638
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Electron Energy-Loss Spectroscopy for Designing Plasmonic Catalysts

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The energy barrier for most of the chemical reactions is overcome by heating the reactants in the presence of a suitable catalyst, where the thermal energy provided by heat helps in overcoming the reaction barrier that has been reduced by the adsorption of the reactant molecules on the catalyst nanoparticle surfaces. In recent years, localized surface plasmon (LSP) resonance energy has been used to replace the thermal energy to initiate reactions at low temperatures, even at room temperature, mimicking photocatalysis.[1,2] So far, optical methods have been used to excite different LSP modes with photons at specific wavelengths, and to measure the resonance energies. However, the low spatial resolution, of the order of 100 nm, achievable by near-field optical methods, does not provide sub-particle level distribution of coupling efficiency of various modes at different energies. On the other hand, high energy electrons not only excite all of the LSP modes simultaneously, but also provide high spatial resolution in the nanometer range to resolve the energy-loss probability, measured using electron energy-loss spectroscopy (EELS) that indicates the location-specific coupling efficiency for the electron excitation of the LSP modes at specific resonance energies on the plasmonic nanoparticle.[3] Moreover, core-loss EELS can be used to identify gas adsorption sites and solid reaction products. Here, we demonstrate that the knowledge gained from low-loss and core-loss EELS measurements can be used to design catalyst-plasmonic particle combination for selected chemical reactions.

We use a monochromated electron source in an environmental scanning-transmission electron microscope (ESTEM), combined with metal nanoparticle boundary element method (MNPBEM) [4] to characterize various LSP modes and their coupling efficiency distribution within the shape and size-controlled Al and Au nanoparticles. We first use the MNPBEM simulations to find the electron energy-loss probability, responsible for generating LSP resonance modes in Al nanoparticles. Figure 1a shows the model of a round Al nanoparticle with different oxide layer thickness for the simulation. Simulated electron energy-loss probability spectra from a 160 nm nanoparticle, without any oxide layer, show that the electron beam can excite multiple modes simultaneously (Figure 1b). While no change is observed in the peak positions or the intensity of the low energy modes (Figure 1c), a red shift and reduction in intensity is present for two high energy modes (approximately around 9 eV and 7.5 eV, respectively). On the other hand, some of the low energy modes do not show up as the particle size increases (Figure 1d and 1e), most probably due to the photon adsorption by large particles. However, the particle size has a pronounced effect on the dipole and quadruple mode energies.

We use commercially available Al nanoparticles and shape-controlled Au nanoprisms synthesized in our lab, to measure the coupling efficiency distribution of various LSP modes at sub-particle level. For plasmonic catalysis, there are three preliminary steps for a reaction to proceed: (1) adsorption of reactant molecules on the nanoparticle surfaces; (2) adequate LSP resonance energy to overcome the reaction barrier; and (3) desorption of product molecules. We use a combination of core-loss and low-loss EELS to observe the first two steps. Figure 2a shows an annular dark field (ADF) -STEM image of a typical ≈

160 nm Al nanoparticle. Elemental analysis of the particle shows a core-shell structure of Al-Al_2O_3, where crystalline and facetted Al core is enclosed in varying thickness of an oxide (Al_2O_3) shell (Figure 2b). Core-loss EELS map of H_2, collected after introducing ≈ 100 Pa of H_2 in the sample chamber, shows that it is mostly adsorbed in the amorphous Al_2O_3 shell around Al core (Figure 2c), indicating a possible pathway for room temperature H_2 dissociation by LSP resonance energies of Al nanoparticles. Low-loss spectra (Figure 2d) shows an energy shift (from ≈ 7.12 eV to ≈ 6.1 eV) and intensity drop for the high-order mode as a function of Al_2O_3 layer thickness in the spectra collected from points 1, 2, and 3 (marked in Figure 2b). Low-loss maps (Figure 1e and 1f), extracted using non-negative matrix factorization (NMF) algorithm, show the locations for high coupling efficiency of electron excitation to the LSP resonances at ≈ 5.47 eV and ≈ 7.12 eV on the particle, respectively. The methodology described above is also employed to study CO disproportionation and CO_2 reduction reactions.

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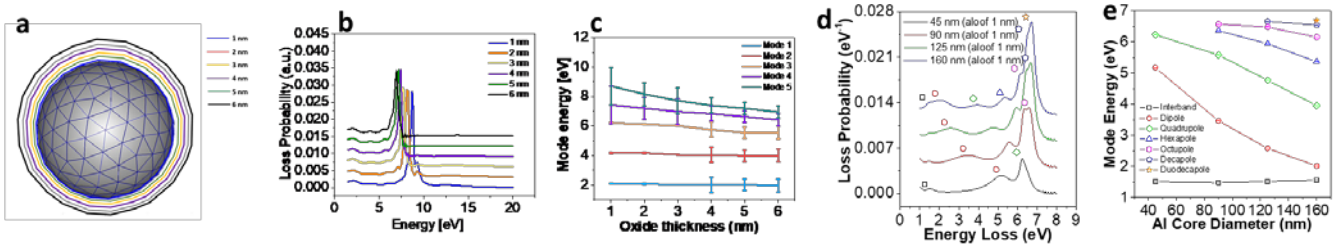

Figure 1. (a) Model of 160 nm Al nanoparticle with different oxide layers (color coded) used for MNPBEM simulations; (b) Loss probability spectra of Al nanoparticle without any oxide shell showing excitation of multiple modes; (c) LSP resonance energy of different modes as a function of oxide layer thickness. (d) Loss-probability spectra for different size of nanoparticles show the number of modes excited by electrons decreases with increasing particle size; (e) energy of different modes as a function of particle size.

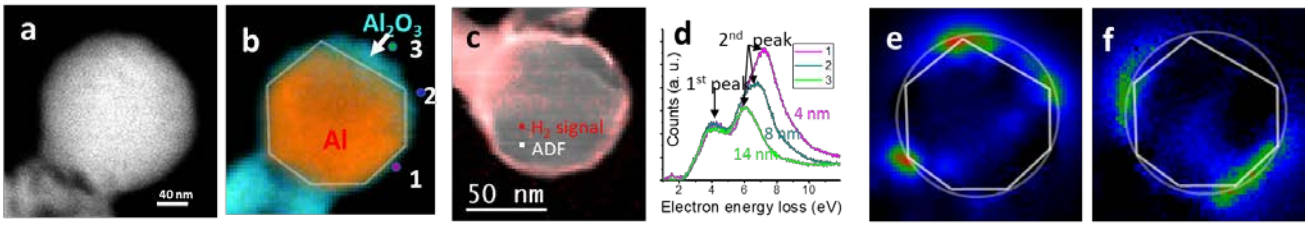

Figure 2. (a) Annular dark-field (ADF) image of an aluminum nanoparticle recorded using scanning transmission electron microscopy (STEM); (b) core-loss STEM-EELS map showing the core-shell (Al-Al_2O_3) structure of the particle. Note that the thickness of Al_2O_3 layer changes due to the facetted nature of the core; (c) H_2 core-loss map showing the distribution of H_2 adsorption in the oxide region; (d) LSP resonance peaks identified in the low-loss EEL spectra showing an energy shift and attenuation of intensity with increasing oxide thickness; (e-f) LSP resonance maps obtained using NMF showing the intensity (coupling efficiency) of electron excitation to LSP modes with resonance energies at 5.47 eV and 7.12 eV.

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