

In-situ Nanoscale Characterization of Catalytic Reactions Promoted by Localized Surface Plasmon Resonance Energy

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Surface plasmons are generated in certain metals such as Au, Ag, and Al due to the interaction of photons or electrons with the surface electrons. Recently, optical methods have been used to show that the decay process of surface plasmons can trigger various chemical reactions at low temperatures, demonstrating the potential of using plasmonic nanostructures to harvest and convert light into chemical energy. (1-2) Understanding the reactions promoted by localized surface plasmon resonance (LSPR) at the nanoscale is important for designing efficient photocatalytic systems for a wide range of energy and environmental applications. However, many important questions related to this type of reaction process remain unclear due to the complexity of the reaction kinetics, and lack of spatial resolution available with optical methods. Details of the reaction process such as the location of gas adsorption sites, how energy is being adsorbed and released, and how those details are correlated to the structure of the catalytical nanoparticles, remain elusive and are only hinted by theoretical calculations.

Here we combined an ensemble of data acquisition and processing techniques to characterize LSPR-promoted chemical reactions at high spatial resolution using an aberration-corrected environmental transmission electron microscope (ETEM) equipped with a monochromated electron source. In particular, we focus on the LSPR promoted dissociation of hydrogen using Al nanoparticles. Atomic-resolution movies and time-resolved electron energy-loss spectra (EELS) are acquired to monitor the crystallographic and chemical changes in the particle as well as LSPR locations and shifts during the reaction. Under gaseous environments we observe structural and oscillatory morphological changes in the Al nanoparticles. EELS imaging, with different energy dispersions, is used to acquire both elemental and LSPR maps from the same particle. These combined spectrum images show correlations between the LSPR profile and the morphology of different compounds in the nanoparticle. Machine learning algorithms, such as Non-negative matrix factorization (NMF), are used to decouple the entangled signals between different modes of the LSPR, which allows us to map the coupling coefficient of each mode on the nanoparticle. The comparison between the EELS maps of the particle, before and after H₂ is introduced in the environment, also show the effect of the gaseous environment on the LSPR generated on the nanoparticle surface locally. Gas adsorption maps show a predominant adsorption of H₂ on the Al₂O₃ shell, while the LSPR peak FWHM analysis reveals direct electron transfer as the LSPR decay pathway, leading to energy transfer from the LSPR to the adsorbed gas. This combined approach to decipher LSPR-promoted reactions provides time-resolved, atomic-scale information on the reaction kinetics. The results provide improved understanding of the dynamics of LSPR promoted reactions, and give insights into nanoparticle engineering for optimizing reaction efficiency. [3]

[1] Sil, Devika, et al. ACS Nano 8(8) (2014), 7755-7762.

[2] Zhou, Linan, et al. Nano Lett. 16(2) (2016), 1478-1484.

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