Application of Electron-Beam-Excited Localized Surface Plasmon Resonance to Unveil Catalytically Active Sites on Au Nanoparticles

Wei-Chang D. Yang¹,², Canhui Wang¹,², Lisa A. Fredin³, Pin Ann Lin¹,², Lisa Shimomoto¹, Henri J. Lezec¹ and Renu Sharma¹*

¹ Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, USA.
² Maryland NanoCenter, University of Maryland, College Park, Maryland, USA.
³ Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, USA.
* Corresponding author: renu.sharma@nist.gov

Recent reports of gas dissociation, such as H₂ and O₂, mediated by optically-excited localized surface plasmon (LSP) resonances demonstrate the potential application of plasmonic nanostructures for harvesting light to initiate catalytic reactions [1, 2]. Theories have assumed that plasmonic catalysis is driven by the energy transferred from nanoparticles to adsorbed molecules during the dephasing of LSP modes [3]. However, LSP-induced chemical processes have not been resolved at a sub-nanoparticle scale to identify active sites responsible for the energy transfer.

Here, we exploit the LSP resonance, excited by electron beam, on shape-controlled Au nanoparticles on TiO₂ support to drive CO disproportionation: 2COₙ → CO₂ + C (s), at room temperature (commonly driven by thermal energy at 400 °C to 600 °C) in an environmental scanning transmission electron microscope (ESTEM), and the carbon product is used to identify the catalytically active sites on Au surfaces. The shape of Au nanoparticles was designed based on two principles. First, using density-functional theory (DFT) calculations, Au nanoparticles with a triangular bi-prism shape (Fig. 1a) are identified to provide varied CO adsorbing ability on individual facets. Second, electromagnetic boundary element method (BEM) calculations using MNPBEM [4] was used to predict the LSP modes that can be coupled with aloof electron beam positioned (Fig. 1b) at the sub-nanoparticle level. We find that the optimal beam position for exciting the dipole mode is at the cantilevered nanoprm corner (Fig. 1c), and the induced plasmonic electric field is located at the three corners with the maximum electric field amplitude outside the cantilevered corner when the electron beam is placed at P1 (Fig. 1d).

Au nanoparticles with a triangular bi-prism shape were synthesized and loaded on TiO₂ support in a cantilevered configuration as shown in the STEM annular dark field (ADF) image (Fig. 2a). High-resolution TEM (HRTEM) and nanobeam electron diffraction (NBED) were performed at a series of tilt angles to confirm that the facets on a Au nanoprm match with those used in DFT calculations (Fig 1a). In situ core-loss electron energy-loss spectroscopy (EELS) was used to observe CO adsorption on the Au surfaces. A stronger C K-edge was measured at the nanoprm edges (Spectrum 1, Fig. 2b) than the region without either Au or TiO₂ (Spectrum 2, Fig. 2b) in CO environment (P₃₀ = 110 Pa). The EELS map of C K-edge intensity integrated from 285 eV to 315 eV (Fig. 2c) shows areas (green and yellow, respectively) where the spectra are taken. After removing the spectral contribution of environmental CO from individual pixels in Fig. 2c, an adsorbed CO map is obtained and indicates that the preferable CO adsorption sites are located at selective edges (Fig. 2d). Low-loss EELS was used to investigate the excitation of LSP modes on the Au nanoprisms on TiO₂ support. The EELS spectra measured using aloof beam positions (Fig. 3a) agree well with the simulated loss probability. More importantly, the
EELS map from 1.8 eV to 3.8 eV confirms the prediction that the most efficient electron beam position for exciting the dipole mode is located at the nanoprisim corner and few nanometers beyond in the vacuum (Fig. 3b). In situ low-loss EELS spectra measured using electron beam position at P1 show an energy shift of LSP resonance in CO environment ($P_{CO} = 110$ Pa) that disappears after CO evacuation ($V_f$), indicating a change in electron density of the Au particle as CO is adsorbed and desorbed at the selective edges, respectively. Carbon deposits, detected by core-loss EELS (Fig. 3c) at the cantilevered corner edge after evacuating CO, were produced from room-temperature CO disproportionation mediated by the LSP resonance excited in CO environment ($P_{CO} = 100$ Pa) by either scanning the electron beam across the entire particle (Fig. 3d) or placing it at the optimal position P1 (Fig. 3e). This shows that the active sites on Au nanoprisms are where the preferable CO adsorption sites and the locations of maximum field amplitude (resonance antinodes) superimpose.

The findings of this work provide an unprecedented insight in the plasmonic catalysis and will be valuable in designing plasmonic antennae for low-temperature catalytic processes.

References: