SUPPLEMENTARY INFORMATION

Mechanism of hydrogen adsorption on gold nanoparticles and charge transfer probed by anisotropic surface plasmon resonance

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Calculation of the optical properties of flat supported Au nanoparticles.

Let us consider a Au NP with a flat ellipsoidal shape, close to the spheroid but with a slight anisotropy, with half-axes corresponding to the average values determined by AFM and MEB: $a = 5.5 \text{ nm}$, $b = 6.5 \text{ nm}$ and $c = 2.25 \text{ nm}$ (Fig S.1). Here we neglect the interaction between the NPs, which is another way to take into account an overall anisotropy of the substrate. It is known that the interaction with the substrate yields a red shift of the LSPR of a NP. However, taking into account rigorously such effect is not simple and, to our knowledge, treatment has been developed for spheroids only and cannot be applied for ellipsoidal particles.\textsuperscript{1,2} Nevertheless, a simple way to introduce approximately the effect of the glass substrate is to consider, an intermediate dielectric function $\varepsilon_{emb}$ between those of air ($\varepsilon_{air} = 1$) and of the substrate ($\varepsilon_{glass} = 2.25$) , for the embedding medium of the NPs.\textsuperscript{3} Moreover, an increase of the damping of the free electrons of Au, due to the small size of the NPs, has been considered in the calculation, which damps out and enlarges the LSPR. With the above values, the transmittance square is given in Fig.S2, for a mass thickness equal to 2 nm. The resonance is located around 600 nm along the x direction (the short size of the ellipsoid parallel to the surface) and shifted to 700 nm along the y direction (the long size), as illustrated in Figure S1. This is in agreement with the experiment. Here, the aim of the calculation was not to perfectly reproduce the experiment but to demonstrate that the measured sizes of the NPs could explain the observed positions of the LSPR. For a better agreement, several leads could be followed: (i) taking into account the distribution of size and of shape of the particles would enlarge the resonances; (ii) taking into account the electromagnetic interaction between the particles (as the apparent chains of particles observed in Fig.2) would increase the anisotropy and redshift the LSPRs. Finally, treating more rigorously the interaction with the substrate could be done, either by using approaches developed for spheroids and considering that the present NPs have shapes close to
spheroids, or by using finite element methods such as Discrete Dipole Approximation, although in this model too, the interaction with the substrate is not easily taken into account.

**Fig. S1.** Ellipsoid diagram representing an anisotropic shape. The x (short) and y (long) axes show the directions of the polarised light in relation to the particle.

**Fig. S2.** Transmittance squared of an ensemble of Au ellipsoids on a glass substrate, with mass thickness of 2 nm
TAS results for different samples.

Fig S3: Graphs for different samples. Each pair is for a given sample of Au nanoparticles of average diameter: a. 10.5nm b. 10.8nm c. 11.6nm d. 13.7nm e. 14.1nm f. 16.3nm. The figure on the left hand side of a pair correspond to a TAS spectrum of the sample and its corresponding pair is a real time measurement of the change in intensity of the TA signal when exposing the sample to Ar and H\textsubscript{2} in 100s cycles. As each sample qualitatively displays the same behaviour, detailed results are only given for sample (a) in the paper.

