doi:10.1017/S1431927613004339
Microsc. Microanal. 19 (Suppl 2), 2013

In Situ Measurement of Localized Surface Plasmon Resonance of Metal Nanoparticles in different surrounding

Pin Ann Lin[1,2], Jonathan Winterstein[3], Henri Lezec[1], Renu Sharma[1]

[1.] Institute for Research in Electronics and Applied Physic, University of Maryland, College park, USA
[2.] Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, USA
[3.] FEI Co., Hillsboro, OR, USA

The high-field regions that occur at metal nanoparticle (NP) surfaces as a consequence of their localized surface plasmon resonances (LSPR), make them attractive for catalysis, optical, and waveguide applications as well as nanosensors. Optical spectroscopic methods, currently employed to measure the dependence of LSPR modes and intensity on metal nanoparticle size, shape and surrounding (support and gaseous environment), are limited to a spatial resolution of approximately 100 nm [1,2]. On the other hand, the LSPR of particles with various morphologies has been measured with nanometer resolution using electron energy-loss spectroscopy (EELS) with a monochromated electron source in the scanning transmission electron microscope (STEM) [3]. Such a detailed understanding of the effect of the local environment on LSPR is essential in order to optimize particle morphology and particle-support interactions for various applications [4]. We have employed an environmental scanning transmission electron microscope (ESTEM)) to combine high spatial with high energy resolution to measure the effect of support material and gaseous environment on particle LSPR.

Shape-controlled 20 nm Au NPs were synthesized by reducing Au precursor in the presence of surfactant, Cetyl trimethylammonium bromide and ascorbic acid. Au colloids were mixed with NPs of the support material with different dielectric constants (i.e. TiO_2, HfO_2) and loaded on lacy carbon TEM grids. All samples were plasma-cleaned to remove the residual surfactant on the Au NP surfaces. *In situ* STEM-EELS spectra were acquired using an ESTEM equipped with a monochromated, high-brightness electron source (X-FEG) with a 1 nm beam size and 100 meV energy resolution. LSPR from Au NPs of different shape on different substrates were first measured in vacuum. Then we introduced H_2 in the sample area at pressures from 10 Pa to 100 Pa. Both STEM-EELS spectra and high resolution TEM images were also acquired after the gas was introduced.

Figure 1 is a representative spectrum collected from Au on TiO_2 and Au on HfO_2. It is clear that only one plasmon mode at 2.4 eV (Figure 1a) can be excited for Au on TiO_2 (Figure 1b) while two different modes, 1.5 eV and 2.4 eV (Figure 1a), are excited for similar size and shaped Au NPs supported on HfO_2 (Figure 1c). Figure 2a shows the STEM dark-field image of a triangular Au NP on TiO_2 support. LSPR measured at two locations, the corner (b) and side (c), of the Au NP were observed to shift to lower energy when the H_2 pressure was increased up to 1 mbar (Figure 2b and c). However, the extent of energy shift at the corner (Figure 2b) was observed to be more than that at the side (Figure 2c) of the NP. Moreover, atomic resolution TEM images show that the surface structure changed after H_2 was introduced (Fig 3). Detailed discussion of the LSPR energies for different metal NP-support systems in vacuum and a variety of gases will be presented.

References:
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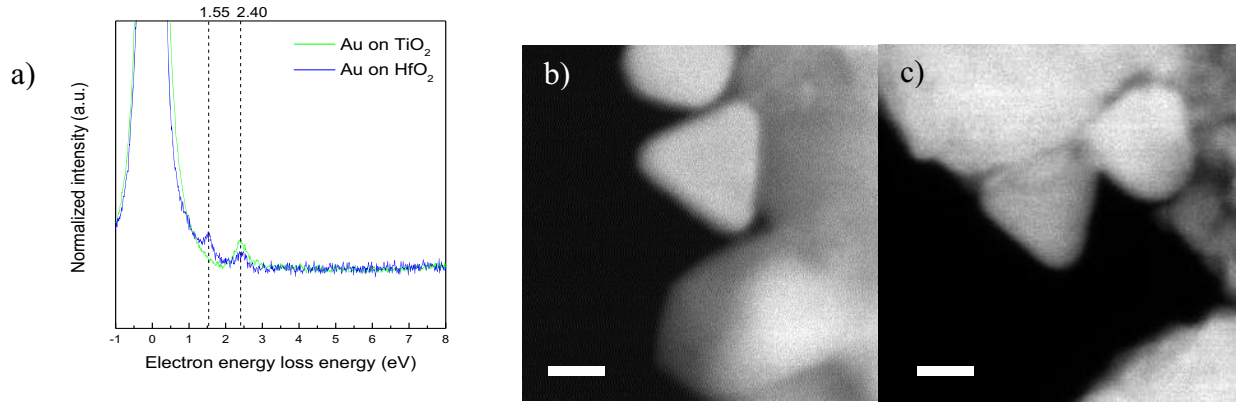

Fig 1. a) STEM-EELS spectra of shaped Au-NP on TiO_2 (green) and HfO_2 (blue). B) STEM image of Au on TiO_2 c) STEM image of Au on HfO_2. Intensity and position of two spectra are normalized using zero-loss peak. Scale bars are 20nm.

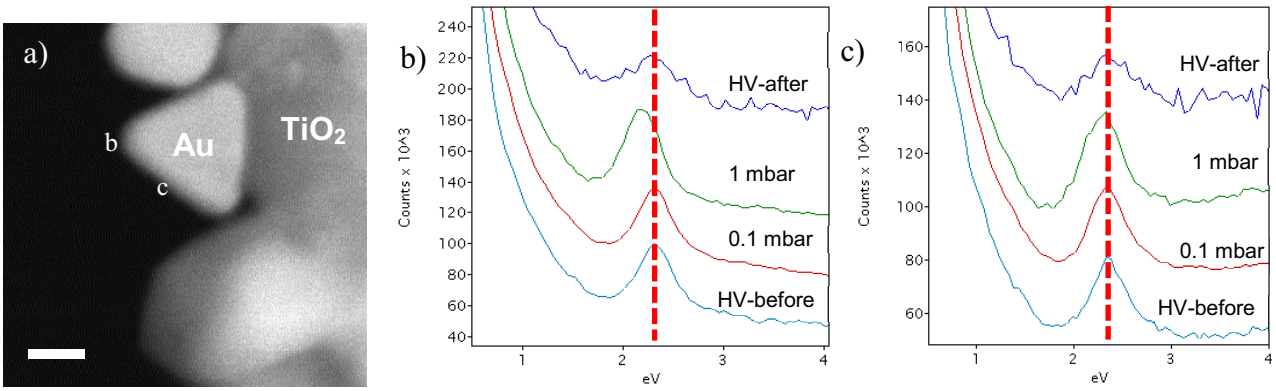

Fig 2. STEM image (a) and EELS spectra (b and c) for Au on TiO_2 substrate in high vacuum (HV), in 0.1 and in 1 mbar H_2, and after H_2 pumpint out H_2 (HV conditon). a) STEM image, scale bar is 20 nm. b) and c) EELS spectra aquired at location marked 'b' and 'c' in the STEM image. The intensities are are shifted arbitrarily and red-dot line aligned at the LSPR energy in HV condition before condition.

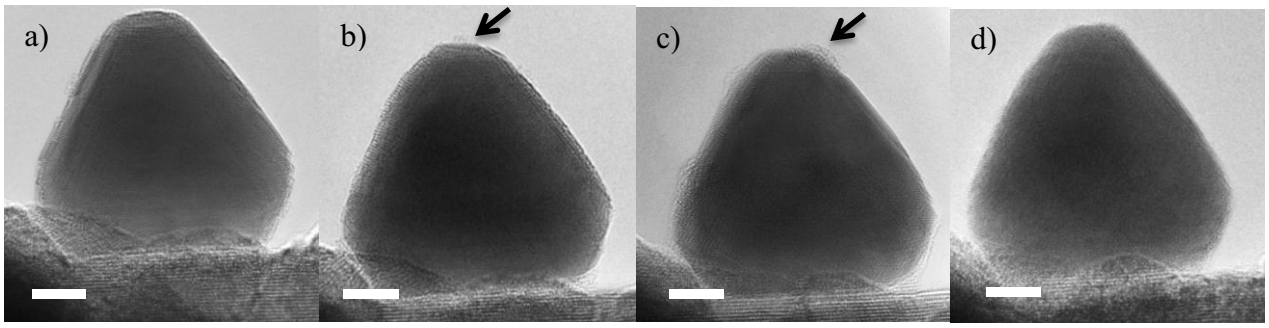

Fig3. High resolution TEM images of a triangular Au NP in (a) HV, before introducing H_2 (b) 0.1 mbar H_2 (b) 1 mbar H_2 (d) HV, after pumping out H_2. Note the surface structure change in H_2 (marked by arrows). Scale bars are 5 nm.

https://doi.org/10.1017/S1431927613004339 Published online by Cambridge University Press