Optimization of self-assembled multilayer polymeric structures based on Neutral Red for pH-sensing applications

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Currently, the optical fiber sensors are becoming more attractive as the domotics and the intelligent networks are being developed and installed. 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. Most of the times, the price is still a handicap, but this technology is getting cheaper and a more extensive use of this kind of sensors will be observed in the immediate future [1]. In this particular field, the fabrication of functionalized coatings for the optical fibers is a promising field for optical fiber sensors compared to other sensing mechanisms, because of the simplicity of the final devices, which makes the costs lower. One of the key points of the fabrication of a fiber optic sensor is the reproducibility. Using the Electrostatic Self-Assembly (ESA) technique, ultra-thin multilayer structures of a lot of materials (polymers, nanoparticles, ceramics, etc.) with almost independence of the size or shape of the substrate can be built up[2][3]. Therefore, the ESA technique is a powerful tool for the fabrication of functionalized thin films, with a big number of degrees of freedom to tune the final properties of the composite coating.

In this work, an ultra-thin film is build up onto the end-face of an optical fiber in order to make it sensible to pH of water solutions. The sensing principle is the change of the absorption spectrum of a colorimetric pH indicator; the Neutral Red (NR). This dye changes its color depending on the pH of the surrounding medium, and this change of color can be measured using a optical fiber setup. The molecules of the NR indicator are immobilized in a polymeric matrix fabricated on the end-face of a cleaved optical fiber using the ESA technique. Water based solutions of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) were used as polyelectrolyte dipping solutions for the ESA protocol. The NR was added to the PAH solution, in order to incorporate the indicator to the polymeric matrix.

The optimization of the sensitive coatings was focused on the tuning of the fabrication parameters, more specifically the pH of the polyelectrolyte solutions used to build up the self-assembled film. As it has been previously reported, the degree of ionization of weak polyelectrolytes dramatically affects to the morphology of the resultant structure [4], and this plays an important role in an optimization process. A optical fiber interferometric technique is used to estimate the properties of the created multilayer structure. This technique is based on the formation of a nanoscale Fabry-Perot cavity onto the end-face of an optical fiber (Fig. 1). The thickness and the roughness of the assemblies was also measured with conventional techniques for comparison with the predictions of the optical fiber setup; a precision profilometer for the thickness, and an AFM for the roughness. Furthermore, absorption spectra of the coatings were also measured, and the changes in the composition of the active coating were analyzed (Fig. 2). Finally, some sensors have been successfully fabricated, in the range of pH4 to pH7, with fast response times (less than 9 seconds).

References:

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Figures:

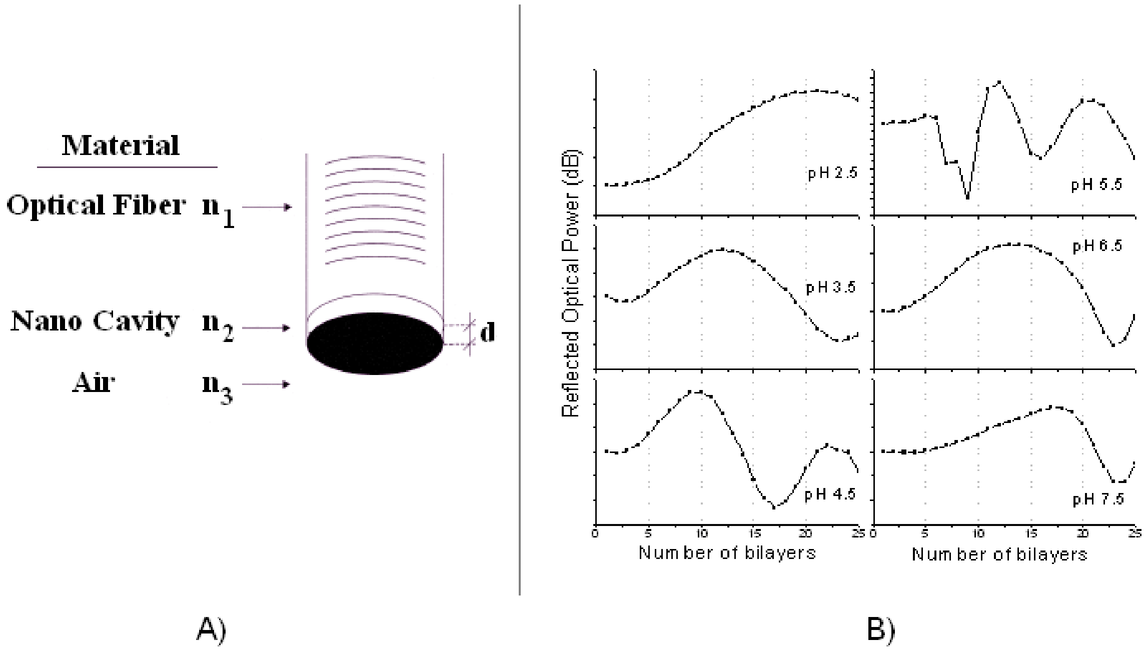

Figure1.- A) Scheme of the Nano-Fabry-Perot cavity formed onto the end-face of the optical fiber. B) Reflected optical power of the optical fiber setup as the structure is built up.

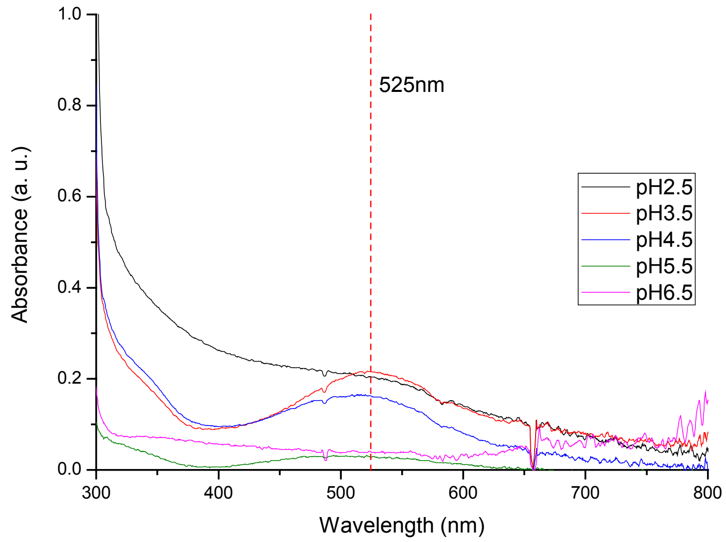

Figure 2.- Emission spectrum of the fabricated devices. Both electroluminescence (EL) and photoluminescence (PL) are shown in the same plot.