doi: 10.1017/S1431927609097451
Microsc Microanal 15(Suppl 2), 2009


# Atomic Resolution STEM and EELS Studies of Interfaces of Model Gold-Titanium Dioxide (Au-$TiO_2$) Catalysts

S. Sivaramakrishnan*,**, J. G. Wen**, B. Pierce*,**, M. Scarpelli*,** and J. M. Zuo*,**

* Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, 1304, West Green Street, Urbana, IL 61801
** Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana-Champaign, 104, South Goodwin Avenue, Urbana, IL 61801

A good part of the multi-billion dollar catalyst industry relies on the chemistry at the surfaces and interfaces of metallic nanoclusters supported on oxide substrates. Model systems consist of metal nanoclusters supported on well defined facets of oxide substrates. The interfaces of nanoclusters play a definitive role in determining the chemistry of these systems [1-2]. Charge transfer and band bending are two common phenomena that have been observed at nanocluster interfaces using spectroscopic tools like X-Ray Photoelectron Spectroscopy (XPS), Extended X-Ray Absorption Fine Structure (EXAFS) (for reviews see [1],[2]). These tools rely on data collected from a number of clusters and therefore average out 'nano-scopic' phenomena. Weak effects at the interfaces of small clusters get buried in the signal from bigger clusters. In order to advance the science of nanoclusters, the atomic structure and electronic structure of their interfaces have to be probed in isolation.

In this work, we show results from gold nanoclusters supported on titanium dioxide, a well-known model catalyst [3] whose ability to catalyze the conversion of carbon monoxide to carbon dioxide has drawn the interest of multiple research groups and has been the subject of heated discussion for the mechanism behind the reaction. We have therefore selected this model system for atomic level characterization by probing the local charge transfer and band shifts at interface of epitaxial Au nanoclusters on $TiO_2$(110). We have developed a method to grow model nanoclusters (including epitaxial nanocrystals) repetitively on the same planes of a substrate that is suitable for electron microscopy. This technique of making suitable TEM samples combined with the advent of aberration corrected microscopy [5] has now given us a toolset that can be exploited to address the needs of interface characterization of model catalysts.

Figure 1(A) shows an Aberration-Corrected Scanning Transmission Electron Microscope (STEM) image of an epitaxial Au nanocluster on $TiO_2$ (110) taken in a JEOL 2200-FS microscope fitted with a CEOS corrector on the probe-forming side operating at 200kV. The cluster is in the Au [112] zone axis which is the most common epitaxial variety. The advantage of preparing epitaxial nanocrystals for interfacial analysis is that data from different clusters is free from effects of varying interfacial atomic configurations. Figure 1(B) shows typical areas chosen for EELS line scans. Figure 2 shows atomic resolution Electron Energy Loss Spectra (EELS) (A) above the nanocluster and (B) at the nanocluster (including the Au/$TiO_2$ interface). Each plot has three curves, one each from the interfacial/surface layer, one layer below the interface/surface and the bulk of the $TiO_2$ (for reference). The free $TiO_2$ surface is seen to have a dominant Ti (3+) species. Subtle band shifts (<1eV; indicated by arrows) are observed at the

nanoclusters' interface. By measuring the integrated area under the curve, charge transfer from the substrate to the nanocluster at the Au/$TiO_2$ interface could be quantitatively measured.

References

[1] Q. Fu and T. Wagner, Surf. Sci. Rep. 62 (11) (2007) 431.
[2] M. W. Finnis, J Phys.-Cond. Matt. 8 (32) (1996) 5811.
[3] M. Haruta, Cat. Today 36 (1) (1997) 153.
[4] M. Haider et al., Nature, 392 (6678) (1998) 768.
[5] Work supported by NSF DMR 0449790. The electron microscopy was partially supported by the US DOE under grant DEFG02-91-ER45439.

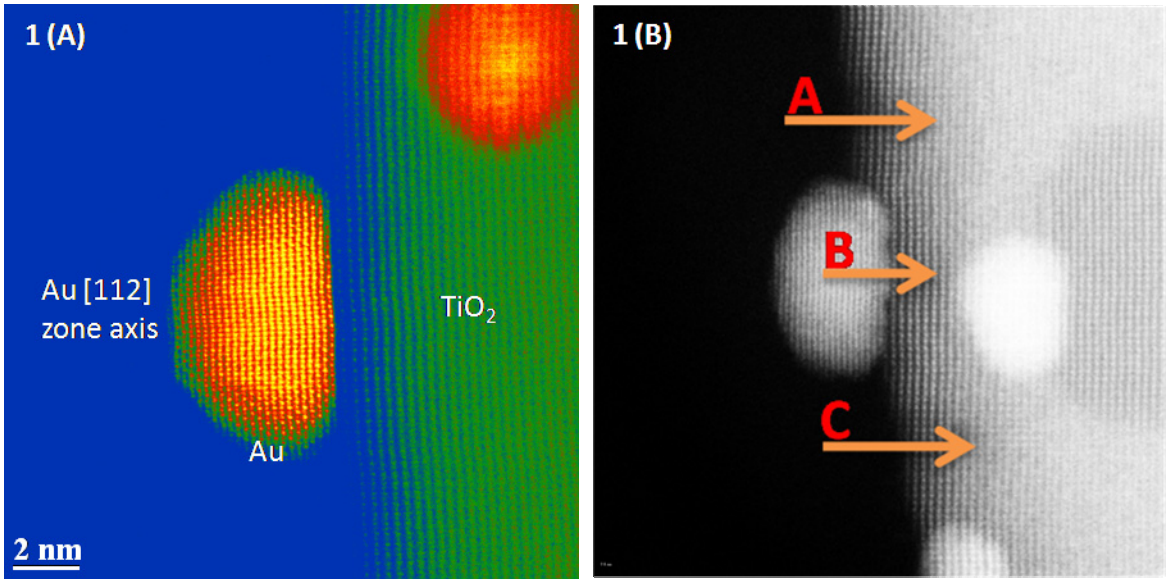


Fig. 1. (A) Aberration-corrected STEM image of epitaxial Au nanocluster supported on $TiO_2$ (110) and (B) Typical areas chosen for EELS line scans.

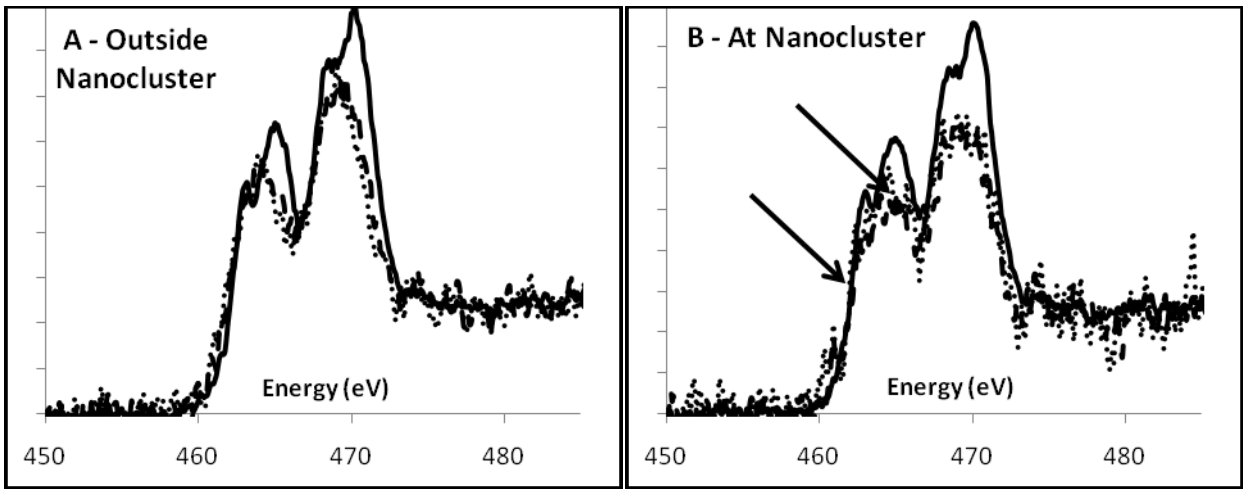


Fig. 2. EELS from the surface/interfacial layer (dotted line), one layer below the surface/interfacial layer (dashed line) and $TiO_2$ bulk (solid line) (A) outside and (B) at the Au nanocluster.

https://doi.org/10.1017/S1431927609097451 Published online by Cambridge University Press