MONITORING NANOSTRUCTURE FORMATION

DTU
Technical University of Denmark

Monitoring Nanostructure Formation atom by atom

As Richard Feynman pointed out in his famous 'There's plenty of room at the bottom' talk in 1959 the properties of materials could be tailored if we control the exact position of each individual atom in the materials. 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 their assembly and here nanoscale imaging research of dynamic processes comes to the fore.

Bottom up processes where materials and nanostructures are formed by building it atom by atom is a viable route to tailor materials. Monitoring the formation of such materials with a spatial and temporal resolution giving insight in the mechanisms controlling the formation is of fundamental interest in order to explore the applications of such.

High resolution transmission electron microscopy serves the basis for atomic resolution imaging. Adding capabilities to such high-resolution imaging instruments allows for the possibilities to monitor formation processes of nanostructures from e.g. gas phases. Examples of such is the formation of carbon nanotubes and metal (oxide) nanowires where the formation is controlled by physical and chemical mechanisms. Another example is electron beam induced deposition of materials, where the positioning of atoms and molecules is controlled directly by a controlled electron beam to directly write nanostructures.

Traditionally, transmission electron microscopy (TEM) has been a high vacuum discipline. However, in both academic and industrial research there is now an increased need to expose samples to more realistic environments during image acquisition, in the form of gas mixtures and elevated temperatures. [1] The so-called Environmental Transmission Electron Microscope (ETEM) is a specially designed microscope allowing for imaging at the atomic scale in the presence of gas at elevated temperature (Figure 1).

The abundance of carbon in nature combined with the variety of assembling the individual atoms into nanostructures with various physical properties such as metallic, semiconducting, semi metallic etc. make carbon nanostructures of particular interest and importance in tomorrow's electronic and optical devices. Single walled carbon nanotubes and graphene show enormous potential in electronic devices and are already incorporated as transparent conductors in touchscreens to name but a few applications.

Single walled carbon nanotubes (SWCNT) consists of a hexagonal lattice of carbon atoms rolled into a tube. The specific diameter and chirality (or helicity) of the carbon tube determine whether the nanotube acts metallic or semiconducting. Tubes are typically grown from metallic seed

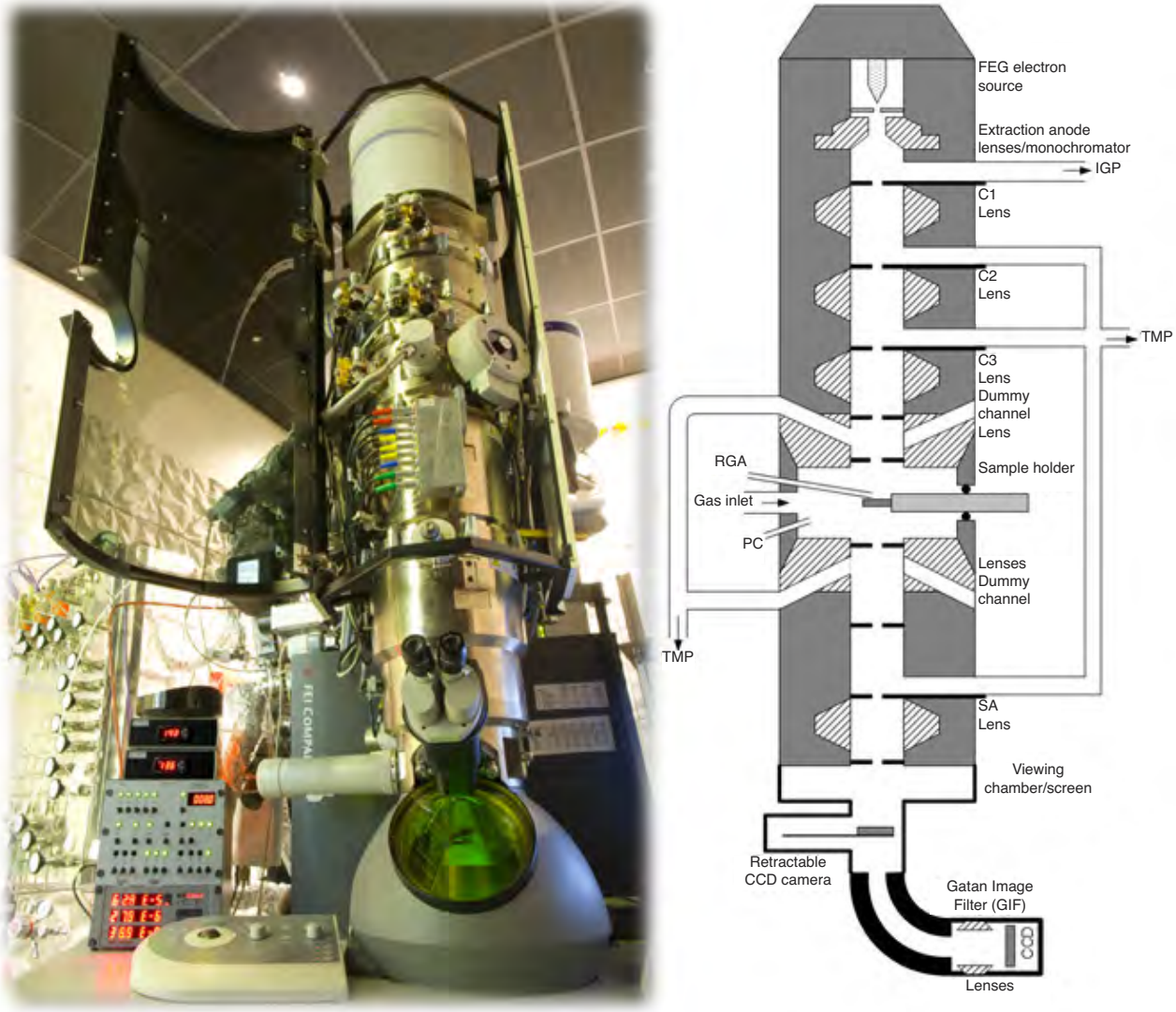

Figure 1: In order to add the capability of monitoring samples in the presence of gases at elevated temperature maintaining the atomic resolution, the electron microscope is equipped with pressure limiting apertures as close to the sample as possible confining the higher pressure (up to 2000 Pa) in a small volume near the sample. This solution has minimal influence on the microscope performance in terms of resolution and electron source stability.

nanoparticles (Fe, Ni, Co, etc). In order to grow the nanotubes selectively (with a specific chirality) for efficient application, a better understanding of the actual growth mechanism is essential. Watching the carbon structure form at the atomic scale gives valuable insight in the key parameters and processes determining the diameter and chirality of the carbon nanotubes and thereby their electronic and optical properties. In situ growth of such carbon structures by means of environmental transmission electron microscopy (ETEM) is a unique opportunity to follow the growth live [1]. At Center for Electron Nanoscopy at the Technical University of Denmark, such growth studies have successfully been carried out in the past years. [2,3]

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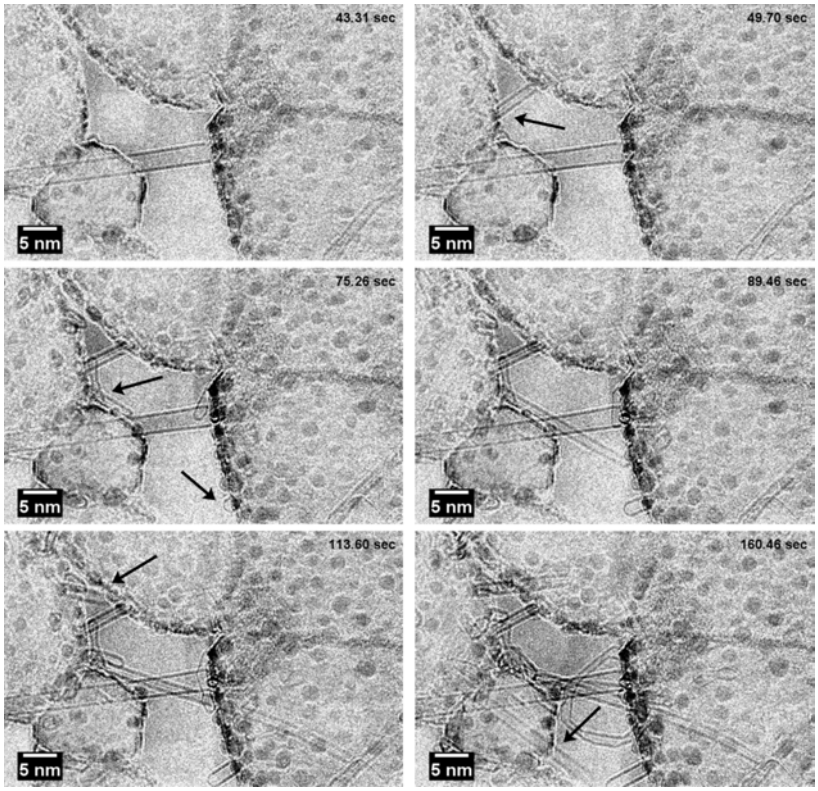


Figure 2: Image sequence of an *in situ* growth experiment performed at 700°C (p(ethanol)=0.1 Pa). Arrows indicate a few newly grown SWCNTs in each frame. The time stamp indicates the time since the valve to ethanol was opened. The images are background subtracted for better visibility of the particles and tubes. *(courtesy of Jens Kling)*

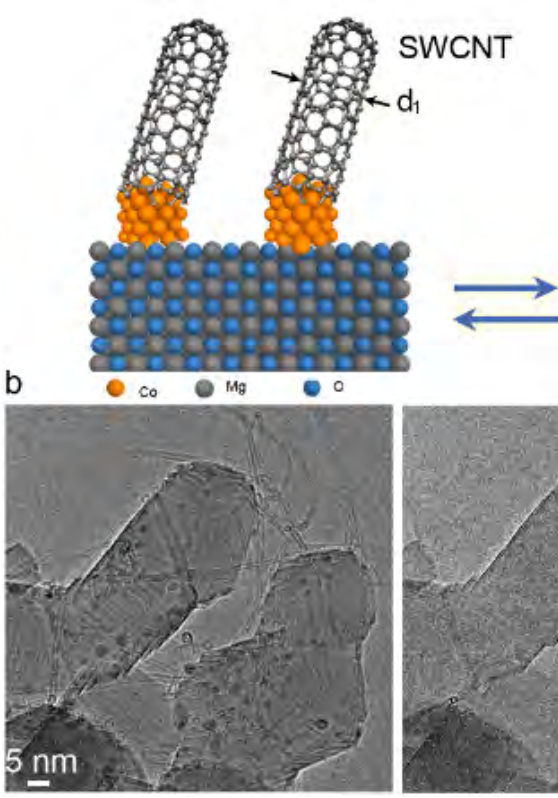
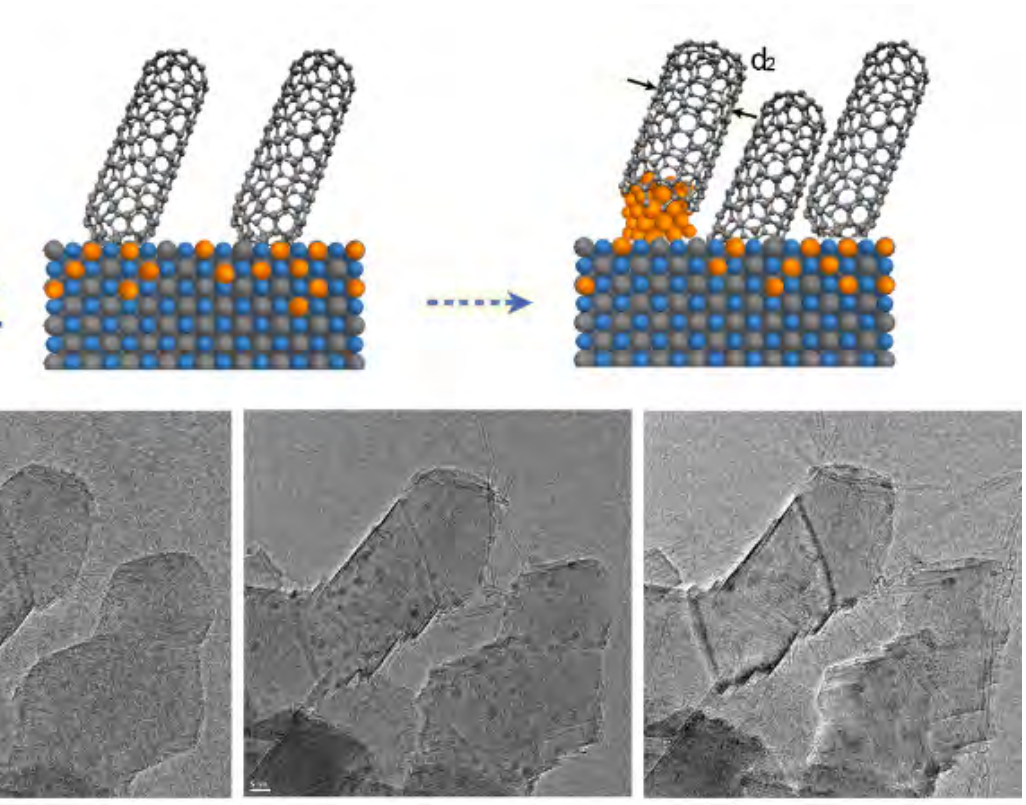


Figure 3: The growth of metal free single walled carbon na pulsing the carbon source (ethanol). The growth is termina carbon supply and the cobalt seed particles are dissolved in leaving the CNTs. Re-introducing the carbon supply re-ini another set of CNTs. *(courtesy of Lili Zhang)*

Figure 2 shows the transition from gaseous carbon to solid carbon forming CNTs. The elongation process of a SWCNT is shown by a series of transmission electron micrographs extracted from a movie, acquired during exposure of a Co/MgO sample to ethanol (C_2H_5OH) at elevated temperature. The diameter and thereby the chirality of the SWCNTs strongly depends on the size and state of the catalytic particles (in this case cobalt) and the access to carbon atoms, which can be incorporated into the tube securing growth. Changes in the amount of accessible carbon either by changes in the carbon supply (gas pressure of ethanol) or by changes in the rate of catalytic cracking of ethanol to free carbon atoms, strongly influence the growth and can be a limiting step for the CNT growth. However, we observe that the same catalyst particle stayed active in terms of nucleating additional solid carbon structures after the growth termination of the first SWCNT (Figure 3). These observations elucidate the importance of an in-depth understanding of the role of catalysts and carbon sources in the continued growth of SWCNTs.

Nanostructures can also be formed by simple oxidation of metals such as copper. CuO nanowires are formed by oxidation of metallic copper in situ in the electron microscope. The exact geometry of the resulting structures depends strongly on the partial pressure of oxygen during the heat treatment. Low pressure results in 2-dimensional copper oxidation in contrast to the 1-dimensional CuO nanowires forming at higher pressures. Post-growth treatment of the oxide nanowires at elevated temperature at reduced partial pressure of oxygen results in dissolution of the formed nanowires [4,5].



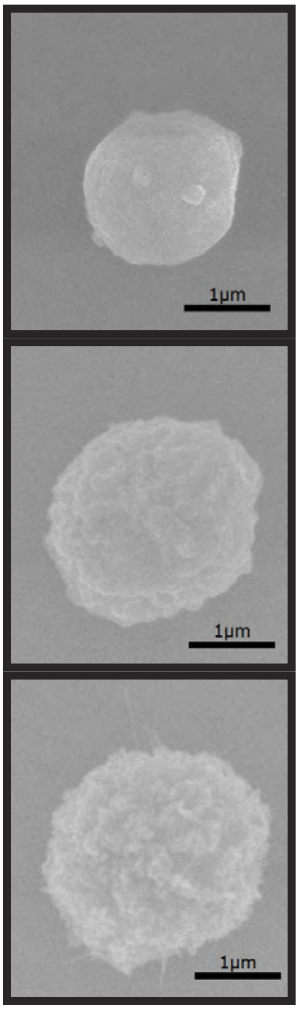


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Figure 4: Oxidation of a metallic copper sphere monitored at elevated temperature (450°C) in presence of oxygen. The scanning electron microscopy (SEM) image reveals a two stage oxidation. First a Kirkedall effect results in a 2-dimensional oxidation followed by an anisotropic oxidation forming high-aspect ratio micrometer long nanowires. *(courtesy Mohammada Ahmed and Mamadou Kone)*

Environmental Scanning Electron Microscopy of the oxidation of a micrometer sized Cu sphere reveals a two stage oxidation process giving rise to different morphologies of the resulting copper oxide. Heating the sphere and introducing oxygen (approx. 1000Pa) result in the sphere to swell uniformly (Figure 4). Metallic copper is transported through the initial copper oxide shell and thereby being trapped as copper oxide on the outside leaving a hollow structure behind (not shown here). This mechanism is known as the Kirkendall effect. After some minutes the transport of copper though the oxide shell follow certain grain boundaries enhancing specific growth directions resulting in pseudo one-dimensional structures / spikes at the surface.

The growth mechanism of the copper oxide nanowires have been studied in detailed using ETEM allowing to follow the atom-by-atom

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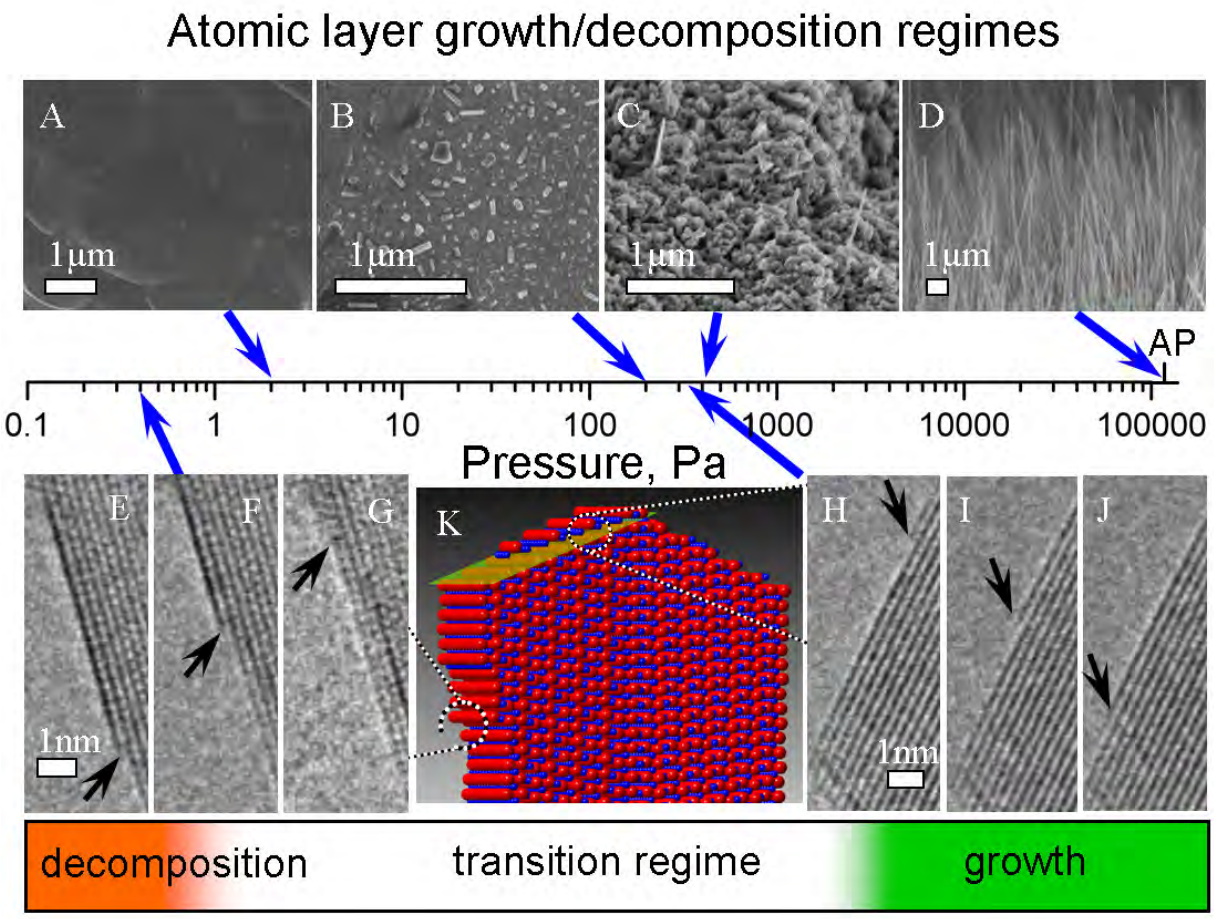
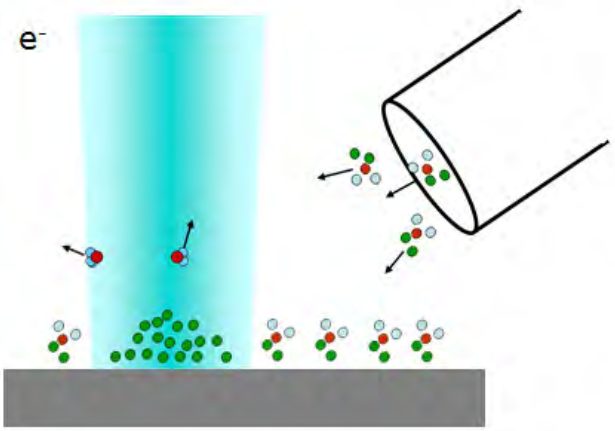


Figure 5: CuO atomic layer (AL) growth/decomposition regimes on NW at different O_2 pressures and constant temperature of 400 °C. (A) to (D) are SEM observation of CuO formation at the indicated pressures. *In situ* environmental transmission electron microscopy (ETEM) decomposition of AL (E) to (G) 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. [5]

growth revealing the growth to happen purely at the tip of the nanowires. A twin boundary formed along the long axis of the nanowires serves as a diffusion path for copper atom, which then are oxidized at the tip of the nanowire extending the structure. [4]

The detailed atomic monitoring of the dynamic processes also give insight into the fundamental concepts of crystal formation suggesting 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 5).

The growth mechanisms described above relies on the self-assembly of the atoms into crystalline material. True control of the atoms forming nanostructures requires external stimuli which can be controlled to the nanometer scale. Individual metal containing molecules can be positioned very precise on a substrate by means of focused electron beam induced deposition. The focused electron beam cracks the adsorbed metalorganic molecules with a sub-nanometer precision (Figure 6).



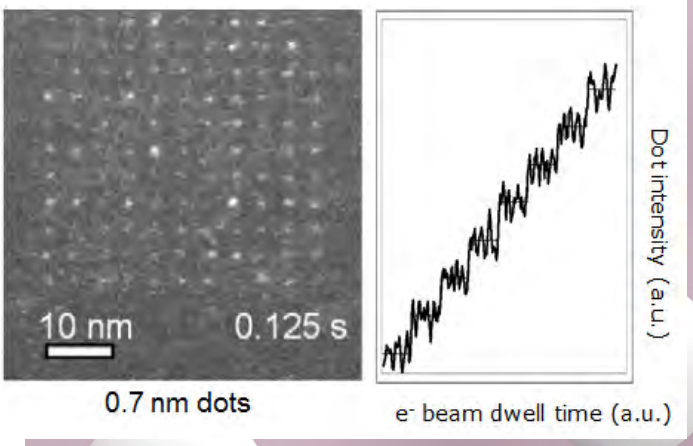


Figure 6: Focused electron beam induced deposition: Gaseous metalorganic precursor molecules are let into the substrate in such way that the fully controlled electron beam writes the metal structure by cracking the adsorbed molecules. The size of sub nanometer structures can be controlled at the single molecule level by the writing speed. [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 characterization tool, which, together with complementary techniques, advances materials science research.

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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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