DTU

Technical University of Denmark

Small is beautiful

If we can see it, we can improve it. Nanoscale imaging research is rapidly growing and within the field of electron microscopy, several developments have improved the performance of the instrumentation, underlying its significance as an extremely versatile characterisation tool for nanostructures.

It has become evident in recent years that nanotechnology is capable of producing materials that have properties that are not found in nature (at least on earth). In order to understand the macroscopic properties of materials, it is essential to gain an insight into the nature of the smallest building blocks and here nanoscale imaging research comes to the fore.

Nanoscale imaging research comes in many guises, but few are as versatile as electron microscopy. Probing nanoscale materials with high energy electrons results in a plethora of different characterisation possibilities. These include morphological and crystallographic information on the nanoscale, as well as elemental, chemical and plasmonic mapping and responses. Furthermore, electron microscopy is also capable of mapping electric and magnetic fields at the nanoscale.

More than eight decades have passed since the first electron microscopes were invented by Ruska and Knoll (1) improving the resolution obtainable by light microscopy by 2-3 orders of magnitude. The probe used to characterise the sample consists of highly accelerated electrons formed into a directional beam where typical energies of the electrons are 1-1000keV.

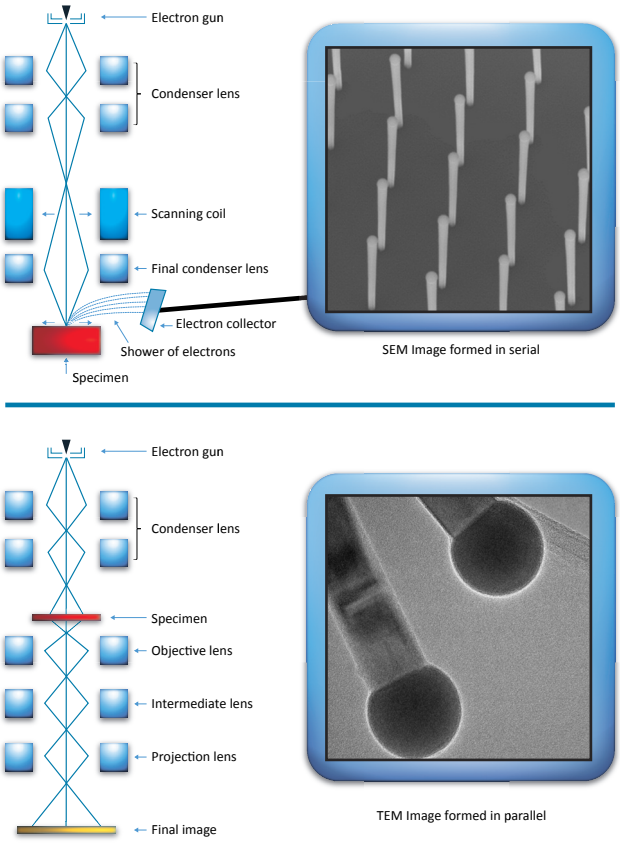


Figure 1. In a Scanning (Transmission) Electron Microscope (S(T)EM) the highly focused electron beam raster over the sample surface defining the field of view and thereby magnification. The image is formed serially by collecting the signal (electrons) escaping from the surface of the specimen giving a pseudo 3D image. In a Transmission Electron Microscope (TEM) the electron beam acts as a plane wave interacting with the specimen and via lens-optics forms a projected image in parallel. The optics (lens-strength) determine the magnification.

Courtesy of Elisabetta M. Fiordaliso, DTU Cen.

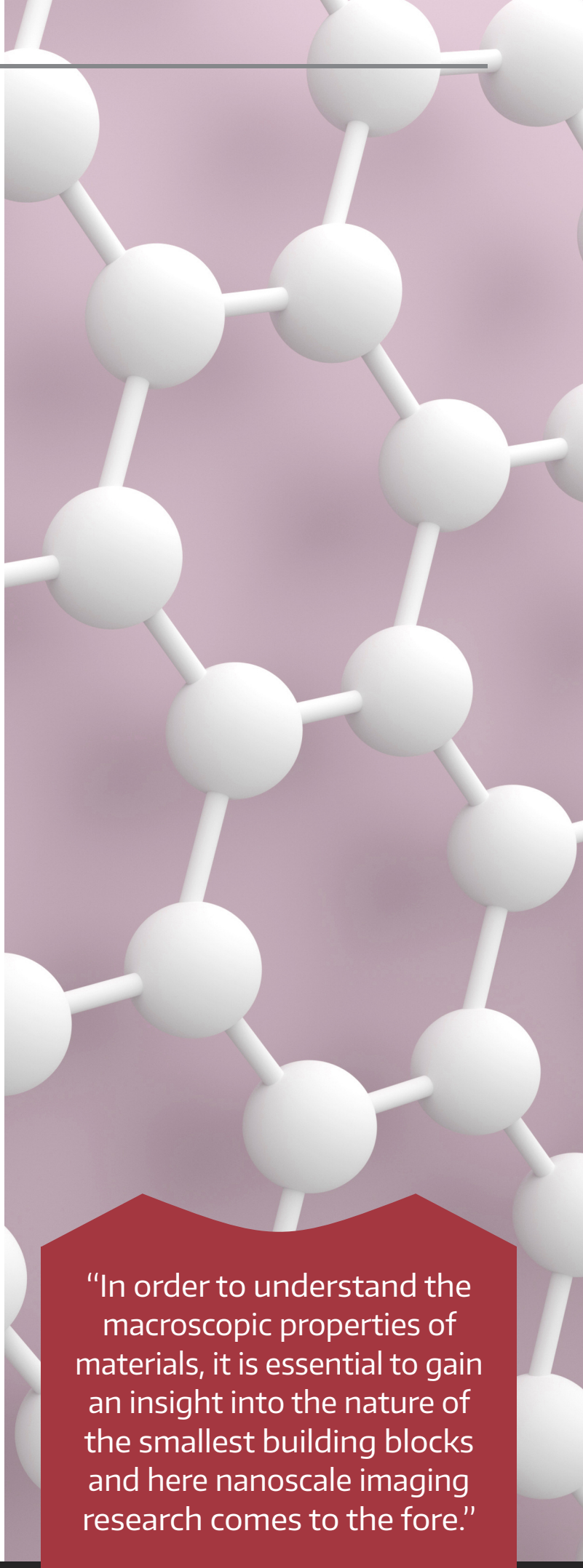
In general, electron microscopes can be divided into two types, corresponding to the image formation principles as shown in Figure 1. In Scanning Electron Microscopy (SEM) a highly focused high-energy electron beam (approx. 1nm in diameter) raster over the surface of a sample. The image is constructed by correlating the signal in the form of escaping electrons from the surface

of the sample to the position of the primary electron beam on the sample surface. In this way an image is formed serially and features down to the sub-nanometer level can be resolved. If the sample is thin enough (<100nm), the transmitted electrons can be used to form an atomically resolved image of the sample.

Transmission Electron Microscopy (TEM), on the other hand, is based on the principle of the electron beam behaving as an electromagnetic wave. Here, a collimated high-energy electron beam is formed and irradiating the sample continuously. The sample is thin (<100nm) in order to have the electron beam transmitted through the sample and an image is formed via a series of lenses. With the latest advancements in electron optics, the resolution matching atomic distances is achievable, i.e. 0.05nm, and thus atomic columns can be resolved.

Over the last couple of decades, instrument development have been dedicated to improvement of the resolution of the electron microscope. Aberrations in the electromagnetic lenses have, since the dawn of electron microscopy, been the limiting factor in the quest for better spatial resolution. With the realisation of aberration correction for both spherical aberration (2) and, more recently, chromatic aberration correction (3) of the image forming lenses, the resolution and interpretability of the formed imaged have reached the ultimate goal – a resolution matching atomic distances.

More recently, detection sensitivity of measurable signals in the electron microscope has undergone rapid development. Game-changing development within fast pixelated electron detectors (4) has allowed for faster



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and more precise imaging and analysis. This has led to vast improvements in time resolution during characterisation, and thereby the response during the dynamic characterisation of materials. Machine-assisted interpretation and analysis of the vast data amount created this way is a hot topic for developments within nanoscale imaging research (5).

Nanoscale functional materials are often tailored by interfacing different elemental compositions with at least one dimension in the nanometer range, e.g. in catalysis and semiconductor research. Nanoscale imaging is an indispensable tool for understanding, development, and failure analysis of these types of materials. The electron microscope's capability to routinely combine structural and chemical information at the sub-nanometer level is indispensable in the understanding of the micro- and nanostructure fabrication and application. Segregation and diffusion of elements in heterostructures under non-ambient conditions are key in order to understand and develop high-performance, sustainable functional materials for current and future applications, see Figures 2 and 3.

An immediate advantage of using electrons as a probe for materials characterisation

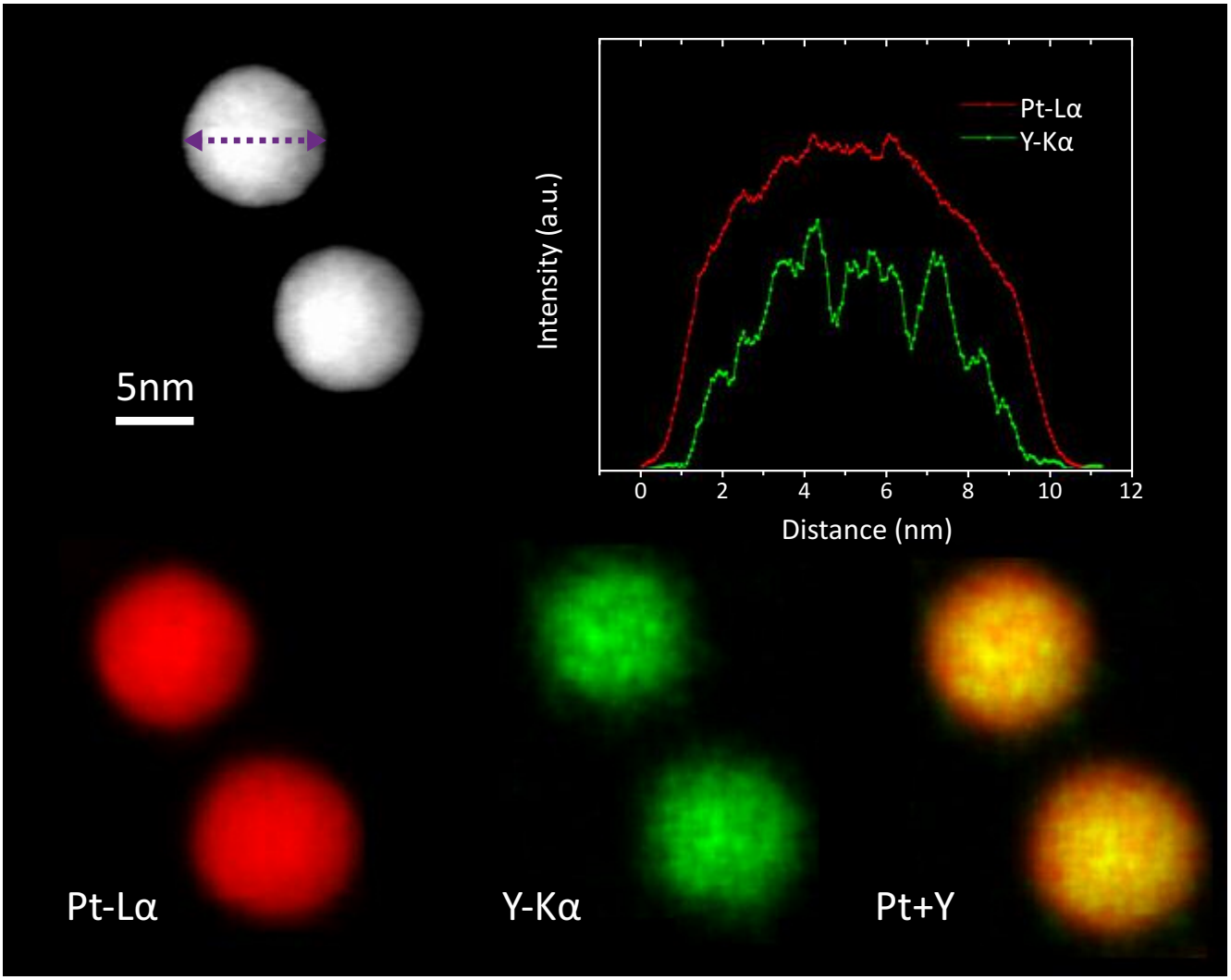


Figure 2. Combining imaging and chemical information at the nanoscale. The enrichment of platinum in relation to yttrium near the surface of synthesised nanoparticles determines the electrocatalytic performance of oxygen reduction reactions used in, e.g. (6). The inhomogeneous composition of the particles is studies in detail by electron microscopy before and after catalytic testing in order to follow the elemental distribution over time.

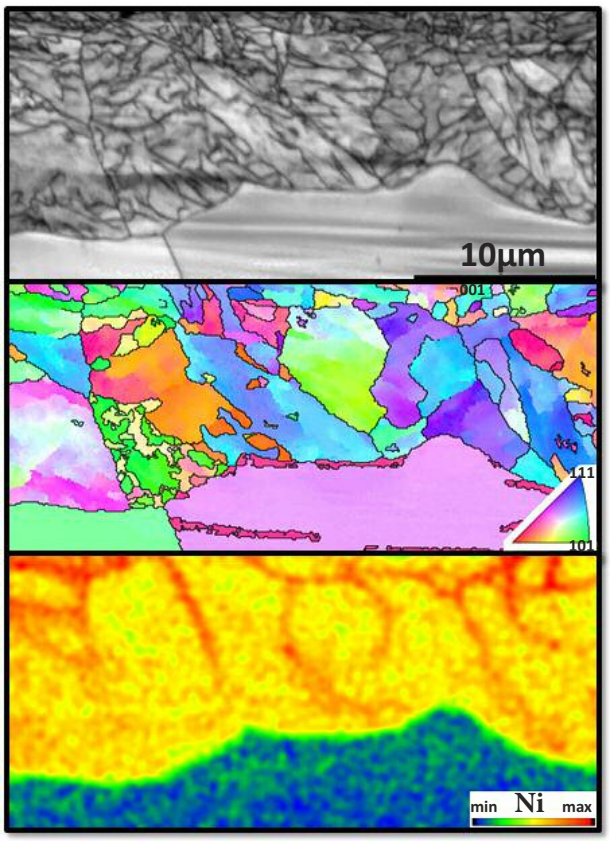


Figure 3. Ferritic steel interconnects in solid oxide fuel cell stacks are often in direct contact with nickel. At an operating temperature of 800˚C, nickel diffusion takes place which brings about a complex evolution both in microstructure and phase. This evolution, among other factors, controls the maximum service time/temperature of the fuel cell. Thus, understanding nickel diffusion into the steel and its mechanism (such as grain boundary diffusion), formation of finer grains, phase transformation from BCC to FCC, etc. is of high importance. All these can be characterised using simultaneous electron diffraction and elemental mapping in SEM (7).

over, for instance, light or X-rays, is the fact that charged particles (swift electrons) interact not only with matter, but also with electric and magnetic fields (Figure 4). Electron holography allows material functionalities such as magnetic and electric fields to be imaged quantitatively while electron tomographyprovides 3D information at the nanoscale. The combination of the two techniques enable us to study nanoscale electromagnetic fields in three dimensions for an understanding of quantum phenomena that occur at the nanoscale and device performance under working conditions. Future applications in, for instance, data storage rely heavily on such characterisations.

The high probability of electrons interacting with matter compared to light or X-rays is the main reason for the high signal and contrast achievable when imaging and analysing nanoscaled materials. However, the same high probability also requires a minimum of scattering objects around the sample. In general the sample is placed in a vacuum chamber in order to achieve the best performance of the microscope. In situ electron microscopy, which describes the imaging and analysis of samples while they are exposed to an external stimuli and environment, is another rapidly developing field (Figure 5). External stimuli include gas exposure, heat treatment, indentation, light exposure, electrical bias, fluid exposure, magnetisation, etc. Monitoring the dynamic processes during nanostructure growth of, for instance, carbon nanotubes provides an insight into bottom-up processes (i.e. building structures atom by atom) of tailor-made materials (9).

Fundamental concepts of crystal formation suggest that the growth and decomposition are determined by simultaneous embedding and removal of the atoms. By changing the crystal formation conditions (temperature or chemical equilibrium) one can switch the regimes from the growth to decomposition (Figure 6).

Building a full laboratory into the confined space of an electron microscope without compromising the general performance of the instrument is an ongoing and necessary step towards moving electron microscopy from a technique providing aesthetically pleasing images to a characterisation tool, which, together with complementary techniques, advances materials science research.

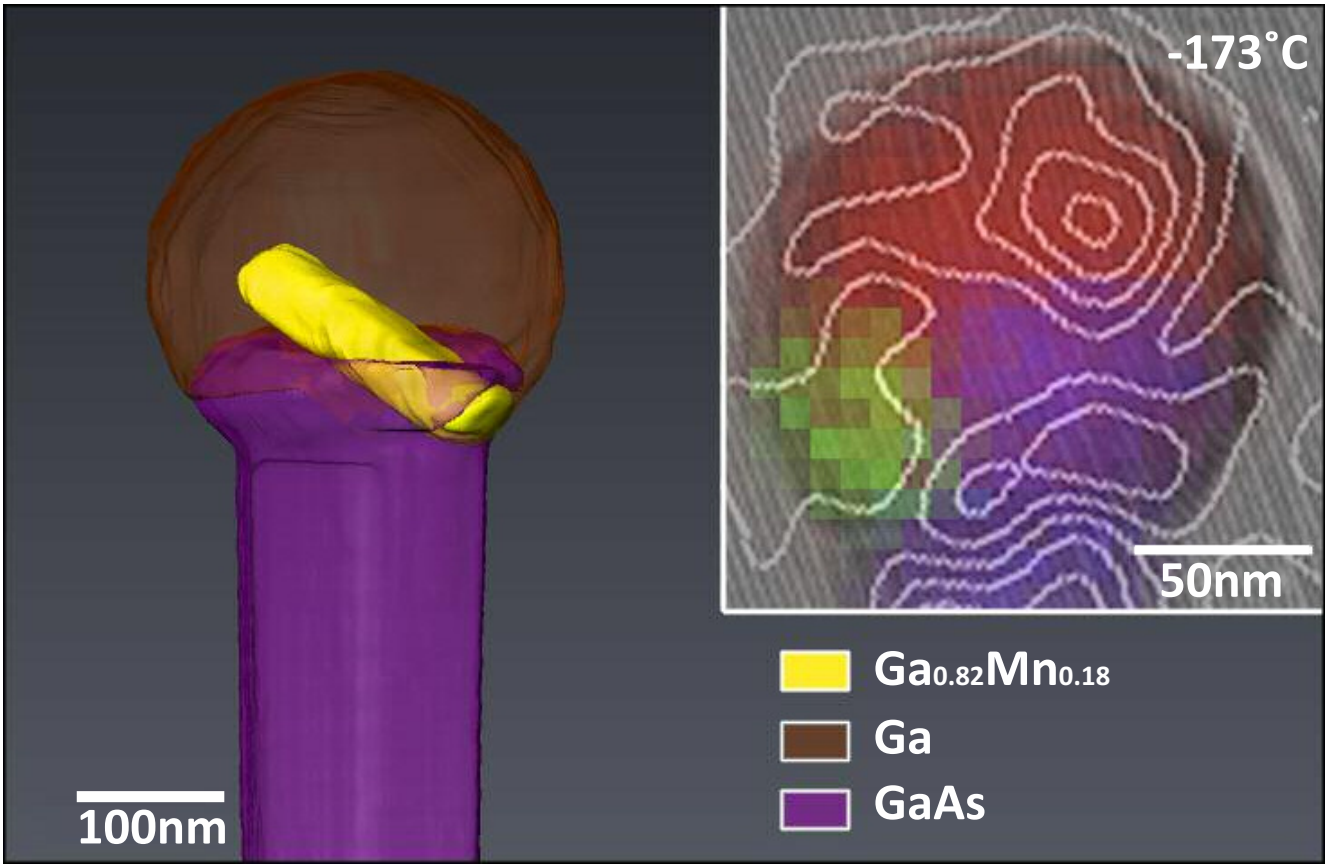


Figure 4. 3D reconstruction of a Mn-doped GaAs nanowire acquired using electron tomography and magnetic contour map. Electron holography revealed that this new phase was not magnetic above -173 ˚C. However, segregated magnetic nanoparticles can in general be an undesired potential magnetic source in diluted magnetic semiconductors compromising their functionality. (8)

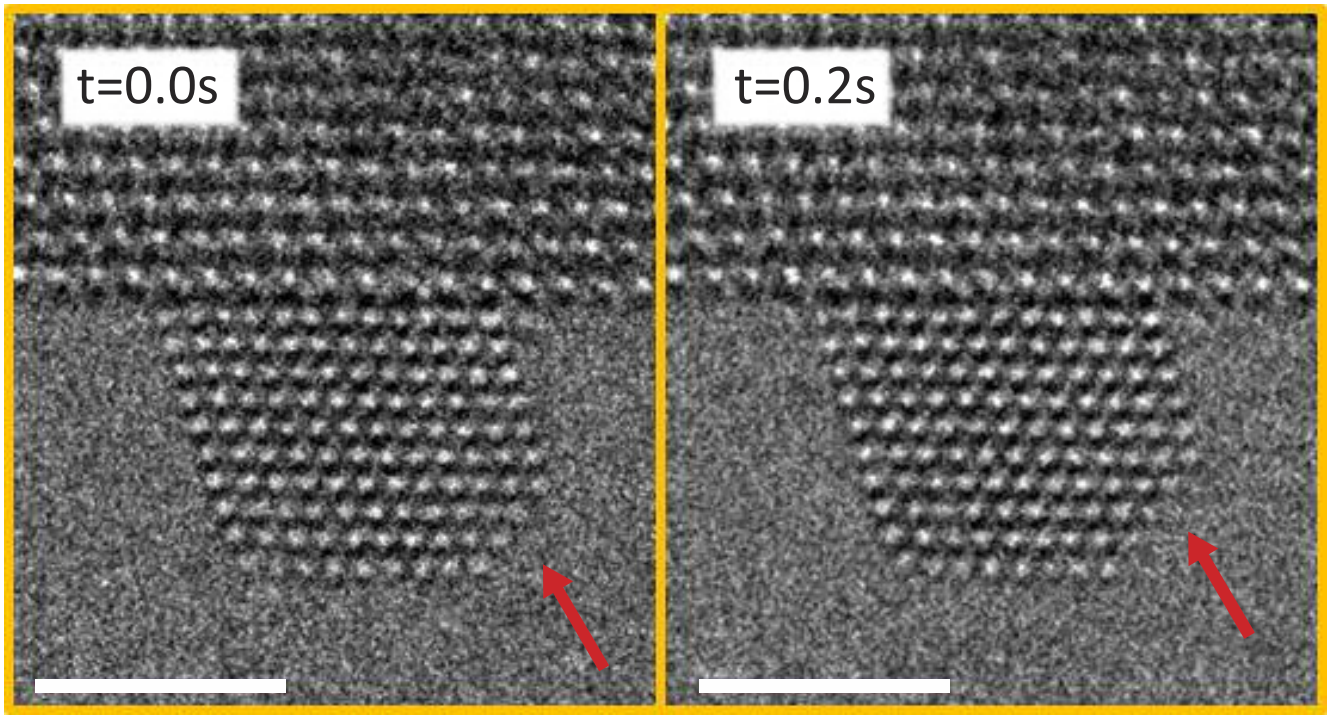


Figure 5. Mobility of atoms at a gold nanoparticle surface. The surface layer indicated by the red arrow disappears during the 0.2s time step between the two images. The bright spots in the gold particle are individual gold atom columns. The apparent joint mobility of surface atoms reveals the increased mobility of undercoordinated atoms exposed to non-vacuum conditions at elevated temperature. The nanoparticles were studied under 4.5 Pa carbon monoxide at 250°C. Scale bar is 2nm. *Courtesy of Pei Liu, DTU Cen.*

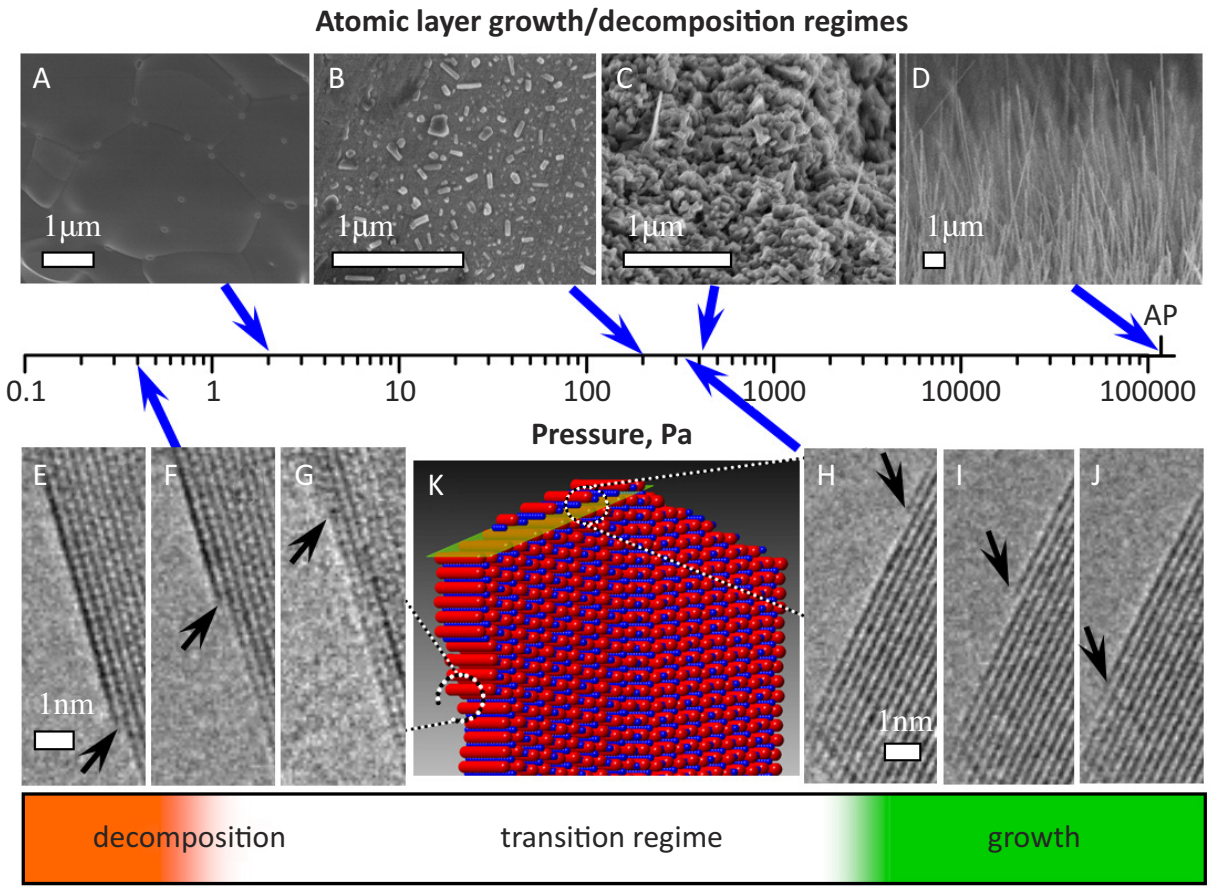


Figure 6. CuO atomic layer (AL) growth/decomposition regimes on NW at different O_2 pressures and constant temperature of 400°C. (A) to (D) are SEM observation of CuO formation at the indicated pressures. *In situ* environmental transmission electron microscopy (ETEM) decomposition of AL (E) to (G) and AL growth (H) to (J) were observed on surfaces, schematically shown on CuO NW model (K). Atmospheric pressure is indicated as AP on the pressure scale (10)

References:

1: The Electron Microscope, M. Knoll, E. Ruska, Zeitschrift für Physik 78, 318 (1932)

2: Electron microscopy image enhanced, M. Haider, H. Rose, S. Uhlemann, B. Kabius, K. Urban, Nature 392, 768 (1998)

3: Chromatic Aberration Correction for Atomic Resolution TEM Imaging from 20 to 80 kV, M. Linck, P. Hartel, S. Uhlemann, F. Kahl, H. Müller, J. Zach, M. Haider, M. Niestadt, M. Bischoff, J. Biskupek, Z. Lee, T. Lehnert, F. Börrnert, H. Rose, and U. Kaiser, Phys. Rev. Lett. 117, 076101 (2016)

4: Comparison of optimal performance at 300 keV of three direct electron detectors for use in low dose electron microscopy, G. McMullan, A.R. Faruqi, D. Clare, and R. Henderson, Ultramicroscopy 147, 156 (2014)

5: Deep Learning of Atomically Resolved Scanning Transmission Electron Microscopy Images: Chemical Identification and Tracking Local Transformations, M. Ziatdinov, O. Dyck, A. Maksov, X. Li, X. Sang, K. Xiao, R. R. Unocic, R. Vasudevan, S. Jesse, S. V. Kalinin, ACS Nano 11, 12742 (2017)

6: Mass-selected nanoparticles of PtxY as model catalysts for oxygen electroreduction, P. Hernandez-Fernandez, F. Masini, D. N. McCarthy, C. E. Strebel, D. Friebel, D. Deiana, P. Malacrida, A.s Nierhoff, A. Bodin, A. M. Wise, J. H. Nielsen, T. W. Hansen, A. Nilsson, I. E. L. Stephens, and I. Chorkendorff, Nature Chemistry 6, 732 (2014)

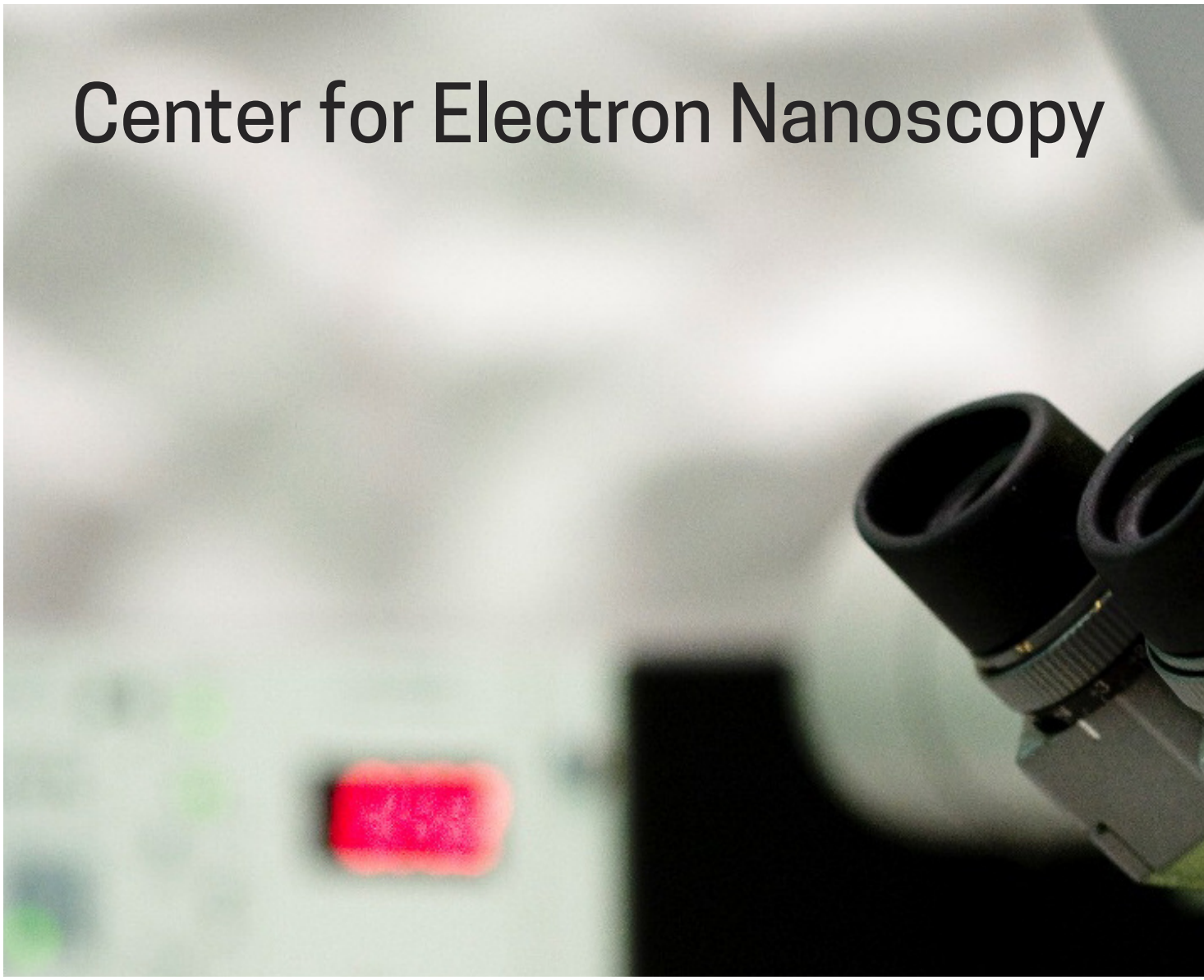
7: Electrical Resistance Measurements and Microstructural Characterization of the Anode/Interconnect Contact in Simulated Anode-Side SOFC Conditions, A. Harthøj, H. Alimadadi, T. Holt, and P. Møller, J. Electrochem. Soc. 162(4), F387 (2015)

8: Direct observation of doping incorporation pathways in self-catalytic GaMnAs nanowires, T. Kasama, M. Thuvander, A. Siusys, L. C. Gontard, A. Kovács, S. Yazdi, M. Duchamp, A. Gustafsson, R. E. Dunin-Borkowski, and J. Sadowski, Journal of Applied Physics 118, 054302 (2015)

9: Growth Termination and Multiple Nucleation of Single-Wall Carbon Nanotubes Evidenced by in Situ Transmission Electron Microscopy, L. Zhang, M. He, T. W. Hansen, J. Kling, H. Jiang, E. I. Kauppinen, A. Loiseau, and J. B. Wagner, ACS Nano 11, 4483 (2017)

10: Direct Observation of Nanowire Growth and Decomposition, S. Rackauskas, S. D. Shandakov, H. Jiang, J. B. Wagner, A. G. Nasibulin, Scientific Reports 7, 12310 (2017)

Center for Electron Nanoscopy



High-end research infrastructure for electron microscopy based characterisation and analysis at Technical University of Denmark.

Following a generous donation from the A. P. Møller and Chastine Mc-Kinney Møller Foundation, the Center for Electron Nanoscopy at the Technical University of Denmark (DTU Cen) was inaugurated in 2007. The center was established as a state-of-the-art electron microscopy (EM) facility with a suite of microscopes housed in a high specification building that only a handful of other labs worldwide could rival. The broad aim of the center is to ensure a balance between advanced research, teaching and training, and fostering collaborations with national and international partners. Now, a decade after the official inauguration of DTU Cen, the center employs 17 researchers (including PhD students and post docs.) as well as 7 technical and administrative staff. Over the years, the activities of the center have been expanding as DTU Cen attracts funding from both Danish and European funding agencies.

Access for academic and industrial scientists to DTU Cen's electron microscopes supports existing research and results in the creation of new research fields and in the sharing of

knowledge for the development of materials, processes, technologies, techniques and instrumentation. The list below gives an idea of the broad research areas that the center is currently pursuing:

- In situ characterisation of individual nanoparticles under controlled atmosphere;
- Nanostructures for Plasmonic sensing;
- Magnetic materials;
- Pore structures in minerals and soil;
- (pseudo) 1-dimensional semiconductor heterostructures for solar cells;
- Growth of 1D and 2D carbon structures;
- Grain boundary mapping and phase transitions of alloy materials.

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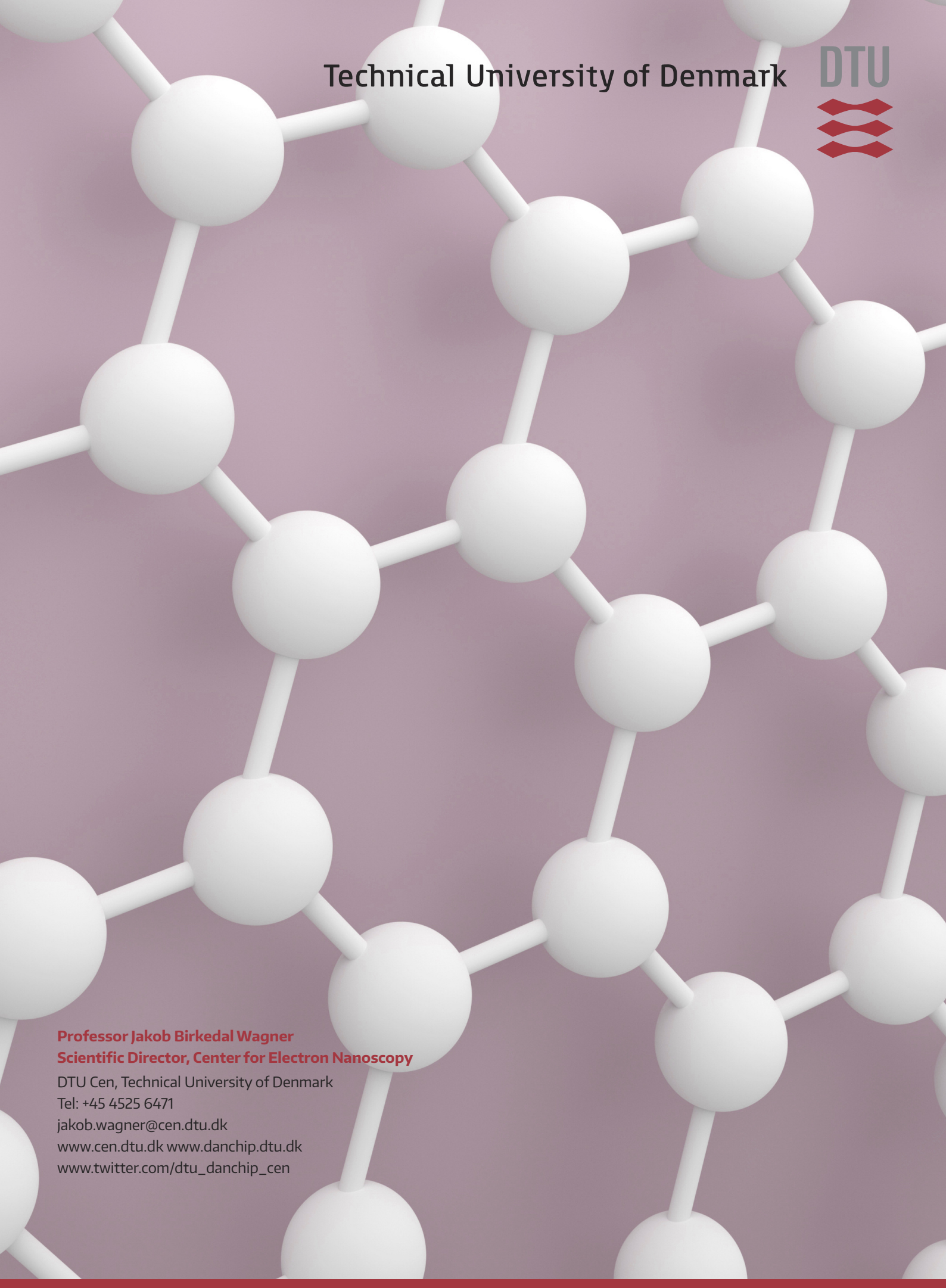

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