Gold and silver nanomaterials based biosensors : a comparative study

Laurent Dreesen, Marjorie Lismont

University of Liege, Physics Department, Biophotonics, 17 Allée du 6 août, 4000 Liège, Belgium

Laurent.Dreesen@ulg.ac.be

Noble metal nanoparticles (NPs) are intensively studied due to their particular optical properties, mainly high optical absorption and diffusion yields, leading to interesting applications in biochemical sensing, molecular tracking and imaging, drug delivery and photothermal therapies [1]. These unique optical properties arise from a physical process named surface plasmon resonance (SPR) which is a resonant coupling of incident light to the collective motion of electrons along the nanoparticles surface [2].

Optical SPR biosensors are able to measure complex formation in real time. Indeed, the SPR absorption spectrum band of the NPs is sensitive to the shape, size, inter-particle distance and composition of the NP as well as the dielectric properties of the surrounding medium [2]. Due to the sensitivity of SPR to the local dielectric environment, plasmonic NPs can thus act as transducers that convert small changes in the local refractive index or in the inter-particle distance into spectral shifts and broadenings of the absorption spectral bands [3].

Among metals, silver and gold NPs have received considerable interest for many reasons. For instance, they are stable in ambient atmosphere and exhibit good biocompatibility even if particular surface treatments are sometimes required. The Ag and Au NPs are also relatively easy to fabricate with different sizes and shapes allowing the tuning of the SPR optical absorption band from the near ultraviolet (400 nm) to the near infrared (1000 nm) wavelengths.

In this study, our aim is to characterize two biosensors based on silver and gold spherical NPs in order to detect which one seems the best. Both NPs have a diameter close to 15 nm. We use the well-known biocytin-avidin complex as a model system because the bonding of avidin with biocytin is extremely strong with a dissociation constant three order of magnitude higher than the typical constants of antigen-antibody interactions. More precisely, we compare the intensities, the band shapes and the spectral locations of the SPR adsorption bands before and after the biomolecular recognition of avidin by biocytin molecules adsorbed on the Ag and Au NPs. The kinetic of the interaction is also discussed.

Before surface treatment with biocytin, the NPs SPR bands are located around 390 and 520 nm for Ag and Au NPs, respectively. The SPR band intensity is higher for silver than for gold.

Biocytin adsorption does not significantly modify the SPR spectral features. NPs do not therefore form aggregates and the local refraction index has not significantly changed.

After avidin addition, a SPR red-shift and a broadening of the SPR bands are observed with both NPs as shown on Figure 1. These parameters evolved with time and reach their final values after around 45 min for each system. The aforementioned spectral changes arise from the biomolecular recognition process between biotin and avidin which leads to the NPs aggregation. The recognition process also induces a variation of the local refractive index around these NPs which contributes to the red-shift. The maximum SPR shifts are equal to 25 nm and 12 nm for silver NPs and gold NPs, respectively. Our results highlight the smaller dielectric sensitivity of gold NPs compared to the silver NPs one for a same particles' size and for an equivalent concentration of avidin. The detection limit, described as the lowest concentration for clear identification of wavelength shift due to biomolecular recognition, is equal to 4 nM for both silver and gold NPs. With this protein concentration, 3 nm is the typical wavelength shift.

The specificity of the biocytin - avidin biosensors is verified by replacing avidin by Bovine Serum Albumina (BSA). When BSA is added, we observe a SPR band shift which is smaller than the detection limit of 3 nm attesting the biosensor selectivity.

Our work demonstrates the superiority of Ag over Au NPs for the elaboration of biosensors based on SPR. However, it is well-known that Ag NPs are less biocompatible than gold. This problem can be circumvented by an appropriate coating of the NPs surface prior ligand adsorption.

References

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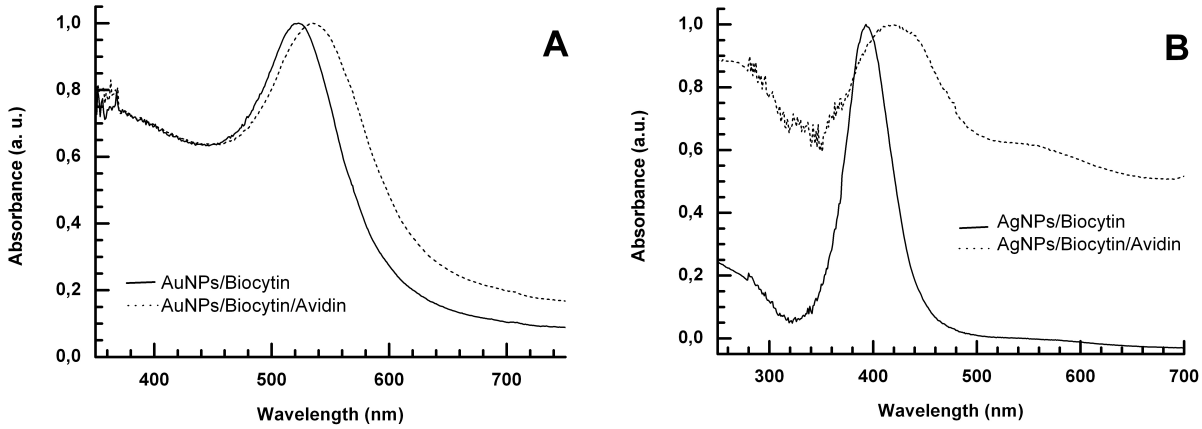
Figure 1



UV-VIS absorption spectra of biocytin - AuNPs (spectra A) and biocytin – AgNPs (spectra B) before (continuous line) and after (dashed line) avidin interaction. The spectra are normalized by the adsorbance maxima.