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Direct Observation of Interfacial Au atoms Using STEM Depth Sectioning

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Interfacial atoms located between metal nanoparticles and supports are proposed active sites in catalysis, because of their distinct physical and chemical properties [1-3]. However, the atomistic details are difficult to resolve in the interface; the lack of knowledge has been a major obstacle toward unraveling their roles in chemical transformations. Here we report the detection of interfacial Au atoms on the rutile (TiO_2) (110) surfaces thanks to the improved spatial resolution and depth of focus brought by aberration corrected scanning transmission electron microscopy (STEM).

Au on TiO_2 is selected because it shows remarkable catalytic activity as the sizes of Au particles reduce to ~3 nm or below, for the oxidation of CO. The Au catalysts are typically prepared by Au precipitation on titania support, followed by calcination in air or reduction under H_2 at elevated temperatures. Extensive study has been done concerning the mechanism of CO oxidation catalyzed by gold and the role of interfacial gold atoms. However, direct observation of interfacial Au atoms has not been reported before. A major obstacle is the TiO_2 support surface, which is often highly complex, undetermined and varies at the nanometer scale. With atomic resolution images recorded at different focuses along TiO_2 [001], we have reconstructed the 3D intensity profiles of interfacial atoms. The results lend to direct support to the presence of interfacial Au atoms, embedded in a single interfacial layer.

The experiment started with forming epitaxial Au nanocrystals (NCs) on rutile (110) by e-beam evaporation deposition followed by annealing in air. The sizes of the Au NCs ranged from 3.5 to 12 nm in width depending upon the annealing conditions. The samples are observed by aberration corrected (AC) scanning transmission electron microscopy (STEM) using the JEOL 2200FS installed at the Center for Microscopy and Microanalysis, Frederick Seitz Materials Research Laboratory, at 200kV. The microscope is capable of resolving atoms separated by 1 Å. Figure 1 shows a Z-contrast image recorded along TiO_2 [001] direction. Au atoms are brighter then Ti atoms due to its larger Z. An atomic model of Au nanocrystal on TiO_2 [110] surface is shown in the inset, with Ti atoms in grey, O atoms in red and Au in yellow. The arrow indicates a distinct interfacial layer between Au NCs and the TiO_2 (110) surface, with Au atoms embedded inside the layer.

To locate the interfacial Au atoms in 3D, a focal series of Z-contrast images were recorded first from the Au nanocrystal near the interfacial region shown in Figure 1. The images were aligned using the cross-correlation method. The intensity profiles in the interface layers were then used to form the depth-sectioning images shown in Figure 2, for the Au, TiO and interfacial layers respectively. The intensity bands were marked using the color boxes to identify the column as a Au-column, Ti-column or an interfacial-column. Notably, at the interface, the depth-sectioning image shows intermediate intensities between these of Ti- and Au-columns. Furthermore, there are intensity variations along the focus direction in the interfacial layer. For example, the column marked as *A* in Figure 2 resembles the intensity of Au columns observed in the Au layer, while the columns marked as *T* have similar intensities as that of Ti columns in the Ti layer. Regions marked as *I* show distinct

intensity peaks that are very different from either the TiO or Au layers. Detailed interactions between Au NCs and the TiO_2 support are thus revealed from these results.

References:

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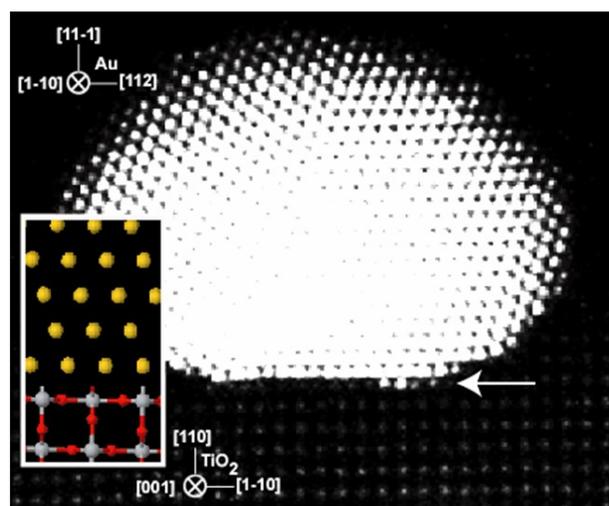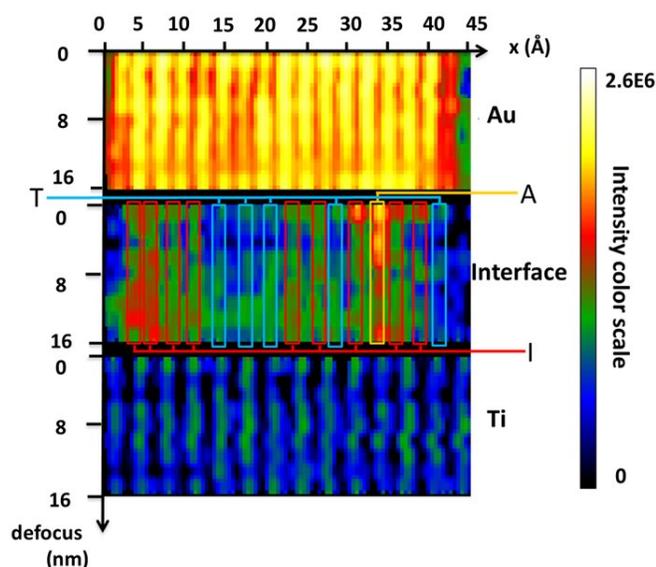
Figure 1   Figure 2

Figure 1, a Z-contrast image recorded along TiO_2 [001] direction. Au atoms are brighter then Ti atoms due to its larger Z. An atomic model of Au nanocrystal on TiO_2 [110] surface is shown in the inset, with Ti atoms in grey, O atoms in red and Au in yellow. A distinct interfacial layer is observed and indicated by the arrow.

Figure 2, the focal series of Z-contrast images recorded from the Au nanocrystal near the interfacial region shown in Figure 1. The images were aligned using the cross-correlation method. These intensity profiles were then used to form the depth-sectioning images shown in Figure 2, for the Au, TiO and interfacial layers respectively. The intensity bands were marked using the color boxes to identify the column as an Au-column, Ti-column or an interfacial-column.