Role of the environment on the quantum plasmonic resonances of sub-10 nm silver nanoparticles

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The optical properties of noble metal nanoparticles are dominated by the surface plasmons (SPs), which are collective oscillations of the free electrons confined at the surface. For sizes between ten nanometers to a few hundred, the plasmon resonance is very well described in purely classical models. On the other hand, a cluster of few tens of atoms behaves as a quantum system where new effects must be taken into account (electron spill-out, d-band transition screening and non-local effects). Nowadays the transition between the purely plasmonic regime and a quantum regime is of great interest [1] and several controversies have been found in the literature [2]. Furthermore, the immediate environment of the cluster (substrate, matrix, oxidation) can modify the energy position of the surface plasmon and its role on the quantum regime is not so clear at the moment.

Optical absorption techniques have been widely employed to study the optical properties of clusters. However in these techniques the measurements are made for a set of particles. This implies an inhomogeneous broadening of the surface plasmon resonance which largely prevents observing the influence of quantum phenomena. In this work we have approached this problem using the electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) in order to measure in parallel the optical and structural properties of individual nanoparticles with a high spatial and spectral resolution. In order to compare our STEM-EELS results, optical absorption experiments have been performed on the same system. Silver nanoparticles were fabricated by physical evaporation techniques (magnetron sputtering and laser evaporation). A quadrupole mass spectrometer was employed to size select the particles. Layers of silica, deposited by electron evaporation, are used in order to enclose the clusters and provide a homogeneous environment and protect them against oxidation as much as possible. The only difference between the samples studied experimentally is their thickness of <100 nm for STEM-EELS and ~ 1 µm for optical absorption.

The silver nanoparticles studied in STEM-EELS (from 1.7 to 9 nm diameter) showed very clear surface plasmon resonances as presented in figure 1 for 6.5 and 2 nm silver nanoparticles in silica. In a more detailed observation, the surface plasmon energy blue shifts with the increase of the electron dose as it is shown in figure 2. In the largest particles, the surface plasmon appears at around 2.7 eV, which corresponds to Ag/Ag_xO particles in silica. Then, the increase of electron dose removes the oxide and modifies the local environment of the particle and the plasmon blue shift until 3.3 eV. In the smaller particles (<5nm), the surface plasmon arrives to higher energies (~3.6 eV) with the increase of electron dose which shows the extreme sensitivity of the surface plasmon to the local environment on the quantum regime. The comparison of the STEM-EELS and optical results, as well as the use of a theoretical model which take into account classical and quantum effects, allowed us to find the compatibility of both techniques and understand the controversies found in literature.

References:

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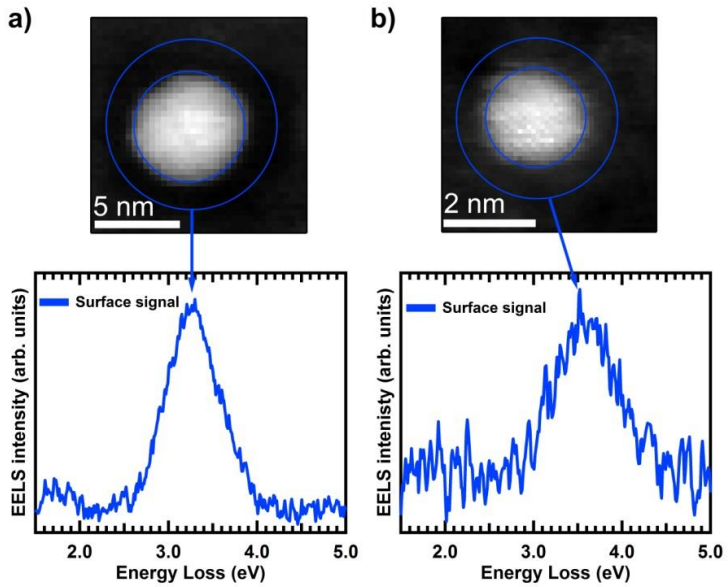

Figure 1. a) STEM-HAADF image of a 6.5 nm particle embedded in silica and the EEL spectrum associated to the surface **b)** STEM-HAADF image of a 2.0 nm particle embedded in silica and their EEL spectrum associated to the surface.

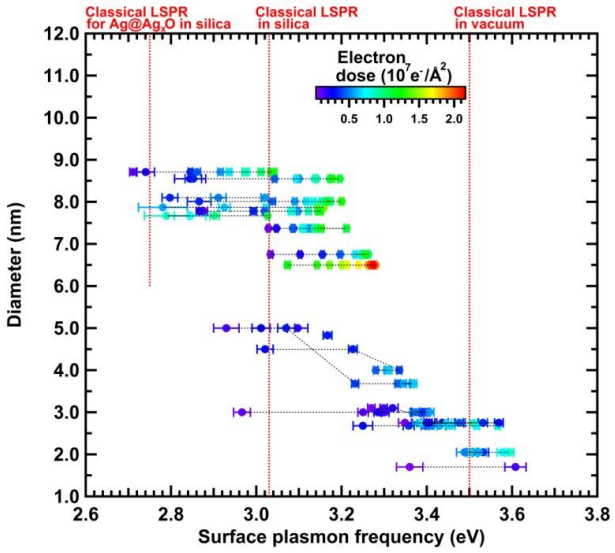

Figure 2. Evolution of the surface plasmon frequency of silica-embedded Ag particles as a function of electron dose, indicated in color code. The interaction with the high energy electron beam modifies the local environment and shifts the plasmon to higher energies, the values for each particle being connected by a black dotted line. At highest doses the size of some nanoparticles also decreases. The central and right vertical lines depict the classical (size-independent) values for the Mie plasmon of free and silica-embedded Ag nanoparticles in the quasi-static limit. Left vertical line has been obtained for core@shell Ag@AgxO nanoparticles at 75% oxidation ratio.