Aberration corrected STEM analysis of Nanowires

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Analysis of nanomaterials, such as nanowires, is a task that is ideally suited to electron microscopy because of the ability to perform high-resolution analysis of individual nanostructures. Furthermore, it is possible to image and obtain spectroscopic information from different locations on each nano-object of interest.

However, the resolution of all transmission electron microscopes is determined by the aberrations of the objective lens. In 1936, Scherzer proved that the spherical and chromatic aberrations of conventional round lenses will always be greater than zero and thereby limit the resolution of the microscope [1]. Thus the recent success in aberration correction is probably the most exciting development to have occurred in the field of electron microscopy for the last few decades. By using non-round lenses, it is possible to eliminate the spherical aberration of the objective lens and obtain a greatly improved resolution [2,3].

Scanning transmission electron microscopy (STEM) has particularly benefited from this achievement because of the availability of the Z-contrast imaging mode. Z-contrast imaging is so called because the intensity in the image is approximately proportional to the thickness of the sample and the square of the atomic number. This allows far easier interpretation of the images than for conventional TEM, facilitating the identification and characterization of unexpected or even unknown structures [4]. This allows a variety of new materials to be examined with unprecedented resolution [5] and even single atom sensitivity [4, 6, 7].

The other key benefit of STEM is that a wide variety of signals can be recorded simultaneously with the Z-contrast image. A schematic of a STEM is shown in fig. 1. A small electron probe that can have a diameter smaller than 1 Å [5] is formed on the sample and scanned in order to generate the image, with signals recorded as a function of probe position. Z-contrast, bright-field imaging and convergent beam electron diffraction can be used to analyze the structure at atomic resolution. At the same time, it is possible to collect other signals, such as X-rays, light emission and electron energy loss spectra (EELS). EELS provides a convenient way to probe both the electronic and chemical structure on an atomic scale. Recently single atoms have been detected in EELS [7]. Cathodoluminescence combined with Z-contrast imaging allows the light emitting properties to be correlated with individual nano-objects (fig. 2).

Nanowires have a variety of exciting applications in nanoscale electronics and photonics. Furthermore, embedding quantum structures in a nanowire is likely to enable exciting new properties to be exploited [8]. However, a detailed understanding of the macroscopic physical properties of such systems relies on their analysis at the atomic scale. Fig 2 shows some low resolution pictures of zinc oxide nanorods and the simultaneously acquired intensity of light emitted. This initial examination raises several important questions:

Firstly not all of the nanorods were bright. Although not all or the emitted photons were collected, the different emission properties are most likely due to different characteristics of the rods. Quantitative analysis of the composition and comparison of the defects and impurities present in different rods will illuminate this interesting problem.

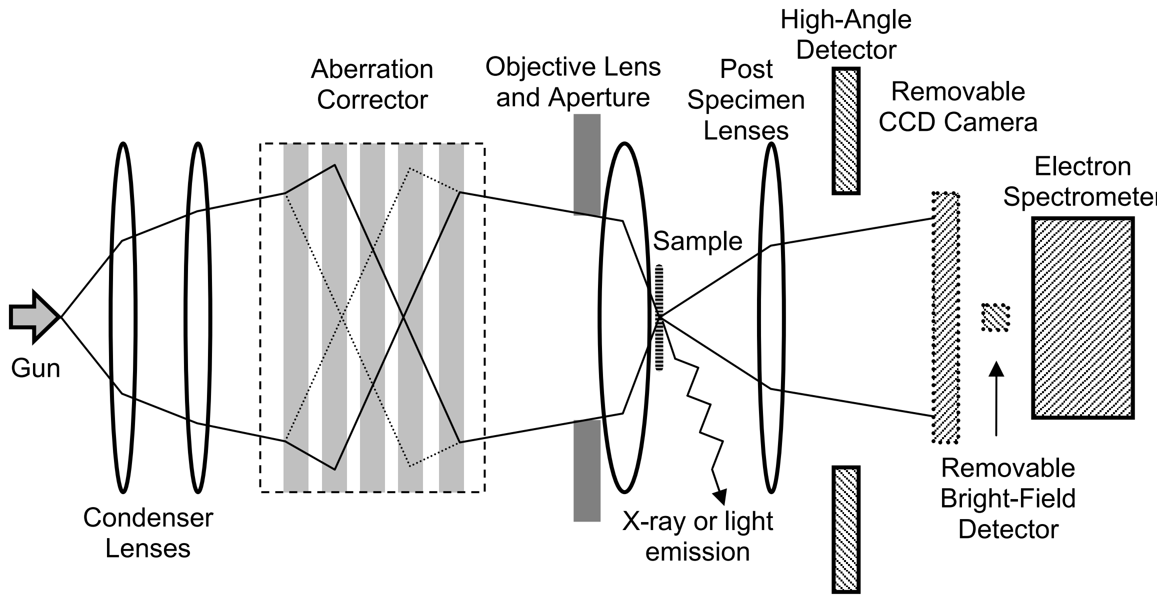

Figure 1. Simplified schematic of an aberration corrected STEM. The aberration correction and probe-forming optics are before the sample. After the beam interacts with the sample, the transmitted electrons and other generated signals can be recorded on a variety of detectors.

One of the problems of analyzing any sort of 3-dimensional nanostructure is that the image obtained in an electron microscope is approximately a 2-dimensional projection of the structure. One consequence of aberration correction is that the depth of focus is reduced. This also occurs in conventional light optics: As the aperture size is increased, the depth of focus decreases with the square of the aperture angle. In a present aberration corrected STEM, the depth resolution is of the order of a few nm. In future machines, the depth resolution should approach 1 nm. van Benthem et al [6] have shown that in some cases, this can allow the location of single atoms in 3 dimensions. When applied to bundles of nanorods or nanowires, such as those shown in fig. 2, this technique will help correlate the emitted signal with particular nanowires.

One dimensional nanostructures are potentially ideal for nanometer scale electronic or structural components [8 and references therein]. Constructing quantum components inside nanowires will enable novel physical properties to be exploited. Future work will include optical spectroscopic analysis of individual nanotubes to probe such exciting areas as quantum confinement [8] and provide a deeper understanding of the structure-properties relationships of these exciting materials.

Nanotechnology is an area that holds great promise to affect almost every area of modern life. One area in which nanotechnology has already had an impact is in catalysis and indeed many catalysts work because of their complex nanostructure. In order to study such complicated systems, it is necessary to be able to detect single atoms on thick and possibly irregular or insulating supports, something that presents difficulties for a conventional TEM or a scanning tunneling microscope.

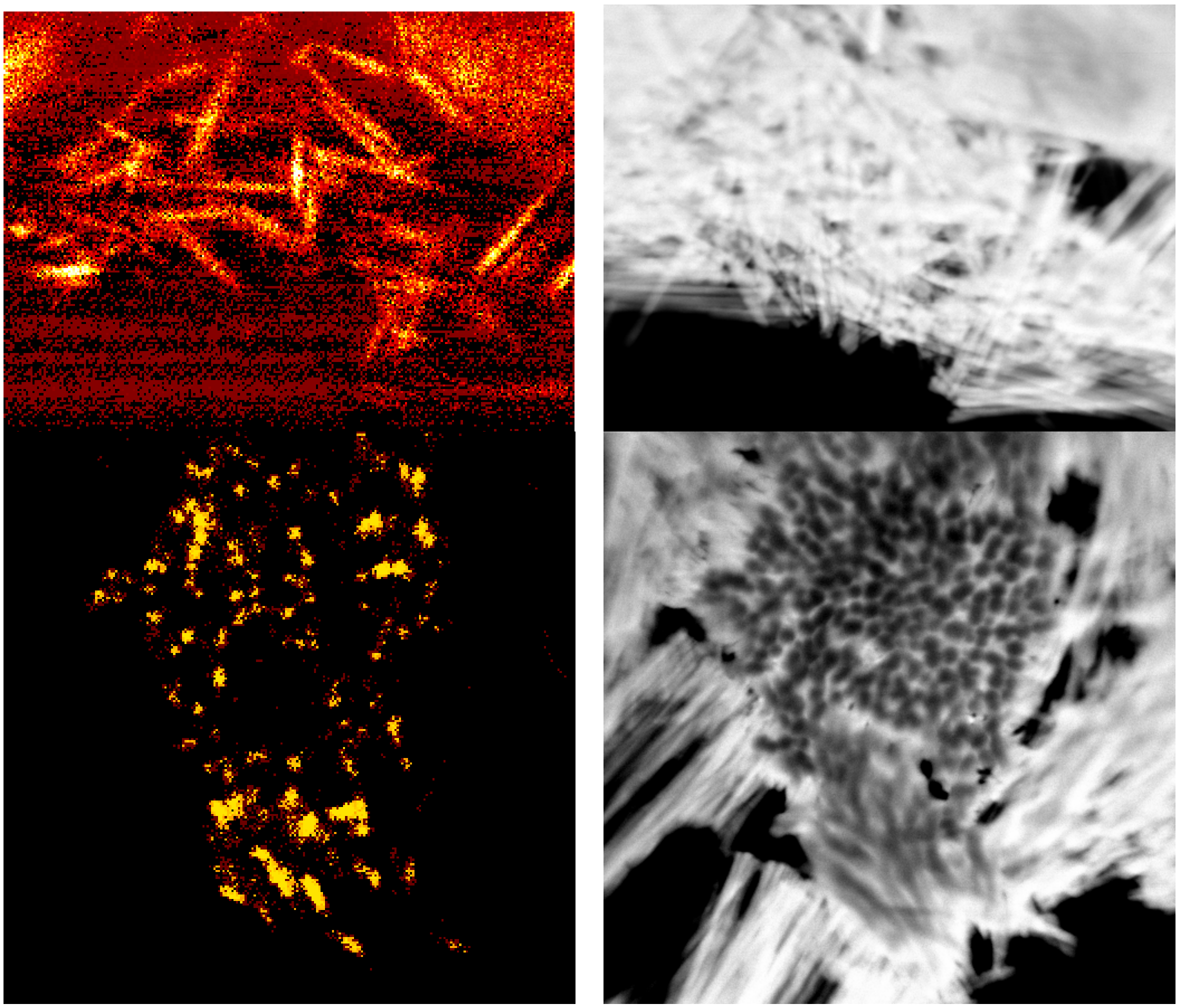

Figure 2. Images of zinc oxide nanorods showing the intensity of emitted light (left) and intensity of electrons scattered out to high angles (right).

One relevant example is that the catalytic converters fitted to almost all modern cars consist of an alumina support covered with metal nanoparticles. However, a problem with this system is that the alumina undergoes an undesirable phase transition at high temperature. Doping the alumina with lanthanum helps prevent this phase transition, although there was some dispute over the mechanism. Z-contrast imaging combined with first principles calculations was able to resolve this conflict. STEM images revealed that the lanthanum was present as dispersed atoms. Even more revealingly, through-focus Z-contrast images were able to demonstrate that the lanthanum atoms were on the surfaces. Combined with density functional theory, this was able to provide a mechanism for the lanthanum-induced stabilization [9].

Another example application is the oxidation of carbon monoxide by supported nano-gold particles. This is a useful reaction because it has several applications relating to air purification and breathing apparatus. It is also a scientifically interesting example because gold in bulk form is not a good catalyst, but when prepared as oxide-supported nano-sized particles, particularly on titania, it becomes one of the most active catalysts for this reaction [10]. In fact the reaction rate depends critically on the size of the gold nanoparticles.

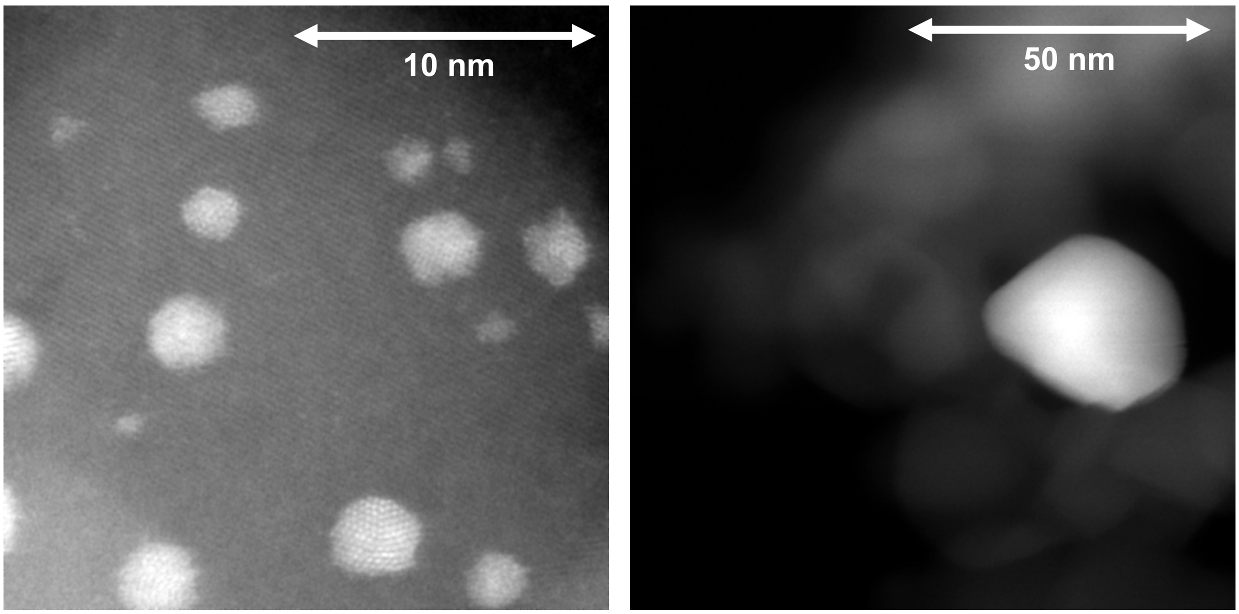

Figure 3. Z-contrast images of gold nanoparticles on titania prepared by G.M. Veith and N.J. Dudney using the method in [11]. The sample on the left shows a high-magnification image of an active catalyst. Some of the smallest spots are single gold atoms. Larger gold particles (right) are far less active.

Z-contrast STEM is an ideal way to investigate these catalysts because even single atoms of gold are visible on relatively thick supports (fig. 3). Combined with a series of reaction rate measurements and other techniques, Z-contrast STEM images were able to provide a basis for first principles calculations. These calculations revealed that the ability of low-coordinated gold atoms on the smaller particles to bond oxygen molecules, in just the right manner, may be critical to the catalytic properties. By combining atomic resolution analysis and detailed calculations it should in future be possible to design more efficient catalysts or other novel nanomaterials.

In conclusion aberration corrected STEM has found applications in the analysis of a variety of nanomaterials and been able to solve several real problems. Analysis of nanowires through Z-contrast STEM promises to provide new insight into the properties of these systems.

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[12] Research sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725, by an appointment to the ORNL Postdoctoral Research Associates Program, and by the Laboratory Directed Research and Development Program of ORNL.