

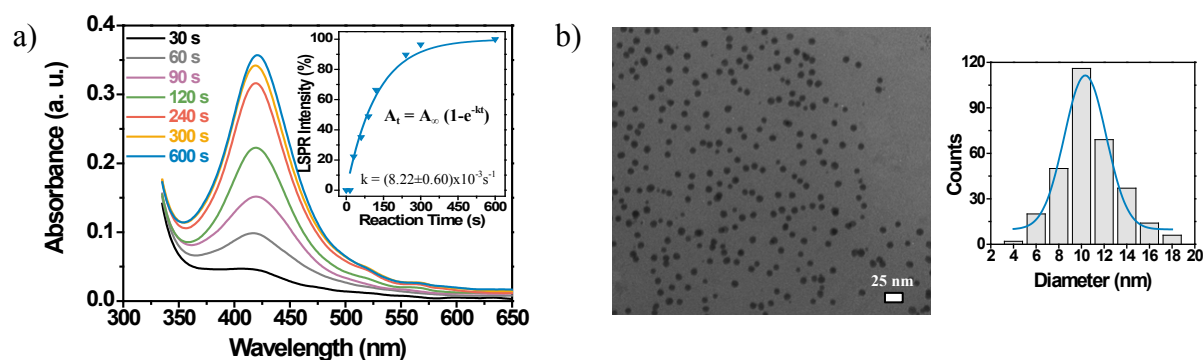


Figure 1. a) Absorbance spectra of a 1 mm² square pattern of Ag-PVA baked at 160°C for different times. Inset: LSPR intensity evolution with bake time. (b) TEM image and nanoparticle size distribution once the reaction is complete.

Figure 1.a shows the formation of Ag NPs in a 1 mm² square pattern (Figure 1.e), as a function of the baking time at 160 °C. The reduction of Ag(I) to Ag(0) was evident after just 30 s, indicated by an absorption band centred around 400 nm, which is the characteristic LSPR absorption feature associated to spherical Ag NPs. The intensity of this band increases fast with increasing baking time from 30 to 240 s and reached its maximum around 600 s. Data analysis reveals (inset of Figure 1.a) that the synthesis of Ag NP in PVA exhibits a pseudo-first-order reaction kinetics, because PVA is in excess. Experimental data can be well fitted to the expression:

$$A_t = A_\infty (1 - e^{-kt}) \quad \text{Eq. 1}$$

where A_t and A_∞ stand for the LSPR absorbance intensity at a given time and when the reaction is completed, respectively, and k is the reaction rate constant. The best fit of experimental data to Eq. 1 yields $k = 8.22 \pm 0.60 \text{ ms}^{-1}$. As can be seen, the LSPR band slightly shifts to the red from 411 to 420 nm, as the reaction takes place. This effect can be attributed to an increase in the average size of the NPs attributed to the Ostwald ripening mechanism [i]. Once the reaction is finished, the resulting Ag-PVA nanocomposite structures showed a symmetric and narrow plasmonic absorption band centred at 420 nm.

Transmission electron microscopy (TEM) was carried out in order to determine the shape and size of the resulting Ag NPs and their distribution within the PVA matrix. Figure 2.b shows TEM images of a small piece of a nanocomposite pattern with Ag NPs embedded in the polymer (case of completed reaction) and the corresponding size distribution. We can observe how Ag NPs are spherical, uniformly distributed and isolated from each other within the polymer matrix. This is in total agreement with the observed symmetric LSPR narrow

absorption band exhibit by the nanocomposite patterns (Figure 2.a). The average diameter of Ag NPs was found to be 10.8 ± 2.9 nm.

Figure 2 shows the chemical structures of the diamines used for the sensing experiments

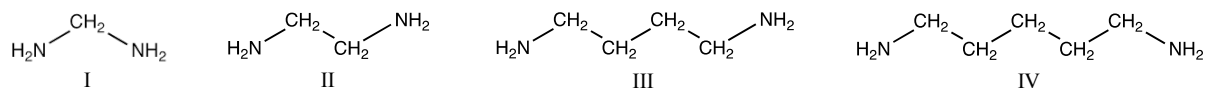


Figure 2. Structures of linear α,ω -aliphatic diamines: I. Methylenediamine (MDA), II Ethylenediamine (EDA) ,III. Putrescine (PUT) and IV Cadaverine (CAD)

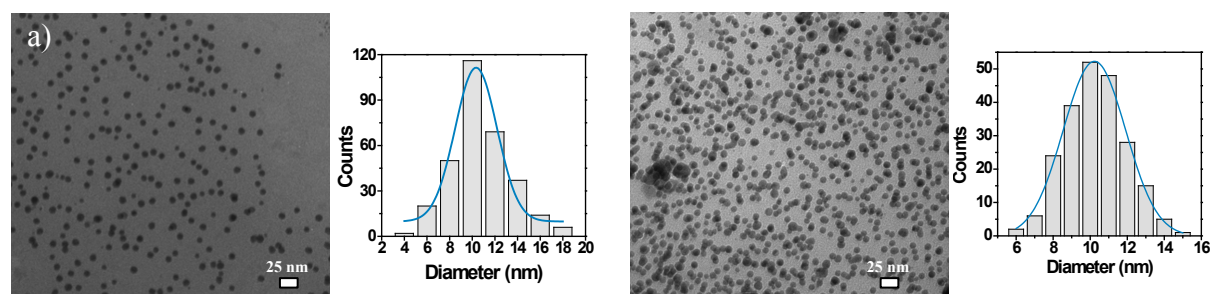


Figure 3. TEM and size distribution before and after sensing a solution of EDA 10^{-4} M.

Figure 3 shows TEM images and the corresponding size distribution of Ag-PVA patterns before (10.8 ± 2.9 nm) and after (10.4 ± 2.1 nm) sensing a solution of 10^{-4} M EDA for 30 minutes. We measured a similar size of Ag NPs after the amine binding.

Figure 4 shows the LSPR curves of the Ag-PVA label before and after exposure to chicken meat for 18 and 24 hours (corresponding to images of Figure 5).

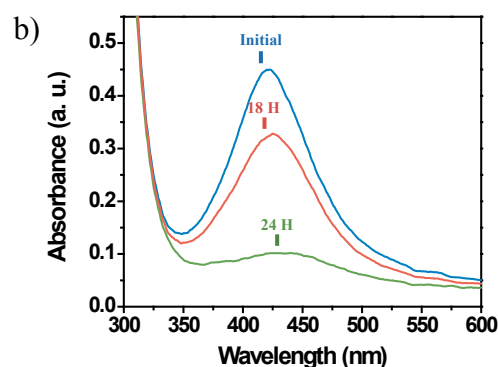


Figure 4. UV-Vis spectra of 1 mm^2 -square Ag-PVA label before and after exposure to chicken meat for 18 and 24 hours.

Figure 5 shows the Ag-PVA label (0.25 mm^2 square pattern) before and after exposure to chicken meat for 18 and 24 hours. Sensor response saturation takes place after 18 hours.

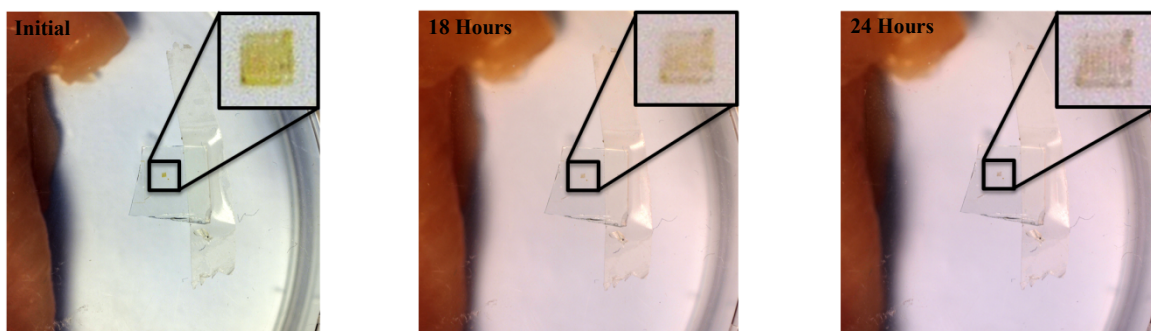


Figure 5. Optical images of the 0.25 mm²-square Ag-PVA label before and after exposure to chicken meat for 18 and 24 hours.

[i] C. B. Murray, C. R. Kagan, M. G. Bawendi *Annu. Rev. Mater. Sci.*, 30, 545, (2000)