

## Measuring Gas Adsorption on Individual Facets of a Nanoparticle by a Surface Plasmon Nanoprobe

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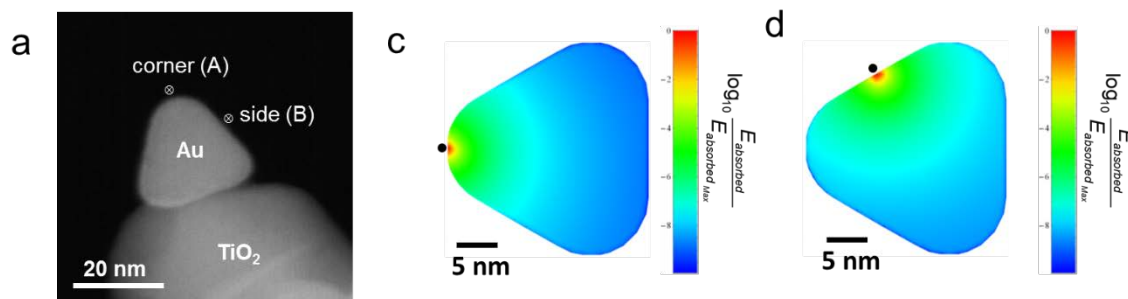
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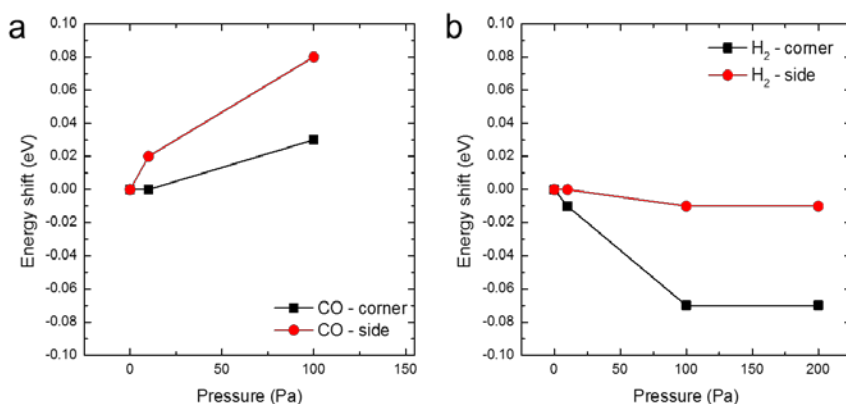
Gas adsorption on metal nanoparticles is a fundamental step that controls a number of gas-solid reaction processes, important in applications ranging from catalysis to gas sensing. Gas adsorption depends on the nature of the gas molecules and atomic arrangement of the surface facets. These factors control the gas binding energies, which have not, so far, been directly measured. Here we show that electron-density changes, induced by gas adsorption on the active metal nanoparticle facet, cause shifts in surface plasmon (SP) energies that can be measured by electron energy loss spectroscopy (EELS). We employ a 1 nm-diameter electron beam from a monochromated 80kV electron source to locally (< 2 nm) excite SPs and measure their energies with 100 meV energy resolution. This high spatial and energy resolution allows us to resolve SP energy shifts in the range of a few meV, localized to individual nanoparticle facets. Using this technique in an environmental scanning transmission electron microscope (STEM), we are able to map *in situ* SP responses on different facets (i.e. corners and sides) of individual Au nanoparticles in vacuum, CO, and H<sub>2</sub> at various gas pressures. Our results were further confirmed by finite-difference-time-domain (FDTD) simulations for the spatial localization of the electron beam excited SP nanoprobe.

Figure 1a shows the STEM dark-field image of a triangular Au nanoparticle on a TiO<sub>2</sub> support and the local SP excitation at the corner location A and side location B. Energy loss maps in the Au nanoparticle, obtained by FDTD simulations, reveal the highly-localized excitation volumes near the edge of the particle in both locations (Fig. 1b and c). SP-EELS spectra at both locations were collected in vacuum, and over a range of gas pressures. In the CO environment, the SP energy was observed to shift to higher energies and the magnitude of the energy shift was larger when probing location B than location A. (Fig. 2a). In contrast, in the H<sub>2</sub> environment, the SP energy shifted to lower energies and the magnitude of the energy shift was larger when probing location A than location B. To confirm that energy shifts measured with such localized excitation are sensitive only to the electron density variations of the probed location, two models of electron density variations in a 1 nm skin depth at the corner and the side, respectively, were applied in our FDTD simulations. When the electron density varies at the corner, the SP energy varies only for probing location A (Fig.3a) but not when probing location B (Fig.3b). Similarly a variation in the electron density at the side yielded energy shifts in location B (Fig.3c), whereas no changes in location A (Fig. 3d).

Therefore, we can conclude that the difference in magnitudes of gas-induced SP energy shifts reports a local phenomenon, and indicates crystallographically-specific absorption of the different gases on the Au nanoparticle facets. A detailed discussion of the SP energies measured for different facet-gas interactions and quantitative measurements of binding energies and number density of molecules adsorbed for different gases on various facets of Au nanoparticles will be presented.



**Figure 1.** (a) STEM image, scale bar is 20 nm. Simulated energy-loss intensity maps, normalized at the maximum adsorbed intensity in log scale represents the SP excitation intensity throughout a nanoparticle via a 1 nm beam (mark as a black dot) excitation at (b) the corner and (c) the side.



**Figure 2.** Measured SP energy shifts as a function of gas pressure of (a) CO and (b) H<sub>2</sub> when probing at corner location A and side location B.

**Figure 3.** Nanoparticle models with surface charge density change in either (a,b) at the corner or (c,d) the side regions. Rainbow plots below each models are corresponding simulated spectra as a function of fractional surface charge density changes, where the most intense dark red represents the energy loss peak position of the sampled area of the nanoparticle.

