Watching Atoms Work: Nanocluster Structure and Dynamics

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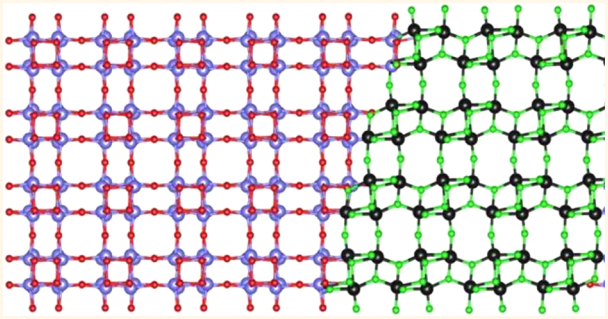
ABSTRACT In the space of little more than a decade, the resolution of the electron microscope has improved to provide clear views of the atomic world. Not only can atomic arrangements be imaged, but with a little gentle provocation from the electron beam, atoms can be energized and their dynamics can also be revealed. In this issue of *ACS Nano*, Chen *et al.* image Si atoms growing under the beam into cubic crystalline arrangements.



Around 400 BC, Democritus thought that matter could not be divided indefinitely and hypothesized that "all matter consists of invisible particles called atoms." Almost 2000 years later, John Dalton reinvented the theory based on experimental observations; for example, that atoms of different elements combine in constant ratios to form compounds. Richard Feynman, in his famous *Lectures on Physics*,[1] said that the most important scientific fact is that all things are made of atoms. What is so remarkable today is that we can put anything into an electron microscope and see for ourselves that, indeed, everything is made of atoms (see Figure 1). In the space of one generation, the human race has gained the ability to see atoms clearly, which is truly a historic accomplishment.

The inventor of the transmission electron microscope, Ernst Ruska, in his Nobel Prize lecture[2] said "As engineers we did not know yet the thesis of the "material wave" of the French physicist de Broglie (1924)... When I first heard of it in the summer of 1931, I was very much disappointed that now even at the electron microscope level the resolution should be limited again by a wavelength." However, inserting his microscope parameters into the equation for the resolution of an optical microscope, he came up with a resolution of around 2 Å, close to typical atomic spacings. In 1939, the inventor of the scanning transmission electron microscope, Manfred von Ardennes, was even more specific,[3] "In particular, the ultramicroscopy technique will sooner or later be able to show the presence of single atoms and their distribution in the object."

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The quest for atomic resolution turned out to be a major engineering challenge. For the next half century, resolution was limited by intrinsic aberrations of the round electron lenses used as the objective lenses. Unlike a glass lens in an optical microscope, electron lenses cannot be produced in arbitrary shapes; they must obey certain symmetries, and it was soon discovered by Scherzer that spherical aberration in a round lens is intrinsically positive.[4] Compensation optics would need to use higher order elements

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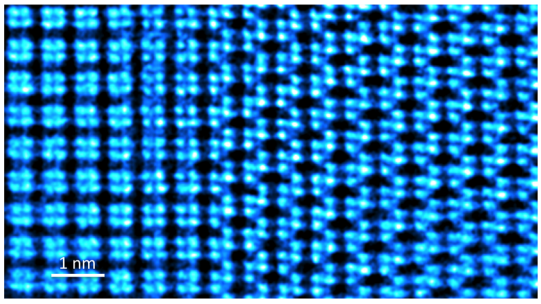

Figure 1. A domain boundary in a VO_2 thin film seen in an aberration-corrected scanning transmission electron microscope. JEOL ARM200F with ASCOR corrector, image courtesy of Noriaki Endo; sample and structure model courtesy of T. Venkatesan and Amar Srivastava, National University of Singapore.

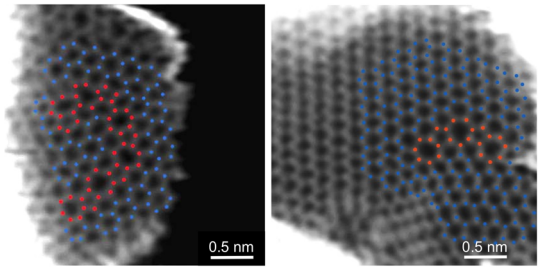

Figure 2. Nanoporous carbon is shown to comprise defective graphene sheets containing 5- and 7-membered carbon rings, red dots. Blue dots mark 6-fold rings. Images obtained with a Nion UltraSTEM at 60 kV beam voltage. Reproduced with permission from ref 13. Copyright 2012 Wiley.

such as quadrupoles, hexapoles, and octapoles, making the design complex, and its alignment beyond human capability.[5] The only practical way to achieve higher resolution was to push the operating voltage to higher and higher values, giving shorter wavelengths, and resolution below 1 Å was actually achieved.[6] However, such machines were large and expensive, and tended to damage specimens rapidly.

Now, in the age of the fast computer and sensitive charge-coupled-device detectors, it has become possible to diagnose and to tune aberrations, and successful aberration correction was achieved first in the transmission electron microscope (TEM)[7] and then in the scanning transmission electron microscope (STEM).[8] Resolution advanced to unprecedented levels, below 0.5 Å in the STEM case,[9,10] but equally important, resolutions of around 1 Å could now be achieved at voltages of only 80 or 60 kV, much lower than before, greatly reducing beam damage.[11,12] To appreciate how this has changed our understanding of materials structure, consider activated carbon, an old material used in diverse applications such as the water filter in your refrigerator. While it was known for decades that the key to its properties was the high surface area, the true atomic structure was not known. Looking at the atoms in a low-voltage aberration-corrected microscope showed the structure clearly for the first time (see Figure 2).[13] It was made of crumpled sheets of defective graphene! And had been, of course, long before graphene was even identified. The 5- and 7-member rings seen in the image create rumples that stop the graphene sheets from stacking close together into graphite; they are the reason for the extended, slit-like pore structures that were long suspected to be responsible for the useful properties.

Much attention has been paid to graphene, of course, with the ability to image point defect configurations and even to interrogate the nature of impurity configurations through electron energy loss spectroscopy.[14] Oxygen has been seen to form crown ether structures in graphene[15] and silicon has been shown to stabilize graphene nanopores.[16] Even a two-dimensional (2D) glass has been observed.[17] But while low beam voltage reduces beam damage enough so that we do not destroy the material the moment we image it, it does not prevent damage completely. A 60 kV electron can impart a considerable momentum to an atomic nucleus, and it can still break atomic bonds. Therefore, things do happen under the beam while we watch, but it is not all bad. What we ultimately see is exploration of metastable cluster configurations; in other words, we can explore nanocluster dynamics. See, for example, the case of a Si_6 cluster observed by Lee *et al.*[18] or the rotating trimer observed by Yang *et al.*[19] In this issue of *ACS Nano*, Chen *et al.*[20] take such observations one step further by imaging Si clusters evolving and growing under the beam into crystalline cubic phases. They grow anisotropically due to the higher stability of the Si−C bond under the beam compared to the Si−Si bond, and they can even rotate perpendicular to the graphene plane. They report essentially a bond-by-bond picture of how the cluster grows from a couple of atoms into a small crystalline ribbon, a fascinating revelation of atomic-level dynamics.

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Density functional theory (DFT) is a valuable complement to such observations by providing insights into the energetics of the nanosystem. Not only does it confirm

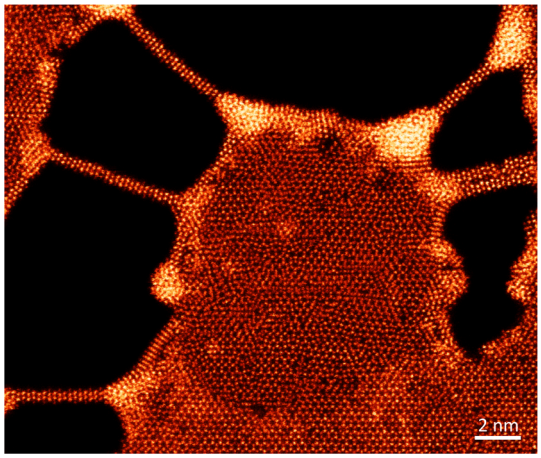

Figure 3. MoSe nanowires sculpted by the electron beam in monolayer $MoSe_2$. Nion UltraSTEM at 60 kV. Reproduced with permission from ref 21. Copyright 2014 Nature Publishing Group.

that the observed motions are feasible under the few electronvolts available from the beam, but it can give further information on structure, the available energy landscape, and also electronic properties. Chen *et al.* use DFT to understand the stable rotation angles of their Si nanoclusters, and show that their upright Si dimer configuration is a metastable state induced by the beam. However, it is not only graphene-based nanostructures that are revealing their secrets. Lin *et al.*[21] have investigated the formation of stable, metallic MX (M = Mo or W, X = S or Se) nanowires by direct "sculpting" under the electron beam. In this system, damage is sufficiently high that holes in 2D monolayers of MX_2 can be formed at high magnification, then nanowires can be formed between adjacent holes (see Figure 3). Under further irradiation, the thinnest MX nanowire structure forms, which is stable under the beam; as X atoms are displaced by the beam, enough return to the wire from the adjacent 2D monolayer reservoir to heal the nanowire. Using DFT, Lin *et al.* further show that the contacts are Ohmic and invariant under rotation of the nanowires.

Chen *et al.* speculate that metal atoms could be used instead of Si to grow nanoclusters with new catalytic properties.[20] Indeed, recent observations of single Nb atoms incorporated into graphitic nanostructures have explained how useful catalytic activity can emerge while the covalent bonding between the metal and the graphitic layer leads to higher stability.[22] Extending such work to other nanocluster geometries, and to other elements and alloy nanoclusters, is likely to be a fertile field for future investigation.

OUTLOOK AND FUTURE CHALLENGES

Watching nanoclusters dance and assemble in the high vacuum of an electron microscope does provide helpful new insights; however, most chemical reactions do not take place under high vacuum, but at high pressures or in liquids. Can we actually see atoms under true operating conditions, *operando*, while reactions are occurring? Gai *et al.* have shown long ago that we may see quite different structures under actual reaction conditions.[23] Much progress has been made in recent years in this regard using environmental cells or thin membranes, but there is a trade-off, as high gas pressure or liquids tend to degrade resolution (for reviews see refs 24 and 25). Even when atomic resolution is observed,[26] it may be challenging to distinguish which reactions are beam induced and which occur in the absence of a beam. Perhaps, we can observe at different doses and extrapolate to zero dose. Perhaps, as with nanocluster dynamics, beam-induced chemical reactions will give equally informative insights into chemical reaction pathways.

In the biological area, where bonding is much weaker than in typical materials, the challenges are vastly amplified. The SALVE (Sub-Å Low-Voltage Electron microscope) project in Germany[27] is aiming to image biological systems at very low beam energies, and the JEOL company in Japan has developed a new Delta (dodecapole element triple aberration) corrector[28] which provides correction of higher order aberrations and shows increased resolution at low beam energies. In addition, there is much recent progress in statistical methods of image processing using manifold-embedding[29] or Bayesian methods[30,31] to allow lower electron doses.

Our ability to view the atomic landscape has only recently emerged, and it represents a new way to inspire novel materials and processes. If we understand how things work at the fundamental atomic level, can we avoid reinventing the wheel and move from trial and error synthesis and processing to more efficient means, learning from what we see? Hopefully so, but in the mean time, the atomic world presents a fascinating new vista.

Conflict of Interest: The authors declare no competing financial interest.

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