

Hydrogen Storage in Palladium Nanoparticles - Thermodynamics

Introduction

There is a rapidly growing general interest in nanoscale hydrogen storage systems since they may offer faster response and advantageous thermodynamics compared to, for example, bulk or micrometer-sized metal hydrides.

In the following application note the thermodynamics of hydrogen stor-

age in palladium (Pd) nanoparticles is investigated using the highly sensitive and versatile Indirect Nanoplasmonic Sensing (INPS) technique.

Experimental

The gold nanodisk arrangement on the INPS sensor chip was covered with thin (10 nanometers) spacer

layer of silicon dioxide (SiO_2) before depositing Pd nanoparticles on the chip surface. Three different Pd nanoparticle sizes ($D_{\text{mean}} = 5.35, 2.47,$ and 1.81 nm) were investigated.

In the experiments presented in this application note, the INPS chip was placed in a heated stainless steel chamber and optical extinction was measured as a function of hydrogen

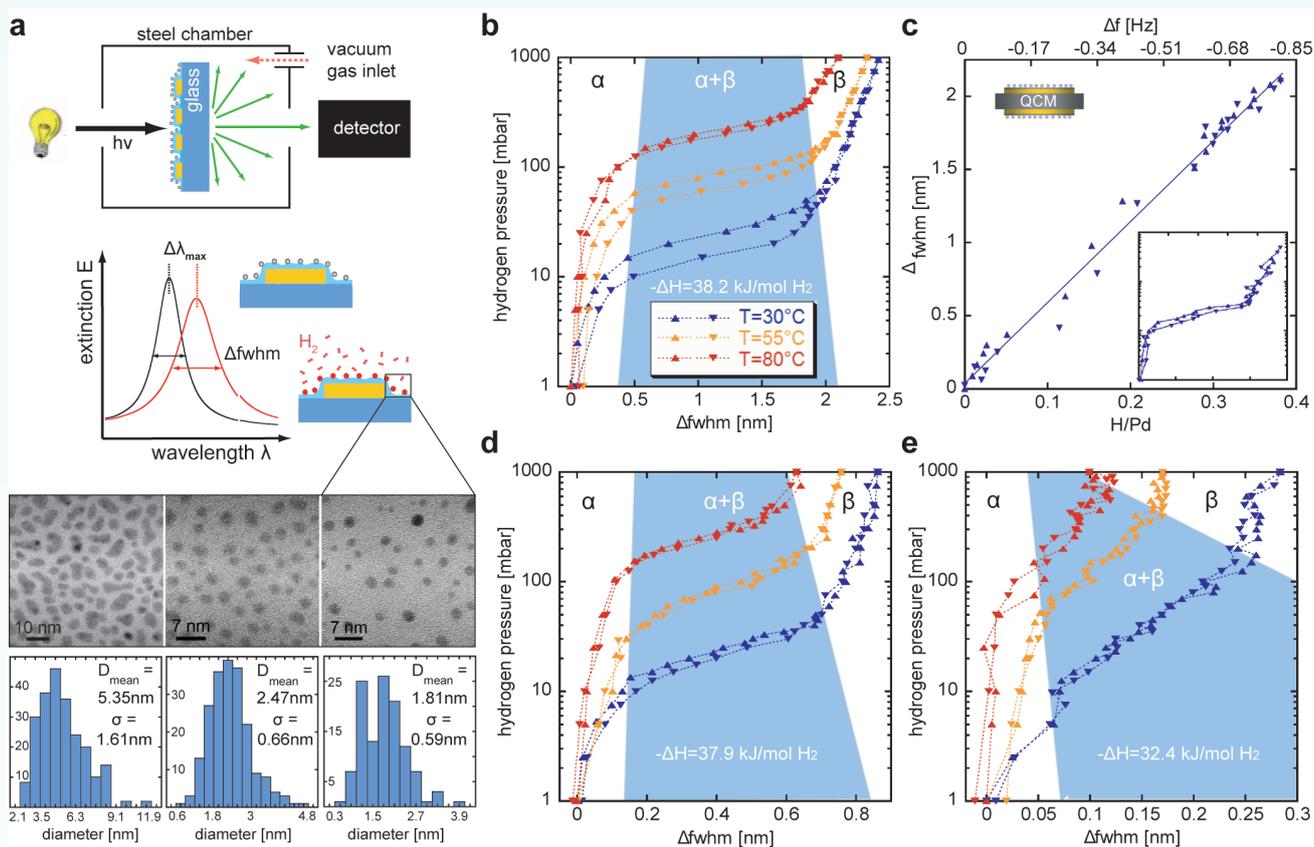


Figure 1: Thermodynamics of hydrogen storage in small Pd nanoparticles. (a) Schematic depiction of the used experimental setup and TEM images of the studied Pd nanoparticles, as obtained by evaporation and hydrogen annealing of thin granular Pd films. (b) p - Δfwhm isotherms for $D_{\text{mean}} = 5.35 \text{ nm}$ Pd nanoparticles. Triangles correspond to hydrogen absorption and inverted triangles to hydrogen desorption. The isotherms show distinct α -, $\alpha+\beta$, and β -phase regions with sloping plateau. (c) The hydrogen concentration (H/Pd ratio), obtained from a QCM measurement, is plotted vs the Δfwhm measured by INPS for identical $D_{\text{mean}} = 5.25 \text{ nm}$ particles. The corresponding QCM-isotherm measured at 30°C is shown as an inset. A clear linear dependence between Δfwhm and the hydrogen concentration in the Pd nanoparticles is found. In the p - Δfwhm isotherms for (d) 2.47 nm and (e) 1.81 nm Pd nanoparticles, a further broadening of the α -phase region, increasing plateau-slope, and narrowing hysteresis is observed. The enthalpies of hydride formation obtained from Van't Hoff analysis for the different Pd particle sizes are displayed together with the respective isotherms.



pressure (Fig. 1a).

The absorption and desorption of hydrogen in/from Pd nanoclusters cause measurable shifts of the spectral peak position ($\Delta\lambda_{\max}$) or of the peak full-width-at-half-maximum (Δfwhm) of the Au sensor nanoparticles (Fig. 1e). Δfwhm was used as the readout parameter in these experiments due to the experimentally found higher sensitivity compared to the spectral peak shift, $\Delta\lambda_{\max}$.

Results

INPS measurements of hydrogen absorption and desorption isotherms are shown in Fig. 1 for Pd nanoparticles with mean diameters 5.35 nm (Fig. 1b), 2.47 nm (Fig. 1d) and 1.81 nm (Fig. 1e). The p- Δfwhm isotherms show distinct α - (hydrogen in solid solution), $\alpha+\beta$ (mixed phase), and β -phase (hydride) regions with sloping plateau. This slope is a clear signature for significant deviation from bulk behavior and is induced by lattice strain, surface tension effects, and the polydisperse particle size distribution.

An increased slope of the plateau, accompanied by a successively narrowing hysteresis, can be observed as particle size decreases. The width of the plateau is decreasing, creating wider α - and β -phase regions for decreasing Pd particle size; both typical signatures of significant particle size effects on the storage thermodynamics. Van't Hoff analysis, where the "center of mass" of the sloping plateaus was used as reference point for reading out plateau pressures, yielded enthalpies for hydride formation for the different Pd cluster sizes clearly indicating the expected destabilization of the hydride phase in small clusters.

To determine the scaling of Δfwhm

with the absolute hydrogen concentration in the Pd nanoparticles, complementary quartz crystal microbalance (QCM) measurements were performed at 30°C. For this purpose $D_{\text{mean}} = 5.35$ nm Pd nanoparticles were prepared on a 10 MHz SC-cut quartz sensor crystal and the measured frequency shift was converted to hydrogen concentration in the Pd using the Sauerbrey relation. In Fig. 1c, Δfwhm (from the 30°C isotherm in Fig. 1b) is plotted versus the QCM frequency shift, Δf , and the corresponding hydrogen concentration in the Pd nanoparticles. A very clear linear relationship between the Δfwhm INPS signal and the hydrogen concentration in the Pd nanoparticles is found. The QCM-isotherm measured at 30°C is shown as an inset and is in excellent agreement with what has been measured for Pd nanoparticles of similar sizes using other experimental techniques.

It should be noted that contributions to localized surface plasmon resonance (LSPR) shifts stemming from hydroxyl group formation in the SiO_2 spacer and/or from charge transfer from chemisorbed hydrogen to the Au nanodisks upon exposure of the sensors to hydrogen gas are negligible in the experiments presented here because the hydrogen partial pressure is never lower than 1 mbar when varied. This means that the hydrogen coverage on the Au surface (if present) and in the SiO_2 is saturated and thus does not give rise to a signal in the LSPR response of the sensor.

Conclusions

Nanoscale systems offer promising advantages for hydrogen storage but require characterization techniques with high sensitivity for the detec-

tion of the small amounts of hydrogen absorbed by these systems.

As illustrated in this application note, Insplorion's INPS platform enables quantitative studies of the particle size-dependent thermodynamics of hydrogen absorption and desorption in/from Pd nanoclusters.

References

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

More information about thermodynamics of hydride formation:

Y. Fukai, *The Metal-Hydrogen System*, Springer-Verlag: Berlin, 1993.

