

Hydrogen Storage in Palladium Nanoparticles - Size Dependent Kinetics

Introduction

Hydrogen storage in metal hydrides is an important issue to be addressed to facilitate a transition from the present fossil fuel based systems towards more sustainable hydrogen based ones.

Two major challenges in this area are to find suitable stability of hydrides (thermodynamics) and fast enough storage and release kinetics. Both these aspects can be investigated with Insplorion's Indirect Nanoplasmonic Sensing (INPS) platform.

For instance, the real time kinetic measurements of hydrogen uptake and release for palladium (Pd) nanoparticles is illustrated in this Application Note.

Experimental

The INPS chip consists of an array of nanofabricated plasmonic gold disks covered by a 10 nm film of SiO₂ (Fig. 1). The Pd nanoparticles are deposited on the SiO₂ surface. TEM images of Pd nanoparticles, resulting from different evaporated film thickness, are shown in Fig. 1

with corresponding size distribution histograms. The dielectric changes in the Pd nanoparticles due to the absorption/release of hydrogen induce a change in the Localized Surface Plasmon Resonance (LSPR) of the Au disk nanosensors. The variation of the optical extinction is monitored at constant wavelength (640 nm) on the peak of the Au disk LSPR with 0.05 s integration time.

Results

The hydriding and dehydriding kinetic curves for Pd nanoparticles with a mean diameter of 1.81, 2.47, and 5.35 nm, measured at 30°C, are shown in Fig. 2. The normalized variation of the extinction coefficient, proportional to the amount of absorbed hydrogen, is plotted as a function of time. The significant difference in signal-to-noise between the curves for different nanoparti-

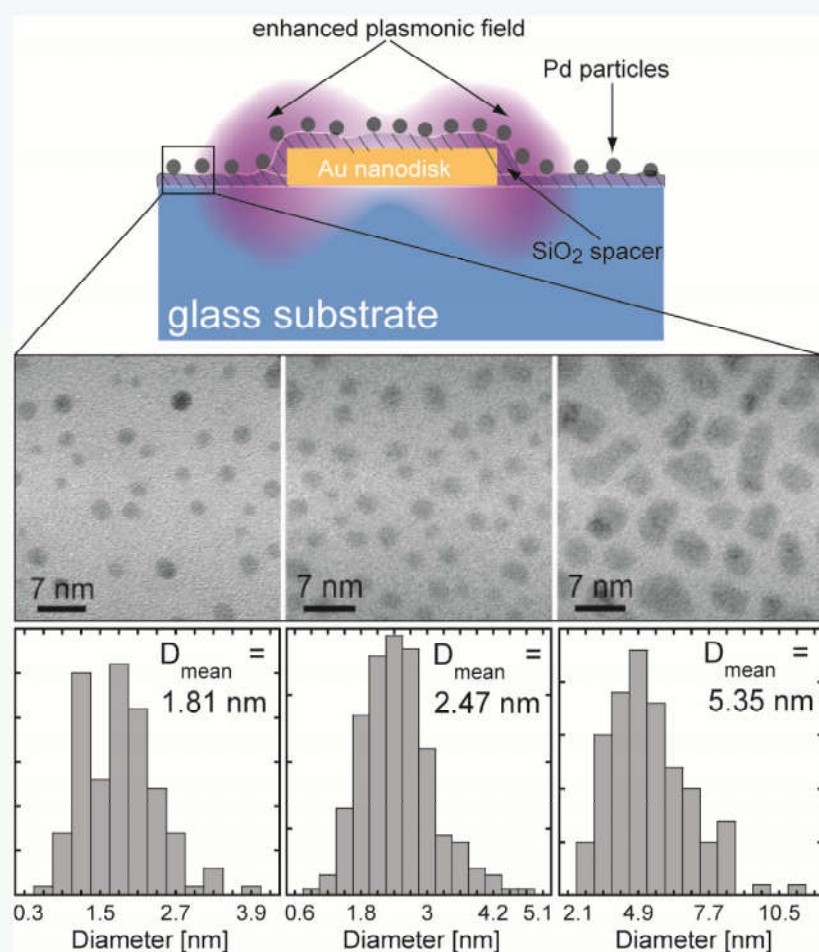


Figure 1: Scheme of Insplorion's INPS platform. The Localized Surface Plasmon Resonance (LSPR) of gold nanodisks is used as "a sensor" to characterize a material (here Pd nanoparticles) which undergoes some change upon hydrogen absorption. The Pd nanoparticles are deposited onto a thin dielectric spacer layer, separating the optically active sensor nanodisks from the material to be studied and the hydrogen environment. The change of hydrogen concentration in Pd nanoparticles is detected through coupling of the enhanced plasmonic near field of the Au nanodisk plasmons to the changing dielectric properties of Pd nanoparticles upon H absorption and desorption. The TEM images below show three examples of Pd nanoparticles used in the experiments presented in this application note, together with the corresponding histograms of the size distribution.



cle sizes has its origin in decreasing observed LSPR shift for smaller nanoparticles (less material) and thus represents the noise level in the raw data. The strongly particle size dependent hydrogenation kinetics, on a time scale ranging from a few to several tens of seconds, is easily resolved in real time by INPS.

In Fig. 3a normalized hydrogen absorption kinetic curves are shown for $D_{\text{mean}} = 5.35$ nm at $T = 30, 55$ and 80°C . The rate-limiting step in the

hydrogenation process is the diffusion of hydrogen atoms through a hydride shell, which is formed around a Pd core. Fig. 3b shows an Arrhenius analysis for four measurements at each temperature ($t_{0.5}$ corresponds to the time for 50% conversion), which yields an activation energy of 24 kJ/(mol H) for hydrogen sorption. For the dehydrogenating process, the rate limiting step is associative desorption of hydrogen from the Pd nanoparticle surface. The Arrhenius

plot for desorption yields an activation energy of 62 kJ/(mol H).

Conclusions

The real-time measurements of hydrogen ab-/desorption in Pd nanoparticles presented in this application note illustrate the unique possibilities offered by Insplorion's INPS platform for the sensitive measurements of fast kinetics at the nanoscale.

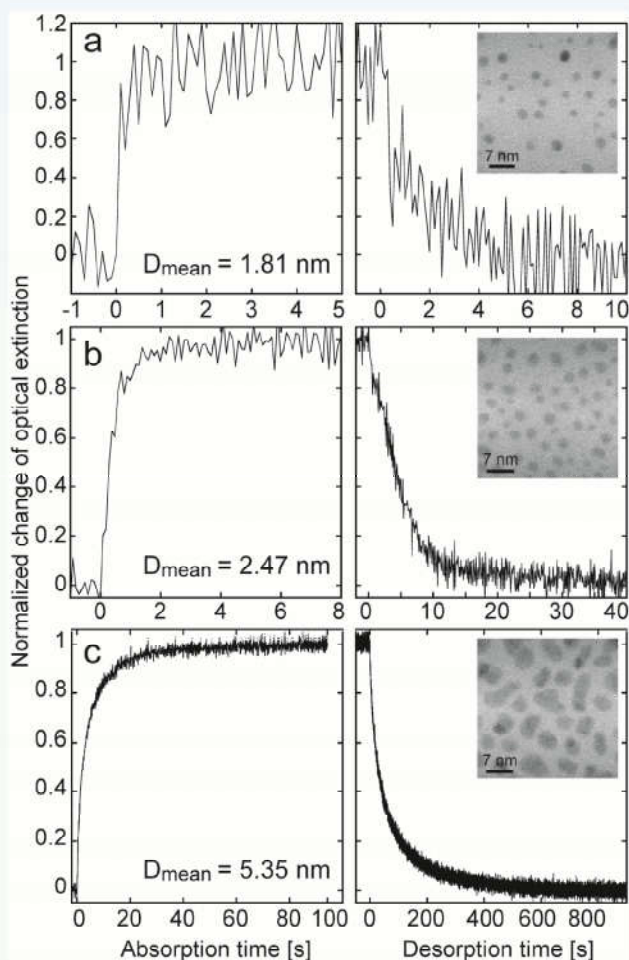


Figure 2: Experimental hydrating (left column) and dehydrating (right column) kinetic curves for three Pd particle diameters: $D_{\text{mean}} = 1.81$ (a), 2.47 (b), and 5.35 nm (c). The change of the optical extinction, measured at 640 nm, is normalized that "1" corresponds to 100% conversion of the Pd nanoparticles to the hydride phase.

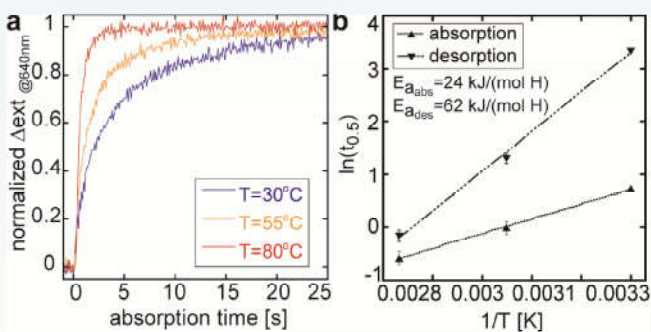


Figure 3: Kinetics of hydrogen storage in small Pd nanoparticles. (a) Normalized kinetic curves for hydrogen sorption in Pd nanoparticles with a mean diameter of 5.35 nm at $30, 55,$ and 80°C . The normalized optical signal is proportional to the amount of hydrogen in the nanoparticle (1 corresponds to the fully hydride state). (b) Arrhenius plots yielding activation energies of the rate limiting steps for absorption and desorption.

References

Size-Dependent Kinetics of Hydriding and Dehydriding of Pd Nanoparticles, Christoph Langhammer, Vladimir P. Zhdanov, Igor Zoric, Bengt Kasemo, *Physical Review Letters* 104 (2010) 135502.

Indirect Nanoplasmonic Sensing: Ultrasensitive Experimental Platform for Nanomaterials Science and Optical Nanocalorimetry, Christoph Langhammer, Elin M. Larsson, Bengt Kasemo, Igor Zoric, *Nano Letters* 10 (2010) 3529-3538.

More information about the thermodynamics of hydrogen storage in Pd nanoparticles:

Application note "Hydrogen storage in Pd - Thermodynamics", available on www.insplorion.com

