Ag-polymer nanocomposites for LSPR sensing

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In the past decade, plasmon-based optical sensors have been one the most preferred sensing platform for detection of biomolecules with high sensitivity and low cost. It is well-known that SPR/LSPR strongly depends on the refractive index of the surrounding medium (substrate, solvent, and adsorbates) of the surface/nanostructure [1]. In this work, we present a novel LSPR sensing platform based on Ag nanoparticles (NPs) embedded in a polymer thin film [2]. Ag NPs are in situ synthesized inside the host polymers by a one-step procedure during the bake step of the formation of a nanocomposite thin film (Fig. 1).

We have used polyvinyl alcohol (PVA) and Novolac as the host polymers for Ag NPs due to the ability of the secondary alcohol and phenolic groups to reduce Ag(I) to Ag(0), their excellent film forming properties and optical transparency. Moreover, they are hydrogels, this is, they can swell in aqueous medium and retain a significant amount of water within its structure without dissolving. As a result, water and analyte diffusion is allowed. Additionally, these materials can be also the basis to fabricate biochip sensors since they can be patterned by e-beam and UV lithography [3,4,5]. To validate the use of Ag nanocomposite thin film as a potential chemosensor/biosensor, we used 2-mercaptoethanol ($HSCH_2CH_2OH$) as analyte, because thiols interact very strongly with metal surface. The typical procedure for the analyte binding reaction simply consists on immersing the nanocomposite thin film in the analyte solution for several minutes to achieve the maximum chemisorption of the analyte molecules.

Fig. 2a exhibits the LSPR absorption curve of the Ag-PVA nanocomposite thin film before and after immersing into an analyte aqueous solution of $5x10^{-6}$ M for 180 min. As can be observed, the LSPR of an Ag-PVA film significantly changes in wavelength, intensity and FWHM. These curves can be nicely fitted by Lorentzian functions in order to obtain more precise values of all spectroscopic parameters: λ_{LSPR}, FWHM (Γ_{LSPR}) and peak intensity, before/after immersing the thin film into the analyte solution for a given concentration. The chemisorption of 2-mercaptoethanol on metal NPs embedded in the polymer thin film is irreversible due to the strong interaction of the Ag-S bond. As a result, the analyte cannot be desorbed to return the nanosensor to its initial state. This is not a limitation since this nanocomposite-based sensor is easy-to-prepare, easy-to-use and low-cost, which are the bases of a fully disposable sensing platform technology

We demonstrate chemosensing capabilities of Ag-PVA nanocomposite with a LOD below 20 nM, by measuring either the LSPR wavelength shift ($\Delta\lambda_{LSPR}$) as a function of the analyte concentration (Fig. 2b). $\Delta\lambda_{LSPR}$ is taken as representative of the change in the dielectric environment of the NPs. The sensor response to the analyte can be tuned by varying the nanocomposite properties such as film thickness and nanoparticle concentration.

We observed a similar behaviour for Ag-Novolac nanocomposite. Fig. 3a shows the LSPR absorption of an Ag-novolac film for different immersing times into a 2-mercaptoethanol aqueous solution of 0.01 M. The analyte binding at Ag NPs is strongly time-depending. The main advantage of this nanocomposite is the possibility of miniaturization due to its lithographic properties. Fig. 9b shows an example of the fabrication of LSPR-based microsensors by menas of UV-lithography. We observe in Fig.3b an optical microscope image of a 100 µm-side square structure of Ag-DNQ-novolac nanocomposite before and after the analyte binding reaction. We notice a significant difference in the absorption of the nanocomposite after 48 hours of immersion into the analyte solution.

PVA and Novolac-based Ag nanocomposites can be used as qualitative or semi-quantitative sensor for thiol molecules (and possibly quantitative for other molecules). Moreover they provide a fast, non-expensive and large-scale fabrication method for plasmonic devices. Because the proposed nanocomposites are easy-to-prepare, easy-to-use and low-cost, a fully disposable sensing platform technology may be developed on it.

References

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Figures
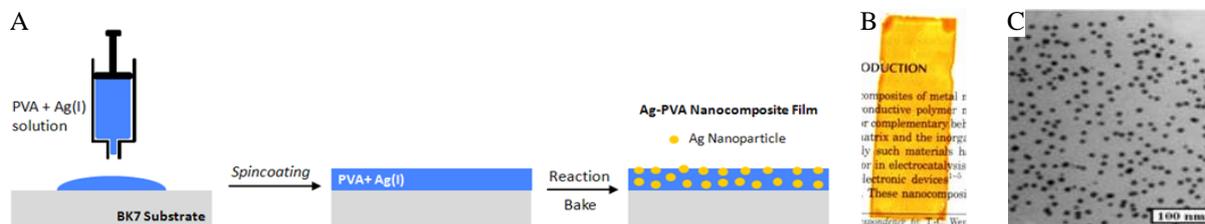
Fig 1. A) Schematic steps involved in the formation of Ag-PVA nanocomposite thin film; B) Image of the Ag-PVA film spincoated on soda-lime glass and C) TEM image..
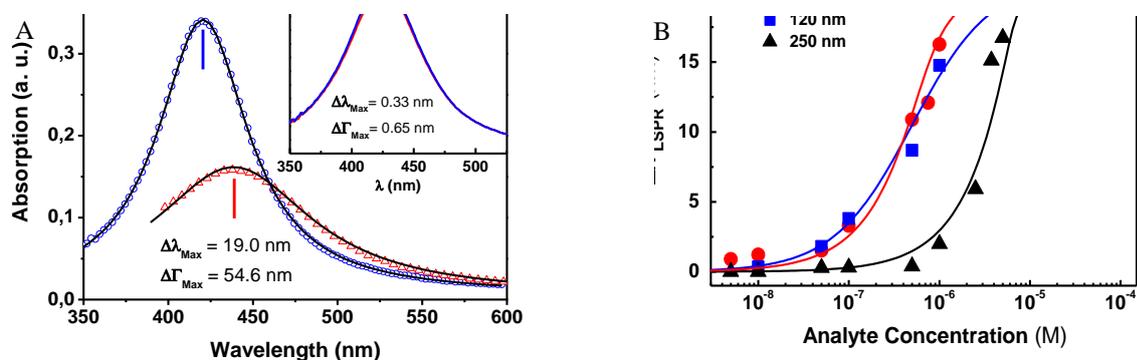
Fig 2: a) LSPR curve of a Ag-PVA thin film before and after immersing on an aqueous solution of mercaptoethanol during 180 min. The effect of pure water is shown as an inset of this figure. B) $\Delta\lambda_{LPSR}$ response of Ag-PVA nanosensors as a function of the mercaptethanol concentration for different film thickness: 80, 130 and 250 nm.
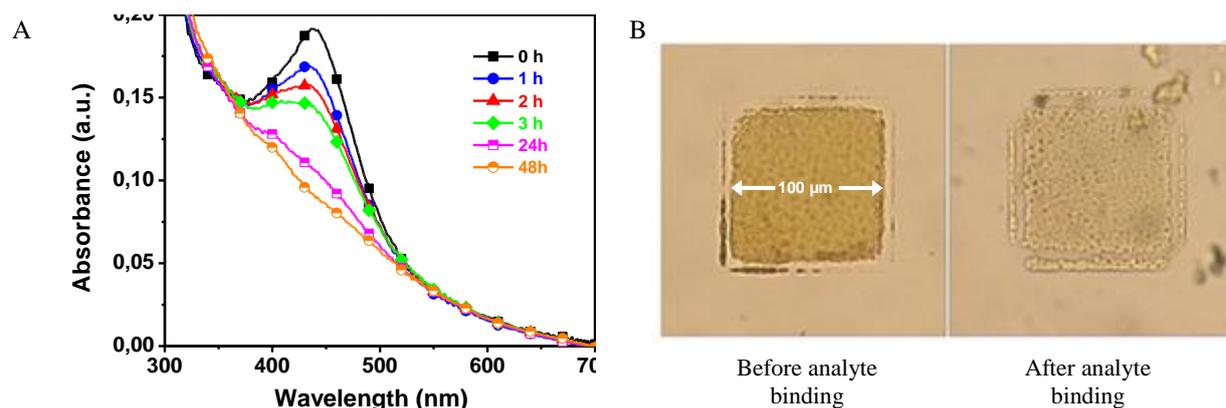
Fig 3. Absorbance of a Ag-Novolac film immersed in a 0.01 M Mercaptoethanol-water solution. b) 100 µm-side square microstructures of Ag-Novolac nanocomposite before (left) and after (rigth) immersion in the mercaptoethanol solution.