Optical and structural characterization of Fe-Ag clusters: monitoring the iron oxidation state through LSPR shifts

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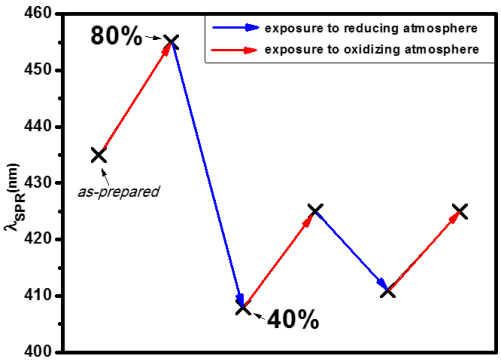

Figure 1: Plasmon energy shifts after exposure to various atmospheres. Percent values denote the reached limits of Fe oxidation state with respect to stoichiometric Fe_3O_4.

The structural and optical properties of small iron-silver clusters have been investigated by TEM and *in situ* plasmonic spectroscopy, respectively. The optical absorption spectra is dominated by a broad and strong surface plasmon resonance (SPR), the features of which are dependent on the sample aging and the surrounding medium. These clusters have been synthesized in a laser vaporization source and co-deposited in silica. According to both the bulk alloy phase diagram and their respective chemical and thermodynamic properties, silver and iron are expected to segregate at the nanoscale. Segregation is confirmed by the combination of HRTEM observations, optical measurements, and analytical (Mie theory) and numerical (FEM) calculations. Fe oxidation in ambient air leads to formation of an amorphous or partially crystallized magnetite (Fe_3O_4) shell surrounding a crystalline Ag core. Changes in the oxidation state of iron induced by the exposure of oxidizing (air, RT) or reducing (H_2+N_2 gas mixture, 200°C) atmospheres could be followed through plasmon shifts (figure 1). The latter were measured with a new *in situ* transmission spectroscopy setup, based on the highly sensitive Spatial Modulation Spectroscopy (SMS) technique.[1]

We have demonstrated that changes in the surface plasmon resonance of clusters provide information about the restructuring processes that occur when they are exposed to a reactive environment. Our approach could be extended to the investigation of catalytic processes. Moreover, segregated Ag-Fe clusters may be promising as a bifunctional system for magneto-optical devices.

1. P. Billaud et al., *Absolute optical extinction measurements of single nano-objects by spatial modulation spectroscopy using a white lamp*, Review of Scientific Instruments 81, 043101, 2010