Plasmonic optical sensors printed from Ag-PVA nanoinks as intelligent labels for food control

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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 its surrounding medium (substrate, solvent, and adsorbates) [1]. Recently, we proposed a novel LSPR sensing platform based on nanocomposite of Ag nanoparticles embedded in 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 [3,4] and UV lithography [5], which may form the basis to the microfabrication of biochip sensors.

In the present work we extend the sensing capability of Ag nanocomposites to and quantify trace amounts of amines in gas and water [6]. Sensing of amines is of great importance not only for environmental and industrial monitoring applications but also for the safety and quality control of food. The transduction mechanism of the sensor is based on the changes of the LSPR band of Ag NPs when analyte molecules are chemisorbed on their surface. The Ag-PVA sensors are fabricated by means of a high-precision microplotter, a direct-write technology developed for printing materials from solution. The nanoink is formulated with a metal precursor ($AgNO_3$) and a polymer (PVA) using an adequate mixture of solvents to meet the rheological requirements for the fluid dispensing process (Figure 1 a).. The LSPR intensity is the most sensitive magnitude to follow the interaction between Ag NPs embedded in PVA and amines. Ag-PVA patterns are tested as a plasmonic optical sensor for the detection of ethylenediamine (EDA) in solution showing a limit of detection as low as 0.3 ng or 6 ppt. We also observed a linear sensing behaviour within a concentration range between 10^{-10} and 10^{-4} M, which allows us to use Ag-PVA as quantitative sensor for EDA. Moreover Ag nanocomposite patterns are also used for sensing vapours of several biogenic (cadaverine, putrescine) and synthetic (ethylenediamine and methylenediamine) amines, where shorter amines exhibit the largest sensor response (Figure 1 b)..

Finally, the Ag-PVA plasmonic optical sensor was tested for real-time monitoring of chicken meat spoilage at room temperature. After 24 hours at room temperature we observed to the naked eye a noticeable colour change of the Ag-PVA label from yellow to colourless, because of the increasing amount of volatile compounds released during the chicken spoilage (Figure 1 c).

We believe that Ag-PVA nanocomposite can be the basis for the development of sensor spots, bar-codes and other labels for smart packaging technology, among other sensing applications.

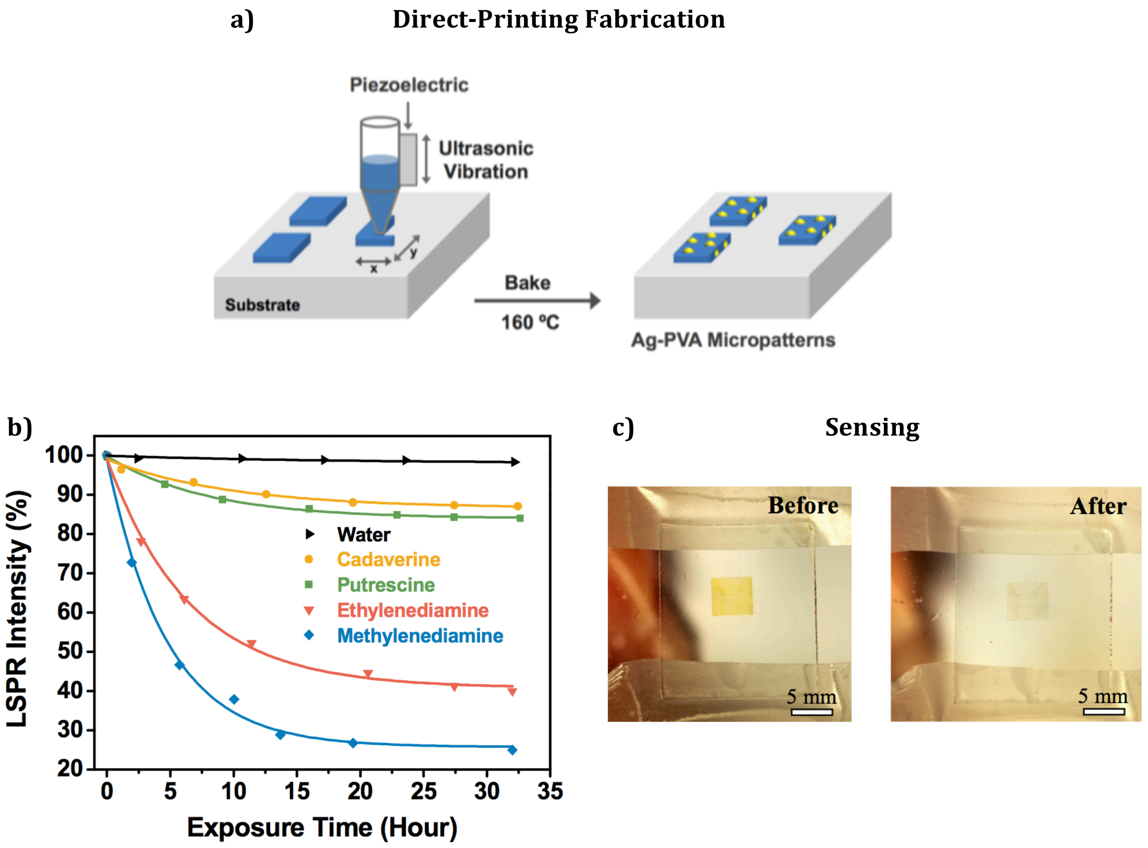

Figure 1. a) Scheme of the fabrication of Ag-PVA nanocomposite sensor by microplotter printing. **b)** Variation of the LSPR peak intensity exposed to the vapours of a 0.1 M aqueous solution of methylenediamine, ethylenediamine, putrescine and cadaverine. **c)** Optical images of the Ag-PVA sensor before and after exposure to chicken meat

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