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Over the last two decades, three-dimensional (3D) imaging by transmission electron microscopy (TEM) or "electron tomography" has evolved into a powerful tool to investigate a broad variety of nanomaterials in different fields such as life science, chemistry, solid state physics and materials science. Most of these results have been obtained with a resolution at the nanometer scale but different approaches have recently pushed the resolution to the atomic level. Such information is a prerequisite to understand the specific relationship between the atomic structure and the physicochemical properties of (nano)materials. We will provide an overview of the latest progress in the field of atomic resolution electron tomography. Different imaging and reconstruction approaches will be presented and state-of-the-art results will be discussed. In this manner, we will demonstrate the power and importance of electron tomography with atomic scale resolution.

Keywords: Atomic resolution, Electron tomography, Discrete tomography, Compressive sensing, Strain mapping

Introduction

Solid matter is a three-dimensional (3D) agglomeration of atoms. The properties of materials are determined by the positions of the atoms, their chemical nature and the bonding between them. If one is able to determine these parameters in 3D, it becomes possible to provide the necessary input for predicting the physicochemical properties of these atomic agglomerates. Moreover, it will allow one to guide the synthesis and development of new nanomaterials.

The development of aberration corrected transmission electron microscopes (TEM) enabled the structural investigation of nanostructures with a resolution of the order of 50pm. [1-4] However, TEM images are only two-dimensional (2D) projections of 3D (nano)-objects. Electron tomography has therefore been developed as a powerful tool to investigate the morphology, 3D structure and composition of a broad range of materials of which many examples are presented elsewhere in this issue. [5, 6] Most results have been achieved at the nanometer level, but some open questions in materials science demanded the further development of the technique and have pushed the resolution to the atomic level. For example, it is known that the surface morphology of Au nanocrystals mainly determines their catalytic and optical properties. [7, 8] Although the morphology can be characterized using conventional electron tomography with a resolution of the order of a few nanometers or below, it is impossible to precisely determine the exact type of surface planes from such reconstructions. In addition to the morphology, the crystal structure, including defects and (surface) strain, is equally essential, since it will directly affect plasmonic or catalytic properties. [9, 10] Being able to perform electron tomography with atomic resolution is therefore crucial. Although this is not yet a standard possibility for all structures, significant

progress for samples that are relatively stable under the electron beam has recently been achieved using different approaches, which will be further explained in this paper.

Visualizing atoms in 3D

First reports in which the 3D atomic structure of a nanoparticle was visualized were based on a single 2D projection image. Through a quantitative analysis of the projected intensities in atomically resolved high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images, acquired from an isolated Au nanocluster, Li et al. were able to extract a thickness profile and a 3D model could be proposed. [11] It should be noted that it is likely that there are different 3D models matching the 2D image. In 2011, a real breakthrough was performed when Van Aert and coworkers obtained a more unique 3D reconstruction at the atomic scale for a 3 nm Ag nanoparticle embedded in an Al matrix. [12] The reconstruction was based on 2 HAADF-STEM images acquired along different zone axes. As illustrated in Figure 1, these images (Figures 1.a,b) were translated into counting results (number of atoms in each atomic column) using statistical parameter estimation theory (Figures 1.c,d). Next, discrete tomography was used to combine the images into a 3D reconstruction with atomic resolution (Figure 1.e). [13] This approach was proposed earlier as an efficient strategy based on simulated electron micrographs. [13] It was hereby assumed that all of the atoms were positioned on a face-centered-cubic grid and that the particle was connected without the presence of vacancies. An excellent match was found when comparing the 3D reconstruction with projection images that were acquired along additional zone axes.

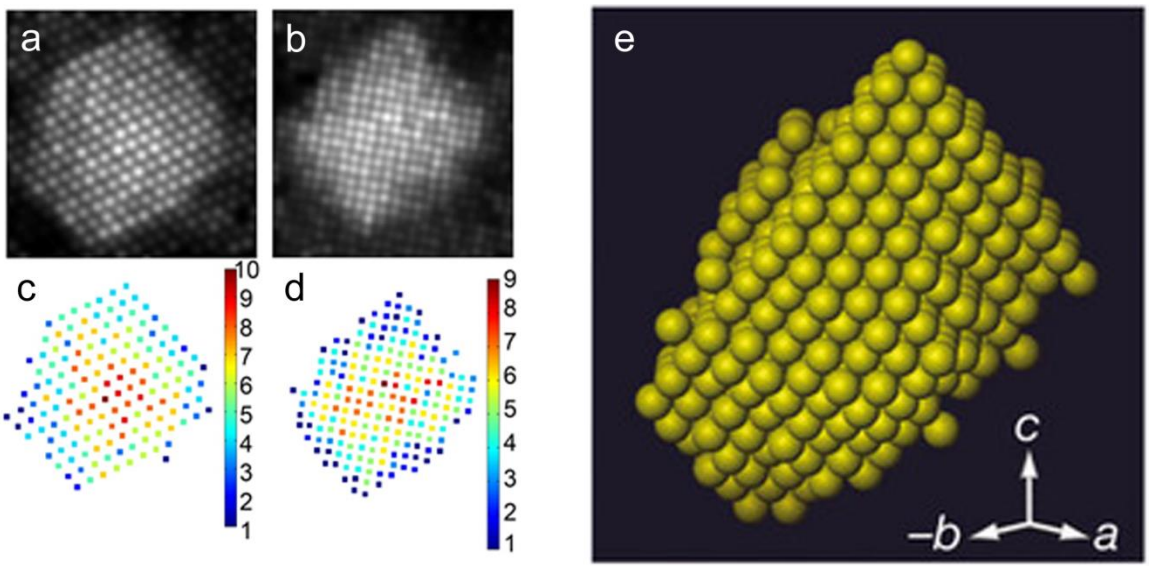

Figure 1: (a, b) Refined models for 2 HAADF-STEM projection images of a nanosized Ag cluster embedded in an Al matrix. (c, d) Number of Ag atoms per projected atomic column for both images. (e) 3D reconstruction of the Ag nanoparticle based on discrete tomography.

The assumptions during the discrete reconstruction provide an excellent start to investigate different nanomaterials. [14, 15] However, deviations from a fixed grid, which is assumed during the reconstruction may be present because defects, strain or lattice relaxation. Such deviations are of great importance as they determine the physical properties of nanomaterials. One may therefore wonder if continuous tomography can lead to visualisation of individual atoms in case the projection images yield atomic resolution. Fullerene-like nanostructures were investigated with a sub-nanometer spatial resolution (0.3*0.6*0.6) nm³ by Bar Sadan and co-workers. [16] In this work, a tilt series was recorded with a tilt range of ±60º and a fixed 3º increment. The series was acquired in bright field (BF) TEM mode using a microscope aligned at negative Cs imaging conditions. The

tomographic reconstruction, which was obtained for MoS_2 octahedral nanoparticles, could indeed be interpreted in terms of the atomic structure. More recently, Scott et al. reported a 3D reconstruction at a resolution of 0.24 nm based on equally-sloped tomography.[17] The main difference in comparison to conventional electron tomography is that the tilt series is not acquired with a constant increment of the tilt angle between two successive projection images, but with a constant increment of the slope. The approach enables one to use a pseudo polar Fourier transform (PPFFT) that renders a pseudo polar grid in Fourier space to a Cartesian grid in real space without the need for interpolation. [18] Although not all atoms in the multiply twinned Au nanoparticle could be located in the reconstruction, individual atoms could be observed in some parts of the nanoparticle. Equally sloped electron tomography does not assume any prior knowledge, but a relatively large number of 69 images is required to obtain high quality results. The technique was also applied to Pt nanoparticles in which dislocations are present. [19]

In order to determine the atom positions using a limited number of projection images, an alternative approach based on compressive sensing was proposed by Goris et al. [20] No prior knowledge concerning the crystal lattice was used, but it was assumed that the reconstruction is sparse at the atomic level. Indeed, for high resolution electron tomography, only a limited number of voxels in the reconstruction are expected to contain an atomic core and most voxels will correspond to vacuum. An important benefit is that because of the incorporation of sparsity during the reconstruction, a limited number of projections is sufficient to create a reliable reconstruction of the atomic lattice. The methodology was applied to Au nanorods and the surface facets of these particles could be precisely determined as illustrated in Figure 2.a. It must be noted that only 4 high resolution

HAADF-STEM images were used as an input. One of the major advantages of equally-sloped tomography and this approach is that the atoms are not fixed on a specific grid during the reconstruction. Therefore, small deviations from a perfect crystal lattice can be detected and measured. Figure 2.b shows the ε_{zz} strain field along the major axis of the nanorod, obtained by applying geometrical phase analysis to the 3D reconstruction. [21] The same approach was used to combine 5 HAADF-STEM images into a 3D reconstruction of core-shell bimetallic Au@Ag nanorods (Figure 2.c). [22] Due to the Z^2-dependence of the intensities in the individual HAADF-STEM projection images, a careful analysis of the intensities in the 3D reconstruction enabled to distinguish between Ag and Au atoms. In this manner, the atomic structure at the interface between the core and the shell could be determined. Recently, Z-contrast in tomographic reconstructions was also used to identify Au- and Ag-rich regions in bimetallic nanoclusters. [23]

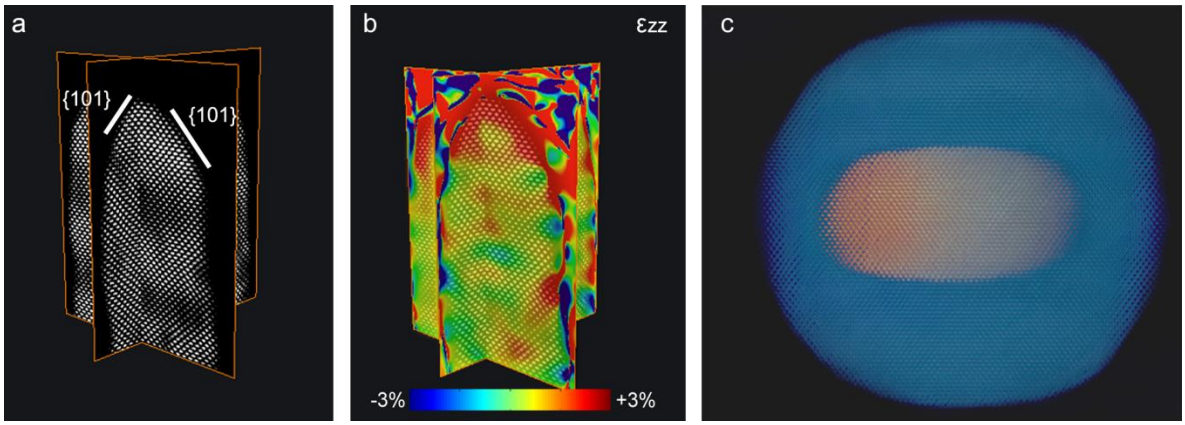

Figure 2: (a) Slices through a 3D reconstruction of a Au nanorod showing the atomic lattice. (b) Corresponding slices through the strain field along the major axis of the nanorod indicating an outwards relaxation at the tip of the nanorod. (c) 3D visualization of a core-shell Au@Ag nanorod where the Au core is rendered orange and the Ag atoms are visualized in blue.

Measuring atom positions in 3D

Although many studies have demonstrated the ability to visualize atoms in 3D, the number of investigations in which atom positions are measured is unfortunately still limited. If one is able to extract the coordinates of every atom in a nanostructure, they can be used as realistic input models for ab-initio calculations. In addition to many technical challenges during the acquisition and the reconstruction, one of the main problems is that 3D reconstructions at the atomic scale often correspond to a continuous 3D volume of intensity values hampering the extraction of the exact coordinates of the atoms inside the nanoparticle. In a recent study, dedicated post-processing algorithms were applied to a 3D reconstruction obtained by equally sloped tomography. [24] In this manner, the 3D positions of the atoms in a needle shaped tungsten specimen were extracted and the strain field could be investigated.

Being able to measure lattice strain in 3D has indeed been an important goal in the field of (high resolution) electron microscopy. A well-known example of strained nanoparticles are nanodecahedra or pentagonal bipyramids. Such particles consist of five segments bound by {111} twin boundaries, yielding a crystallographic forbidden morphology. Therefore, measuring strain fields in nanodecahedra by TEM has been the topic of several studies during recent years. Johnson and coworkers combined atomic resolution TEM and geometrical phase analysis to investigate the strain distribution in a Au decahedron with a diameter of 17 nm. [25] Their results were supported by finite element calculations and revealed a combination of an internal lattice rotation and small shear strains inside each

segment of the nanoparticle. Although many studies provide a good start towards the understanding of the strain distribution inside Au decahedrons, [25, 26] it is important to note that the results are based on a single 2D projection, hereby neglecting the 3D nature of the lattice strain. We therefore aimed at comparing strain investigations using 2D projection images with 3D measurements based on high resolution electron tomography reconstructions. [27]

A continuous tilt series of 2D projection images was therefore acquired in HAADF-STEM mode and a dedicated alignment procedure was applied. During a conventional alignment, the angles at which the images in the tilt series are acquired are mostly fixed according to their nominal values. Here, the angles were estimated during the reconstruction in an iterative manner by calculating intermediate reconstructions. As discussed above, the outcome of a 3D reconstruction at the atomic scale is often a continuous 3D volume of intensity values, from which the center of each atom can only be determined by additional analysis after the reconstruction. Very often, it is therefore far from straightforward to obtain atom coordinates because of the size of the dataset and the lack of objective and automatic segmentation procedures. We could overcome this limitation by assuming that the 3D atomic potential can be modeled by 3D Gaussian functions. Although this is a moderate hypothesis, it significantly simplifies the reconstruction problem to a sparse inverse problem, yielding the coordinates of the individual atoms as a direct outcome of the reconstruction. A similar approach was recently used to determine the positions of more than 10.000 spherical nanoparticles in a nanoassembly. [28] Hereby the assembly was considered as a set of perfect spheres. The use of shape models can therefore be considered as a powerful solution to many problems in the field of electron tomography.

Visualizations of the final 3D reconstruction, obtained for the Au nanodecahedron containing more than 90,000 atoms, are presented in Figure 3.a-c along different viewing directions. [27] The inset displays the 3D model of the morphology. Since the coordinates of the atoms are a direct outcome of the reconstruction technique, it becomes straightforward to calculate the 3D displacement map. The displacements were calculated with respect to a reference region in the middle of the segment. We computed derivatives of the displacement map in such a manner that 3D volumes were obtained corresponding to ε_{xx} and ε_{zz}. [29] Slices through the resulting ε_{xx} and ε_{zz} volumes were acquired through the middle of the segment and the results are presented in Figure 3.d and Figure 3.f. Furthermore, the variation of the lattice parameters was investigated along x and z based on the same slices (Figure 3.e and Figure 3.g). Both along the x and z direction, a systematic outward expansion of the lattice can be observed. The expansion along z is limited to a few of the outer atomic layers and shows an asymmetry (Figure 3.f-g) that is likely to be related to the fact that the decahedron is deposited on a carbon support.

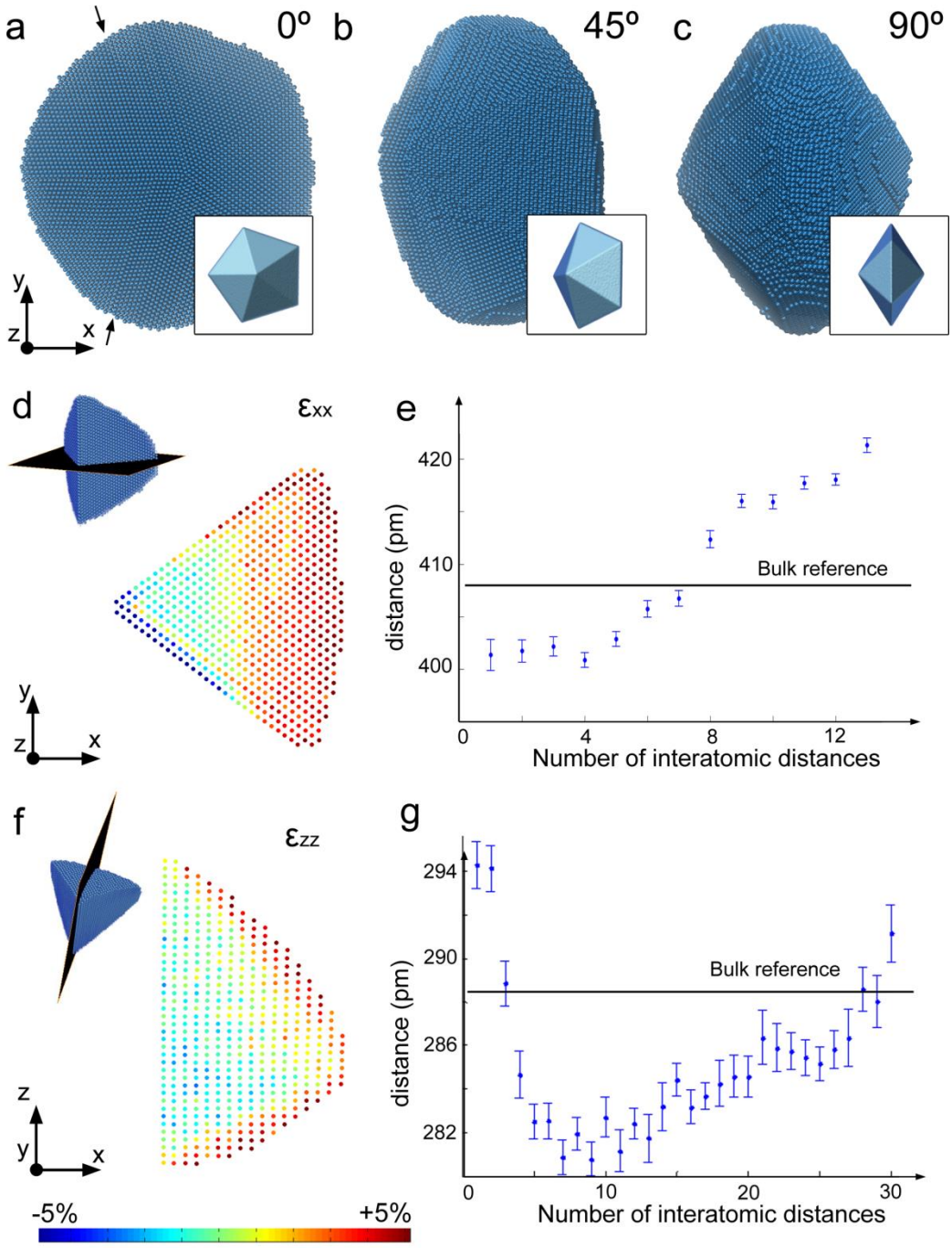

Figure 3: (a-c) 3D visualizations of the reconstruction showing the atomic lattice of a Au nanodecahedron. (d,f) ε_{xx} and ε_{zz} strain field showing a surface relaxation in both directions. (e,g) This surface relaxation is

confirmed by measuring the lattice parameter on slices through the reconstructions.

3D information from 2D projections

As discussed above, the first attempts to obtain 3D reconstructions using electron tomography at the atomic scale were based on single 2D projection images. The ever increasing complexity in composition of novel nanostructures is often accompanied by an increasing sensitivity towards the electron beam. Therefore, it is far from straightforward to acquire a large number of TEM images since samples tend to degrade. Also for very small clusters it is nearly impossible to avoid rotations or structural changes due to the energy transfer from the electrons to the cluster. The possibility to determine the 3D atomic structure of nanomaterials based on a single projection image has therefore received renewed interest. Van Aert and coworkers showed that the number of atoms in a given atomic column can be counted with single atom sensitivity. [30] The technique is based on a statistical analysis of the scattering cross sections, which can be obtained at the atomic level when using an empirical model-based approach. In this manner, the scattering cross sections for each atomic column can be related to the number of atoms that are present in each column. This approach was used to investigate the dynamical behaviour of ultra-small Ge clusters, consisting of less than 25 atoms. [31] Aberration corrected HAADF-STEM images were acquired and the number of atoms at each position was determined. In order to extend the 2D images into 3D, ab initio calculations were carried out. As an input, different starting configurations, in agreement with the experimental 2D HAADF-STEM images, were used. All of the relaxed cluster configurations, illustrated in Figure 4, stay relatively close to the input structures. However, only those configurations in which a planar base

structure was assumed, were found to be still compatible with the 2D experimental images. In this manner, reliable 3D structural models were obtained for the ultra-small clusters.

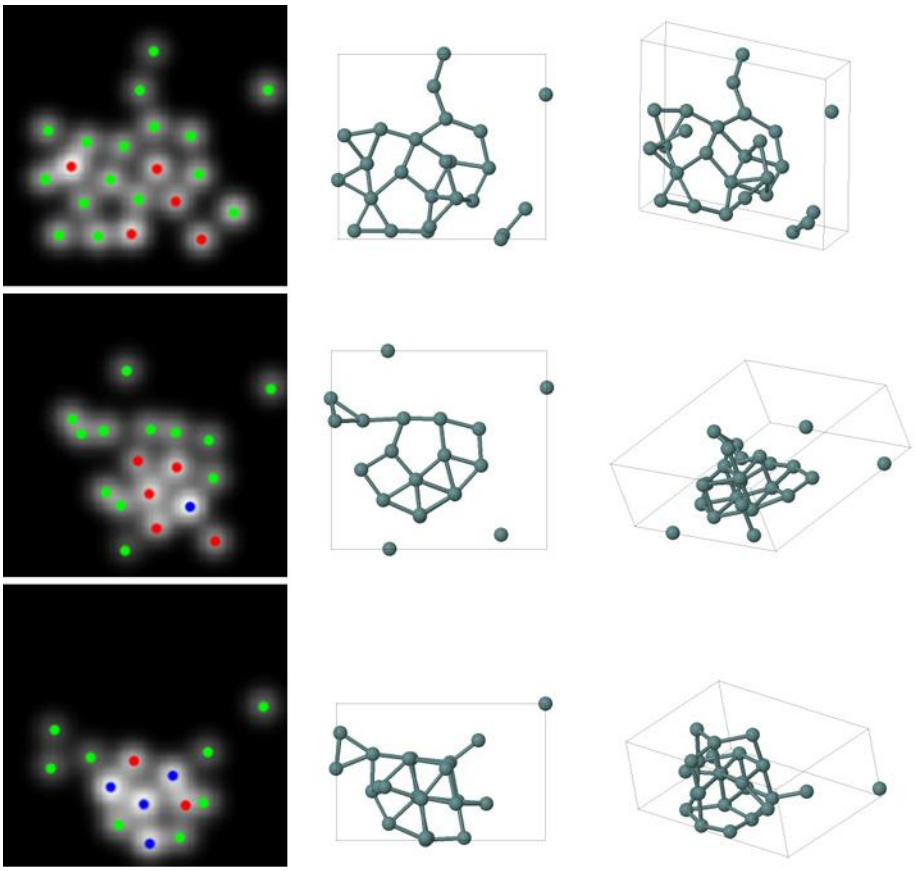

Figure 4: The left column presents the counting results obtained for 3 different configurations of a single ultra-small Ge cluster. Green, red and blue dots correspond to the presence of 1, 2 and 3 atoms respectively. The 3D results of the ab-initio calculations are shown at right along different viewing directions.

Also for larger clusters or nanoparticles, counting results can be used to generate a starting configuration where each atomic column is positioned symmetrically around a central plane. Using a monte-carlo based energy minimization, a 3D model for the structure of the nanoparticle can be proposed. This technique was applied by Jones and coworkers to visualize the 3D atomic structure of a catalytic Pt nanoparticle. [32] Furthermore, Jia et al. determined the shape of a MgO nanocrystal using a single high resolution TEM projection image acquired with the negative spherical aberration imaging technique. [33] Van Dyck and coworkers analyzed the stacking of 2 graphene layers with atomic resolution from a single restored exit wave. [34] The technique is based on the fact that the phase of the exit wave increases linearly with the distance of propagation and as a result, the third dimension of each atom can be estimated by a linear fitting model. A similar study was performed to obtain a 3D atomic model of the active sites on Pt catalytic nanoparticles. [35]

Clearly, these different approaches will become increasingly important in the future field of atomic resolution electron tomography and will open up a whole new range of experiments that will enable researchers to link the crystal structure, including defects to functional properties.

Summary

Electron tomography has been used in an increasing number of studies to investigate the 3D structure of nanomaterials. Recent advances by different groups and using different techniques have pushed the resolution of the technique to the atomic level. Although many of these results have been obtained for model-like systems, innovative studies also enable the investigation of interfaces, defects and lattice deviations with the same resolution. One

of the future challenges will be to also investigate the chemical nature and valence for every atom in a given nanostructure. The achievement of atomic resolution in 3D should therefore not be considered as the end of a quest, but as the start of a new journey in the field of 3D electron microscopy and materials science in general.

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Author biographies

Sara Bals received her PhD from the University of Antwerp (Belgium) in 2003. Next, she joined the National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory (Berkeley, California). Currently she is a Professor at the Electron Microscopy for Materials Research (EMAT) group of the University of Antwerp. Her main research interest consists of the application and further development of electron tomography for advanced nanostructured materials. In 2013 she received an ERC Starting Grant.

Bart Goris received his PhD degree at the University of Antwerp in 2014. He is currently working as a post-doctoral researcher at EMAT. His current interests include new developments in the field of electron microscopy and electron tomography in order to obtain three dimensional (3D) structural and chemical information on different nanomaterials with a resolution down to the atomic scale.

Annick De Backer received her PhD degree at the University of Antwerp in 2015. She is currently working as a post-doctoral researcher at EMAT. Her research focuses on new developments in the field of model-based atomic resolution electron microscopy

aiming at quantitative structure characterization of nanostructures with the highest possible precision using advanced statistical techniques.

Sandra Van Aert received her Ph.D. from the Delft University of Technology (The Netherlands) in 2003. Thereafter, she joined the EMAT group at the University of Antwerp where she became a Professor in 2009. Her research focuses on new developments in the field of model-based electron microscopy aiming at quantitative measurements of atomic positions, atomic types, and chemical concentrations with the highest possible precision.

Gustaaf Van Tendeloo graduated from the University of Antwerp in 1974. Currently, he is a Full Professor at the University of Antwerp and a guest Professor at Wuhan University in China. His research focus is on the application of electron microscopy to different aspects of materials science. His work has resulted in an extraordinary number of publications, citations and prizes including an ERC Advanced Grant and the prestigious FWO Excellence Prize.

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