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Electron Imaging of Interfacial Oxygen by Aberration Corrected TEM: Possibilities and Scientific Opportunities

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Imaging light atoms requires optimization of electron optics, detector configuration and electron acceleration voltages. Here we report progress in imaging oxygen atoms at the interface between gold nanocrystals (Au NCs) grown on rutile TiO_2. Au NCs on rutile TiO_2 surfaces have attracted considerable interest for their remarkable size-dependent catalytic activities, especially for catalyzing the oxidation of carbon monoxide [1]. Several mechanisms have been proposed to explain such surprising chemical activities and almost all of them involve interactions at the Au NCs and support interface [2], which renders the study of interfacial structure tremendously important. Thus it is essential to use advanced characterization technique to determine the atomistic registry in the interface. While high-angle scattering of electrons (Z-contrast) in scanning transmission electron microscopy (STEM) with aberration correction (AC) can characterize interfacial cations with atomic resolution, oxygen atoms are difficult to detect due to its low value of the nuclear charge Z. The chromatic aberration corrector equipped on ACAT (Argonne Chromatic Aberration-corrected TEM) located in Argonne National Lab improves information transfer and image resolution; the flexibility of adjusting individual aberration coefficients with C_c corrector also allows precise control of contrast transfer function and greater contrast between heavy and light atoms, which helps to enhance the sensitivity to light elements for thin samples using phase contrast. This technique provides a new way to image oxygen atoms at atomic resolution, even in instances where the oxygen atoms are situated a short distance away from strong scattering heavy atoms like gold and titanium.

To enable high resolution C_c-corrected TEM investigation of NC interfaces, we have developed a novel NC synthesis technique for preparing Au NCs on vicinal rutile (TiO_2) surfaces. Au nanoparticles about 2~5 nm in diameters, were first deposited onto the single crystal TiO_2 substrate, pre-thinned and annealed in air, by e-beam evaporation deposition at room temperature. Then the sample was annealed in air at 500°C to form epitaxial Au NCs. The same annealing procedure is used for the activation of Au catalyst. Benefiting from the high signal and noise ratio and absence of scan distortion in high resolution TEM, we have detected oxygen atoms and measured their positions with high accuracy, while we used STEM to obtain positions of cations by HAADF imaging. We characterized different surface structures prior to deposition and the interface after deposition. Oxygen terminated TiO_2 (110) surface has been observed after ion-milling and before deposition; and at the interface the oxygen structure is also observed in details, as shown in the figure. By comparing these results, the effect of surface and interfacial oxygen has been addressed and so has been the influence of Au NCs on surface reconstruction of TiO_2, which provided a large impact on our understanding of the atomistic mechanism of catalytic activities. The results will be presented and discussed in the context of gaining better understanding about interfacial effect in real catalysts.

In addition, we carried out aberration corrected annular bright field (AC-ABF) STEM imaging and compared the images with the HREM images. Explorations of the optimum imaging condition for surface and interface oxygen atoms on HREM with help of electron optical and dynamic simulation programs and reconstruction of exit wave were also performed and will be discussed as well [4].

References:

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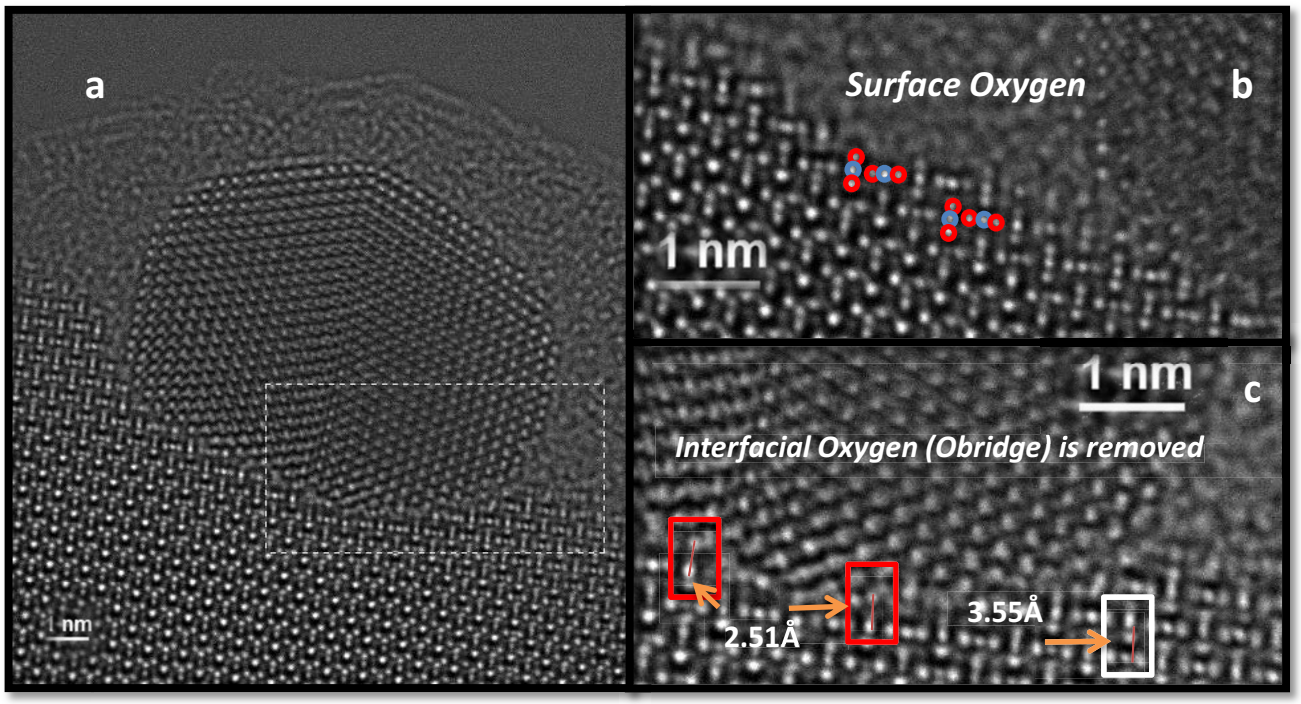

HREM images of gold NC on TiO_2 (110) surface from aberration corrected TEM at Argonne National Lab. Figure a) shows a gold NC located on TiO_2 surface steps. All gold, titanium and oxygen atoms are resolved. Figure b) shows the bridge oxygen on TiO_2 surface. The blue circles here indicate the titanium atoms and red circles for oxygen atoms. Figure c) is a magnified image of the area indicated by the box in figure a). The interfacial atoms are resolved. The red boxes show where the interfacial oxygen is reduces. In TiO_2 lattice marked by the white box, the distance between two nearest titanium atoms is measured to be 3.55 Å, while in the interface the distances between nearest gold atoms and titanium atoms are approximately 2.51 Å, which confirms that there are no oxygen sites in between.

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