Electron Microscopy

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Multi-Dimensional Electron Microscopy

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Dedicated to the MPI für Kohlenforschung on the occasion of its centenary and to the memory of R. J. M. Griffiths

Even though Ernst Ruska's pioneering work led to the transmission electron microscope (TEM) in the 1930s,[1] and shortly thereafter Manfred von Ardenne produced a primitive form of a scanning electron microscope (SEM),[2] it was not until the 1960s that Charles Oatley's SEM became a commercial reality.[3] It proved spectacularly successful because, through its relatively large depth of focus, it yielded 3D topographic images of materials such as minute parasites, nematodes, blood cells, pollen, etch pits, corrosion products, radiolaria and the compound eye of a fly. Soon it became indispensable for nanolithographers and manufacturers of integrated circuits. Biological, medical, physical and engineering sciences have each benefitted incalculably from SEM; and nowadays civilized life relies on TEMs and SEMs to design and assemble computers and the myriad other electronic accoutrements of 21st century electronic and domestic gadgetry. In the 1960s also, Heinz Bethge introduced his ingenious topographically sensitive gold decoration technique[4] which one of us deployed to identify emergent screw dislocation, and mono- and multilayers of graphene, on oxidized surfaces of graphite.[5]

From the outset, TEMs required ultra-thin specimens and they yielded 2D projected images. With them, in the mid-1950s, Cambridge and Geneva scientists established incontrovertibly the reality of dislocations in solids. The notion of dislocations, proposed in 1934 (by G. I. Taylor,[6] E. Orowan[7] and M. Polanyi[8]) to account for the plasticity and unexpectedly low strength of solids, was confirmed by the high resolution images taken by J. W. Menter of an edge dislocation.[9] Moreover, M. Whelan[10] and W. Bollmann[11] separately recorded the movement of dislocations in metals, thereby elucidating the enigmatic phenomena of strain- and work-hardening.

Subsequently, TEMs and their scanning variants (STEMs) have comprehensively revolutionized large segments of the natural sciences, for example: the identification of individual atoms (or clusters thereof) of Pt and its congeners in catalysts widely used to convert oil to fuels for transport or heating; the existence of carbon nanotubes and their importance in new, mechanically strong composites; intergrowths at sub unit cell level in minerals that had hitherto defied elucidation by X-ray analysis; the structure of membrane proteins and viruses; direct, atomically-resolved images of nanoporous synthetic materials (adsorbents and catalysts) long before they could be studied by X-rays; and direct proof (by TEM imaging) of the graphitic layers in heat-treated coals, as envisaged in the pioneering X-ray studies of Rosalind Franklin.[12]

With appropriate instrumental modification, both SEMs and STEMs can be used to follow some chemical and physical processes in situ. But the great power of EM lies in its ability to yield information in real space, in reciprocal space (diffraction) and in energy space, by recording signals using inelastically scattered electrons as well as concomitantly emitted X-rays. The most modern electron microscopes, equipped with aberration-corrected lenses and ultrasensitive detectors, can easily probe specimens as small as zeptograms (10^{-21} g). Moreover it readily yields the chemical composition, structure, bonding, valence states of constituent atoms as well as the dynamics of minute atom clusters and some surface characteristics including plasmonic oscillations. When images are recorded under high-angle annular dark-field (HAADF) conditions, an atomic number (Z-contrast) picture results. Such images, taken at various angular settings also yield tomographic (3D) information, which is invaluable in probing the microporosity and fractal dimensions of the ever-expanding family of ordered mesoporous catalysts.[13] Tomographic resolution has recently been pushed to the atomic level using different approaches: firstly, by quantifying individual atomic column intensities and essentially counting the number of atoms therein,[14] and secondly, by a conventional tilt series applying 3D Fourier filtering methods, to elucidate, for example, the atomic structure close to a dislocation core.[15] Recent work, using a "big-bang" approach attains also, under favorable circumstances, atomically resolved electron tomograms that can distinguish chemically distinct peripheral atoms in layers of graphene.[16]

Modern STEM-based X-ray and energy loss spectroscopic techniques can generate "spectrum-images" in which behind every image pixel lies a complete (X-ray or energy loss) spectrum. By recording a tilt series of such spectrum-images, 4D "spectrum tomograms" provide spectral (and thus chemical) information at every real space voxel. Early work[17] using an equivalent energy-filtered TEM method ("volume spectroscopy") was followed soon after by 4D STEM methods enabling, for example, the different chemistry of silicon (elemental, oxide, silicide) to be mapped in 3D in a commercial semiconducting device. Applying this method

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to the low loss spectrum, which encodes information regarding local optical properties, can yield 3D images of localized surface plasmon resonances (LSPRs) which control the optical properties of nanostructures smaller than the wavelength of light (see Figure 1 a).[18] The recent introduction of high solid angle X-ray detectors in the STEM, coupled with higher brightness guns, has improved enormously the efficiency of X-ray (EDX) mapping and thus the ease with which X-ray spectrum-tomography can now be undertaken.

The exquisite sensitivity of dark-field imaging, using STEM or TEM, to small deviations from the Bragg condition allows a variety of crystal defects to be readily imaged; using a tilt series of such images, it is now straightforward, for example, to map the geometry of a dislocation network in 3D.[19] However, encoded within the image series is a wealth of additional information pertaining to the Burgers vector and strain local to the dislocation core. Such 3D information is not projected in a simple way and to extract it would require more sophisticated treatment than currently used. Mapping strain in 3D using sensitive dark-field images (or other EM techniques such as electron holography described below) presents a formidable but very worthwhile challenge.

Another powerful and sensitive EM technique is electron holography, an interferometric technique, in which using a charged biprism as a beam splitter, electron wavefronts from neighboring regions of the specimen (or from the specimen and vacuum) interfere and produce a "hologram". The intensity and frequency modulation in the hologram can be used to recover the amplitude and phase, respectively, of the exit wavefunction, the latter being especially important, for example, for the retrieval of local electromagnetic potentials. By recording a tilt series of such holograms the 3D potential can be recovered and this has proven to be especially successful in mapping the 3D built-in potential across p–n junctions in semiconductor devices.[20] To reconstruct magnetic potentials (or fields) more than one tilt series is necessary and vector tomographic techniques to enable this are actively under development. One recent application of vector electron tomography used phase-reconstructed Lorentz microscopy to elucidate the 3D magnetic induction of a micrometer-sized permalloy element.[21]

Provided specimens are sufficiently beam-stable, electron crystallography becomes a powerful approach to solving the structure of many minute crystals in 3D using diffraction patterns and the images formed in the EM. The transforma-

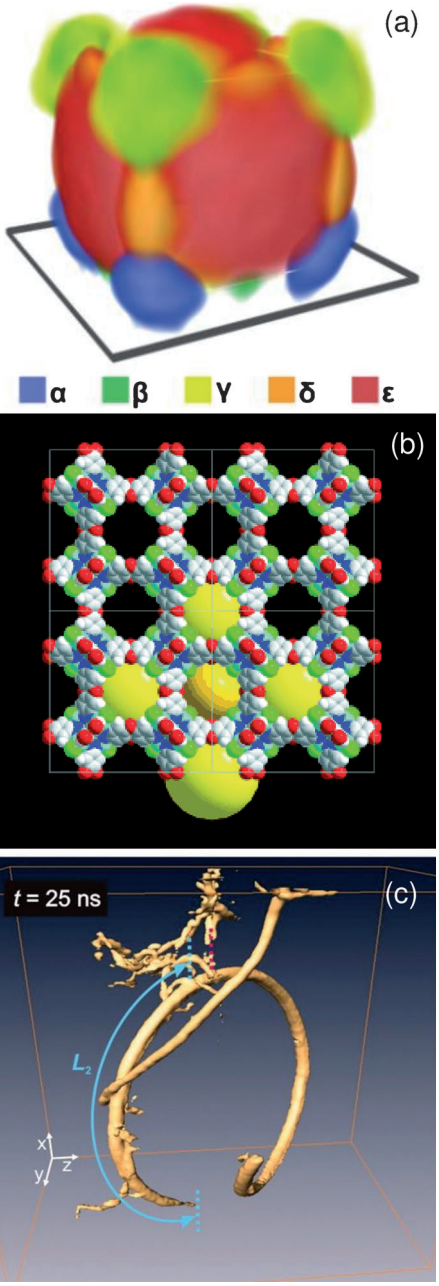

Figure 1. a) Composite color image showing five surface plasmon modes (labeled α–ε) on a silver nanoparticle reconstructed using 4D spectrum-tomography.[18] b) MFU-4L (a metal–organic framework) structure solved using PED and diffraction tomography.[24] Color code: light blue Zn, green Cl, blue N, gray C, white H, red O. c) Multi-walled carbon nanotube dynamics captured using 4D electron tomography.[28]

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tive work of Aaron Klug using this approach enabled the detailed architecture of viruses and a host of macromolecular entities of major biological significance, including membrane proteins to be solved. Until relatively recently, the structure of crystals that were unstable for high resolution EM studies were often solved through an amalgamation of 2D EM images, computer simulation and X-ray powder diffraction.[22] However, with the advent of precession electron diffraction (PED),[23] in which the electron beam is scanned in a hollow cone above the specimen and then de-scanned below the specimen, the net effect being equivalent to precessing the sample about the optic axis, it is now entirely possible to solve, often in combination with diffraction tomography, the 3D structures of organic crystals, zeolites and metal–organic frameworks (MOFs) (such as that shown in Figure 1 b), many of these being new kinds of synthesized materials that have vast potential as catalysts, photocatalysts, semiconductors and novel selective adsorbents.[24] MOFs, in particular, as recently demonstrated, are exceptionally good examples of single-site Lewis heterogeneous catalysts in organic synthetic chemistry.[25] By scanning the precessed beam, hybrid 4D "diffraction-imaging" maps can be acquired in which a diffraction pattern is recorded at every real space pixel within a 2D image. By acquiring a tilt series of such maps it is possible to create a 6D data set whereby, at each real space voxel, 3D reciprocal space (and thus local 3D crystal orientation) information is available. A complementary technique using many (ca. 10^5) conically scanned dark-field images leads to similar information.[26]

The inception of 4DEM a decade or so ago led to a revolution in acquiring time-resolved structural and dynamic data. Up until then, images were recorded (in 2D and 3D) statically or by using video recording on the millisecond time-scale. With pump–probe, laser-stimulated photoemission EM (and specimen perturbation) it is possible to reach the femtosecond domain.[27] This means a 10 orders of magnitude increase in temporal resolution, yet retaining the spatial resolution to the atomic scale. Key to the success of doing so is Ahmed Zewail's introduction of single-electron imaging (which avoids the complications of Coulomb repulsion and consequential loss of resolution). Zewail's advance has led to imaging of atomic motions in nanomaterials, the mechanical motions of nanostructures (Figure 1 c),[28] direct visualization of phase transitions, melting and recrystallization, and new insights into the behavior of biological structures ranging from DNA to proteins to amyloids. His introduction of photon-induced near-field EM (PINEM) has uncovered new phenomena pertaining to the interaction of nanostructures with electric fields. For irreversible behavior that cannot be studied with stroboscopic methods, alternative "single shot" electron imaging methods have been devised in which a single pulse, a few nanoseconds in duration, is used in a pump–probe fashion.[29]

As a final thought, we must remember that a significant challenge with all multi-dimensional microscopy techniques is to develop efficient ways to handle and process the huge quantity of data generated. By combining real space, reciprocal space, time and perhaps also a spectral domain, Gigabytes of data are generated very quickly. One solution is to simply acquire less data through "smart" acquisition and reconstruction schemes. In essence, we can build in to any experiment, or post-acquisition analysis, knowledge about the object under consideration—so-called "prior information"—which may take many forms, ranging from knowledge of the chemical composition, morphology (e.g. convexity), a zero background signal, or the need to obey physical laws (e.g. Maxwell equations). One method, increasing in its popularity, is "compressed sensing" in which the key prior is the ability to describe the object as being "sparse" in some domain. Such prior information, some of which at first sight may appear trivial, can impose remarkably strong constraints on the reconstructed object, thus requiring far fewer images (perhaps an order of magnitude fewer) to produce high-fidelity electron tomographic reconstructions.[30]

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