

In situ Scanning Transmission Electron Microscopy with Atomic Resolution under Atmospheric Pressures

Pan, X.¹, Dai, S.¹, Zhang, S.¹ and Graham, G.¹

¹ University of California Irvine, United States

In situ transmission electron microscopy (TEM) under gaseous environment has attracted attention not only for basic scientific research but also for important industrial applications of materials and catalysts. Although differential pumped environmental TEM (ETEM) is a well-established platform to investigate the dynamic gas-solid interaction, some constraints still exist at the current stage: (1) The maximum gas pressure allowed in ETEM is no more than 1/100 of the atmospheric pressure, which is not favorable for building a bridge between the *in situ* results and real applications; (2) It is difficult to obtain atomic-resolution high angle annular dark-field (HAADF) images in scanning transmission electron microscopy (STEM) mode since no probe corrector is available in commercialized ETEMs while normal annular dark field (ADF) imaging is limited to the low-angle regime due to the post-specimen differential pumping apertures. Recently, it has become possible to overcome these limitations through the use of a MEMS-based, electron-transparent windowed gas cell. Using this instrumentation, the gaseous environment is normally sealed between two silicon nitride windows, reaching the pressure of 760 Torr (1.0 atm) under static gas conditions or with low flow rates. The gas cell holder can be safely inserted in any state of art TEMs without any modification to the column and vacuum system, thus removing the limitation of HAADF-STEM imaging encountered in differentially pumped ETEMs. In this talk, we illustrate the advantages of the windowed gas cell as applied to our *in situ* study of two important systems: (1) CO-induced Pt nanoparticle surface reconstruction at saturation coverage (2) Facet-dependent oxidation of Pt₃Co fuel cell catalysts.

It is well-known that different geometric configurations of surface atoms on supported metal nanoparticles have different catalytic reactivity and that the adsorption of reactive species can cause reconstruction of metal surfaces. Thus, characterizing metallic surface structures under reaction conditions at atomic scale is critical for understanding reactivity. Here, we observed the truncated octahedron shape adopted by bare Pt nanoparticles undergoes a reversible, facet-specific reconstruction due to CO adsorption, where flat (100) facets roughen into vicinal stepped high Miller index facets, while flat (111) facets remain intact (Fig. 1). It is noticeable that high partial pressure of CO (> 20 Torr) allowed in the gas cell, ensuring the saturation CO coverage, triggered the surface reconstruction of Pt nanoparticles.

By taking advantage of the Z-contrast STEM imaging, we studied of surface composition and the dynamics involved in facet-dependent oxidation of equilibrium-shaped Pt₃Co fuel cell catalysts in an initially disordered state. Using our *in situ* gas cell technique, evolution of the surface of the Pt₃Co nanoparticles was monitored at the atomic scale during their exposure to an oxygen atmosphere at elevated temperature, and it was found that Co segregation and oxidation take place on {111} surfaces but not on {100} surfaces. These results may prove useful for a better understanding of the catalyst durability and possible further attempts at surface engineering of Pt-metal fuel cell catalysts.

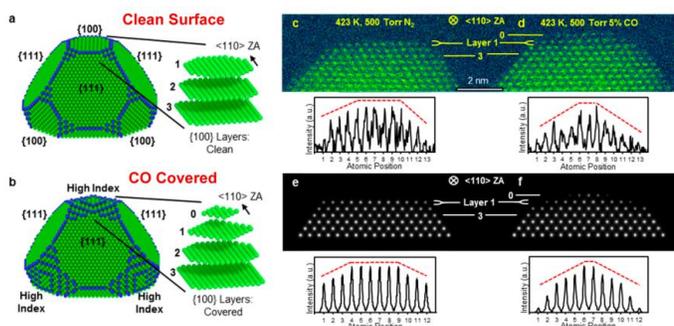


Figure 1. Visual comparison of DFT-calculated (a-b) and *in situ* STEM measurements (c-f) of facet-specific CO-induced Pt nanoparticle surface reconstruction. Intensity analysis of layer 1 was presented.