Spectroscopy in STEM/TEM

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Probing materials one atom at a time with low-voltage scanning transmission electron microscopy

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An essential corollary to the exciting instrumentation developments electron microscopy has witnessed over the last decade is the significant increase in detection limits and signal-to-noise ratios achieved on the new generation aberration-corrected microscopes, which provide improved data collection ability and greater flexibility. The development of so-called 'gentle', dose-controlled STEM techniques, for instance, has been particularly beneficial for the field of two-dimensional materials [1]. By reducing the acceleration voltage to overcome knock-on damage limitations, many of these structures can be imaged directly at atomic resolution with annular dark field (ADF) detectors, revealing for instance unique structure reconstructions at the edge of MoS_2 nano-catalysts [2] or the propensity of graphene to spontaneously 'heal' itself when perforated (Fig. 1a) [3]. Having shown what atomic species are present and where single atom impurities or defects are located using spectroscopy [4], some fundamental questions remain: how exactly are these atoms bonded to one another and how do structural differences affect their electronic configuration? Answers to these questions can be provided one atom at a time by EELS fine structure analysis, which can distinguish unambiguously between bonding configurations (Fig. 1b) [5]. This truly marks the start of single-atom physical chemistry.

In addition, the wealth of complementary analytical signals available from a single experiment provide unprecedented insights into the properties of materials. Minute changes in the composition of complex oxides can dramatically alter the local atomic configuration and thus transform their physical properties. For instance, the dielectric response of microwave ceramic $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ can be fine-tuned by adjusting the Ba and Nd content [6], while the spontaneous polarization of magneto-electric oxide gallium ferrite $Ga_{1-x}Fe_xO_3$ is dependent on the distortions caused by the structural asymmetry of the cation sites [7]. When combining Z-contrast imaging, bright field STEM imaging and true routine 2D EELS chemical mapping with advanced statistical image analysis [8] it is possible to determine statistically variations of only a few atoms in the chemical distribution of the different sites in these structures across a range of compositions, and to relate those to accurately measured small local atomic displacements generated by these compositional changes (Fig. 2).

1. O.L. Krivanek et al., in "Low Voltage Electron Microscopy", D. Bell and N. Erdman Eds., Wiley, London, 2013.
2. L.P. Hansen et al., Angew. Chem. Int. Ed. 50 (2011), p. 10153.
3. R. Zan et al., Nano Lett. 12 (2012), p. 3936.
4. T.C. Lovejoy et al., Appl. Phys. Lett. 100 (2012), 154101.
5. Q..M. Ramasse et al., Nano Lett. Art. ASAP (2013) doi:10.1021/nl304187e.
6. N. Rejab et al., Journal of Mater. Sci. 22 (2011), p. 167.
7. A. Roy et al., J. Phys.: Condens. Matter 23 (2011), p. 325902.
8. M.C. Sarahan et al., Ultramicroscopy 111 (2011), p. 251.
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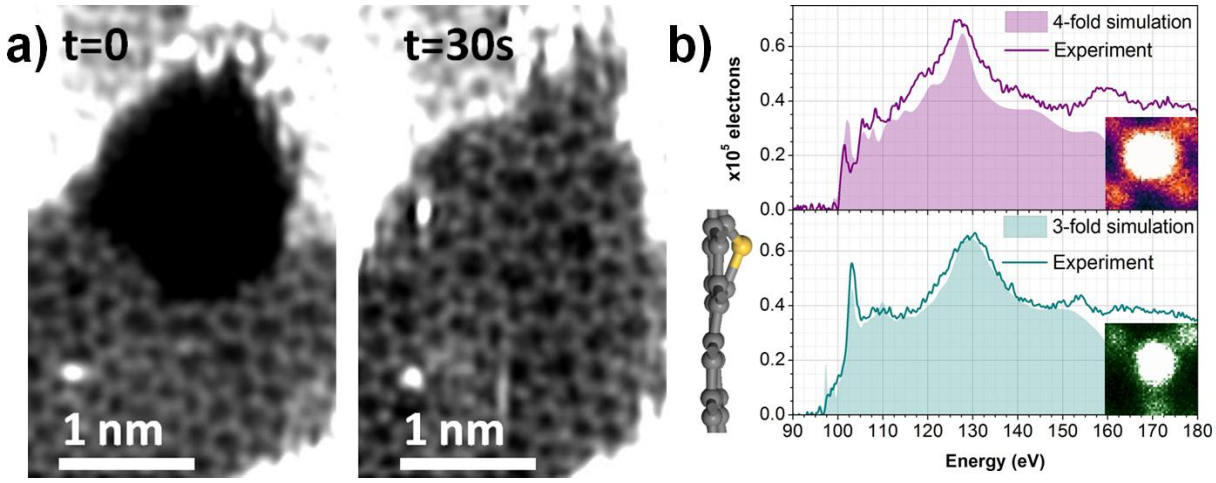

Figure 1. (a) Hole in single-layer graphene heals spontaneously by filling itself with loose carbon atoms to form a 2D amorphous patch. [3]. **(b)** Experimental and simulated EEL spectra acquired from a single Si atom in graphene in two different bonding configurations: trivalently bonded to the graphene lattice (top, inset) or tetravalently bonded to the graphene lattice (bottom, inset). [5]

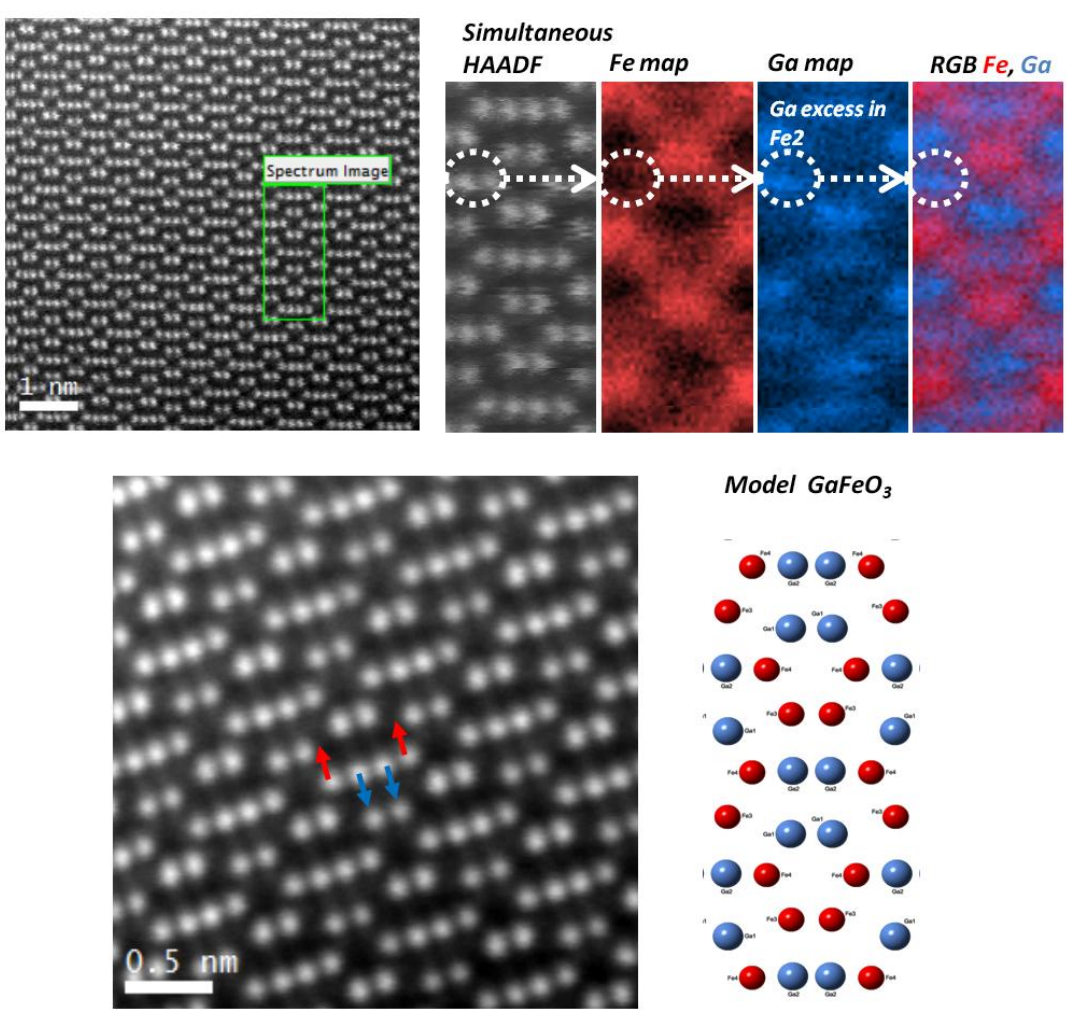

Figure 2. HAADF survey image and atomically-resolved EELS maps of a $Ga_{1-x}Fe_xO_3$ complex oxide revealing excess Ga located at the so-called Fe2 lattice sites. Quantitative analysis of bright field/HAADF images through template matching algorithms suggests these chemical variations are linked small atomic displacements of the Ga sites.