Nanoplasmonics for Nanomaterials Science and Catalysis

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Nanosized systems (particles and films) are essential ingredients in many established or envisioned technological applications, including sensing, heterogeneous catalysis, 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 effects.

Indirect Nanoplasmonic Sensing (INPS) is a novel experimental technique fulfilling the above criteria *[1-3]*. The remarkably sensitive and very versatile INPS platform consists of plasmonic sensor nanoparticles (Au nanodisks or truncated nanocones, prepared on a transparent substrate), covered by a thin dielectric spacer layer onto which the nanosized system to be studied is deposited. The key to the sensing is utilization of localized surface plasmon resonances (LSPR) in the Au sensor nanoparticles. The spacer layer exerts the following functions:

- protection of the Au nanosensors from structural re-shaping;
- protection of the Au nanosensors from chemical interaction with the sample material;
- protection of the Au nanosensors from harsh/reactive environments;
- providing a tailored surface chemistry of the sensor chip, and thereby
- be either an inert substrate for the sample material, or
- participate actively in the studied process.

In this presentation I will give an overview of how INPS can be used to, via shifts in the sensor extinction or dark-field scattering spectra, sensitively measure numerous processes in/on nanomaterials and nanocatalysts.

For example, kinetic phase transitions in the H_2+O_2 and CO+O_2 reactions were followed in real time with INPS by probing 5-20 nm Pt *catalyst* particles *[1]*. In *[2]*, using Pd as catalyst, and exploring different particle sizes, it was possible to demonstrate size dependent catalytic activity by INPS optical nano-calorimetry.
The power of LSPR/INPS for *hydrogen storage* studies was demonstrated through work with H_2/Pd particle systems, exhibiting bulk properties for particles in the size range 10-300 nm (direct sensing using the LSPR in Pd nanoparticles *[4]*), and non-bulk behavior for particles < 10 nm. In the latter case we demonstrated particle size dependent thermodynamics and kinetics relying on INPS *[2,3]*. Furthermore, *single particle* dark-field scattering INPS experiments on 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 *[5]*.
Finally we show how INPS can be used to monitor *sintering* in real time and under realistic temperature and pressure conditions *in-situ*. We monitor the sintering of model catalysts, consisting of Pt clusters on SiO_2 and Al_2O_3 surfaces at atmospheric pressure. The use of INPS can be extended to industrially relevant catalyst structures and realistic catalyst working conditions *[6]*.

The demonstrated examples open up a whole new field of nanoplasmonic sensing for nanomaterials science and catalysis due to the generic nature of the INPS approach.

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[5] Manuscript submitted; [6] in preparation.