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Electron energy-loss spectroscopy for direct visualization of gas adsorption sites

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Over the last two decades, environmental scanning-transmission electron microscope (ESTEM) has become a method of choice for measuring and understanding atomic scale mechanisms of heterogenous catalytic reactions. The adsorption of reactant molecules on selective metal catalyst surfaces is the first step of fundamental importance at it indicates catalytically active sites. Although the gas molecules do not cause strong electron scattering to generate enough contrast for imaging, surface modulation of the Au nanoparticles due to CO adsorption has been reported an indirect method to identify gas adsorption sites [1]. Recently, water adsorption on reconstructed TiO_2 surfaces has also been reported [2]. Here, we show an alternative method using the core-loss electron energy-loss maps to directly visualize the gas adsorption locations.

We employ an ESTEM equipped with a monochromated high brightness field-emission gun (X-FEG) with 0.08 eV energy resolution, dual-EELS, operated at 80 keV for acquiring STEM-EELS maps. Spectrum images acquired in gaseous environments are a three-dimensional data cube that includes energy-loss information in the Z direction at each pixel of a STEM-ADF image. Environmental contribution of the gaseous component was extracted from a square area where only relevant gas is present in the original STEM-EELS map. The rescaled image is subtracted from the original STEM-EELS map to obtain the adsorption of the gas molecules. Background subtraction method depends on the complexity of the energy-loss region. For example, a multiple linear least square fit using reference spectra was employed for the H K-edge while a power-law fit was used for C k-edge.

In order to discern the active sites for a room temperature CO disproportionation reaction by Au localized surface plasmon resonance (LSPR), we have successfully applied this procedure to identify the location of CO adsorption on shape-controlled Au nanoprisms (Figure 1a-c) in various gas pressures using C K-edge maps [3]. Interestingly, the C K-edge intensities (marked green) were located on the edges, where two crystallographic planes meet, instead of the surface as revealed by a series of images at varying tilted angles (Figure 1a-c). Furthermore, we used the same method to obtain H_2 adsorption maps on Al nanoparticles (Figure 1 d-f), surrounded by a shell of Al_2O_3, to probe H_2 dissociations assisted by Al LSPR, which have been reported at room temperature in the literature [4]. The presence of H K-edge (13 eV, Figure 1e, red line) in the low-loss region complicates the extraction of its contribution as the Al bulk plasmon peak and other spectral features associate with Al_2O_3 are also present in the same region. Therefore, the multiple linear least square fitting was used to extract the H_2 adsorption map (Figure 1f) where H_2 adsorption was found to be limited to the amorphous Al_2O_3 shell surround the Al core. A detailed discussion of the procedure will be further evaluated using other examples, such as CO_2 adsorption on graphite, oxygen adsorption of boron nitride nanotubes.

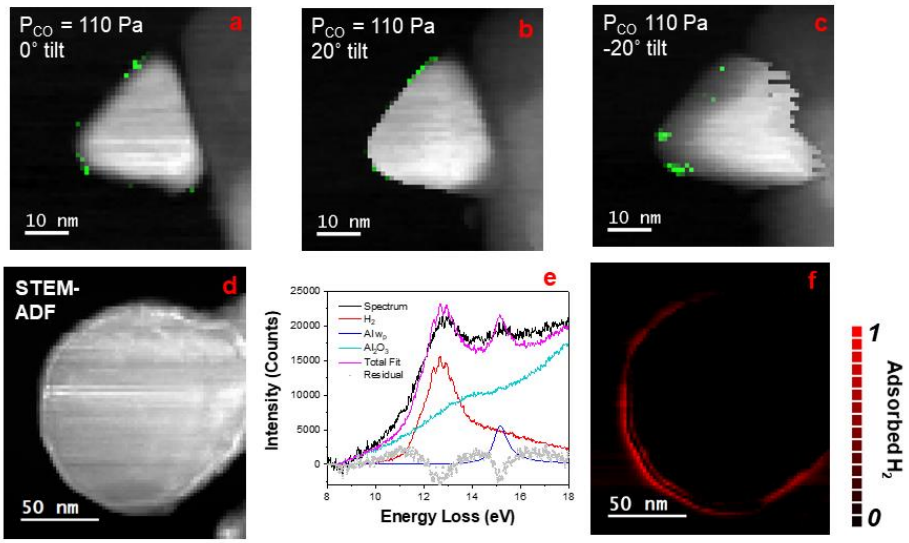

Figure 1. Figure 1 (a-c) Carbon maps (green), acquired by tilting the particle by ±20º and after removing the environmental contribution of CO from the images, showing the CO absorption on specific edges of an Au nanoprism (see reference 2 for details). (d) An ADF image of an Al nanoparticle in 100 Pa of H2 (e) EELS spectra showing the contributions from H2, Al (metal), Al2O3 obtained after multiple linear least square fitting, (f) H2 map showing the H2 adsorption is confined to the Al2O3 shell.

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