Angew. Chem. Int. Ed. 49 (2010) 9569 – 9571

Electron Tomography: From 3D Statics to 4D Dynamics

Dang Sheng Su

Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society,
Faradayweg 4-6, 14195 Berlin, Germany

* Corresponding author: e-mail dangsheng@fhi-berlin.mpg.de,

Received 27 July 2010; Published online: 8 October 2010

Abstract

4D-electron tomography enables the study of transient states of materials, structural dynamics of big molecular objects, and biological systems under controlled conditions.

Keywords: dynamics; electron microscopy electron tomography; nanomaterials; stroboscopy

Human beings are used to see in 3 dimension-we are born to live in a 3 dimensional (3D) world. As we live, “time” is the fourth dimension that we do not feel, but experience. This 4 dimensional (4D) observation and experience is so obvious in our daily life, yet not apparent in physics, chemistry and biology, especially not for details at the nanoscale at a time-interval of sub-millisecond. We need additional instruments for observation and recording. Note that the transmission electron microscope (TEM), one of the two most powerful imaging instruments with resolution below 0.1 nm, produces only two dimensional images of a nano object (either biomolecules, viruses, or minutes of inorganic materials). The third dimension information of the object along the direction of the incident electron beam is lost by projection, along with any time-resolved information at a scale of sub-millisecond interval.

There were biologists, biophysicists and biochemists who pioneered to “retrieve” 3D information from 2 dimensional (2D) TEM projections. Already in 1960´s, Klug et al reconstructed 3D biostructures of high symmetry from one or more projections,[1] another group reconstructed asymmetric protein structure from a sufficient number of projections.[2] Hart reconstructed the 3D structure using a recorded tilt series of images of the tobacco mosaic virus with a resolution of 0.3 nm.[3] Gorden et al. introduced an algebraic reconstruction technique (ART) which could handle completely asymmetric objects.[4] Many theoretical refinements followed, e.g. image reconstruction from projections by Zwick and Zeitler,[5] and reconstruction with orthogonal functions by Zeitler.[6] While 3D electron tomo

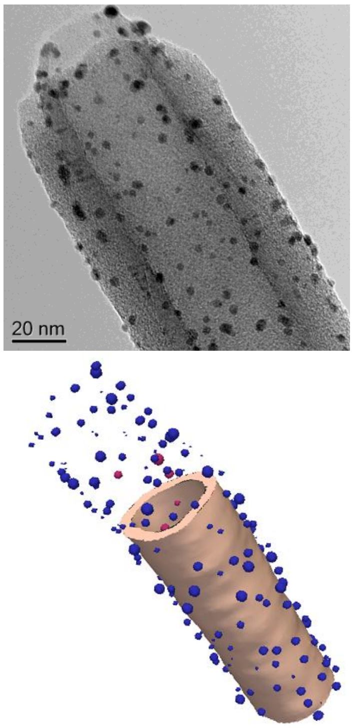

Figure 1. (a) Typical 2D-TEM image of a CNT with Ni nanoparticles. The information, whether the Ni particles are outside or inside the tube, is lost due to the projection. (b) Reconstructed tomogram from a titled series: in pink: carbon nanotube, in red: Ni particles inside the tube; in blue: Ni particles on the external surface. Reproduced from Ref. [13] with permission.

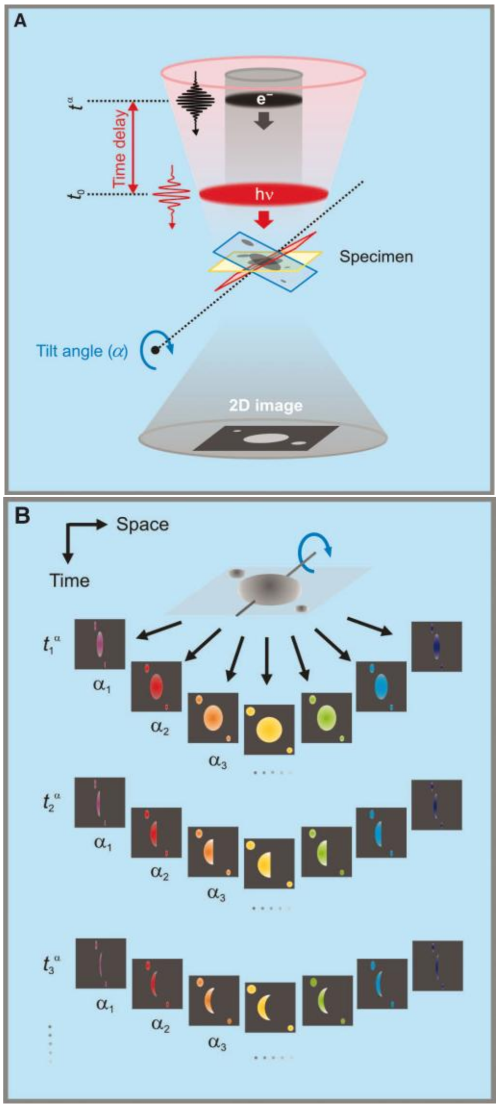

Figure 2. (A) Schematic representation of time-resolved 4D electron tomography. The heating pulse initiates (at t_0) the structural change and acts as a clocking pulse, whereas the time-delayed electron packet (at t^a), with respect to the clocking pulse, images the structure at a given tilt angle (α). (B) A series of 2D images at various projection angles and time steps are taken to construct the tomograms. In this work, increments of 1° and scannings from −58° to +58° were used to define a and its range; the time scale ranged from femtoseconds to microseconds. The number of total spatiotemporal projections made was near 4000, and these were used to construct the tomographic movies of the object in motion. Reprinted from Ref. [14] with permission. Copyright 2010, AAAS.

graphy remains a field of research in biology since that time,[7] its wide spreading in other fields only started in this decade.[8] The driving force is the rapid development of nanoscience and catalysis,[8, 9] where the 3D-morphology of a nano object and the spatial distribution of supported nanocatalysts become essentially important to understand certain physical properties of the nanodevices, or to develop catalysts with designed structure and performance. Advances in electron microscopy, especially the availability of large-area charge-coupled device (CCD) cameras, microscope automation and finally the advances in computational methods were required to bring the field into the state of the art in high resolution electron tomography with applications in various fields.[10] Just to remember that Hart could only use 12 tilted images for the reconstruction.[3]

Due to their tubular morphology and high aspect radio, carbon nanotubes (CNTs) induce peculiar properties for materials trapped inside (confinement effect).[11] While the selective deposition of metal particles only inside of CNTs is already highly demanding,[12] the characterization, whether the particles are really inside the tubes or outside the tubes, remains even more challenging. A 2D electron micrograph does not distinguish particles inside or outside the tube; the third dimension information along the electron beam is lost (Fig. 1a). However, a 3D-tomogram can be reconstructed from a tilt series of 2D electron micrographs, thus revealing the spatial distribution of Ni nanoparticles inside or outside the CNT.[13]

So far so good, but the image and the tomogram in Figure 1 (and in all of these studies so far) is obtained from a static object representing the time-averaged equilibrium state of the structure. Any dynamics, for instance the breathing motion of the supporting CNT or transient process of the particles, if any, are lost in such experiment. In a recent paper published in Science,[14] A. Zewail and coworker realized for the first time 4D electron tomography by integrating the dimension of time into the electron tomogram, allowing real-space and real-time visualization of dynamics of nano objects. This requires the recording of various 2D- projections of an object (the conventional 3D tomography) at a given time with a time resolution that is high enough to capture any transient process of the object. The reconstructed 3D tomogram obtained as a function of time gives then the 4D tomogram. The breakthrough was the result of obtaining the high spatial resolution of conventional electron microscopy but simultaneously enable the temporal resolution of atomic-scale motion.[15]

As conventional TEM could not provide any temporal information down to sub-milliseconds, Zewail and coworks have developed ultrafast electron microscopy (UEM) by combining ultrafast lasers to a modified electron microscope.[16] The technique is based on the fundamental concept of timed, coherent single-electron packets, or electron pulses, which are liberated with femtosecond durations.[17] This new UEM has been successfully applied to study time-resolved image and diffraction,[18] and timed resolved electron-energy-loss (-gain) spectroscopy.[19]

For 4D electron tomography, the time dimension is then integrated into any electron tomogram that spans a whole tilt series. This simultaneous real-space and real-time resolved images are obtained stroboscopically with single-electron coherent packets. As it is shown in Fig. 2A, a specimen tilt arrangement is configured in an UEM to enable the recording of various 2D-projections of an object at a given time. The frames are taken for each degree of tilt with time intervals of femtoseconds or nanoseconds, as dictated by the time scale of the motions involved. The

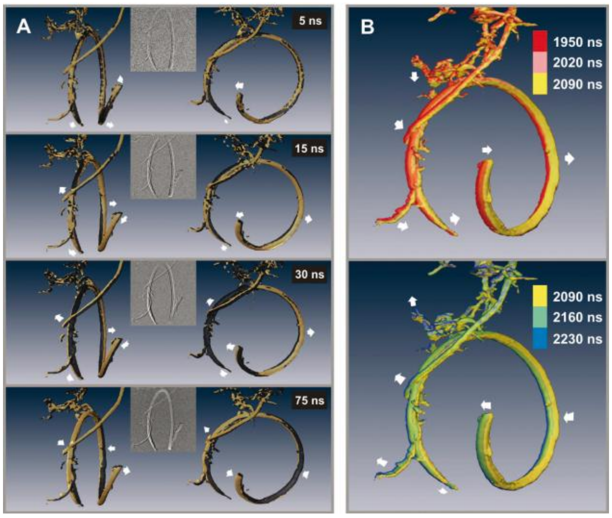

Figure 3. 4D tomographic visualization of motion. (A) Representative 3D volume snapshots of the nanotubes at relatively early times. Each 3D rendered structure at different time delay (beige) is shown at two view angles. A reference volume model taken at t = 0 ns (black) is merged in each panel to highlight the resolved nanometer displacements. Arrows in each panel indicate the direction of motion. (B) The time-dependent structures visualized at later times and with various colors to indicate different temporal evolution. The wiggling motion of the whole bracelet is highlighted with arrows. Reprinted with permission from ref. 14.

concept is illustrated in Fig. 2B, which depicts the construction of tomograms from the 2D projections at different angles and times. Because of the various dimensions involved, at a given time each 2- projection represents a 3D frame (including time), whereas a 3D tomogram when constructed from all the 2D projections represents a 4D frame.

4D-electron tomography allows the constitution of movies of objects in motion, thus enabling studies of non-equilibrium structures and transient processes. The method was demonstrated using carbon nanotubes of a bracelet-like ring structure for which 4D tomograms display different modes of motion, such as breathing and wiggling, with resonance frequencies up to 30 megahertz (Figure 3).[14] The breathing motion of a single- and double walled CNT leads to well-known fingerprint peaks in the Raman spectra for their identification.[20] The 4D electron tomography of Zewail gives now the first observation of breathing vibration for multi-walled CNTs.[14]

With the new development of 4D-electron tomography, we should be able to view the “movie” of dynamics of various nano objects. It enables the study of transient states of materials, structural dynamics of big molecular objects, and biological systems under controlled conditions. Performing the 4D-electron tomography under environmental conditions, i.e. with the presence of atmospheric gases suitable for chemical reaction, would allow for recording of the response and dynamics of nanocatalytic particles and “view” 4 dimensionally their behaviour during the reaction. Truly new understanding and discoveries for catalysis, chemistry, and nanoscience are now on the horizon.

References

[1] (a) D. J. Derosier, A. Klug, *Nature* **1968**, *217*, 130-134; (b) R. A. Crowther, L. A. Amos, J. T. Finch, D. J. Derosier, A. Klug, *Nature* **1970**, *226*, 421-425.

[2] W. Hoppe, R. Langer, G. Knesch, C. Poppe, *Naturwissenschaften* **1968**, *55*, 333-336.

[3] R. G. Hart, *Science* **1968**, *159*, 1464-1467.

[4] R. Gordon, R. Bender, G. T. Herman, *J. Theor. Biol.* **1970**, *29*, 471-481.

[5] (a) M. Zwick, E. Zeitler, *Optik* **1973**, *38*, 550-565; (b) E. Zeitler, *Optik* **1974**, *39*, 396-415.

[6] E. Zeitler, in *Electron Tomography* (Ed.: F. J.), Plenum Press, New York and London, **1992**, p. 63.

[7] (a) A. J. Koster, R. Grimm, D. Typke, R. Hegerl, A. Stoschek, J. Walz, W. Baumeister, *J. Struct. Biol.* **1997**, *120*, 276-308; (b) V. Lucic, F. Forster, W. Baumeister, *Annu. Rev. Biochem.* **2005**, *74*, 833-865; (c) R. McIntosh, D. Nicastro, D. Mastronarde, *Trends Cell Biol.* **2005**, *15*, 43-51.

[8] J. M. Thomas, P. A. Midgley, *ChemCatChem* **2010**, *2*, 783-798.

[9] G. Mobus, B. J. Inkson, *Mater. Today* **2007**, *10*, 18-25.

[10] (a) H. Friedrich, P. E. de Jongh, A. J. Verkleij, K. P. de Jong, *Chem. Rev.* **2009**, *109*, 1613-1629; (b) P. A. Midgley, E. P. W. Ward, A. B. Hungria, J. M. Thomas, *Chem. Soc. Rev.* **2007**, *36*, 1477-1494.

[11] (a) X. L. Pan, Z. L. Fan, W. Chen, Y. J. Ding, H. Y. Luo, X. H. Bao, *Nat. Mater.* **2007**, *6*, 507-511; (b) X. L. Pan, X. H. Bao, *Chem. Commun.* **2008**, 6271-6281.

[12] E. Castillejos, P. J. Debouttiere, L. Roiban, A. Solhy, V. Martinez, Y. Kihn, O. Ersen, K. Philippot, B. Chaudret, P. Serp, *Angew. Chem.* **2009**, *121*, 2567-2571; *Angew. Chem. Int. Ed.* **2009**, *48*, 2529-2533.

[13] J. P. Tessonnier, O. Ersen, G. Weinberg, C. Pham-Huu, D. S. Su, R. Schlogl, *ACS Nano* **2009**, *3*, 2081-2089.

[14] O. H. Kwon, A. H. Zewail, *Science* **2010**, *328*, 1668-1673.

[15] A. H. Zewail, *Science* **2010**, *328*, 187-193.

[16] A. H. Zewail, J. M. Thomas, *4D Electron Microscopy*, Imperial College Press, London, **2010**.

[17] (a) B. Barwick, H. S. Park, O. H. Kwon, J. S. Baskin, A. H. Zewail, *Science* **2008**, *322*, 1227-1231; (b) F. Carbone, O. H. Kwon, A. H. Zewail, *Science* **2009**, *325*, 181-184.

[18] P. Baum, A. H. Zewail, *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 18409-18414.

[19] B. Barwick, D. J. Flannigan, A. H. Zewail, *Nature* **2009**, *462*, 902-906.

[20] R. Saito, C. Fantini, J. Jiang, *Top. Appl. Phys.* **2008**, *111*, 251-286