Applications of STEM and EELS to Nanoscience

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Nanotechnology is one of the most important areas of modern science, which already affects many aspects of everyday life, from semiconductors to sensors and catalysts, and is set to produce ever more new and exciting developments. The electron microscope has long represented one of the best ways to obtain information on the composition or electronic configuration of nanoscale structures, materials, or technology. The fundamental problems with the conventional transmission electron microscope (TEM) are: that the images can be difficult or even impossible to interpret for unknown or complicated structures; the limited resolution due to the lens aberrations; and that the images are 2-d projections of 3-d structures; all of which hinder the accurate identification and analysis of nanostructured materials.

The scanning transmission electron microscope (STEM), shown in fig. 1, addresses some of these problems. Collecting the electrons scattered to high angles on a high-angle annular dark field detector provides the Z-contrast imaging mode. This is called Z-contrast because, to a good approximation, the image is a projection of the structure with the bright spots representing atoms and an intensity depending on the square of the atomic number, Z. Thus interpretation of the images is far simpler than for a conventional TEM [1].

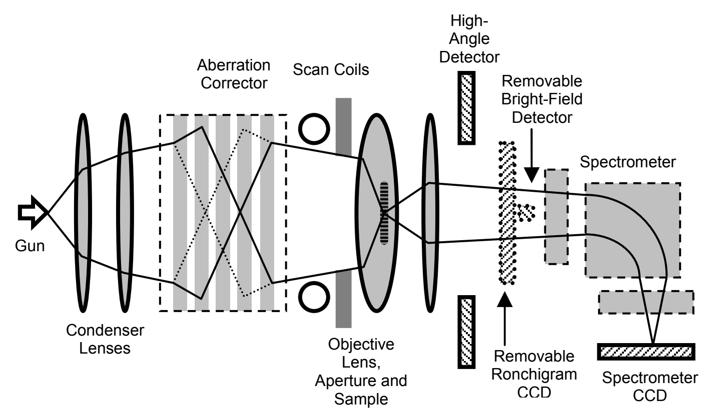

Figure 1. Simplified schematic showing the important components of an aberration corrected STEM, fitted with a variety of detectors and an EEL spectrometer.

Aberration correction is perhaps the most exciting advance happening in the field of electron microscopy at the moment. The resolution of an electron microscope is normally limited by the aberrations (imperfections) of the lenses. An aberration corrector, as shown in fig. 1, is a device which introduces negative aberrations to cancel the unavoidable, positive aberrations of the electron lenses. This results both in an improved resolution [2] (fig. 2) and a greatly increased sensitivity for single atom detection [3].

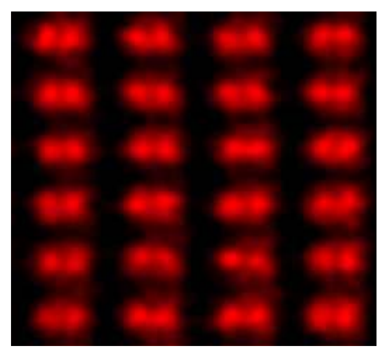

Figure 2. Z-contrast image showing Si viewed down the [112] axis. Bright spots are the atomic column locations. The 0.8 Å [444] (dumbbell) spacing is resolved.

Catalysis, despite its importance to the modern world, is in many cases still not well understood. Gold is a remarkable catalyst, because in bulk form, or as large particles, it is not catalytically active. Yet when present as nano-sized particles on an oxide support, it becomes one of the most active catalysts for oxidation of CO. It is clear that something important happens at the nanoscale. Using an aberration corrected Z-contrast STEM, we obtained images as shown in Fig. 3. These showed that the active gold particles are 1-2 nm in diameter and quantifying the thicknesses in comparison to image simulations revealed that they are mostly 1-2 layers thick, agreeing well with previous work on model systems. Having an accurate idea of the active form of the gold catalyst then allowed us for the first time to calculate their properties, which revealed that the nanoparticles are capable of bonding both CO and O_2, thereby allowing the high catalytic activity [4].

Perhaps the most significant advantage of the STEM over a TEM is that it is possible to obtain electron energy loss spectra (EELS) at the same time as the Z-contrast image. EELS has been shown to allow detection of single atoms even within the bulk of a sample [5], and can be obtained at atomic resolution [6], and can measure important properties such as the distribution of charges in a mixed valence material at an atomic level. Delocalization arises due to two main causes: as the probe propagates through the sample it spreads out; and the non-local nature of the ionization interaction. Full dynamical calculations are showing how this second factor is less important than was sometimes previously believed. In one exciting development, Varela et al. [5] used the beam spreading to estimate the depth of a single dopant atom in a semiconductor, detected by EELS, by comparing the integrated intensity recorded on different columns (fig. 4). This demonstrates the unique ability of EELS in a STEM to obtain spectra from individual nanostructures, even inside a matrix.

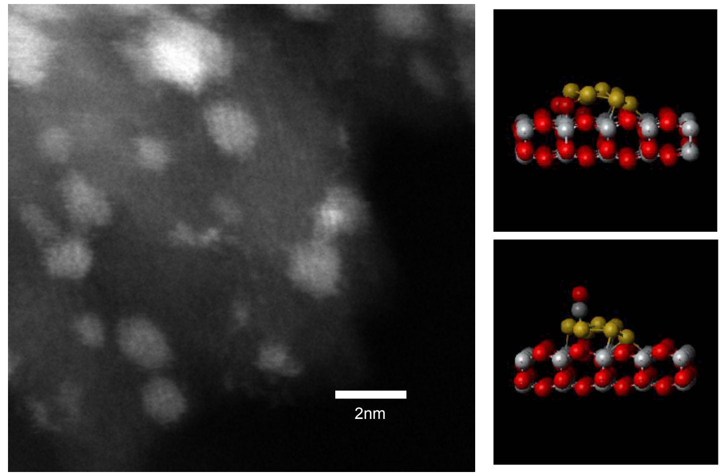

Figure 3. (Left) Z-contrast images of a gold (bright spots) on titania catalyst. The particles are mostly 1-2 nm across, and 1-2 layers thick. (Right) First principles calculations used to calculate the properties of the observed particles shows that they are capable of bonding both CO (top) and O_2 (bottom).

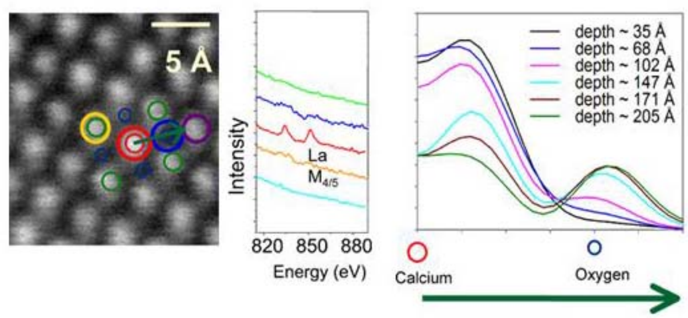

Figure 4. EEL spectra obtained from individual columns of a $CaTiO_3$ crystal. The red spectrum reveals the presence of a single La atom within the calcium column circled in red. The signal is substantially reduced at neighboring columns (blue and yellow). (Right) Dynamical simulation of the La EELS intensity along the green arrow. The ratio of signals on adjacent columns indicates the depth of the atom in the crystal. This atom is approximately 100 Å below the surface.

One often neglected feature of aberration correction is that the enlarged aperture used to obtain the improved resolution also results in a smaller depth of field. This means that under the right conditions, an electron microscope moves from the regime in which it provides a 2-d projection of the real structure to one in which it allows true 3-dimensional analysis [7]. This technique has the potential to revolutionize electron microscopy in the same way as confocal microscopy has revolutionized optical microscopy.

Thus, we have shown how the aberration corrected STEM represents a truly unique way to obtain information on both the structural and electronic configuration on a wide variety of materials with atomic resolution and sensitivity to single atoms.

References

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