Gold Nanoparticles on TiO$_2$ (110): Exploring the Imaging Capabilities of Aberration Corrected Scanning Transmission Electron Microscopes through Simulation

S.D. Findlay$^1$, N. Shibata$^{1,2}$, Y. Ikuhara$^{1,3}$

$^1$Institute of Engineering Innovation, The University of Tokyo, Tokyo, 116-0013, Japan
$^2$PRESTO, Japan Science and Technology Agency, Saitama, 332-0012, Japan
$^3$Nanostructures Research Laboratory, Japan Fine Ceramic Center, Nagoya, 456-8587, Japan

The Z-contrast nature of high angle annular dark field (HAADF) imaging in scanning transmission electron microscopy (STEM) makes it well suited to identifying heavy atoms in and on relatively light surrounds. This is particularly useful for imaging nanoparticle catalysts on supporting specimens. For example, Nellist and Pennycook used this approach to image trimer and dimer configurations of Pt on the surface of $\gamma$-alumina [1], providing insights later used to explain the catalytic properties of this system [2]. The development of spherical aberration correctors [3] has since brought STEM to the point where HAADF imaging of single atoms both on and within material samples is possible. One catalyst system of particular interest is that of nanoparticle gold. Gold nanoparticles on metal oxide supports prove to be active catalysts for a variety of chemical reactions, and their catalytic activity depends strongly on the nanoparticle size and on its interaction with the support [4]. HAADF STEM imaging was recently applied to small gold nanoparticles on TiO$_2$ (110) to show directly that, for sufficiently small nanoparticles, the gold atoms preferentially attach to specific sites [5], as seen in Fig. 1.

We discuss a range of HAADF STEM simulations carried out to explore the conditions which maximize the visibility of the gold nanoparticles relative to the moderately strongly scattering TiO$_2$ substrate. Fig. 2 shows some explorations of the visibility of a single gold atom atop either the TiO$_2$ column or a pure O column as a function of probe-aperture size. Substrate thickness was also considered, as evident in Fig. 2B. Detector size was found to have very little effect on the visibility of a single gold atom on the surface, provided the inner angle was large enough that little elastic scattering contributed directly to the HAADF image. We also note that the larger the thermal vibration of the atoms in the nanoparticle, the less visible it will be relative to the substrate, an effect which becomes more pronounced with increasingly fine probes. As the vibrational properties of the nanoparticles are generally not known in advance, a range of plausible values is explored to assess this effect. Depth sectioning was found unlikely to provide useful information about the three-dimensional structure of such small nanoparticles. One alternative is to use a quantitative analysis of the HAADF intensity to assess the number of gold atoms present. The simulation presented in Fig. 3 supports the principle of this approach.

References

FIG. 1. A typical HAADF STEM image of gold nanoparticles deposited on a TiO$_2$ (110) surface. The conformation of the smaller nanoparticles to the substrate lattice is evident.

![Image of HAADF STEM image of gold nanoparticles on TiO$_2$ (110) surface.]

FIG. 2. A. Simulated ADF signal from various columns in the case of a single gold atom on the surface of TiO$_2$ (110). The 200 keV probe is aberration-free, the crystal thickness is 97 Å and the ADF detector spans the range 70–196 mrad. B. The ratio of the signals from a single Au atom on the TiO$_2$ column to that of the TiO$_2$ column alone.

![Graph showing simulated ADF signals and ratios for various column thicknesses (32 Å, 97 Å, 162 Å).]

FIG. 3. Line scan across a fictitious structure where one, two and three gold atoms respectively are placed atop three TiO$_2$ columns. The monotonic trend with the number of atoms is clear, suggesting a well-quantified experiment would be able to assess the number of gold atoms present. The 200 keV aberration-free probe is taken to have a 23 mrad probe-forming semi-angle, the substrate to be 32 Å thick and the HAADF detector to span the range 81-228 mrad.