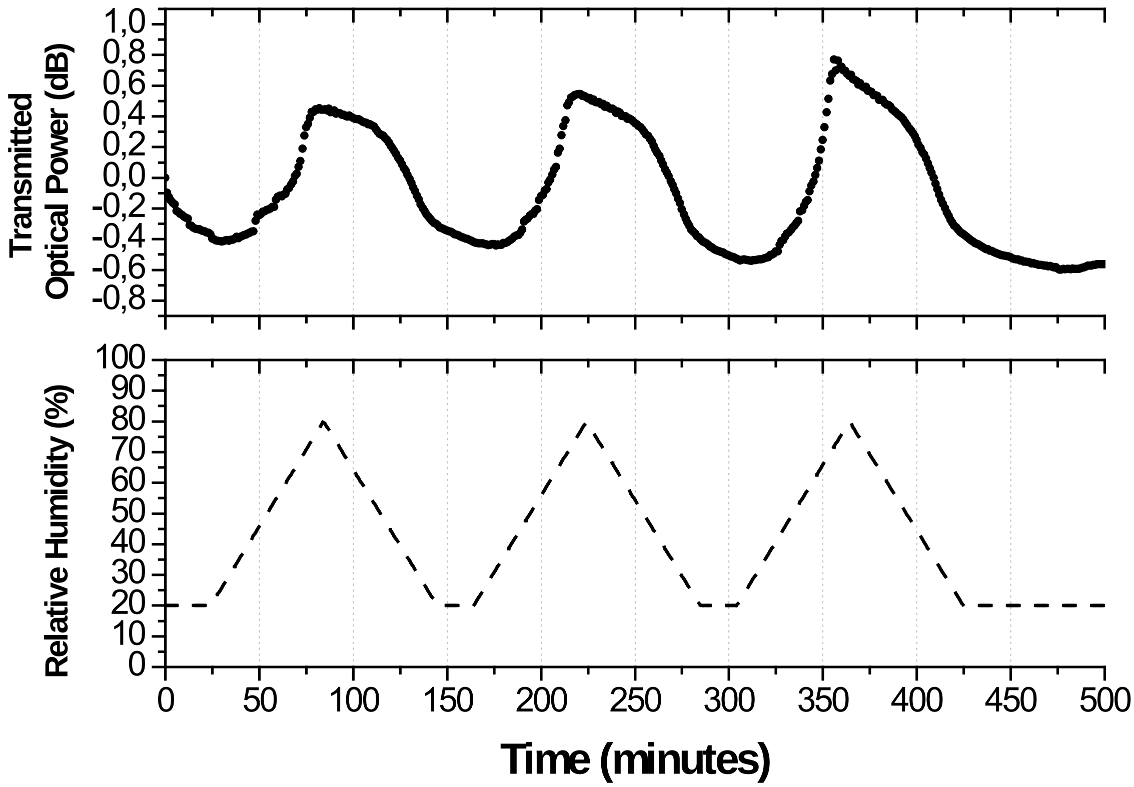

Figure 9. Optical fiber sensor response at 410 nm wavelength resonant peak (top) compared with the Set-Point Climatic chamber RH (bottom).

The results shown in both figures indicate that an increase or decrease of the RH produces a change in the index refraction of the sensitive region due to the previously swelling/deswelling phenomenon. In addition, the sensor exhibits humidity-dependent losses in the visible range due to the SPR phenomenon, as it can be seen in Figures 8 and 9. The sensor showed 1.6 dB of dynamic range and a slight drift of a 5% in the first operation cycles. Nevertheless, as the sensor is submitted to more RH cycles, a more stable response is observed. Additionally, the response time of the optical fiber RH sensor was estimated by exposing the active area to a human breath exhalation. The response time was 600ms approximately which is faster than most of the conventional RH sensors.

IV. CONCLUSIONS

In this work, a new humidity sensor based on silver nanoparticles embedded in a polymeric coating deposited onto an optical fiber core is reported. These nanoparticles have been successfully synthesized at room temperature without any particle aggregation into the sensor film. In addition, the antibacterial behavior of the Ag NPs prevents the growth of microorganisms what is very likely in high humidity environments.

The sensitive coating was fabricated using the LbL assembly. It has been experimentally demonstrated that the fabrication of these functional coatings are humidity sensitive due to changes in their optical properties with Relative Humidity (RH) variations. The sensitive coating changes the refractive index and thickness as a function of the RH variations and therefore, changes in the resonance are observed as a function of the number of bilayers added depending on RH variations. Such RH fluctuations can be detected by a shift of the LSPR intensity with a fast response time which makes possible to control RH for high performance applications such as human breathing monitoring.

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