High spatial resolution tomographic reconstruction from STEM high angle annular dark field (HAADF) images

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ABSTRACT: A technique for high spatial resolution three dimensional reconstruction from STEM HAADF images using electron tomography is presented. 'Z-contrast' images are shown to be ideal projections for tomography and examples are shown from nanostructured catalysts and magnetotactic bacteria crystallites. Results prove that accurate reconstruction is possible of both internal positions and exterior shapes. Given sufficient projections over a wide tilt range a reconstruction resolution of 1nm is possible in all directions for a reconstruction volume of $100nm^3$.

1. INTRODUCTION

The analysis of structure by TEM is limited by the nature of the microscope as a structure projector; a three dimensional (3D) object is reduced to a two dimensional (2D) projection. While a projection often contains sufficient information to make valid materials conclusions there are an increasing number of systems whose structural complexity requires 3D analysis at high spatial resolution. Similar problems are routinely solved in the biosciences by electron tomography (Frank 1992), mathematically reconstructing the object from tilt series of bright field (BF) images. For most materials specimens, however, BF images are unsuitable for reconstruction due to the effects of diffraction contrast. A tomography method is introduced that uses tilt series of scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) images to achieve high spatial resolution 3D reconstruction. The advantages of HAADF images for tomographic reconstruction will be covered, illustrating them with two different experimental applications and a number of conclusions made as to the limits and power of the technique.

2. SUITABILITY OF STEM HAADF IMAGES FOR TOMOGRAPHY

The effects of crystalline diffraction contrast make BF images unsuitable for tomographic reconstruction of materials science specimens. This is because tomography requires that the images are 'true projections' of structure; the contrast observed has to have, at the very least, a monotonic relationship with the amount of material in projection. Diffraction contrast does not show this kind of relationship and therefore BF images are not 'true projections' of structure. The few examples that exist of BF electron tomography being applied to materials systems are generally on amorphous or very weakly scattering specimens (Koster et al. 2000).

STEM HAADF images are formed predominantly from electrons scattered to high angles by interactions close to the atom core. For annular detectors with large inner radii (>30 mrad) the scattering is predominantly incoherent and the intensity is approximately proportional to the square of the atomic number (Z). An image so formed, a 'Z-contrast' image, shows contrast related directly to the atomic number and the total amount of that material through which the beam has passed: as such it meets the projection requirement.

3. ELECTRON TOMOGRAPHY

Although electron tomography was developed initially using BF images the actual methodology is almost identical for STEM HAADF images. Indeed the reconstruction tools are general enough to have also been used for tilt series of EFTEM elemental maps (Weyland and Midgley 2001) as well as electron holograms (Stolojan et al. 2001).

To acquire a tilt series a specimen is rotated about a single axis by small increments, usually of between 1° and 5°. The resolution of the eventual reconstruction is a factor of both the maximum tilt angle and the number of projections recorded, both of which should be maximised. At each increment an image (projection) is recorded. However, as the specimen rarely rests on the mechanical tilt axis corrections are needed for focus and position of the object of interest. A further fine alignment of the projections is required before reconstruction; this stage is crucial to the quality of the final results and is often repeated with reference to an initial reconstruction. Two types of tomographic reconstruction have been implemented: weighted backprojection (Frank 1992) and iterative solution (Gilbert 1972). In both approaches the reconstruction is by consecutive 2D slices perpendicular to the tilt axis. Visualisation of the 3D dataset can then be either an iso-surface rendering, where a polygonal surface is generated from all values above a certain threshold, or a voxel projection, which can be enhanced by giving distinct contrast bands different opacity and colour values.

4. NANOSTRUCTURED HETEROGENEOUS CATALYSTS

To understand the activity of heterogeneous catalysts based on metal nanoparticles embedded in mesoporous silica requires structural analysis at high spatial resolution. Whilst previous analysis by using a combination of STEM ADF imaging and EDX mapping (Ozkaya et al. 1999) has proved somewhat successful the structural complexity of these catalysts means there exists a need to analyse them in full 3D. The atomic number difference between silica support and the metal nanoparticles provides ideal contrast for HAADF STEM imaging and for subsequent tomographic reconstruction from a tilt series of such images.

A STEM HAADF tilt series was acquired from a catalyst containing 1-2nm Pd_6Ru_6 nanoparticles anchored on the walls of a mesoporous MCM-41 silica framework, composed of a hexagonal array of 3nm diameter pores. A typical HAADF image of the structure is shown in Fig. 1 a). The series was acquired using a Philips CM300-FEG(S)TEM, operating at 300kV, using an on axis Fischione HAADF detector. The tilt series was acquired from an isolated area of catalyst with images every 2° from 60° to -48°. Images were aligned using a cross-correlation algorithm applied sequentially to images stretched using an inverse cosθ function. After determination of the tilt axis, 3D reconstruction was achieved by weighted back-projection of consecutive 2D slices.

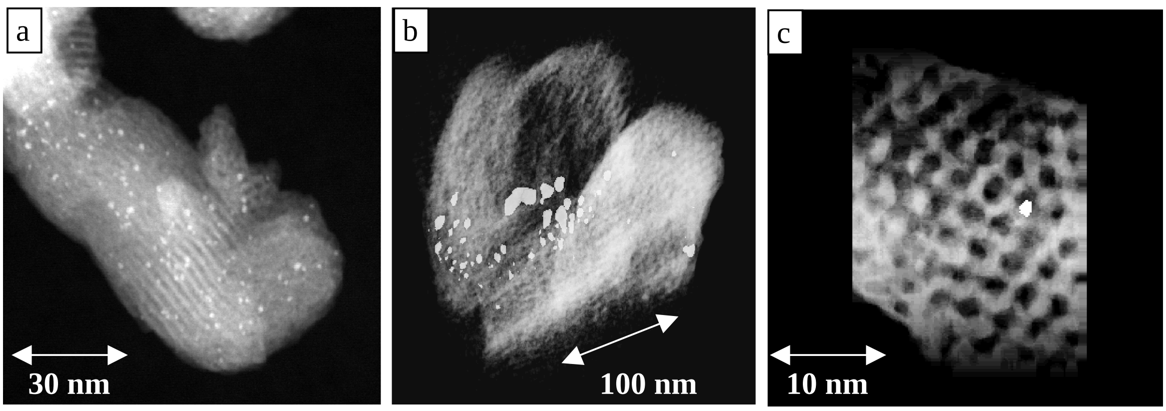

Fig. 1.a) STEM HAADF image of a typical area of MCM-41 containing Pd_6Ru_6 nanoparticles. b) Contrast selected voxel projection from a tomographic reconstruction of the catalyst. c) Voxel projection from a sub-section of reconstruction shown in b) showing clear reconstruction of the hexagonal channels of the MCM-41 and a single particle anchored to the inner wall of one mesopore.

Contrast selected voxel projections of the reconstructed dataset, Fig. 1 b) and c), clearly show the position of the nanoparticles in relation to the mesopores. The larger particles are resting on the surface of the silica framework because they are too large to be incorporated in the channels. Full colour animated versions of both Fig. 1 a) and b), are available online at: *http://www-hrem.msm.cam.ac.uk/Research/CETP/STEM_Tomo.html.*

5. MAGNETOTACTIC BACTERIA

Magnetotactic bacteria have been the subject of recent research because they contain chains of magnetite (Fe_3O_4) crystallites, see Fig. 2 a), that are allegedly similar to those found in a Martian meteorite (McKay et al. 1996). The shape of these crystallites is thought to be key to determining whether they are organic or inorganic in origin. Until now only conventional imaging methods have been applied to the Martian specimens to ascertain their 3D structure. It is far better to use a tomographic approach and as such STEM HAADF tomography has been applied to terrestrial specimens to show its superiority. A tilt series was acquired from two chains of large (100-200nm in length) crystallites, see Fig. 2 a), with images every 2° over ±56°. Images were aligned as before. Tomographic reconstruction was carried out by a simultaneous iterative reconstruction technique (SIRT) (Gilbert 1972). An initial assessment of the quality of the reconstruction is possible by observing the similarity between Fig. 2 b) and c), in which the faceting visible in the original projection is retained in the reconstruction. Generating iso-surfaces from the reconstruction then allows unbiased analysis of the crystal shape and indexing of the major facets of the crystal, see Fig. 2 d)-f).

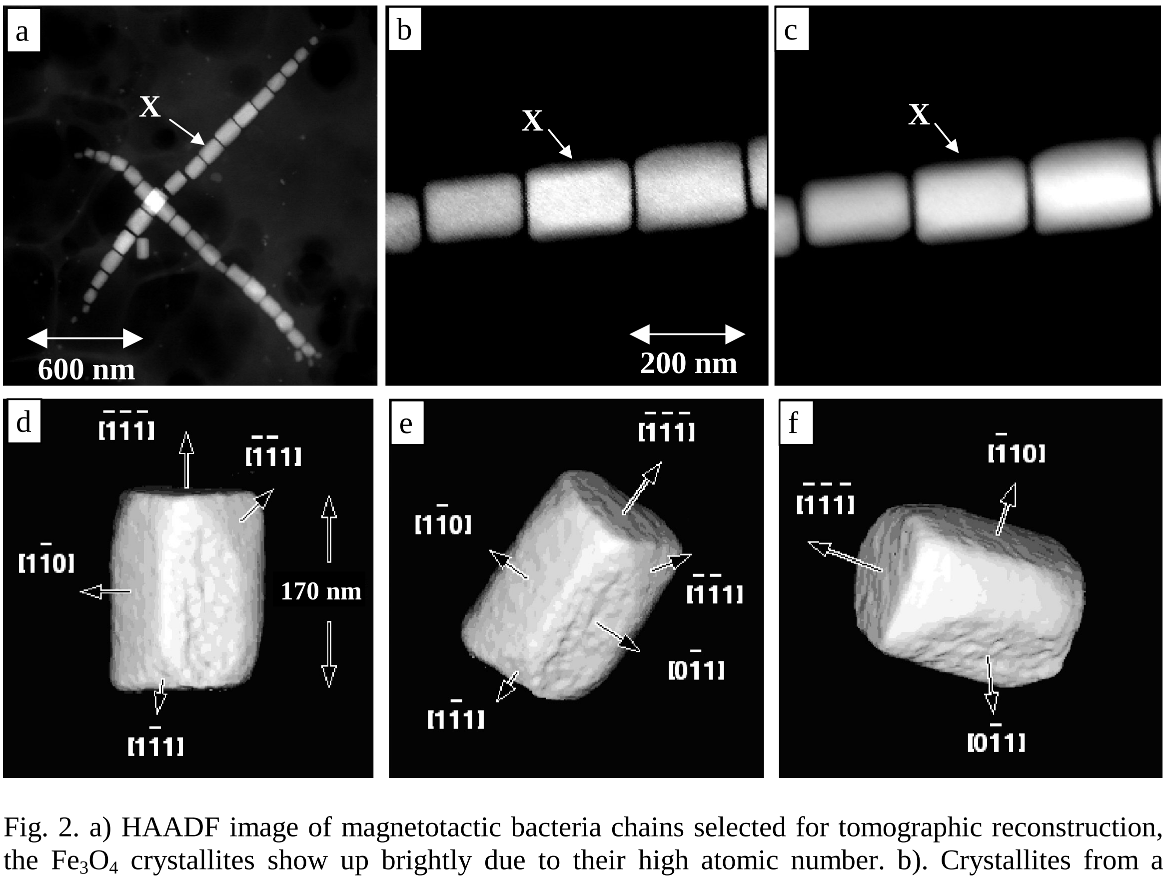

Fig. 2. a) HAADF image of magnetotactic bacteria chains selected for tomographic reconstruction, the Fe_3O_4 crystallites show up brightly due to their high atomic number. b). Crystallites from a selected area of the zero degree projection of the tilt series. c) Reprojection of the tomographic reconstruction of the same area as b) showing close agreement between the original and the reconstruction. d)-f) Iso-surface visualisation of the reconstruction from a crystal, marked X in a)-c), clearly showing that the major crystal facets, whose normals are indexed, have been reconstructed.

An animation, from which Fig. 2 d)-f) are taken, that allows a better visualisation of all the facets is available online at: *http://www-hrem.msm.cam.ac.uk/Research/CETP/Images/Facets_anim.gif.*

6. DISCUSSION

Two very different examples of STEM HAADF tomography have been used to examine the effectiveness of the technique. The nanostructured catalyst results demonstrate that reconstruction of the internal structure of an object is possible. It also shows the high spatial resolution achievable, 1nm in all directions, given a sufficient number of projections within a wide tilt range and a relatively small reconstruction volume (around $130nm^3$ for the demonstrated dataset).

Whilst the interest in the catalysts is in the relative positions of the nanoparticles and channels, with the magnetite crystallites it is in the shape of the object. The reconstruction of these crystallites was enhanced by use of iterative reconstruction routines (Gilbert 1972) that are particularly powerful at removing artifactual intensity outside the real object, improving the clarity of iso-surface visualisations, and in this case allowing unbiased indexing of the facets.

STEM HAADF tomography is powerful where large differences in atomic number, Z, exist. However in objects containing structures with similar Z it is of less use and EFTEM tomography may be more revealing (Weyland and Midgley 2001). As with all tomography experiments the extended acquisition time can cause problems with specimen damage, and while no significant damage was observed in these systems, for some specimens beam damage may be the limiting factor.

7. CONCLUSIONS

The potential of STEM HAADF tomography as a method of 3D analysis at high and medium resolution has been examined. High resolution reconstructions of both the position and shape of structures has proved to be possible by the application of weighted backprojection and iterative reconstruction routines. Such reconstructions would have been impossible with BF tomography.

The development of automated acquisition routines is required to allow a greater number of projections to be recorded over a shorter amount of time to improve both the quality of reconstruction and to reduce potential beam damage. A further improvement in resolution would result from an increase in the maximum tilt range of our specimen holder from ±60° to ±70° and we intend to implement this in the near future.

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