Nanomaterials for Sustainable Energy

Towards Understanding and Controlling Structure at the Atomic Scale

The atomic structure of nanomaterials and the energy needed for their function can be optimised by a fundamental understanding of catalytic behaviour of nanoparticles and of the physical, atomic-level properties of materials for solar cells, fuel cells and light sources. This requires advanced tools that can see down to the individual atoms and sense their chemical environment, show information in three dimensions and allow experiments *in situ* to follow specific reactions.

With conventional global energy resources under increasing pressure, developing renewable energy sources and increasing the efficiency of existing energy production technologies are crucial aspects of efforts to ensure long-term energy supplies and preserve and protect the Earth's environment. New nanomaterials promise to play an important role in accomplishing these goals, and their development requires exploration of material properties at the atomic scale to precisely understand, accurately control and truly visualise structure-property relations of surfaces, defects and interfaces. Researchers are using knowledge of physical, chemical, structural and energy relationships at the atomic scale to optimise the performance of catalytic nanoparticles, solar cells, fuel cells and light sources. Acquiring this knowledge requires advanced tools that can see individual atoms and sense their chemical environment, analyse and present the information in three dimensions and perform experiments *in situ* to follow specific chemical reactions and physical processes.

Keywords:

S/TEM, Nano particles, Catalysts, Atomic structure, Atomic resolution

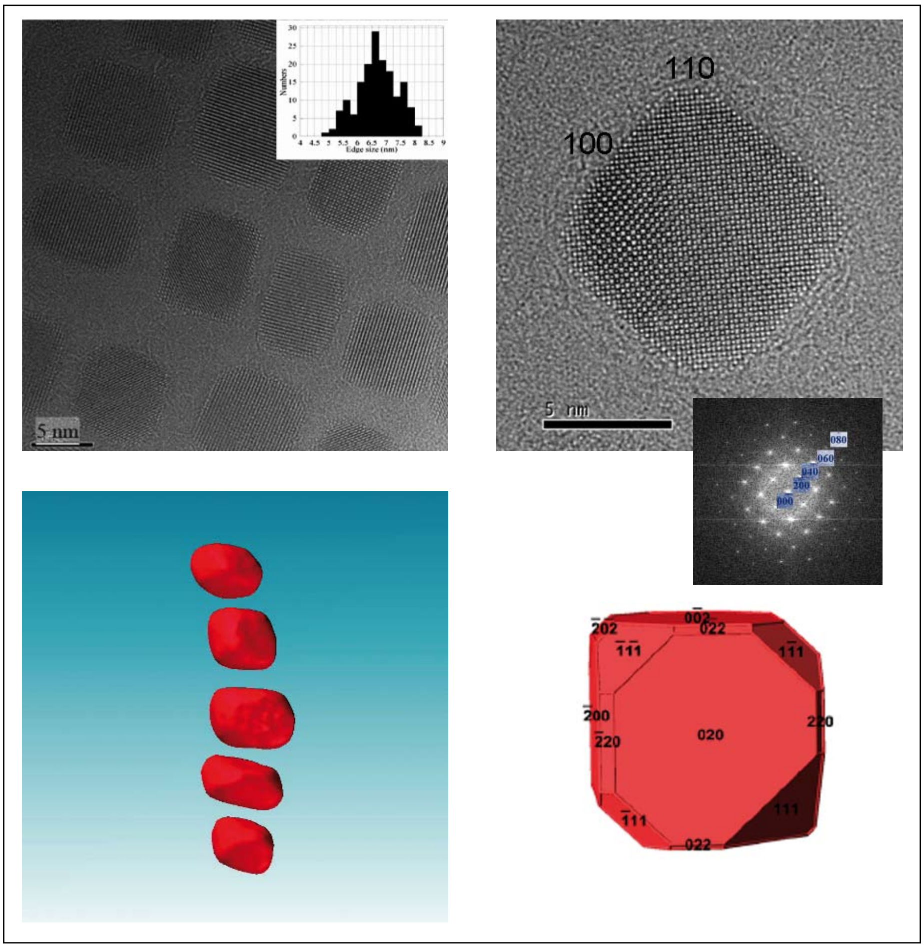

Fig. 1: Components of a solid oxide fuel cell (SOFC): CeO_2 nano particles in a polymer matrix. Aberration corrected TEM gives unambiguous, atomic resolution images of the particles, allowing determination of particle size distribution and indexing of crystal planes along facets. These facets are a crucial aspect of catalytic activity. TEM tomography means that 2D projections can be transformed into a 3D representation, as demonstrated by the reconstruction of five CeO_2 particles, lower left. [2]

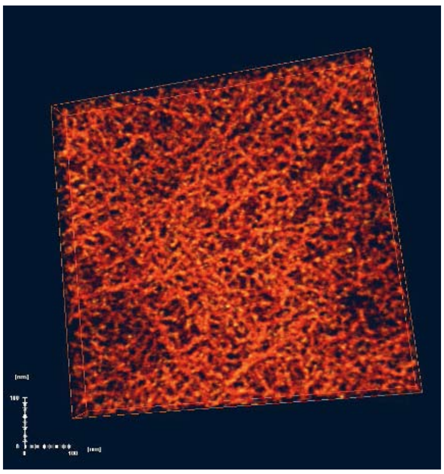

Fig. 2: A 3D reconstruction from a series of STEM tomograms showing a polymer semiconductor nano network that forms part of an organic photovoltaic device. [3]

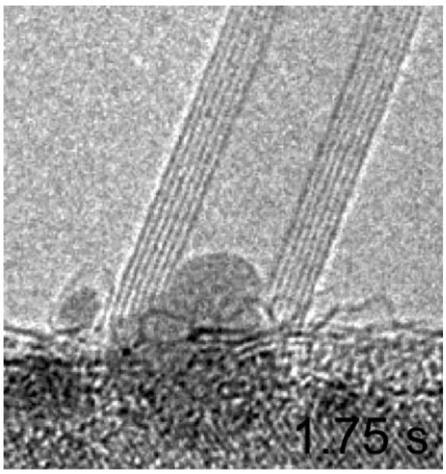

Fig. 3: *In situ* dynamic observation of the growth of a multi-walled carbon nanotube in the TEM. Courtesy of S. Takeda and H. Yoshida, Osaka University, Japan.

Solid Oxide Fuel Cells

Among the new generation of energy-efficient and environmentally-friendly energy production technologies is the solid oxide fuel cell (SOFC), which can be used in electrocatalytic reactions as a conductor of oxygen and to produce hydrogen directly from methanol. For catalytic reactions, a large surface area with plenty of active sites is a must, and one way to achieve this is by the formation of tiny nanocrystalline particles, which improve performance by providing a large surface area with many active sites. The nature of the exposed crystal facets at the surface determines the degree of activity. Precisely characterising these facets requires the ability to clearly observe the positions of atoms at the edges of the nano crystals in both two and three dimensions. Aberration-corrected, high-resolution scanning/transmission electron microscopy (S/TEM) provides these capabilities (fig. 1).

Next generation 3D nano characterisation is enabling similar progress in areas such as materials for solar cells. Figure 2 shows a 3D reconstruction from STEM tomography of a semiconductor polymer nano network. The morphology, phase distribution and connectivity of the network affects the electrical efficiency of photovoltaic devices. The percolation pathway of the individual polymer blends only becomes clear when visualised in three dimensions.

Nanotube Synthesis

S/TEM can provide more than just static observations of materials. A unique new TEM specifically designed for "environmental" (ETEM) *in situ* studies of dynamic processes permits gases in the specimen chamber at pressures up to 4 kPa (40 mbar, 30 torr) and a wide range of temperatures (max. 1,000°C). Up to four different gases can be used, and a gas analyser precisely monitors the actual composition of the gases in the sample environment. The ETEM accommodates double tilting, for crystallographic alignment and can be equipped with a spherical aberration corrector to provide atomic resolution capabilities. ETEM enables the *in situ* dynamic synthesis and reaction of materials in the TEM, allowing direct analysis of chemical information, growth kinetics and catalytic processes using both imaging and spectroscopic techniques at ultra-high resolution. This promises to give a deeper understanding of the reaction mechanisms at the nanoscale, even down to the atomic level. For example, in the case of nanotube synthesis, ETEM studies can be used to directly investigate the shape of the catalysts responsible for nano tube nucleation (fig. 3) under reaction conditions (i.e. at temperature and pressure). In the case of catalyst characterisation, real time observations of catalyst crystallinity, physical structure and electronic structure can be made in both oxidising and reducing environments.

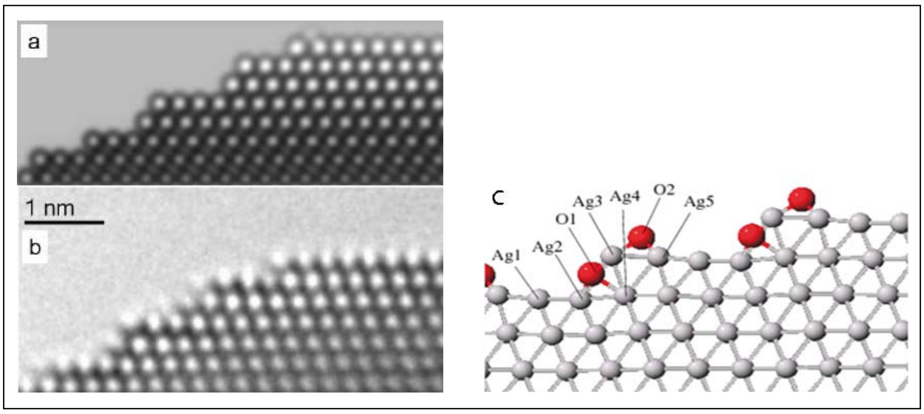

Fig. 4: TEM image simulation (a), aberration-corrected TEM imaging (b) and density functional theory (c) combine to reveal new information on Ag nano catalysts. The presence of sub-surface O atoms causes certain Ag atoms to protrude slightly, making a huge difference to catalytic activity. [4]

Silver Nanoparticle Catalyst

Seeing and measuring exact atomic positions, and any irregularities in position, is casting new light on the catalytic activity of, for example, silver nanocatalysts that play a crucial role in producing ethylene oxide (a major component in flexible plastics) and formaldehyde (a major component in rigid plastics), purifying drinking water, collecting solar energy and storing oxygen. The catalytic action of silver also finds use in converting methanol-containing waste gas from pulp mills: instead of being burned off into the atmosphere, the waste products are efficiently transformed into formaldehyde. However, the precise reason for the catalytic activity of silver nano particles was not known until recently, when aberration-corrected TEM was used to measure interatomic distances (fig. 4). This revealed a surprise: certain atoms at steps or edges were found to protrude (by a mere 0.3Å) where they might be expected to be slightly recessed. This seemingly insignificant detail has a major effect on catalytic activity. Theoretical simulations using these measurements confirmed that oxygen atoms placed at certain sites within the surface and subsurface of the crystal would give rise to the distances measured experimentally. The presence of oxygen had been predicted by Nobel prize winner Ertl using spectroscopic methods, but could not be directly visualised until the advent of advanced, aberration-corrected TEM.

These are but a few examples of how, with the world's energy needs in mind, technological and scientific insights using aberration-corrected S/TEM are advancing progress in the understanding, development and control of new nanomaterials and are a vital component in helping to realise the potential of smart materials and energy efficient devices.

References

[1] Stokes D.J. *et al.:* NanoTech Northern Europe (2008)

[2] Kaneko K. *et al.:* Nano Letters 7(2), 421–425 (2007)

[3] van Bavel S.S. *et al.:* Nano Letters (in press)

[4] Su D.S. *et al.:* Angewandte Chemie, 47 (2008)

Authors:
Debbie Stokes, Bert Freitag, Dominique Hubert

Contact:
Debbie Stokes
FEI Company
Eindhoven, The Netherlands
debbie.stokes@fei.com