Nanostructure Functionality through Aberration-Corrected STEM

S. J. Pennycook,[1] M. F. Chisholm,[1] A. R. Lupini,[1] Y. Peng,[1] M. Varela,[1] K. van Benthem,[1] A. Borisevich,[1] S. D. Findlay,[2] M. P. Oxley,[2] L. J. Allen,[2]

[1] Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA
[2] School of Physics, University of Melbourne, Victoria 3010, Australia

The 300 kV VG Microscopes' HB603U STEM at Oak Ridge National Laboratory with a Nion aberration corrector has achieved the first direct image of a crystal at sub-Angstrom resolution, using the incoherent Z-contrast or high-angle annular dark field (HAADF) mode, as shown in Fig. 1a,b. [1] To validate use of the Fourier transform to measure a resolution limit of 0.61Å, Fig. 1c compares Fourier transforms of a simulated image and the probe used for the simulation. Excellent agreement is seen for a thin crystal where ideal incoherent imaging applies. Thicker crystals show reduced high frequency transfer, but no spurious sum or difference frequencies [2]. The sub-Ångstrom probe allows Z-contrast imaging of oxygen columns next to heavy columns (Fig. 1d). Furthermore, an efficient, simultaneous, aberration corrected, phase contrast image is available using a small axial detector giving improved oxygen visibility, although spurious features are seen between the Sr columns (Fig. 1e). The STEM has become a viable means of acquiring aberration-corrected phase contrast images, with the advantage of simultaneous Z-contrast imaging and EELS.

These capabilities are ideal for the investigation of nanostructure functionality. Fig. 2 shows a Z-contrast image of the mixed valence material $Bi_{0.37}Ca_{0.63}MnO_3$, revealing a random distribution of Bi^{3+} dopants on the Ca^{2+} sites. EELS, which can provide information on orbital occupation via the $L_{2/3}$ ratio, reveals that the additional dopant electrons are localized in Mn d-orbitals, arranged in linear stripes. These observations represent the direct observation of a nanoscale charge ordering phenomenon [3]. The small probe also provides significantly enhanced sensitivity to *single* atoms, not only their imaging and lattice location by inspection [4,5], but also their spectroscopic identification by EELS [6], with significant applications to catalysis [7].

An unanticipated advantage of aberration correction is the enhanced depth resolution. Transverse resolution improves linearly with increasing aperture angle whereas depth resolution improves quadratically. This makes possible for the first time the 3D reconstruction of nanostructures through depth sectioning while maintaining sensitivity to single atoms. A precision of 0.1 x 0.1 x 1 nm has been achieved for Hf atoms in a $HfO_2/SiO_2/Si$ gate dielectric structure [6]. Figure 3 shows one frame from a 3D reconstruction of a functionalized multiwall carbon nanotube with the functional sites labeled by gold. The same methods should be applicable to EELS and X-ray spectroscopies providing 3D nanoanalysis for grain boundaries, dislocation core structures and nanoscale phase separation phenomena. For atoms not well-separated in depth, quantitative image simulations can determine the thickness of a nanocrystal, column by column, thus revealing its 3D shape [8,9].

References:

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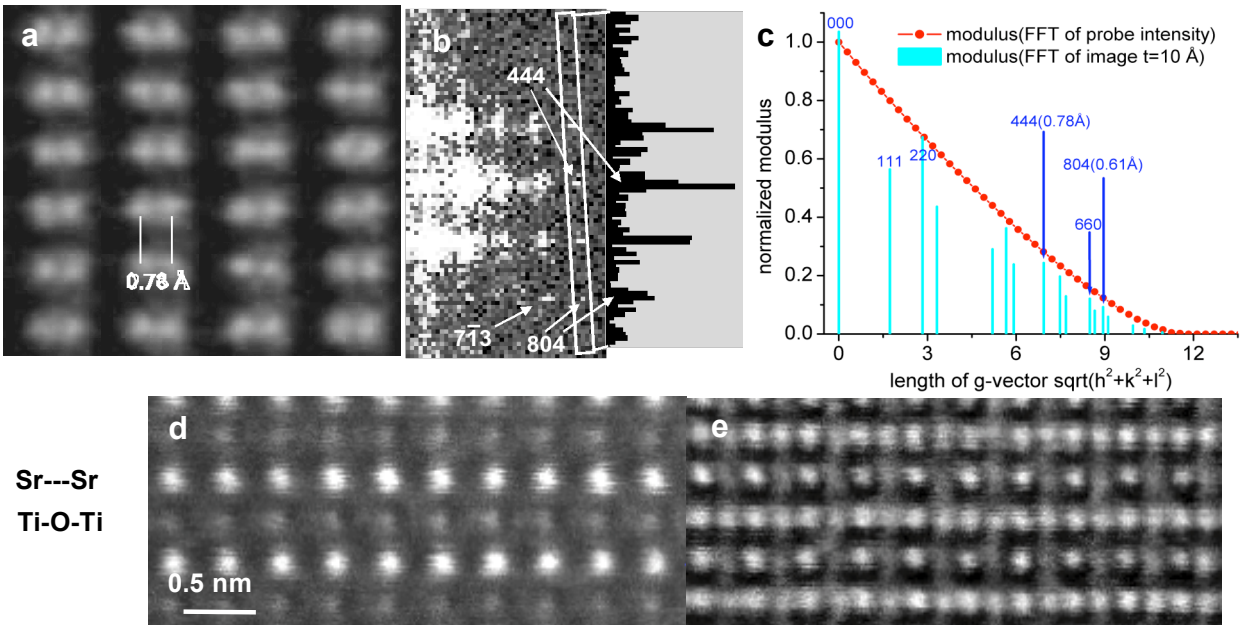

Fig.1: (a) Z-contrast image of Si⟨112⟩ resolving the 0.78 Å dumbbell, with (b) Fourier transform indicating information transfer to 0.61 Å. (c) Fourier transforms of a simulated image and the probe used for the simulation. (d) Aberration-corrected Z-contrast and (e) phase contrast images of $SrTiO_3$ ⟨110⟩ showing oxygen columns taken at a defocus of +2 and +6 nm respectively (raw data).

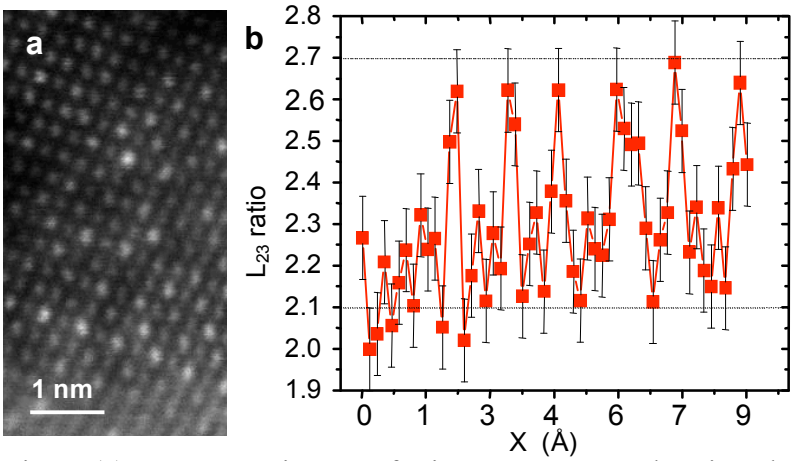

Fig.2: (a) Z-contrast image of $Bi_{0.38}Ca_{0.62}MnO_3$ showing the random locations of Bi atoms on Ca sites. (b) $L_{2/3}$ ratio on the Mn edge plotted along [100] showing approximately a 15-Å periodicity due to charge ordering. Horizontal lines represent the ratio for bulk Mn 4+ (lower) and 3+ (upper) compounds.

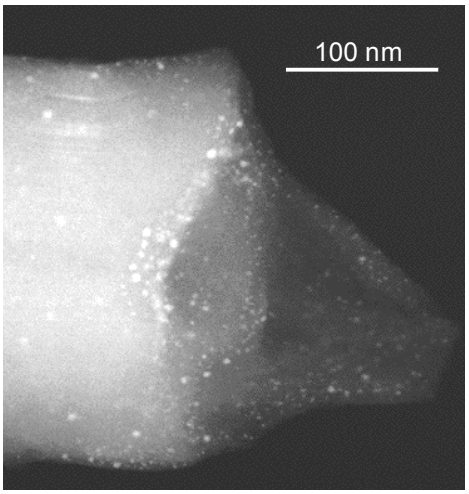

Fig.3: Multiwalled carbon nanotube functionalized with gold nanoparticles.