Dichroic surface plasmons in Au and Au-Pd nanoparticles: reactivity towards gas molecules and application to high-performance H₂ sensing.

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Gold nanoparticles (NPs) are of great interest for multiple applications, including their reactivity to catalytic reactions, as well as localized surface plasmon resonances (LSPRs), which can be excited by incident light. It is well known that the LSPR depends on a number of parameters, such as the size and shape of the NPs, the local environment and its interaction with them. In particular, the presence of molecules adsorbed on the surface of the Au NPs can induce a modification of the refractive index of the immediate environment, but also can be accompanied by charge transfers, which both strongly influence the wavelength position of the LSPR.

Therefore, the study of the LSPR changes of Au NPs placed in a gas makes it possible to follow the presence and the adsorption of the gas molecules on the NPs. However, the reactivity of the Au, even with nanometric scale, remains low, leading to very small displacements of the LSPR, which can be much less than 1 nm and therefore hardly measurable. Here, we use a very sensitive optical surface technique, known as reflectance anisotropy spectroscopy, to study such minute changes in the LSPR. The anisotropic samples of Au are formed of nanoparticles elaborated by oblique angle evaporation on a glass substrate, leading to dichroic NP films showing two different plasmon resonances as a function of the polarization of the light (Fig. 1).

We have applied this approach to several studies. (i) In order to demonstrate the performance of the method, we first studied its sensitivity to detect very small variations in the refractive index of the environment (water with alcohol). (ii) We conducted a comparative study of the adsorption of dioxygen and dihydrogen on Au NPs. The experiments were well reproduced by calculation, demonstrating the existence of charge transfers between the gold and the adsorbed entities. (iii) By adding palladium to gold, we developed Au-Pd NPs to detect small amounts of H₂ in a carrier gas, showing that this method holds great promise for the development of highly sensitive plasmonic H₂ sensors (fig 1).

Figure 1. Left hand side: Absorbance of the anisotropic Au NPs film for two perpendicular polarizations of the light with respect to the direction of evaporation. Right hand side: Optical anisotropic signal measured during cycles of 2% H₂ in Ar vs. pure Ar, for Au and for Au-Pd NPs.

References

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