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Uncovering Nanoscale Chemical Variations in the Third Dimension; Electron Tomography in the Analytical Mode

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Analytical transmission electron microscopy is arguably the most powerful tool to resolve nanoscale chemical variations in a wide variety of materials systems. However, most analytical TEM techniques suffer a common limitation; they are constrained to offer a two-dimensional (transmitted) abstraction of what is, in reality, a three-dimensional specimen. Often this problem can be minimised by preferential orientation of a structural feature, such as an interface, but there will still be a degree of uncertainty due to the transmission problem. A number of new techniques have been demonstrated that avoid this problem by combining electron tomography, in which a 3D reconstruction of the specimen is calculated from a tilt series of micrographs, with analytical microscopy [1, 2]. The most promising of these is energy filtered TEM (EFTEM); the ability to acquire rapid spatial information making it more suited to tomography than scanning techniques such as EDX or EELS spectrum imaging.

Early studies in EFTEM tomography used only two or three energy-loss images at each core-loss edge to map elementals in three dimensions. This approach is rapid, but it represents only basic use of the information available in the electron energy loss spectra (EELS). It is well understood that improved EFTEM results can be achieved by acquiring an EFTEM image series, an "image-spectroscopy" mode, as opposed to just two or three images [3]. This can result in improved signal to noise ratios (SNR) as well as provide quantitative or semi quantitative maps. Such quantitative elemental maps, which are linear with the amount of a projected element, should also lead to at least semi-quantitative three-dimensional reconstructions. Potentially, there are two routes to a three dimensional map, illustrated in Fig. 1; via processing each individual energy-loss series into a elemental map tilt series or by reconstructing individual energy loss volumes. The latter approach leads to a 4D dataset ($x,y,z,\Delta E$) allowing the extraction of EELS spectra at each 3D voxel [4].

The technique can also be expanded to investigate scattering events other than core-loss transitions. The low-loss region of the EELS spectrum contains information from scattering due to collective excitations, such as bulk and surface plasmons, as well as due to interband transitions. Plasmon energies are particularly sensitive to changes in bonding in the material; there can be significant shifts in plasmon energy for different bonding conditions even in identical chemical species. An example of this plasmon shift mapping has been used for tomography by Gass et el[4], studying the shift between different forms of Carbon. An example is given in Fig. 2 for silicon nanocrystals in a silicon oxide matrix. This material exhibits high efficiency visible luminescence in the visible band, which is thought to arise via quantum confinement effects. Understanding this behaviour would be simpler given a comprehensive analysis of the shape, size, connectivity and density of the nanoparticles. The difference between the bulk plasmon energies for Si and SiO_2, 16.7 eV to 22.4 eV, leads to a significant contrast in the energy-loss images collected over the plasmon peaks. A three-dimensional reconstruction from these images, Fig. 2 c), allows the examination of the morphology of these distinctly asymmetrical nanoparticles.

[1] Mobus, G., et al., *Ultramicroscopy*. 96(3-4) (2003). 433.
[2] Weyland, M., et al., *Microscopy and Microanalysis*. 9(6) (2003). 542.
[3] Thomas, P.J., et al., *Ultramicroscopy*. 88(2001). 179.
[4] Gass, M.H., et al., *Nano Letters*. In Press(2006).
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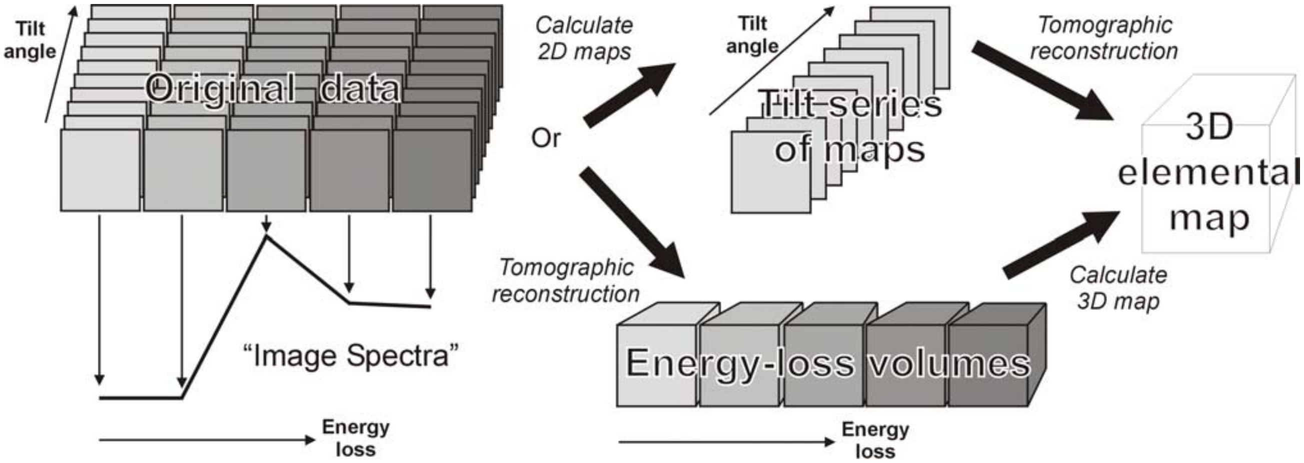

Fig. 1 An illustration of the two processing routes for EFTEM "image-spectra" tilt series, where at each energy loss images are available across a wide tilt range. In the upper route each energy-loss series of images is reduced to a single map for each tilt, and tomographic reconstruction of this series of maps leads to a 3D elemental map. In the lower route tomographic reconstruction is carried out at each energy loss to give a 4D dataset (*x,y,z, ΔE*), from which a 3D elemental map can be generated voxel-by-voxel.

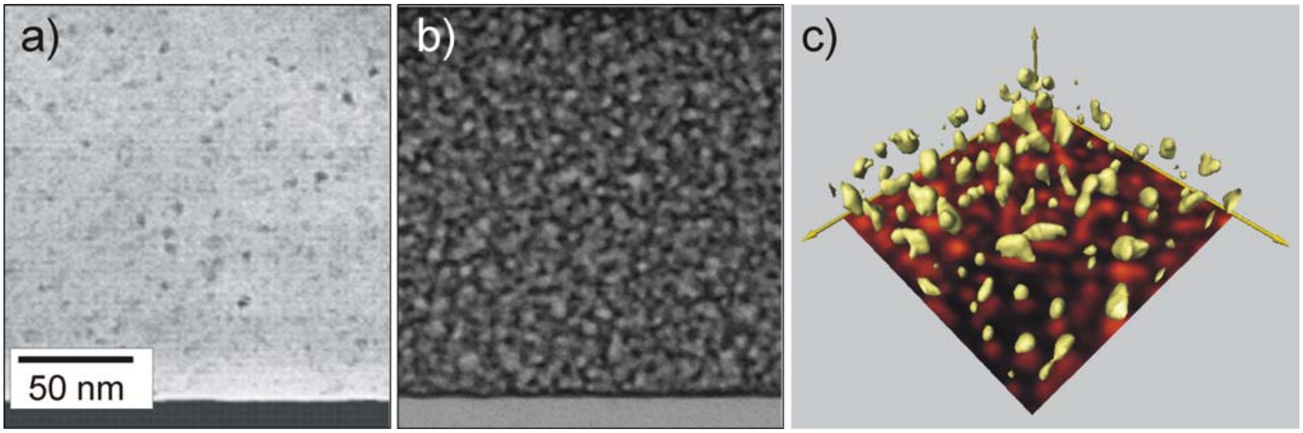

Fig. 2 Plasmon loss tomography of Si nanocrystals in an SiO_2 matrix. a) Conventional bright field imaging significantly underestimates the density of particles, while plasmon loss imaging b) shows strong contrast from the entire distribution of nanoparticles, and is ideal for tomography. c) A tomographic reconstruction, displayed as an iso-surface, from a tilt series of these particles shows their non-equiaxed morphology.