

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

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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: $2\text{CO}_{(g)} \rightarrow \text{CO}_{2(g)} + \text{C}_{(s)}$, 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 a loof 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 nanoprism 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 nanoprism 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 nanoprism edges (Spectrum 1, Fig. 2b) than the region without either Au or TiO₂ (Spectrum 2, Fig. 2b) in CO environment (P_{CO} = 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 a loof 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 nanoprism 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:

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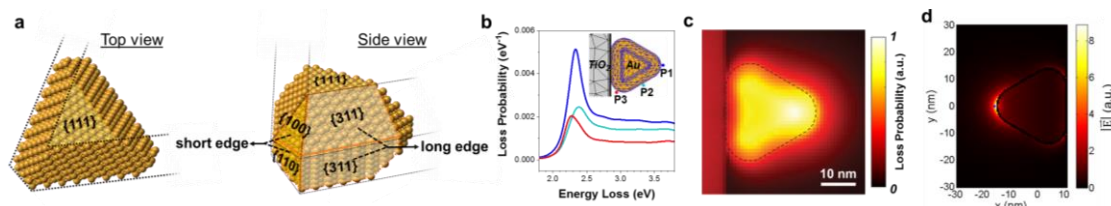


Figure 1. **a**, Crystal model of a Au nanoprism bound by facets used in DFT calculations. **b**, Simulated electron energy-loss probability by placing electron beam at P1, P2 and P3. **c**, Simulated loss probability map from 1.8 eV to 3.8 eV. **d**, Simulated plasmonic electric field with electron beam placed at P1.

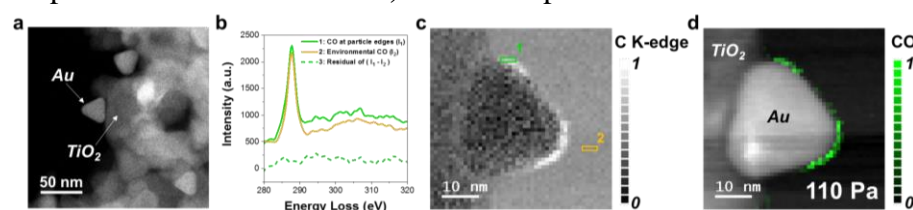


Figure 2. **a**, STEM-ADF image of Au nanoprisms on TiO_2 support. **b**, EELS spectra measured from areas 1 and 2 indicated in **c**, as well as the difference between them. **c**, EELS map of C K-edge (285 eV to 315 eV) in CO environment ($P_{CO} = 110$ Pa). **d**, EELS map of adsorbed CO.

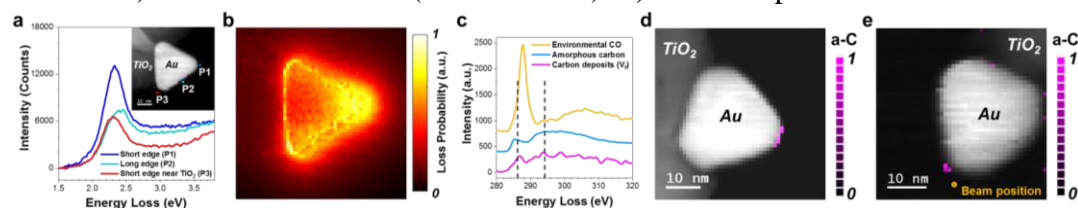


Figure 3. **a**, EELS spectra measured at P1, P2, and P3. **b**, EELS map from 1.8 eV to 3.8 eV. **c**, C K-edge comparison of CO, amorphous carbon and the carbon deposit. **d-e**, Carbon distributions after CO evacuation (V_f) resulting from scanning electron beam (**d**) and fixed electron beam at P1 (**e**) in CO.