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A Combined Experimental and Theoretical Approach to Measure Spatially Resolved Local Surface Plasmon Resonances in Aluminum Nanocrystals

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The optical properties of nanoscale systems are influenced by their ability to excite localized surface plasmons, which are collective oscillations of the free electron gas confined to the metal surface. This property has led to a variety of novel applications in fields such as plasmon-enhanced nanocatalysis [1], sensing of biological molecules [2] and surface enhanced detection techniques [3]. Surface plasmon enhanced nanocatalysis stands out as being a novel and promising field, where single and/or multicomponent nanostructures can lead to new and previously unexplored chemical activities. It has been shown that localized surface plasmon resonances (LSPR) can be used to produce 'hot-carriers' or photothermal heating to promote chemical reactions [4]. Among plasmonic materials, Aluminum stands out due to its affordability and capability to support ultraviolet (UV) plasmon resonances. Al is typically covered by a native Al_2O_3 layer. For Al nanoparticles with controlled shapes, it is not yet clear how the LSPR energies are influenced by the geometry of the nanoparticle as well as the coverage of the Al_2O_3 layer.

In this study, we employed a combined experimental and theoretical approach to characterize LSPR in icosahedral $Al_{core}(Al_2O_3)_{shell}$ nanoparticles [5]. Theoretically, we performed simulations of nanoparticle plasmons using Boundary Element Methods (BEM) where we consider the electron beam passing at a 2.5 nm distance from the surface of an icosahedron-shaped $Al_{core}(Al_2O_3)_{shell}$ nanoparticle. Our analysis emphasizes that the electron energy-loss probability spectra are characteristic of this complex nanoparticle shape, such that for the mode located around 7 eV, both the LSPR energy and intensity have lower values, when the beam is placed near a facet, edge or corner of the nanoparticle, respectively (Figures 1 (a)-(b)). However, different behavior is observed for other modes. These results are in good correlation with our experimental analysis where we collected electron energy-loss spectroscopy (EELS)-LSPR measurements near the surface of the $Al_{core}(Al_2O_3)_{shell}$ nanoparticles using a monochromated electron source with 100 meV energy resolution. Figure 2 (a) shows an experimental EELS map of an Al nanoparticle surrounded by a 4 nm thick oxide (Al_2O_3) layer. Similar to our simulation results, the experimental spectra shown in Figure 2 (b), appertaining to the edge and corner, display a distinct energy shift as a function of position of the electron beam excitation with respect to the nanoparticle. We applied machine-learning based algorithms such as Non-Negative Matrix Factorization (NMF) to de-couple convoluted LSPR signals of the icosahedron-shaped Al nanoparticles and subsequently attribute them to the geometry of the particle, as shown Figure 2 (c)). This allows us to map the coupling efficiency of the electron beam with the LSPR on the nanoparticles, revealing the energy transfer path from the excitation source to the plasmonic nanoparticles. This combined experimental and theoretical method allows a better understanding of the localization of LSPR in nanocatalysts with nano-engineered morphologies as well as a dielectric coating [6].

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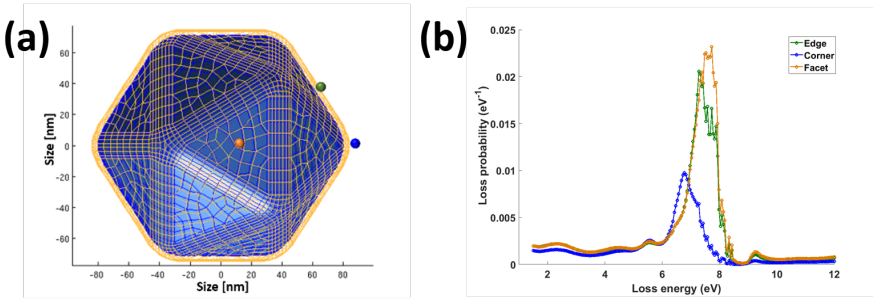

Figure 1. (a) Structural model for 160 nm diameter icosahedron-shaped Al_{core} $(Al_2O_3)_{shell}$ nanoparticle created for BEM-based simulations. The Al_{core} core is surrounded concentrically by 4 nm thick oxide layer; (b) EELS low loss probability spectra collected for a beam placed 2.5 nm away from the surface for edge (green), corner (blue) and facet (yellow) locations on the surface of the icosahedron shown in (a).

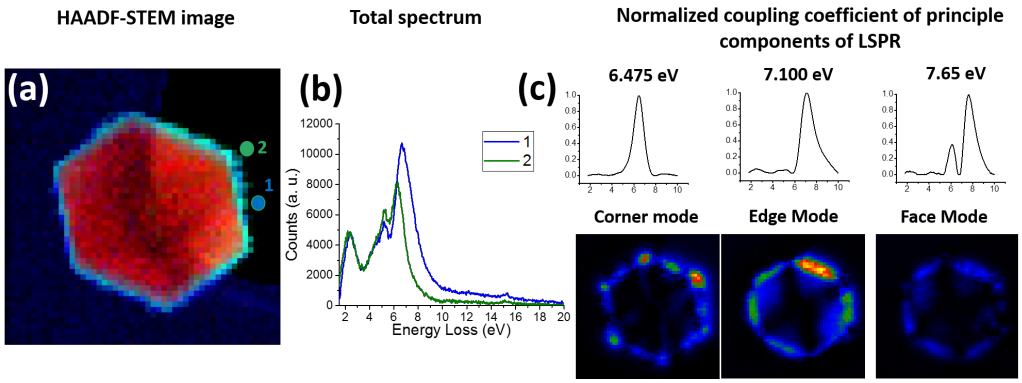

Figure 2. (a) Al (red) and O (blue) elemental map of an icosahedral shaped Al_{core} $(Al_2O_3)_{shell}$ nanoparticle. Marked with blue and green are the two EELS collection points from where the edge and corner spectra have been acquired; (b) Overlapped corner and edge spectra for the Al_{core} $(Al_2O_3)_{shell}$ nanoparticle shown in Figure 2 (a); (c) Normalized coupling efficiencies of principle components of LSPR and mapping of these components on the surface of the Al_{core} $(Al_2O_3)_{shell}$ nanoparticle.

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