Microplotter Printing of LSPR sensor based on Ag-PVA nancomposite for amine detection

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Molecular sensing and detection based on localized surface plasmon resonance (LSPR) have attracted intense interest for detection of biomolecules with high sensitivity and low cost. LSPR of Au and Ag nanoparticles (NPs) strongly depends on the refractive index of the surrounding medium (substrate, solvent, and adsorbates) [1]. Recently, we proposed a novel LSPR sensing platform based on nanocomposite of Ag nanoparticles embedded on a polymer matrix such as PVA and Novolak for the detection of 2-mercaptoethanol [2,3]. The advantage of these materials is that 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. Additionally, these materials can be patterned by e-beam and UV lithography [3,4,5], which may form the basis to the microfabrication of biochip sensors.

Figure 1: a) Scheme of the fabrication of Ag-PVA nanocomposite by microplotter printing. b) 1 mm-side pattern of Ag-PVA fabricated by microplotter printing and the corresponding TEM image.

In the present work we report on the fabrication of Ag-PVA sensors by a high-precision microplotter, a very promising direct-write technology developed for printing materials from solution, which may form the basis to the future microfabrication of LSPR sensors. Thus, we have formulated a novel nanoink based on a solution of the metallic NP precursor ($AgNO_3$) and the polymer (PVA). After the printing procedure, the patterns are bake and the NPs are synthesized inside the polymer. Figure 1.b shows an optical microscope image of 1 mm-side square Ag-PVA structure printed on a glass substrate from the optimized ink formulation and bake conditions and the corresponding TEM image.
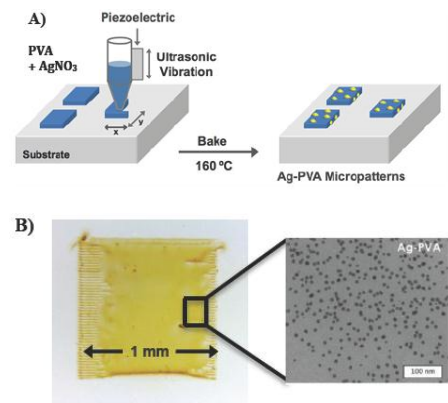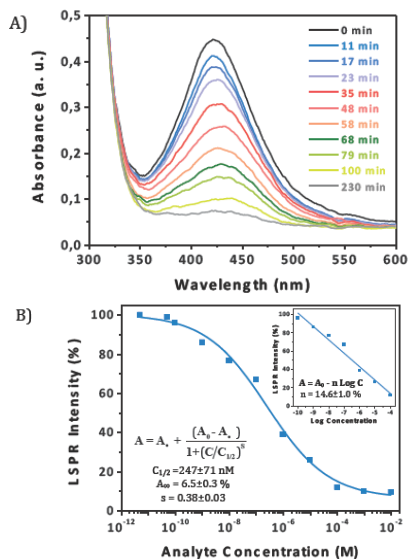

Figure 2: a) LSPR curve of a Ag-PVA thin film before and after immersing on an aqueous solution of 10^{-4} M ethylenediamine. b) Absorption decay response of Ag-PVA sensors as a function of the ethylenediamine concentration for immersing time of 1000 min. Inset: linear regresion of the calibration curve in the linear detection range.

Now, we extend the sensing capability of Ag nanocomposites to the detection of amine-based analytes both in solution and in vapor. Sensing of amine species in aqueous solutions is of great importance not only for environmental and industrial monitoring applications but also for the quality control of food products. Figure 2a exhibits the LSPR absorption curve of the Ag-PVA nanocomposites thin film after immersing into an aqueous solution of 10^{-4} M ethylenediamine for different times. We observed that LSPR intensity and LSPR shift evolve as a function of the immersing time. Analyte binding to Ag NPs is a strongly time-depending phenomenon. Figure 2b shows the LSPR absorption decay response of Ag-PVA sensors as a function of the EDA concentration for immersing time of 1000 min. Calibration curves for analyte binding assays are generally characterized by a sigmoidal relationship between the sensor response and the analyte concentration. Ag-PVA structures exhibit a limit of detection (LOD) of 0.1 nM. The maximum sensor response, this is the sensor saturation, is achieved for an analyte concentrations above 10^{-4} M. The linear detection range for EDA was estimated to be over an analyte concentration of six orders of magnitude, from 10^{-10} to 10^{-4} M. The sensitivity was determined to be 14.6±1.0 % from the slope of the linear regresion of the calibration curve shown in the inset of Figure 2b.

The response of the Ag-PVA was also performed by exposing the nanocomposite patterns to the vapors of several biogenic (putrescine, cadaverine) and synthetic (methylenediamine and ethylenediamine) amines. Because these amines are to a greater or lesser extent volatile, it is expected that a certain amount of diamines can be in the vapor phase. Figure 3 shows the real-time sensor response to different diamines and water. We measured a different sensor response to the amines tested. This can be mainly explained in terms of the analyte relative pressure in the vapor phase but also due to their different binding affinity for Ag NPs. The largest responses were obtained for shorter diamines (methylenediamine>ethylenediamine>>putrescine> cadaverine) because these molecules are more volatile and therefore their concentration in the vapor phase is higher.

This work confirms that a fully disposable sensing platform technology can be developed on this material because the proposed nanocomposite is easy-to-prepare, easy-to-use and low-cost and allows miniaturization.
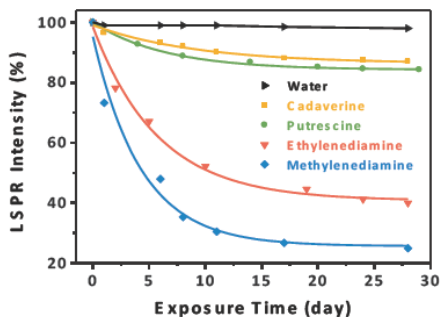

Figure 3: The real-time kinetic response of Ag-PVA exposed to the vapors of methylenediamine, ethylenediamine, putrescine and cadaverine.

References

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