

Predicting Plasmonic Reactions on Faceted Metal Nanoparticles

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With limited natural resources and a growing global population, new materials that lower our energy consumption and its cost are increasingly critical to balance the growing demand for consumer goods and fuels with a sustainable earth. The energy of light-driven localized surface plasmon (LSP) resonances are an effective source of highly energetic electrons which could be harnessed to dramatically reduce the energy required to produce goods or fuels. Noble metal nanoparticle LSPs depend on the size, shape, composition, and environment,¹ making them useful in a range of applications including molecular-scale devices,² biological sensing,³ photovoltaics,⁴ and photocatalysis.^{5,6} By building quantum mechanical models of LSP energetics and reactions on the surfaces of faceted metal nanoparticles we will predict heterogeneous catalytic processes and identify candidate systems that can be used to diversify the production of raw materials and energy.

Recent reports of hot-electron-induced dissociation of small molecules, such as hydrogen, demonstrate the potential application of plasmonic nanostructures for harvesting light to split water,⁷ dissociate molecular hydrogen,^{8,9} isomerize molecules,^{10,11} and rearrange bonds.^{4,12,13} Theories have assumed that plasmonic catalysis is mediated by the energy transfer from nanoparticles to adsorbed molecules during the dephasing of localized surface plasmon (LSP) modes optically excited on plasmonic nanoparticles.^{14,15} However, LSP-induced chemical processes have not been resolved at a sub-nanoparticle scale to identify active sites responsible for the energy transfer. Here, by exploiting the Au LSP resonance, excited by electron beam, to drive CO disproportionation at room temperature. Using density functional theory to characterize the surfaces and reactivity, along with in situ electron energy-loss spectroscopy and electromagnetic boundary element method (BEM) calculations, we show that the active sites on Au nanoparticles are where preferred gas adsorption sites and locations of maximum LSP electric field amplitude (resonance antinodes) superimpose. Our findings provide an unprecedented insight in the plasmonic catalysis and will be valuable in designing plasmonic antennae for low-temperature catalytic processes.

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