

Tunable optical fiber pH sensors based on TE and TM Lossy Mode Resonances (LMRs)

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Abstract

In this paper, a high sensitivity optical fiber pH sensor based on lossy mode resonance (LMR) generated with transversal electric (TE) and transversal magnetic (TM) polarized light is presented. Poly(allylamine hydrochloride) (PAH)/ poly(acrylic acid) (PAA) polymeric thin-films fabricated onto side-polished D-shaped optical fibers are used as pH-sensitive as well as LMR supporting coatings. The adequate selection of the pH-sensitive coating fabrication parameters enables to obtain devices working at different pH regions. Two devices have been obtained in order to measure pH from 4.0 to 5.0 and from 7.0 to 8.0 respectively. Obtained optical fiber pH sensors based on TE and TM LMRs showed a maximum sensitivity of 69 nm/pH, which means a resolution of ~ 0.0008 pH units by using a conventional communications Optical Spectrum Analyzer (OSA) with 0.06 nm resolution.

1. Introduction

Accurate pH control is very important in many industrial applications, such as chemistry, food industries, beverage industry or medicine. As an example, the characteristic range of pH in wines is between 4 and 4.9, whereas pH value in human blood is ideally 7.35. Much research has been made in the development of optical fiber pH sensors in the last decades due to their many advantages such as miniature in size, immunity to electromagnetic interference, remote sensing capability, low transmission losses in the communication windows and wide bandwidth [1-4]. Among these works, different optical interrogation techniques have been described, such as those based on interferometry [3], fiber gratings [4], surface plasmon resonance (SPR) [5] or lossy mode resonance (LMR) [6].

Concerning LMR [7],[8], this type of resonance occurs when the real part of the thin-film permittivity is positive and higher in magnitude than its own imaginary part and the real part of the permittivity of both the optical waveguide and the external medium surrounding the thin-film. The LMRs are generated when a mode guided in the optical fiber starts to be guided in the thin film. LMR-based device is highly sensitive to the refractive index variations in the surrounding medium, which enables their use for different sensing applications [13]. LMR have several advantages over the SPR: multiple resonances can be generated when the thin-film

thickness is increased [9], the resonances can be generated with both TE (transverse electric) and TM (transverse magnetic) polarized light [10] and they can be tuned at any wavelength of the optical spectrum [10].

LMRs have been achieved using a wide variety of materials with low imaginary part of the refractive index, such as metal oxides like indium tin oxide (ITO) [11], [12] or TiO₂ [9], indium oxide [10] or polymers [6]. Thus, an adequate selection of the thin-film to be deposited onto the optical fiber core will enable the fabrication of resonance-based optical fiber pH sensor with defined characteristics [6].

This work describes the utilization of a polymeric (PAH/PAA) thin-film as the LMR supporting coating for the fabrication of a high sensitive pH sensing devices by means of the utilization of D-shaped optical fibers. The combination of D-shape optical fiber structure and PAH/PAA coatings permits to obtain pH sensitivities and spectral widths of LMRs not seen before. Thanks to these improvements, small changes in pH with high accuracy were successfully detected. The separation and characterization of the polarization dependent LMRs (LMR_{TM} and LMR_{TE}) have been studied as a function of the pH.

2. Experimental details

2.1 PAH/PAA coating fabrication

PAH/PAA coatings were fabricated onto D-shaped optical fibers using the layer-by-layer (LbL) nano-assembly technique. LbL consists of the sequential adsorption of oppositely charged molecules. Poly (allylamine hydrochloride) (PAH) (Mw ~ 65,000) and poly (acrylic acid) (PAA) (Mw ~ 15,000) were purchased from Sigma-Aldrich Inc. A 10mM PAH aqueous solution was used as the polycationic solution and a 10 mM solution of PAA in ultrapure water was used as the polyanionic solution. Ultrapure water (18.1MΩ/cm) was obtained from a Barnstead Inc. water purification system. Both anionic and cationic solutions were adjusted at the same pH using an electronic pH-meter (Crison Inc.) and adding a few drops of hydrochloric acid or sodium hydroxide when necessary.

Regarding the optical material, D-shaped fibers were provided by Phoenix Photonics LTD. These fibers consisted of standard single mode fibers (Corning® SMF-28) with a cladding/core diameter of 125/8.2 μm, a polished length of 1.7 cm and an attenuation peak of 5 dB at 1550 nm in high refractive index oil (1.5), as it is represented in the inset of Figure 1. D-shape optical fibers with an attenuation peak of 5 dB are used because PAH/PAA is a material which introduces high optical losses.

The fabrication process comprised a first immersion of the D-shaped optical fiber in 1 M KOH during 10 minutes followed by a wash in ultrapure water in order to acquire a prior negative charge. Once the substrate was negatively charged, it was immersed in the PAH solution and then in a PAA solution for 2 minutes each immersion. The fiber was rinsed repeatedly in ultrapure water between these two immersion steps. The structure obtained after this process is known as a bilayer and it is repeated until the required thickness or number of bilayers is obtained.

The experimental fabrication setup is shown in Figure 1. This setup is used to monitor the thin-film growth by monitoring the wavelength shift of the LMRs as a function of the number of bilayers (thickness of the coating). This configuration consisted of a multi-LED light source (HP-83437A Broadband light source), with an emission range from 1150 to 1680 nm, connected to one end of the optical fiber depolarizer. The other end is connected to the D-shape fiber. Light

passes through the sensitive region and arrives at an optical spectrum analyzer (OSA-HP86142A). The depolarizer is used in order to remove the polarization dependence of the light source. Hence, the light used for the fabrication monitoring is not polarized.

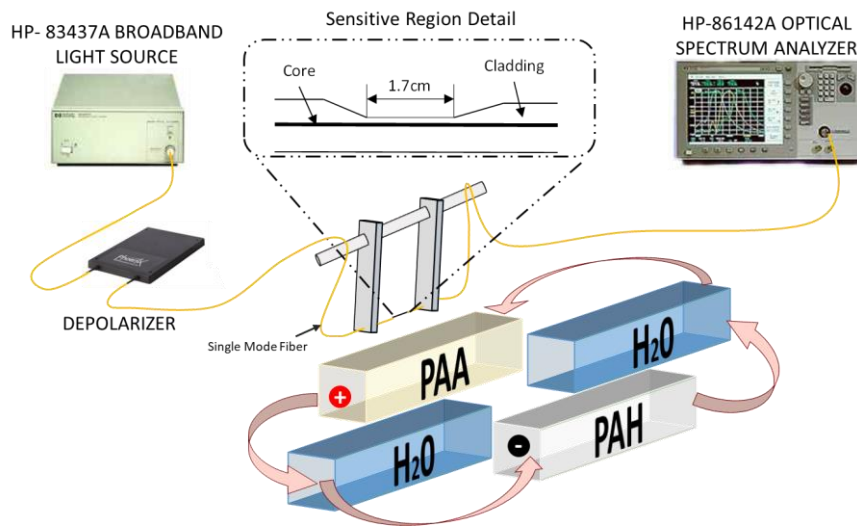


Figure 1

2.2 pH experimental setup

This setup is basically the same as the one described in section 2.1 but in this case we have added a polarization controller (Agilent 9169A) between the depolarizer and the D-shaped fiber input. This polarization control setup, combined with the characteristic geometry of D-shaped fiber, enables to differentiate between TM and TE polarizations and permits to obtain two resonances: LMR_{TM} and LMR_{TE} [13].

The pH response of the device is obtained when the sensitive region is immersed into different solutions with different pH. Phosphate-buffered saline (PBS) buffers with different pH values were purchased from Panreac Inc. Stock pH solutions were prepared by mixing the buffer solutions with ultrapure water in a ratio 1:5 and adjusting the exact value by dropping acid or base as necessary. The pH of the solutions was verified afterwards. The climatic conditions were stabilized at 23°C of temperature and relative humidity of 35% during the fabrication and measuring processes.

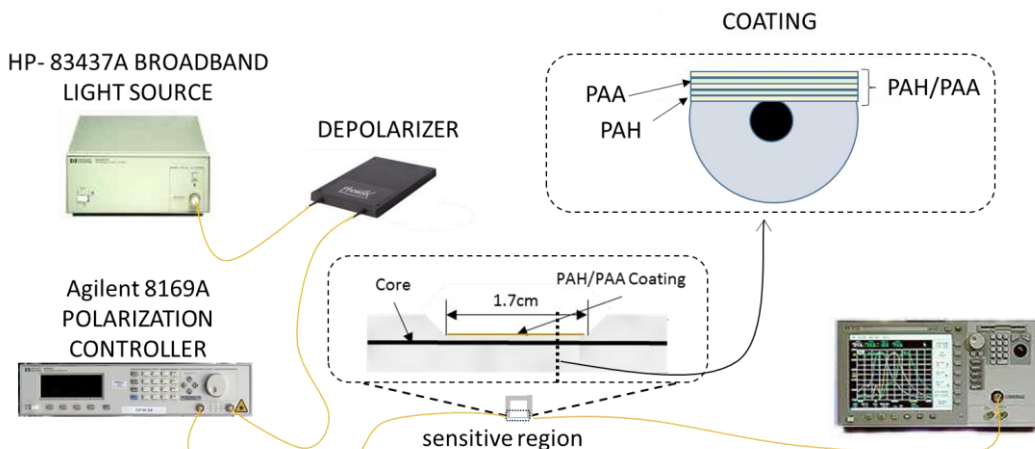


Figure 2

3. Results

The sensing mechanism consisted of maximum absorbance peak shift (resonance wavelength) originated by pH-induced thickness variations of the polymeric coating. When the PAH/PAA coating is dipped into liquid solutions, its thickness is modified as a function of the external medium pH. As a consequence, the effective refractive index of the structure will change, producing a shift of the LMR [14]. The behavior of the coating is dependent on many factors, among others molecular weights, polymer concentration, ionic strength and pH of the solution, and temperature [15]. Rubner and co-workers [14] have shown that the thickness of adsorbed multilayers of PAA and PAH depends sensitively on the pH of the adsorption solution. This effect is considerably stronger than the dependence of the layer thickness on the ionic strength [16]. Since the properties of the PAH/PAA structure differ as a function of the pH of the polymeric solutions employed in the fabrication process [17], two different devices (A and B) have been studied in order to enable measurements at different pH values. Particularly, 'A' device consisted of the fabrication of PAH/PAA bilayers from polymeric solutions adjusted at pH 7.0 while 'B' device was obtained from polymeric solutions adjusted at pH 4.0 (see section 2.1 for more details). Device A was used to measure the pH within the range 7-8. Device B was fabricated to achieve lower pH values. In this way the sensor B is used to measure the pH within the range 4-5. Both devices operate at different pH regions of interest for industrial and biomedical applications.

3.1 Device A

The fabrication of the device A was monitored using the setup described in Figure 1. To do this, the transmission spectrum in every bilayer was monitored during the fabrication process. Figure 3a shows the transmittance response as a function of the number of bilayers added onto the D-shape fiber. Here, the first LMR appears in this spectral window at bilayer number 38 and shows a redshift as a function of the number of layers added onto the sensitive region. Process fabrication monitoring enables to control the device response and stop the process at the required conditions. In this case, the construction was stopped in the bilayer number 43 at the optimal spectral position as it is shown in Figure 3. The spectral response of the last 5 bilayers can be observed in Figure 3b with the resonance wavelength centered in the spectral detection window (1442 nm) of our equipment. To sum up, 'A' device consisted of a [PAH/PAA]₄₃ coating with the first LMR centered within the region 1150-1650 nm (1442 nm).

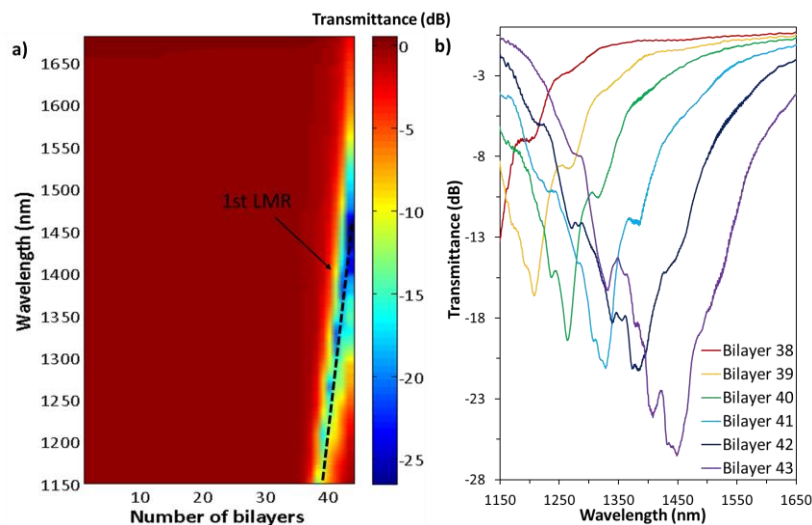


Figure 3

The transmission spectrum of the first LMR after the [PAH/PAA]₄₃ coating fabrication was collected using the setup shown in Figure 1 when the sensitive region is immersed in a solution with a pH 7.8 (see Figure 4). In Figure 4, the resonance wavelength of the first LMR is located at 1384 nm (solid black line). Previous works describe that the utilization of a polarization controller combined with D-shaped fibers, as it is depicted in Figure 2, enable to observe both TM and TE polarization contributions separately [14]. The LMR associated to TM polarization (LMR_{TM}) and the LMR associated to TE polarization (LMR_{TE}) are plotted in Figure 4. LMR_{TM} is located at 1353 nm and the LMR_{TE} is located at 1417 nm, with a separation between them of 64 nm. In order to quantify the spectral widths of the LMRs, the parameter $\Delta\lambda$ is defined as the wavelength range covered by the LMR at a transmission level 3 dB above the resonance minimum. In this case LMR_{TE} shows a $\Delta\lambda$ of 15 nm and LMR_{TM} shows a $\Delta\lambda$ of 9 nm.

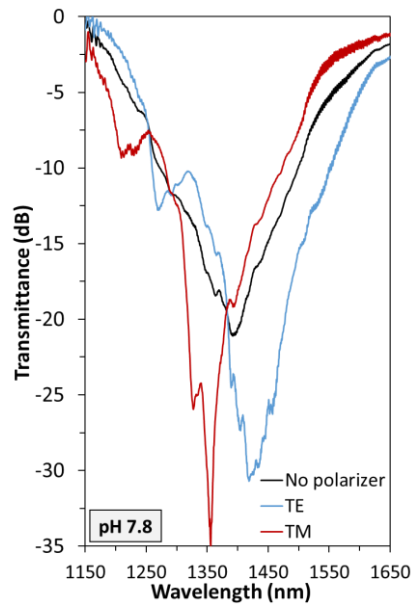


Figure 4

Then, device A was subjected to changes in pH. The experiment consisted of successive immersions of the sensitive region in pH solutions ranging between pH 7.0 and 8.0 (variations of 0.2 pH units) in order to study the hysteresis and sensitivity of the device. The resonance wavelength shift of the first LMR (No polarizer), LMR_{TE} and LMR_{TM} is represented in Figure 5. To obtain this LMRs (LMR_{TE} and LMR_{TM}), we used the experimental setup shown in Figure 2. However, “No polarizer” is the spectral response of the device without polarizer. Here, the maximum absorbance peaks shift to higher wavelengths when the pH value decreases. The wavelength of the maximum absorbance peaks have been obtained applying a least squares parabolic fit algorithm implemented in Matlab®, where the wavelength peak corresponds to the parabola vertex.

In this plot it can be observed a resonance wavelength redshift when the pH decreases. Particularly, LMR_{TM} and LMR_{TE} experiment a shift of 30 and 34 nm, respectively. In other words, the sensitivities of the LMR_{TM} and the LMR_{TE} to pH variations in the range 7.0 and 8.0 pH units are 30 and 34 nm/pH unit respectively, which means a resolution of 0.001 pH units using a conventional optical spectrum analyzer with a spectral resolution of 0.06 nm. Additionally, ‘A’ device shows a hysteresis value of 0.05% in the studied range. As shown in Figure 5, the device presents a non-linear behavior due to non-linearity swelling of PAH/PAA [17]. Each experiment

was repeated four times, and averaged, being obtained a maximum error bar for the measured wavelength shifts of ± 1 nm.

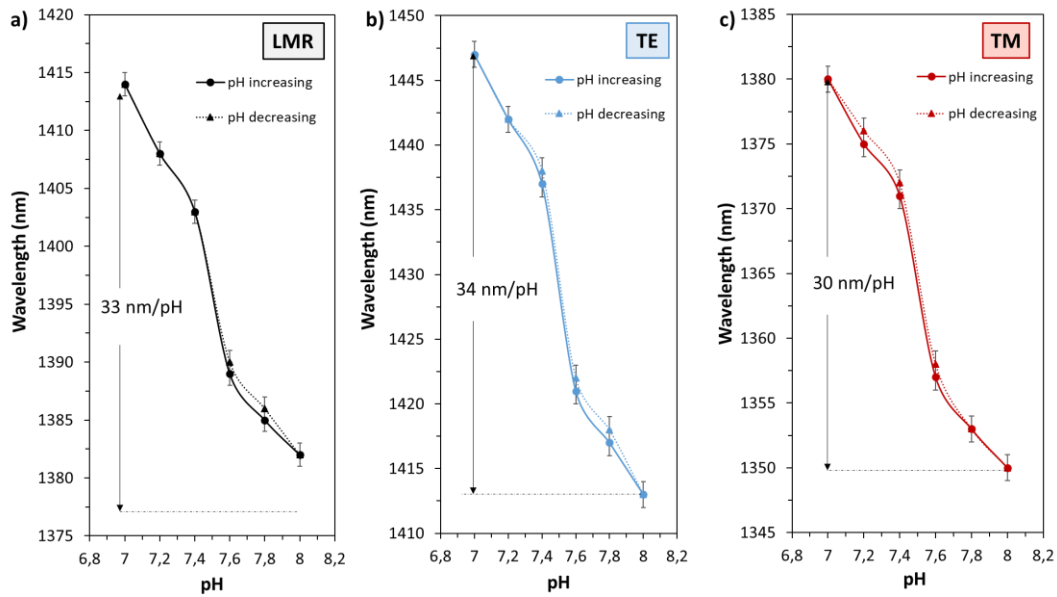


Figure 5

3.2 Device B

The fabrication of the 'B' device was monitored using the setup in Figure 1 as it has been previously described for 'A' device. Figure 6a shows the evolution of the transmittance response as a function of the number of bilayers added onto the D-shape fiber. Here, the first LMR appears at bilayer number 48 and shows a redshift as a function of the number of the layers added onto the D-shape fiber. In order to obtain an optimal position of the resonance centered within the detection window (1150-1650 nm) the fabrication was stopped at the bilayer number 60. The fabrication spectral response from bilayer 50 to 60 is represented in Figure 6b with the resonance wavelength located at 1410 nm at the end of the process. In this case, 'B' device consisted of a $[\text{PAH/PAA}]_{60}$ coating with the first LMR centered in 1410 nm.

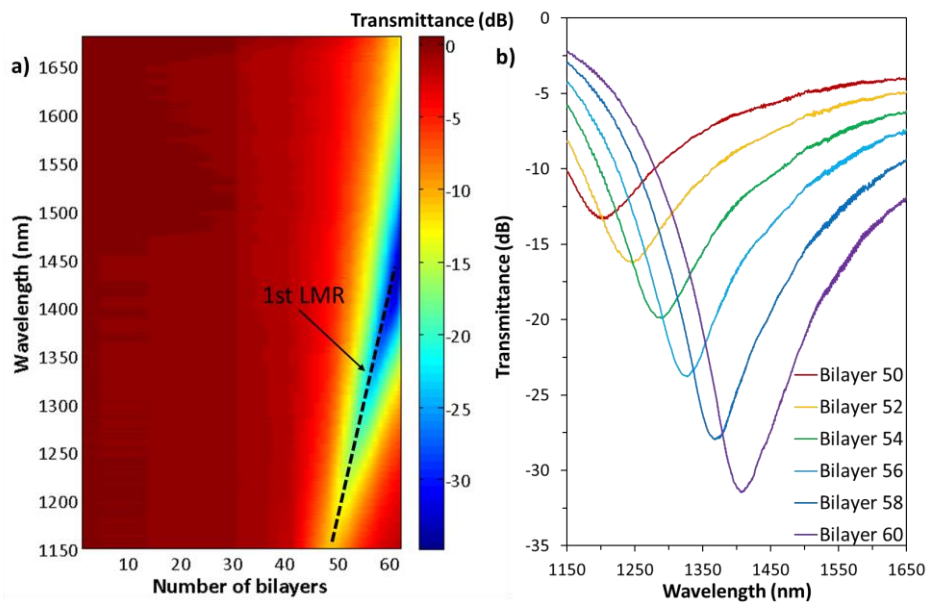


Figure 6

The transmission spectrum of 'B' device when the sensitive region is immersed in a solution with pH 4.2 is represented in Figure 7 (solid black line). As it was explained with 'A' device, the utilization of a polarization controller (see Figure 2) enables to obtain the TM (solid red line) and TE (solid blue line) components of the LMR (see Figure 7). In particular, LMR_{TM} is located at 1342 nm and LMR_{TE} is located at 1397 nm, with a separation between them of 55 nm. In this case LMR_{TE} shows a $\Delta\lambda$ of 16 nm and LMR_{TM} shows a $\Delta\lambda$ of 15 nm.

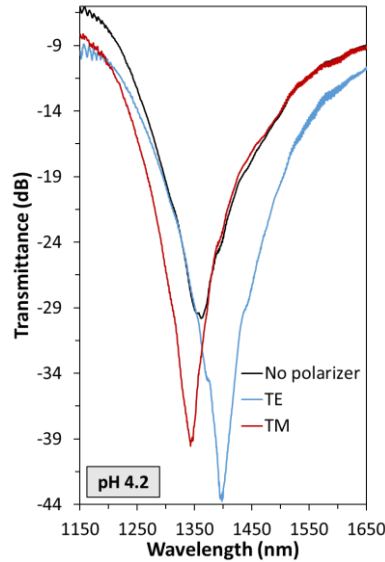


Figure 7

Then, device 'B' was subjected to pH successive pH changes between pH 5.0 and 4.0 (variations of 0.2 pH units) in order to study the hysteresis and sensitivity of the device. Resonance wavelength shift of 'B' device when the sensitive region is immersed in different pH solutions is represented in Figures 8a (LMR without polarization controller), 8b (LMR_{TE}) and 8c (LMR_{TM}).

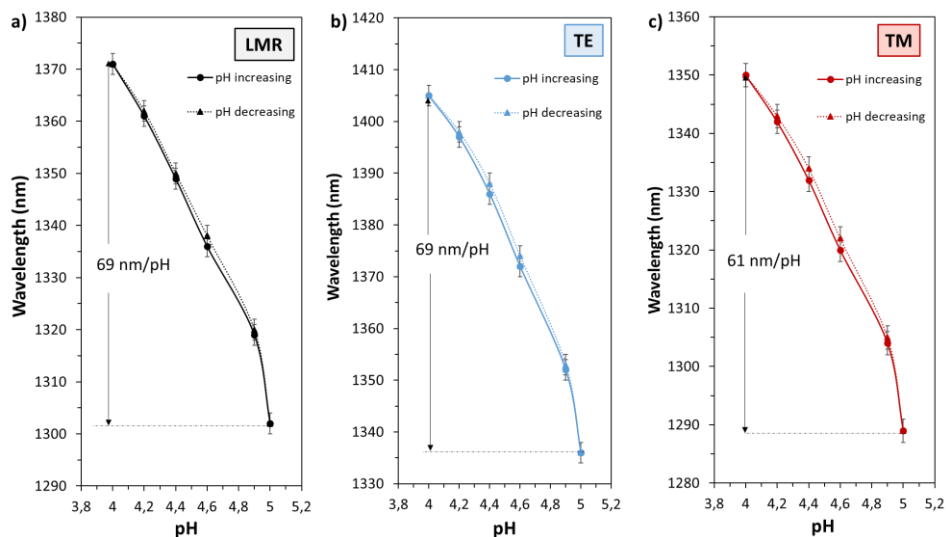


Figure 8

The sensitivities of the LMR_{TM} and the LMR_{TE} are 61 and 69 nm/pH respectively in the pH range from 4 to 5, which correspond to a resolution of ~ 0.0008 pH units using a conventional communications Optical Spectrum Analyzer with a spectral resolution of 0.06 nm (see Figures 8b and 8c). In addition, the device shows low hysteresis (0.04%) in the studied pH range. Each

experiment was repeated four times, and averaged, being obtained a maximum error bar for the measured wavelength shifts of ± 2 nm. To our knowledge, this sensitivity overcomes the highest sensitivity reported in previous works with Lossy Mode Resonance (LMR) [18], long-period fiber gratings (LPFG) [19], surface plasmon resonances (SPRs) [5] and photonic crystal fiber [3] by a factor of 1.2, 2.5, 5.6 and 77 respectively.

4. Conclusions

A pH sensor based on the detection of TE and TM polarization components of LMRs has been obtained by means of the fabrication of thin polymeric films onto D-shaped optical fibers. The characteristic properties of PAH/PAA polymeric films enable to tune the pH detection range by means of adjusting the thin-film fabrication parameters. Two devices working at different pH regions of interest for industrial and biomedical applications have been obtained.

The combination of high sensitive optical fiber structures and pH sensitive coatings permit to obtain pH sensitivities and spectral widths of LMRs not seen before. Thanks to these improvements, small changes in pH with high accuracy were successfully detected. Optical fiber pH sensors have shown high sensitivity (69 nm/pH) and low hysteresis (0.04%), which reveals their potential in many different real-life applications. In addition, the monitoring of LMR_{TM} and LMR_{TE} resonances permits to perform dual measurements, which could be helpful in order to reduce noise or extend the dynamic range of the devices.

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Figure Captions

Fig 1. Experimental fabrication setup used to monitor the PAH/PAA deposition process and detail of the D-shaped fiber.

Fig 2. Experimental measuring setup with the light source, depolarizer, detector and the PAH/PAA coated sensitive region.

Fig 3. Evolution of the transmitted spectra during the deposition of PAH/PAA polymer chains at pH 7.0 on the device A.

Fig 4. Transmittance spectra obtained with 'A' device (solid black line) and TM (solid red line) TE (solid blue line) components when the sensitive region is immersed in a solution at pH 7.8.

Fig 5. Response of the device A a) , LMR_{TE} b) and LMR_{TM} c) when the sensitive region is immersed in different pH.

Fig 6. Evolution of the transmitted spectra during the deposition of PAH/PAA polymer chains at pH 4.0 on the device B.

Fig 7. Transmittance spectra obtained with 'B' device (black) and separation of the TM (red) and TE (blue) mode resonance components when the sensitive region is immersed in a solution at pH 4.2.

Fig 8. Response of the device B a) , LMR_{TE} b) and LMR_{TM} c) when the sensitive region is immersed in different pH.