

Lossy-mode resonance based optical fiber pH sensors

C. R. Zamarreño*, M. Hernaez, I. Del Villar, P. J. Rivero, I. R. Matias, F. J. Arregui
Public University of Navarra, Campus Arrosadia, Pamplona, SPAIN
carlos.ruiz@unavarra.es

Different type of resonances can be supported by thin-film coated substrates [1]. Among them, lossy-mode resonances (LMRs) have been recently explored for the fabrication of indium tin oxide and titanium oxide based optical fiber refractometers [2-3]. These devices take advantage of optical fiber properties, such as portability, light-weight and easy multiplexation in wavelength among others [4], as well as the benefits associated to the LMRs, such as the non-dependence with the polarization of light or the generation of multiple resonances without modifying the optical fiber geometry [2-3]. LMR-based devices also permit the utilization of additional layers onto the sensitive coating in order to detect diverse substances or chemical compounds [5]. However, LMRs can be also generated by the utilization of many other materials different than metal oxides or semiconductors.

Here, it is described the fabrication of LMR-based optical fiber pH sensors by means of the deposition of thin polymeric structures onto the exposed core of 200/225 μm core/cladding diameter optical fibers (FT200EMT, Thorlabs Inc.). The materials used for the coating fabrication are the polycation *poly(allylamine hydrochloride)* (PAH), the polyanion *poly(acrylic acid)* (PAA) and the colorimetric pH indicator known as neutral red (NR). The coatings have been fabricated by using the well-known Layer-by-Layer (LbL) electrostatic self-assembly technique as it has been already described in previous works of our group [5-6]. Moreover, PAH/PAA structure has shown thickness dependence with the pH of the surrounding medium, known as swelling/deswelling [7], which has been exploited before in the fabrication of pH sensors [8].

A white light source (AQ4303-B, ANDO Inc.) was connected at the input of the fiber in a typical optical transmission setup in order to introduce light through the sensitive region, as it is represented in Fig. 1. The output of the fiber was connected to the single end of a bifurcated optical fiber, which was attached at the other end to two spectrometers (HR4000 and NIR512 from Oceanoptics Inc.) in order to obtain the spectral information in the range between 500 nm and 1700 nm.

Absorbance spectra were collected as the coating thickness was increased up to 100 bilayers. Three different resonances were originated during the coating fabrication process as it is observed in Fig. 2. Two of these resonances (2nd and 3rd) remained visible within the studied range at the end of the fabrication process. Then, [PAH+NR/PAA]₁₀₀ coated optical fiber was immersed into different pH solutions in order to observe the shifts of the second and third resonances as a function of the coating thickness variations. As it is represented in Fig. 3, both, second and third resonances, shift forward and backward as the pH of the surrounding medium is varied between 5.0 and 4.0 for different intervals. Hence, wavelength at maximum absorbance or resonance wavelength can be used in order to determine the pH of the surrounding medium. Wavelength based detection technique permits the fabrication of robust and power fluctuation immune optical fiber sensors. Furthermore, the presence of two different resonances permits the realization of dual reference measurements and the associated improvement in the signal to noise ratio. Wavelength shifts of both, second and third resonances, have been obtained by monitoring the maximum absorbance wavelength during the pH variation sequence as it is represented in Fig. 4. Here, it is observed that the second resonance wavelength shift is larger (~30 nm), approximately double, than that of the third resonance (~15 nm), which indicates that the second resonance is more sensitive to pH variations.

To sum up, polymer coated optical fiber has been fabricated and characterized as LMR-based optical fiber pH sensors for the first time. Moreover, these devices take advantage of wavelength detection and the utilization of two references. Finally, the fabrication of LMR-based devices by means of the deposition of polymeric coatings presents a first step towards the application of many other coatings with different properties and applications in chemistry, biology among others.

References:

- [1] F. Yang, J. R. Sambles, *J. Mod. Opt.*, **44**(6), (1997) 1155-1163.
- [2] I. Del Villar, C. R. Zamarreño, M. Hernaez, F. J. Arregui, I. R. Matias, *J. Lightwave Tech.*, **28**(1) (2010) 111-117.
- [3] M. Hernaez, I. Del Villar, C. R. Zamarreño, F. J. Arregui, I. R. Matias, *Appl. Opt.*, **44**, (2010) 3980-85
- [4] B. Lee, S. Roh, J. Park, *Sens. Actuators B*, **15** (2009) 209-221.
- [5] C. R. Zamarreño, M. Hernaez, I. Del Villar, I. R. Matias, F. J. Arregui, *Sens. Actuators B*, (2010)
- [6] J. Goicoechea, C. R. Zamarreño, I. R. Matias, F. J. Arregui, *Sens. Actuators B*, **132**, (2008) 305-311.
- [7] K. Itano, J. Choi, M. F. Rubner, *Macromolecules*, **38**(8), (2005) 3450-3460.
- [8] J. Goicoechea, C. R. Zamarreño, I. R. Matias, F. J. Arregui, *Sens. Actuators B*, **138**, (2009) 613-618

Figures

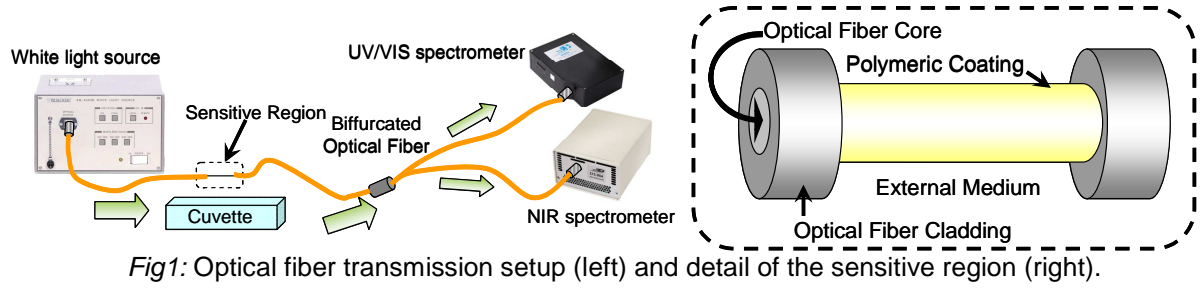


Fig1: Optical fiber transmission setup (left) and detail of the sensitive region (right).

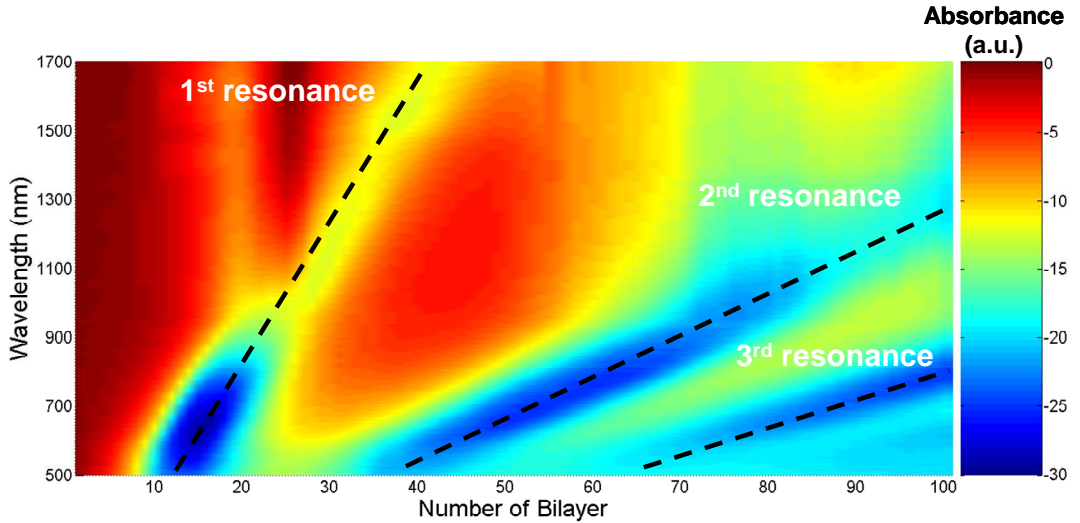


Fig2: Spectral response as a function of the number of bilayers added.

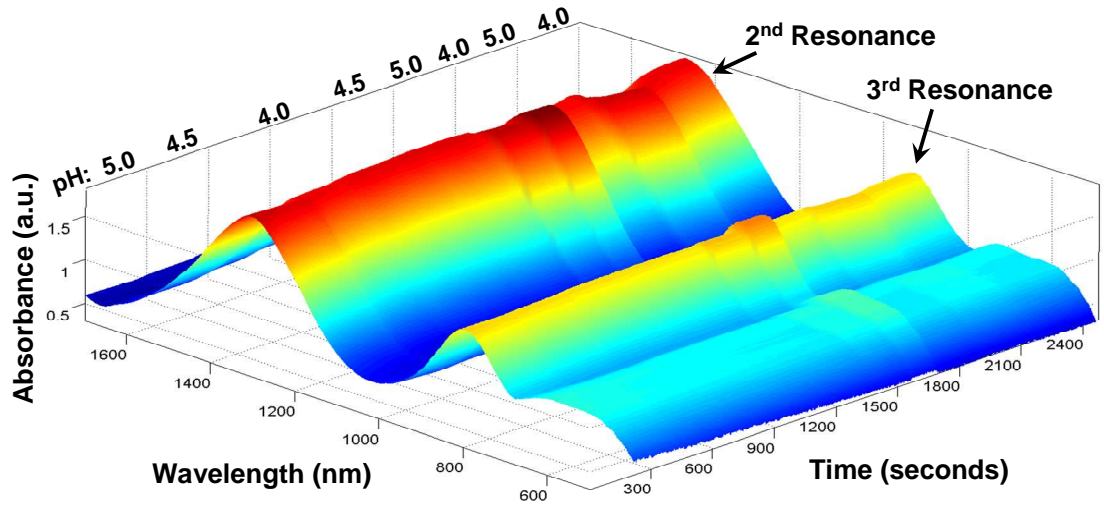


Fig3: Spectral response as a function of the pH of the external medium for a [PAH+NR/PAA]₁₀₀ device.

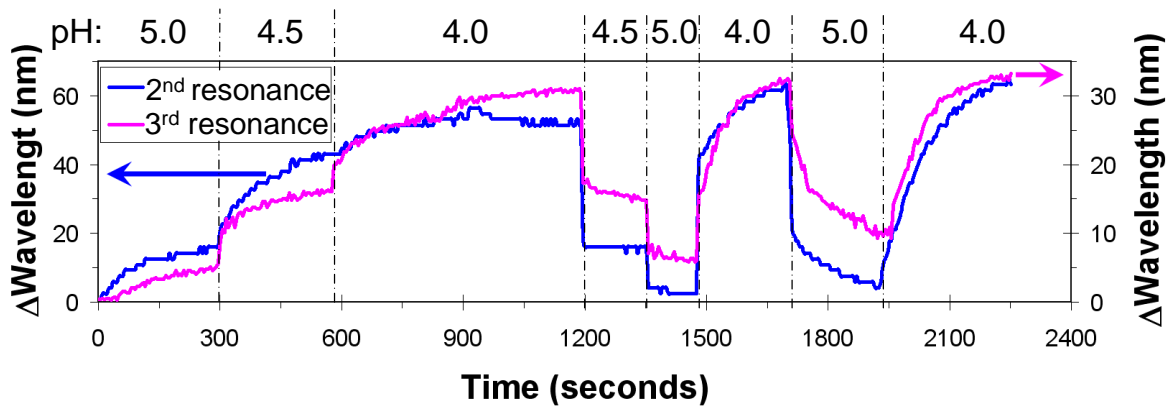


Fig4: Wavelength absorbance maxima shift for the 2nd and 3rd resonances as a function of the pH.