Straightforward nano patterning on optical fiber for sensors development

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A simple method to prepare a nano pattern along the surface of an optical fiber is applied in this work to develop a pH sensor. The template is made of a block copolymer that defines specific locations where gold nano particles (Au NPs) are adsorbed on forming clusters. The average diameter of the resulting agglomerates is 121 nm and the mean distance between centers is 182 nm. The morphology of the gold clusters array produces Localized Surface Plasmon Resonance (LSPR). The absorbance spectrum is affected by pH variations and the ratio between the absorption at two different wavelengths is used to characterize the response, which is repetitive and reversible. This study highlights the potentiality of this type of chemical nano patterning for the development of optical fiber sensors.

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Optical fiber sensors require coatings with specific properties to obtain significant sensitivity and fast kinetics. Films with thicknesses below 100nm and a high surface/volume ratio are demanded to get an increase of the interface area and ease the interaction with the analyte. In this work, we propose the use of a chemical nanopatterning technique that makes the sensing material to be deposited following a template with tunable geometry parameters. There are three main groups of techniques to create nano structures on optical fiber: fiber decoration (self-assembly of nanomaterials), planar fabrication (photolithography, nano imprinting, interference lithography, electron beam lithography, focused ion beam milling), hybrid techniques and through fiber transfer [1]. The method proposed in this letter belongs to the first group and compared to the other techniques, the precision that allows to prepare complex 3D nano structures is sacrificed by its low cost, fast implementation, and simplicity. More specifically, block copolymers can generate uniform nano templates on surfaces with different geometries, which is relevant for the case of optical fiber [2]. The resulting pattern is based on the chemical structure of the copolymer: a monomer is polar whereas the other one is apolar, so that when the copolymer is dissolved, micelles are formed. Once deposited onto a surface, a pattern with specific locations showing an electrical charge is defined. Therefore, particles with an opposite charge get self-assembled onto this kind of nano patterns. Gold nanoparticles (Au NPs) are a relevant example because they have been used for sensing purposes [3]: devices to detect analytes such as toxic metal ions [4], cysteine [5] or hydrogen peroxide [6] are described in the literature. Moreover, Au NPs have been successfully adsorbed into surfaces seeded with block copolymers [7].

The absorption spectrum of the Au NP clusters array is determined by the distribution of the template [8] and by the aggregation state of the NPs [9]. As a consequence, the LSPRs produced by Au NPs are affected by both parameters [10] and it is the transduction mechanism on which many optical devices are based on.

The synergy between block copolymer patterned surfaces and Au NPs offers a great potential for tailoring the features of periodic nanostructures [7]. Thus, it has recently awaken interest for its application on the development of optical biosensors [11]. However, this technology has not been applied to the development of optical fiber pH sensors yet. This work shows the potentiality of this technique to prepare this kind of devices in a simple and straightforward way, without the need of functionalizing the Au NPs. Citrate-stabilized Au NPs have been self-assembled onto a poly(styrene-b-2-vinylpyridine) nano template deposited along an optical fiber. The resulting array gave rise to an absorption spectrum that depended on the state of aggregation of the Au NPs and it was modulated by changes of pH between 2 and 6 [12]. The utilization of this device as a pH sensor opens the door for the fabrication of devices for different applications by controlling the properties of the copolymer template and the morphology of Au NPs clusters onto the surface of an optical fiber.

The sensor was fabricated with a SiO_2 200µm-core plastic cladding optical fiber (PCS). A fiber splicer was used to remove the cladding along 5 mm in a repetitive way, offering an easy access to the evanescent field and so facilitating the transduction. The surface of this segment was firstly cleaned with 2% Hellmanex™ III for 20 minutes and it was then rinsed with ultrapure water. Thereafter, the fiber was sunk in 1M KOH for 20 minutes. Thereafter, the fiber was sunk in 1M KOH for 20 minutes. Then, it was immersed in ultrapure water for another 20 minutes; thereby, the fiber surface was cleaned and activated with OH^- groups.

Nano pattering was prepared by dipping the fiber longitudinally into a 5 mg/ml solution of poly(styrene-b-2-vinylpyridine) (PS-b-P2VP) in o-xylene [9] at a constant speed of 16 mm/s, being immersed for 30 seconds. The block copolymer micelles of the solution got deposited along the fiber surface defining the nano pattern that showed a positive electrical charge density due to the polar head of the block copolymer.

Citrate-stabilized Au NPs were synthesized following Turkevich and Frens reaction [13] by reducing tetrachloroauric(III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$, 99 % purity) with sodium citrate: firstly, 500mL of a 1 mM $HAuCl_4$ solution were heated up to 90 °C under vigorous agitation and thereafter, 50 ml of 38.8 mM sodium citrate ($HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$, purity ≥ 99 %) solution were added. This mixture was kept at the same temperature and agitation for one hour and then it was cooled down prior to its use. The dimensions of the synthetized Au NPs were measured using a Zetasizer from Malvern: their average diameter was 15.85 nm, with a standard deviation of 1.74 nm.

Due to their negative charge, those Au NPs got assembled on the cationic polar heads of the block copolymer. For that, the fiber was introduced in the Au NPs colloid for 1 hour and finally, it was exposed to a plasma treatment for 1 minute in order to remove the micelle apolar tails surrounding the Au NPs [14]. The process is summarized in Fig 1. The polymeric template as well as the Au NPs array deposited onto the optical fiber were characterized with a Scanning Electron Microscope (Carl Zeiss, model Ultra Plus). Image processing package FIJI has been used to measure the different geometrical parameters of the samples.

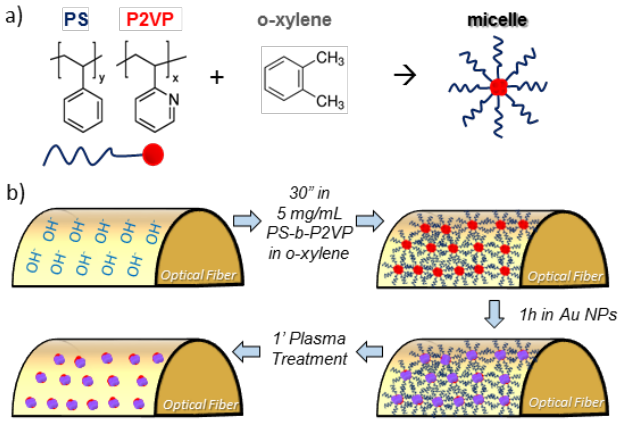

Fig. 1. (a) Schematic of a PS-b-P2VP micelle when it is dissolved in o-xylene: the polar head of the copolymer is colored in red whereas the apolar tale is in blue; (b) Main steps of the sensor fabrication process: Au NPs are represented in purple.

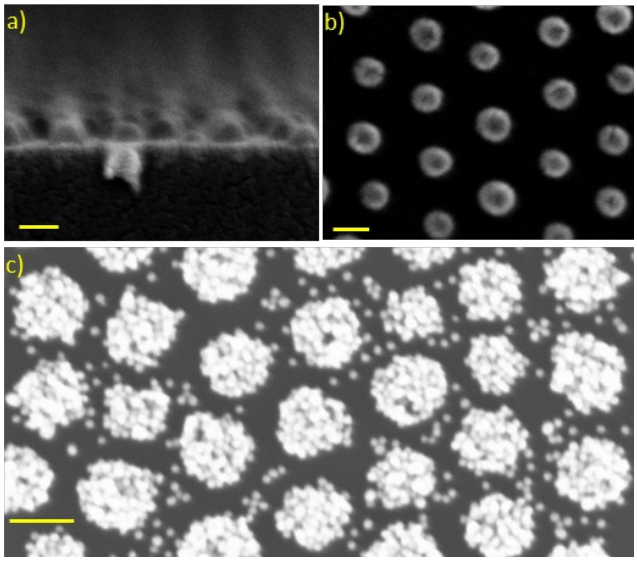

Fig. 2. (a) Section of the fiber with the nano pattern; (b) Top view the PS-b-P2VP template onto the optical fiber; (c) Top view of the Au NPs clusters once the process is over. The scale (yellow bar) is 100 nm.

In order to characterize the polymeric template, a segment of the optical fiber was cleaved and analyzed by SEM images just with the chemical nano patterning. Fig 2.(a) shows a section which gives an idea of the 3D uniform distribution; the top view of the template is displayed in Figure 2.(b) and Figure 2.(c) shows how the Au NPs get attached to the spots defined by the pattern. The height of the deposited micelles is 52.26 ± 3.41 nm whereas the cluster diameter (estimated from several SEM images) is equal to 88.56 ± 7.22 nm; the distance between centers was 155.24 ± 11.25 nm. These parameters depend on the block copolymer concentration and their effect on the sensing features is currently been analyzed. The average clusters diameter after the adsorption of Au NPs is 119.04 ± 8.70 nm and the separation between their centroids is 157.80 ± 14.11 nm. This last parameter disparity before and after the adsorption is below 1.65% and might be produced because it was measures in the distinct areas of the sample: however, this difference does not compromise the uniformity of the nano template. In the case of the diameter, the variation is 30.48 nm and it is because of the adsorption process, so that the radius increase is around 15.24 nm, which matches with the Au NPs diameter. Therefore, the final thickness has an approximated value of 68.11 nm. There are Au NPs between the clusters but their density is low and can be removed by exposing the fiber to a toluene saturated atmosphere [9].

The adsorption of the Au NPs onto the optical fiber as well as the response of the sensor were characterized using a transmission set-up (see Fig 3): an U-holder was used to reduce bending losses. The light source was a halogen lamp DH2000 whereas the receiver was a USB2000 spectrometer (both obtained from Ocean Insight). OceanView software (from the same company) was used to record the spectra evolution during the experiments.

The clusters formation was studied on real time in terms of variations in the absorption spectra of the sensor signal. For one hour, the patterned fiber segment was immersed in the Au NPs colloid and spectra were recorded at different moments (see Fig 4).

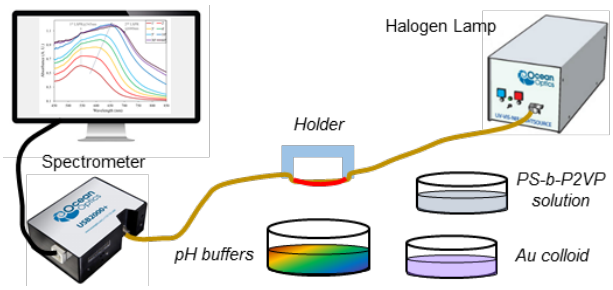

Fig. 3. Experimental set-up used for characterization of the sensor together with the different solutions where the sensor was immersed in.

At minute one, a first LSPR centered at 538 nm is observed: this absorption peak corresponds to the Au NPs [15] and it is determined by their diameter [16] so that it is not shifted during the assembly process. Moreover, it confirms that the NP get assembled onto the nano pattern [17]. A second absorption peak is observable since minute 2 and it is produced by cluster distribution of the NP: as the process continues, it is red shifted from 600 nm to 680 nm. The shape of the spectrum is slightly modified from minute 10 in terms of intensity and its red shift is a consequence of the decrease in the inter-Au NPs distance because of the formation of the clusters [18].

From minute 5 on, it is only possible to monitor the second LSPR because it overlaps the first one. After the plasma treatment, the spectrum does not show significant changes. The immersion time for the adsorption process is currently under optimization to make it as short as possible keeping the final sensing features. In any case, the spectra point out that no more than one hour is required to get the clusters ready.

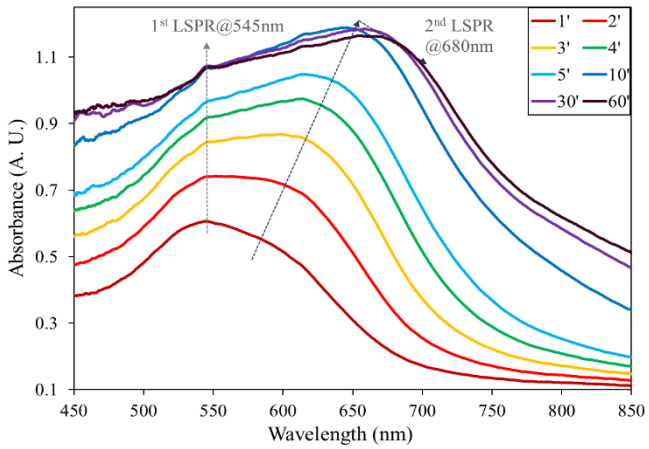

Fig. 4. Spectra recorded during the immersion into the Au NP colloid. The locations of the LSPRs with doted arrows.

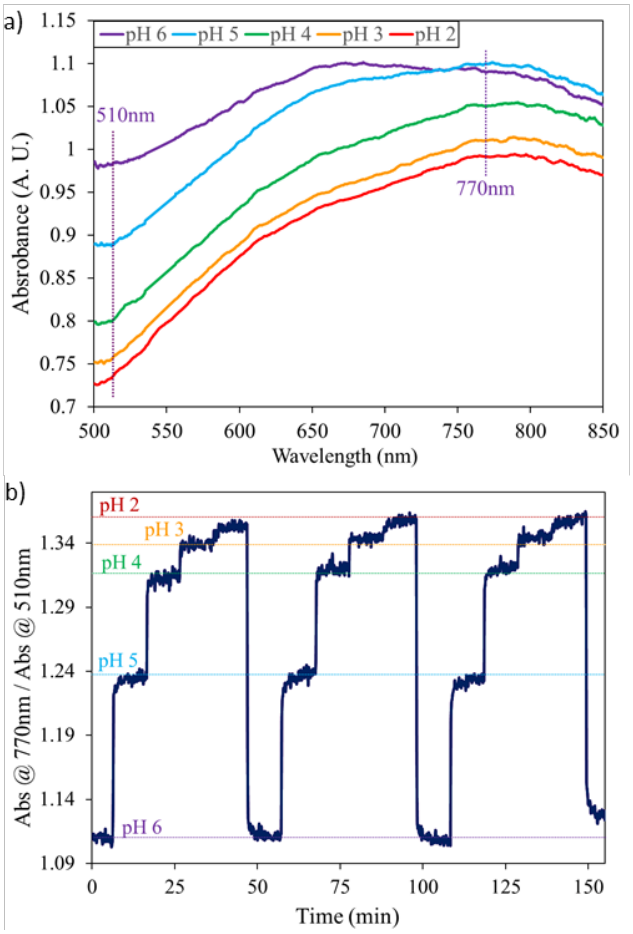

Fig. 5. (a) Absorbance spectra for different pH values; (b) Dynamic response in terms of the ration between the absorbance at 770nm and 510nm.

The response of the sensor to pH variations was studied exposing it to solutions that ranged from pH 6 to 2 with a sampling period of 10 seconds. Fig 5.(a) shows absorption spectra for different pH values. The ratio between the absorbance at 770nm and at 510nm is used to characterize the sensor dynamically to pH sweeps (see Fig 5.(b)): these wavelengths were chosen to maximize the ratio. Furthermore, this self-referenced measurement avoids the effect of undesired intensity artifacts. In Fig. 5(b) it can also be observed that the response of the sensor is the same for each pH value in every cycle, what means that the sensor presents a repetitive and reversible behavior: it is a consequence of the swelling/deswelling process suffered by the P2VP polymer when it is exposed to solutions of different acidities [19]. The relationship between the absorbance ratio and the pH value follows a sigmoidal shape which matches the behavior of pH sensors based on Au NPs [12][20][21][22]. The response is linear in the range between pH 4 and 6, with a sensitivity of -0.1095 Δ((Abs @770nm)/(Abs @510nm))/pH unit ($R^2 = 0.99$).

The theoretical resolution is 0.09 pH units, whereas the repeatability of the response is evaluated in terms of the standard deviation for each pH value: in the worst case, the maximum error is 0.39%. Moreover, the behavior is reversible.

Taking into account these results, it can be inferred that chemical patterning based on block copolymers has a significant potential for preparing nano templates on optical fibers. The method is easy to perform and studied in the literature, so that it can be applied to prepare nano templates on optical fiber instead of using other techniques that are more complex and expensive. Au NPs form clusters at the specific positions defined by the template during a process that is shorter than one hour. The nano template geometric distribution can be adjusted as it is reported in the bibliography.
The resulting Au NPs clusters array shows a fast, repetitive and reversible response to pH variations. The sensing coating shows a thickness lower than 100 nm and a significant surface/volume ratio because of its morphology: these characteristics are required to obtain enhanced sensitivity and faster kinetics. This proof of concept highlights not only the potential development of optical fiber sensors based on Au NPs but also on other metallic NPs or materials able to get assembled on the nano pattern described.

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Disclosures. The authors declare no conflicts of interest.

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