Exploring nanomaterials with 3D electron microscopy

O. Ersen[1,*], I. Florea[1,3], C. Hirlimann[1] and C. Pham-Huu[2]

[1] IPCMS, UMR 7504 CNRS – Université de Strasbourg, 23 rue du Loess, BP 43, 67034 Strasbourg cedex 2, France
[2] ICPEES, UMR 7515 CNRS – Université de Strasbourg, ECPM, 25 rue Becquerel, 67087 Strasbourg cedex 2, France
[3] LPICM, UMR 7647 CNRS – Ecole Polytechnique, Route de Saclay, 91128 Palaiseau Cedex, France

In this review we focus on recent developments in the field of 3D imaging at the nanoscale, when applied to nanomaterials and nanostructures. We demonstrate, by highlighting examples, that recent progress in the use of electron microscopy techniques based on tomography allows one to fill the gap between the development of new materials and their structures and characterization. A special emphasis is put on two new 3D approaches: quantitative and analytical 3D tomography. The first approach gives access to the quantitative exploration of specific parameters within nano-objects and/or nanostructures while the latter, based on electron energy loss spectroscopy, details the 3D chemical composition of such systems at the nanometre scale.

Introduction

The increasing interest in the development of nano-objects and nanostructured materials, at the forefront of materials science, escalates the need for tools dedicated to the characterization of these systems at the nanoscale. It is necessary to explore the fundamental physical and chemical properties of nanomaterials to be able to subsequently exploit these properties at a technological level. The final goal is to integrate such systems into innovative products and devices for real-world applications. Precise characterization is therefore required throughout material synthesis and preparation, and plays a key-role in the definition and the optimization of the processes involved.

Various analysis techniques such as X-ray reflectivity, spectroscopic ellipsometry, SAXS or GISAXS are currently employed to access physical and chemical information about the structure, morphology and/or chemical composition of nanomaterials and structures [1,2]. Unfortunately, they only give information averaged on the volume of the sample of interest, a detrimental inconvenience, which can be overcome by using near field imaging techniques such as STM, AFM or TEM that are adapted for accessing information at the atomic level. The main drawback of these techniques is that they may only explore very limited surfaces with minimal curvature. Atom probe tomography [3] reaches atomic resolution but can only explore very small volumes in a destructive manner, leaving aside complicated structures.

In the present review we will show that electron tomography (or 3D-TEM) is a useful tool that gives access to qualitative and quantitative information at the nanoscale [4–6]. When looking at a transparent and structured object an observer can spontaneously rotate the object in order to get a complete understanding of its internal structure. This idea is at the principle of tomography: recording at various angles, images produced by some kind of wave transmitted through the object of interest. The wavelength of the wave limits the ultimate resolution. Tomography is therefore very general, as light, sound, neutrons, X-rays, etc. can be used as probes, depending on the size and the nature of the objects under investigation. Electron microscopes, providing electrons with wavelengths in the picometre range, are suitable for 3D imaging using the tomographic technique, as they allow the probing details at the nanometre scale. Moreover, when combined with chemical imaging (energy filtered TEM), the technique allows the 3D chemical composition of nano-objects to be solved, correlating their chemical composition with the subsequent properties. As a new technique, unexpected technical

*Corresponding author:. Ersen, O. (ovidiu.ersen@ipcms.unistra.fr)

 http://dx.doi.org/10.1016/j.mattod.2015.04.004

developments will most certainly appear in the near future, closing the gap between nanoscale imaging and advanced materials.

Principle of electron tomography and the current state-of-the-art

Electron tomography is based on the recording of series of projection images of an object that is rotated inside the electron beam of a microscope for a discrete number of incidence angles in the range $\pm 80^\circ$. Each recorded image is a projection in the observation plane of the integrated quantity of interest, such as the mass or the chemical composition of the sample along the electron trajectory. The Radon transformation [7] is applied to these projections allowing the construction of a 3D matrix describing the sample in the real space. This is performed by back projecting the intensity of each corresponding pixel on the set of projection images into a unique voxel of the matrix being constructed (Fig. 1). For example, a 3D image of an object can be extracted from the matrix by recognizing, through contrast measurements, the interface delimiting vacuum and matter, in the case of shape-sensitive volumes. From this image, porosity, for example, can be quantitatively determined with a nanometre scale resolution as well as its distribution inside the solid volume. More generally, from the 3D voxel matrix that is constructed, quantitative or chemical analysis can then be performed.

Electron tomography has been used in the second half of the last century as a powerful instrument for studying the details of the morphology and the inner structures of living cells and structures. The pioneering works of DeRosier and Klug [8] can be considered as the real starting point for 3D imaging in electron microscopy. A brief history of the origin and the development of 3D reconstruction methods can be found in the Nobel lecture of Klug in 1983 [9]. Work published by Baumeister et al. [10] is still an important reference for biological studies [11]. Electron tomography has more recently been applied in the field of materials as the result of the high technological maturity of the electron microscopy techniques. Because soft materials and polymeric nanostructures exhibit true three-dimensional structures, electron tomography applied in a quantitative way at the meso-scale or with a sub-nanometric resolution has become an ideal tool for their characterization [12,13]. A large variety of polymeric structures have thus been studied, including hybrid structures with block copolymers [14] or nanocomposites materials [15]. In the field of inorganic materials, teams, led by

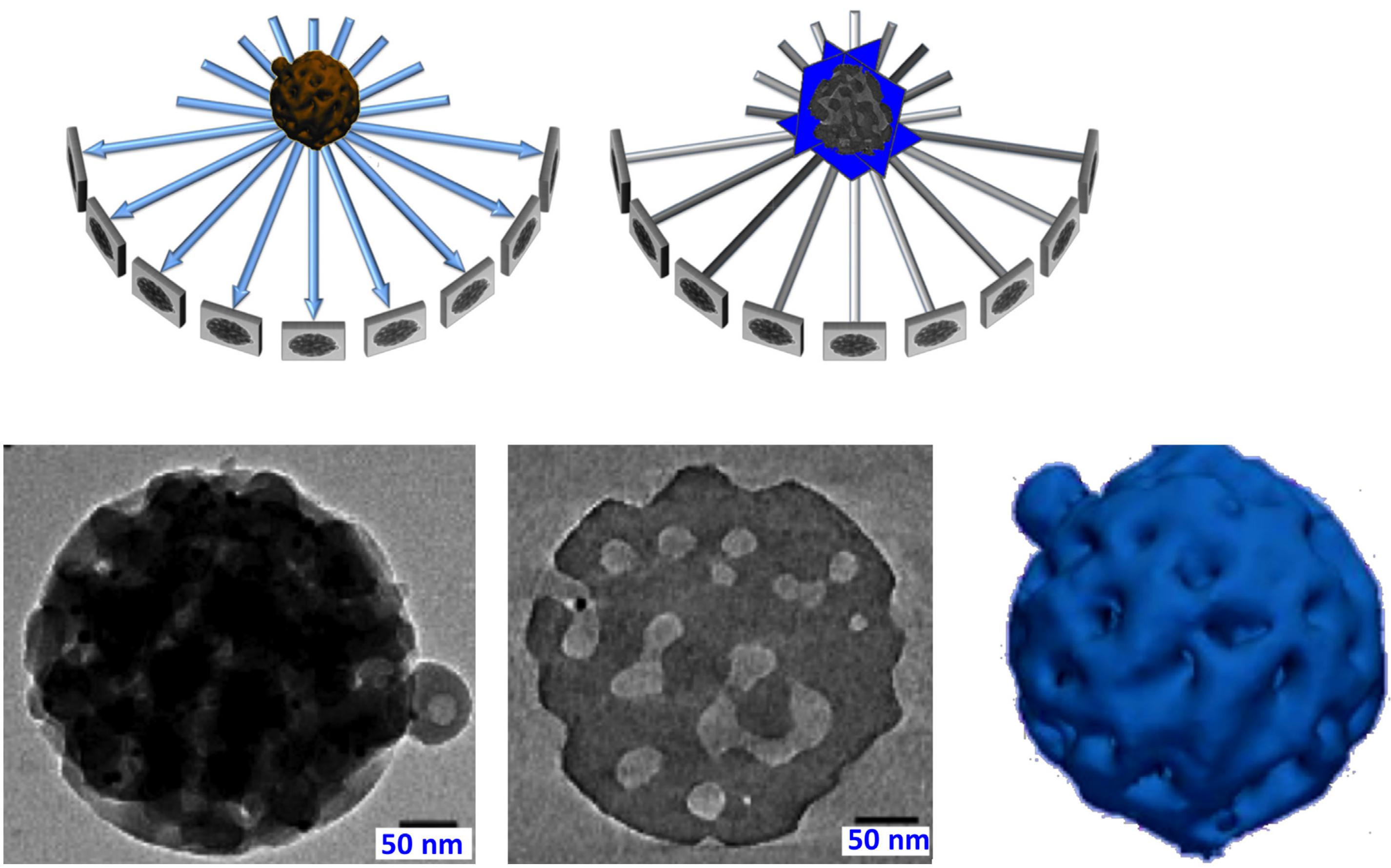

FIGURE 1

Schematic representation of an electron tomography experiment. In a first step a series of projection images is acquired while tilting the specimen inside the electron beam of the microscope (left top), in a second step the object matrix is constructed using a back-projection algorithm (right top). The benefits of gaining information when passing from a traditional 2D image to a 3D model is highlighted in the bottom part of the figure, for the case of a porous zeolite. On the left, one of the recorded projections is shown. In the middle, a slice through the 3D matrix obtained from the projections is shown. On the right, a 3D representation of the object of interest constructed from the 3D matrix is displayed.