Electron Tomography of CeO\textsubscript{2} Nanostructures

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Abstract. The three-dimensional (3D) morphology of two related classes of CeO\textsubscript{2} nanostructures is reconstructed using electron tomography with three image acquisition modes for comparison. The samples include free standing nanoparticles of ~ 40nm diameter with octahedral morphology and nanoscale precipitates of 100-200 nm diameter embedded in glass with dendritic morphology, both of fluorite-type CeO\textsubscript{2}. Tomograms were successfully constructed from (i) bright field (BF) TEM, (ii) a novel single-window energy-filtered TEM (EFTEM), and (iii) annular dark field STEM (ADF) modes. Advantages and disadvantages of the imaging modes are summarized.

1. Introduction
Compared with the destructive techniques of 3D atom probe [1] and focused ion beam (FIB) tomography [2], electron tomography [3] is the major non-destructive technique to reconstruct 3D nano-volumes. Recent progress and shifts in applications from originally biological materials [4-5] to the inorganic materials area [6] have been established. BF TEM has been sufficient for low atomic number and mostly amorphous biomaterials, but its immediate application to crystalline materials would be rather limited to amorphous or porous types of materials. Bragg scattering, which falsifies the projection images, needs to be suppressed and EFTEM, ADF STEM and EDX-mapping have been proposed [7-8]. These incoherent and dark-field-type imaging modes provide up to a maximum object thickness limit some proportionality between object thickness and intensity, ideally suited for tomography. A first comparison of bright field with dark field imaging modes was presented in [9]. In this paper, we study electron tomography using a combination of single energy-window EFTEM and BF images and elaborate their applicability for free-standing nanoparticles. For embedded particles in glass we make use of the high atomic number difference between Ce in the precipitates and the B-Si-O based glass matrix, and apply ADF-STEM.

2. Experimental and Methods
Ceria nanoparticles were suspended in distilled water after at least ten minutes dispersion by ultrasonic vibration. The suspension was immediately dropped onto a home-designed copper grid of 1mm dimension with a thin layer of freshly prepared continuous carbon film to achieve a high range of viewing angles for a TEM with a 2mm polepiece gap. The grid was mounted on a 1.2mm diameter Ti-rod supplied by Gatan for the model 912 holder.

A glass composite material with nanoscale precipitates was produced in house as described in [10]. The bulk glass was crushed by agate mortar and pestle, followed by TEM-sample mounting in the same way as for the CeO\textsubscript{2} nanoparticles.
All specimens were observed using a JEM 2010F TEM (JEOL, Japan) with an ultra-high-resolution polepiece (URP) and Gatan GIF at 200 kV. All tilt series of the above-mentioned model systems were aligned using the cross-correlation method and reconstructed using the weighted-backprojection method, implemented in IMOD software [11]. Projected volume-rendered views and isosurface (threshold) views from the reconstructed 3D data volumes have been calculated and displayed by IDL [12].

3. EFTEM tomography of Free-standing CeO$_2$ Nanoparticles

The electron energy loss spectroscopy (EELS) analysis reveals that the nanoparticles were CeO$_2$ by the characteristic M$_{4,5}$ peak ratio (884eV and 901eV) and the selected-area diffraction pattern indicates the particles are single crystalline of cubic fluorite phase [13]. EFTEM tomography has been originally designed to suppress all element-imaging, except for the selected one, which requires three-window elemental maps or jump ratio images at every tilt angle [7]. For a constant composition nanoparticle, the benefit of EFTEM is reduced to its incoherent suppression of Bragg scattering contrast.

We therefore test in this work “single-window EFTEM tomography”. The first choice for the energy window is a trade-off between short exposure/low drift/good signal-noise ratio and good suppression of scattering contrast. The former leads to low energies, while the latter prefers high energy losses. Our chosen compromise in the case of CeO$_2$ was the strong Ce-N-edge peak near 130eV. Although this signal is a superposition of Ce-atom contributions and the large tail of the plasmon region, we don’t extrapolate and subtract the plasmon background. Its suitability for tomography is entirely based on the proportionality of each partial signal to the thickness of the specimen. This applies up to a certain limit, when multiple-scattering and absorption effects start to flatten off the linear intensity-thickness relationship.

Another major benefit of “single-window” EFTEM is the ease, speed and the opportunity to combine the tomographic tilt series with a parallel acquisition of a BF series, by inserting/retracting the filter slit pair-wise. Two tilt series of EFTEM images and BF images from the same nanoparticle were therefore recorded across a tilt range from -50° to +70° at 5° increment. Samples of these two tilt series at -50°, 0°, and +70° tilt angles are shown in Figure 1(a) and (b), respectively.

To provide a full comparison of methods, a third tilt series of a different particle was acquired using ADF STEM imaging mode [8] and the images at -50°, 0°, and +55° tilt angles are shown in Figure 1(c).

The isosurface views from all three reconstructions by BF, EFTEM, and ADF STEM are shown in Figure 1(d), (e), and (f), respectively. The crystallographic analysis by diffraction and tomographic reconstruction indicate that the free standing CeO$_2$ nanoparticles are almost perfect octahedra enclosed by {111} facets. All three reconstructions are found to be surprisingly similar and successful, in spite of different amounts of artefacts in the input images. The two incoherent imaging modes show reliable intensity-thickness relations, while the BF-images suffer from dark patches, which falsely produce an excess-thickness signal. As further detailed in [13-14], the success of the BF reconstruction is due to a combination of cancellation of artefacts and the sufficiency of “geometric” tomography for a convex particle. In terms of resolution, we estimate an order of the techniques from BF TEM/HREM (highest) over ADF STEM to EFTEM (lowest) resolution. A superposition of BF TEM contours and EFTEM intensity signals seems therefore to be an attractive option.
Figure 1  The tilt series and the tomographic reconstructions obtained by BF and EFTEM of the same particle. (a) BF images, (b) EFTEM images at 130eV loss with a slit of 10eV at -50°, 0°, and +70° tilt angles, and (c) ADF STEM images at -50°, 0°, and +55° tilt angles. The isosurface views (d), (e), and (f) of the tomographic reconstructions were obtained from (a), (b), and (c), respectively.

Figure 2  ADF STEM tilt series of a typical glass fragment with CeO₂ precipitates. (a) ADF STEM images at ±60° and 0° tilt angles at low magnification. (b) ADF STEM images of one of the dendritic structures at high magnification at ±60° and 0° tilt angles. (c) The reconstructed volume with indicated glass matrix and CeO₂ dendrite at low magnification. (d) The volume of one dendrite.
4. ADF-STEM Tomography of CeO₂ nano-precipitates

The dendritic precipitates in the glass matrix were analyzed by selected area diffraction and Ce-M-edge EELS to reveal single crystalline CeO₂ [10]. ADF STEM imaging mode [8] was chosen due to its applicability to both amorphous and crystalline materials and a high atomic number difference between Ce and Si+B from the glass. ADF STEM images were recorded from -70° to +70° at 5° angular increment at both low and high magnifications in order to reconstruct an entire glass fragment and one dendrite, respectively (Figure 2). The distribution of the precipitates and the volume fraction can be estimated from the reconstruction of the entire fragment, while the surface morphology and its relationship to the growth direction in one individual CeO₂ precipitate can only be revealed from its individual reconstruction.

5. Conclusion

In summary, the 3D morphology of CeO₂ nanoparticles was successfully reconstructed by BF TEM, ADF STEM, and the single-window EFTEM modes. ADF-STEM has been show to be most suitable for CeO₂ nanoparticles embedded in glass. The single-window EFTEM imaging mode is fast and intermediate between BF (the unfiltered imaging mode) and the three-window EFTEM elemental mapping method, based on the proportionality to density and thickness of EFTEM intensity. BF TEM is shown to be applicable to crystalline nanoobjects with simplified geometry, such as convex contour and homogeneous composition.

Acknowledgements

This work was supported by a grant from EPSRC, UK.

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