Multiscale Theoretical Modelling of Plasmonic Sensing of Hydrogen Uptake in Palladium Nanodisks

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The study of Hydrogen uptake and its diffusion dynamics in metals has raised a lot of theoretical and experimental research because of its importance in a variety of relevant applications like efficient and safe hydrogen storage [1], hydrogen sensing [2] and nanocatalysis [3]. We analyse theoretically the optical properties of Palladium nanodisks during hydrogen uptake. The theoretical description of the optical response of Pd-H system is not an easy task due to (i) the presence of different phases (α and β phases) that H can adopt when absorbed into Pd and (ii) different length scales involved in the hydrogen uptake process. We first obtain the dielectric response of Pd-H using *ab initio* quantum mechanical calculations [4]. The quantum mechanical calculations consider the atomic scale changes occurring in Pd during hydrogen uptake. The crystal lattice used in the ab initio calculations is shown in Fig. 1(a). The calculated dielectric functions are then used in the full electrodynamical calculations of light scattering by H-modified Pd nanodisks. The electrodynamical calculations include the details of the size, shape and the environment affects of the mesoscopic system. Thus our multiscale theoretical approach address both the atomic level as well as the mesoscopic level changes responsible for the total optical response of the palladium hydride disks during hydrogen uptake.

Two different phases of Pd-H (α with low H concentration and β with higher H concentration) can coexist as the H concentration increases. We follow the spectral evolution of the localized surface plasmon peak of the disks for different admixtures of the Pd-H α and β phases (Fig. 1b) and reproduce the experimental [5] plasmon energy shift produced by the structural inhomogeneity upon hydrogen absorption (Fig. 1c). Our combined theoretical framework provides a solid background to describe plasmonic sensing in the dynamics of structural domains, as well as to identify hydrogen saturation conditions in metal-hydrides.

References

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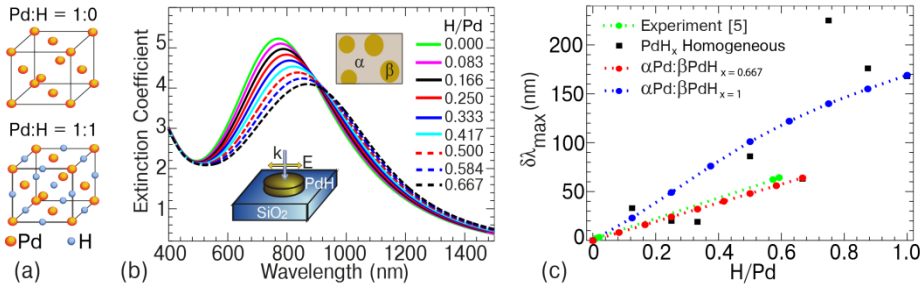

Figure 1: (a) Crystal lattice of $PdH_{x=0}$ and $PdH_{x=1}$ used in the ab initio calculations. (b) Extinction spectra for a PdH disk of 20 nm thickness and 190 nm diameter calculated using Bruggeman's effective dielectric function with α phase of $PdH_{x=0}$ and β of $PdH_{x=0.667}$ for different H/Pd ratios. (c) LSPR shifts calculated for a Pd-H disk of 20 nm thickness and 300 nm diameter placed on SiO_2 substrate plotted as a function of H/Pd using Bruggeman's effective dielectric function with the β phase taken as $PdH_{x=0.667}$ (red dots) and as $PdH_{x=1}$ (blue dots). A comparison with experimental results from Ref. [5] (green dots) is shown. The black dots give the spectral shift for a homogeneous distribution of H in Pd.