**Indirect Nanoplasmonic Sensing for Nanomaterials Science**

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Nanosized systems (particles and films) are essential ingredients in many established or envisioned technological applications, including sensors, heterogeneous catalysts, photovoltaics, electronic and photonic devices, batteries and hydrogen storage systems. In many of these applications the nanosized systems are in contact with gaseous or liquid environments and desired (e.g. in catalysis) or undesired (e.g. corrosion) interactions between gas or liquid molecules and the nanosized system may occur. In this context it is of particular importance to develop experimental tools for fast, sensitive and reliable measurements of processes on/in nanosized systems under realistic, close-to-application, conditions. The latter often means working at high temperatures, at ambient or higher pressure and in harsh and corrosive environments. Furthermore, sometimes measurements would preferably be done on a single nanoparticle to avoid ensemble-averaging related effects.

Indirect Nanoplasmonic Sensing (INPS) *[1-3]* is a novel experimental technique fulfilling the above criteria (in analogy to “traditional” nanoplasmonics for biosensing applications *[4]*). The remarkably sensitive and very versatile INPS platform consists of plasmonic sensor nanoparticles (Au nanodisks or nanocones, prepared on a transparent substrate by Hole-Mask Colloidal Lithography *[5]*), covered by a thin dielectric film onto which the nanosized system to be studied is deposited (Figure 1). The key to the sensing is utilization of localized surface plasmon resonances (LSPR) in the Au sensor nanoparticles. The latter, via shifts in their extinction spectra, sensitively measure, for example, changes in the surface coverage of adsorbed reactant species (sensitivity <0.1 ML) on [1], or the formation of new phases in *[2,3]* the adjacent studied nanosystems on the spacer layer. These already demonstrated examples open a whole new field of *nanoplasmonic sensing for nanomaterials science* due to the generic nature of the INPS approach.

Here, we demonstrate how INPS, (i) in a simple optical transmission/reflection or (ii) dark-field scattering experiment, can be used to monitor and quantify size effects in metal hydride formation on the particle ensemble (i) and, for the first time, *single* particle level (ii) in Mg and Pd nanoparticles, ranging in size from 1 nm to 50 nm. The latter are ideal model systems to scrutinize how nano-sizing of the hydrogen storage entities influences phase diagram, thermodynamics and kinetics of nanoscopic metal hydrides. Furthermore, Mg is a very interesting system for commercial solid-state hydrogen storage due to its lightweight and low cost. The versatility of the INPS method in this context is illustrated with the following examples:

1) INPS measurements of activation energies for rate limiting steps during hydrogen sorption/ desorption in Pd nanoparticles (1-10 nm) illustrate, for the first time, the size dependence of the activation energy for hydrogen diffusion through nanosized Pd hydride and hydrogen desorption

from the nanosized Pd particles, respectively. These results are compared to the ab-initio DFT-based calculations for the respective systems.

2) Measurements of hydride formation thermodynamics and kinetics in Mg nanoparticles illustrate how complex INPS nanostructures (i.e. Au/Ti/Mg/Ti/Pd layered nanodisks) can be studied quantitatively in a convenient way and how nanosizing can be efficiently used to engineer storage thermodynamics and kinetics in storage systems relevant for applications.

3) Single particle dark-field scattering INPS experiments on the two above-described systems, i.e. studies of hydride formation in single Mg and Pd nanoparticles, illustrate the possibility to completely eliminate problems caused by inhomogeneous size-distributions and temperature or mass-transport gradients present in studies of ensembles of nanosized entities.

**References**


[1] E. M. Larsson, C. Langhammer, I. Zoric, B. Kasemo, Science, **326** (2009), 1091.
[2] C. Langhammer, E. M. Larsson, B. Kasemo, I. Zoric, Nano Letters, **10** (2010), 3529.
[3] C. Langhammer, V. P. Zhdanov, I. Zoric, B. Kasemo, Physical Review Letters, 104 (2010), 135502.
[4] J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, R. P. Van Duyne, Nature Materials, **7** (2008), 442.
[5] H. Fredriksson, Y. Alaverdyan, A. Dmitriev, C. Langhammer, D. S. Sutherland, M. Zaech, B. Kasemo, Advanced Materials **19** (2007), 4297.


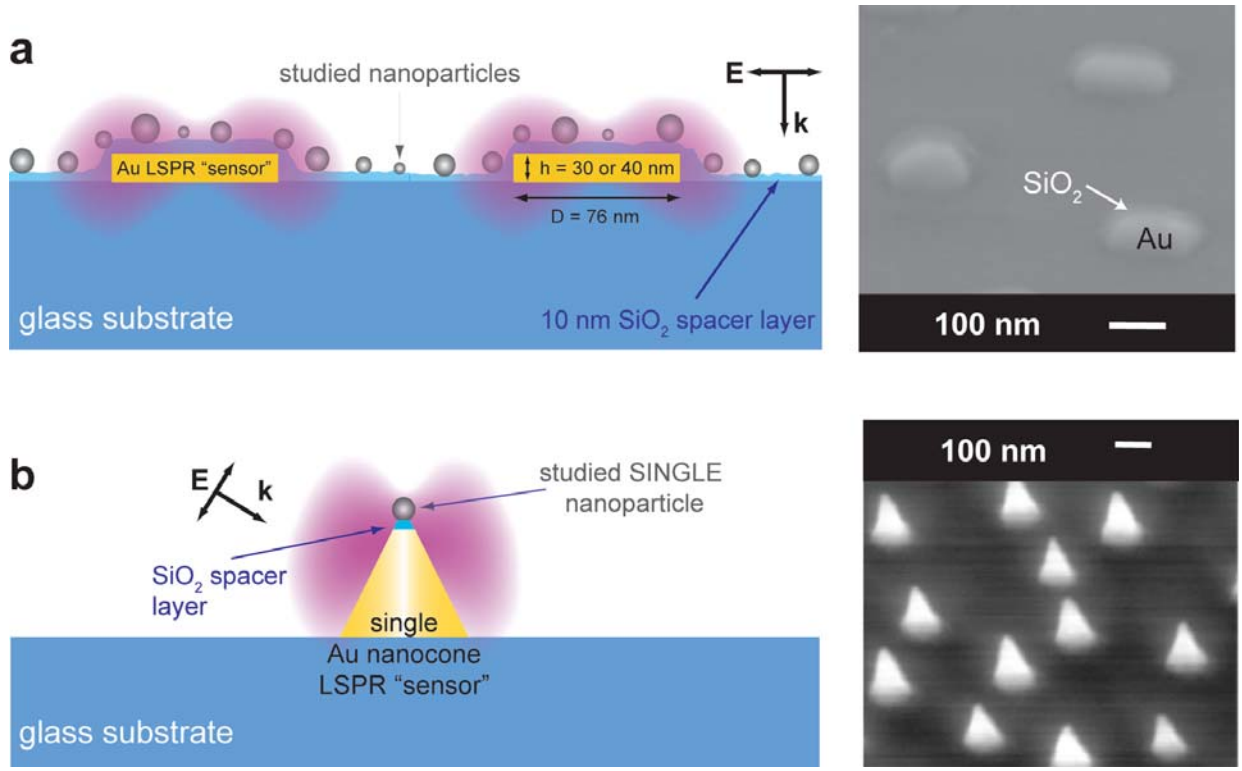


*Figure 1: Schematic depictions of (a) a standard INPS platform and (b) single-particle nanocones sensors. The SEM pictures to the right show the respective real nanostructures.*