Hybrid Tomography for structural and chemical 3D imaging on the nanoscale.

G Möbus, Z Saghi, W Guan, T Gnanavel, X Xu, Y Peng
Dept Engineering Materials, University of Sheffield, Sheffield S1 3JD, UK.
g.moebus@sheffield.ac.uk

Abstract. Electron tomograms can be reconstructed from a variety of projection imaging techniques in TEM, some of which are sensitive to the surface or the bulk, to the structure or chemistry, or operate under different resolution regimes. We introduce a concept of combining two acquisition series using two different complementary modes to form a single hybrid tomogram. As the main application, composite nanoobjects are presented for which a low-resolution 3D chemical mapping mode for the object interior can be combined with a high-resolution surface sensitive mode to precisely define the object exterior shape.

1. Introduction
Electron tomography in materials science is currently the most powerful method of 3D reconstruction of nanostructures. Using projection image tilt series in the TEM, a level of resolution and optional chemical sensitivity can be achieved which is unmatched by any X-ray techniques. Recently, the family of TEM tomography methods has grown rapidly to now include: bright field (BF), dark field (DF) TEM, ADF-STEM, EFTEM, holography, EELS, and EDX [1, 2].

2. The concept of hybrid tomography
In order to be able to exploit the complementary benefits of the different electron tomography modes, applied to the same sample, we outline a strategy of combination-tomograms. At first, we divide the diversity of imaging modes into the following classes or pairs of opposites:

(i) surface sensitive versus bulk sensitive tomography. Here surface refers to the particle shape (or habit in crystallography); surface tomography is the discipline that ideally returns a 3D function with value 1 along all segments (voxels) of the surface and values 0 both inside and outside the surface (or equivalent: value 1 inside and value 0 outside the material). Here bulk refers to the 3D interior density function (e.g. atomic number density) which is determined by bulk tomography, and which has either floating number values or a set of gray levels more than binary.

(ii) structural versus chemical tomography. This classification separates the aim of reconstructing a 3D morphology (both surface and inner microstructure) from reconstructing a 3D chemical map. A core-shell nanostructure with a crystalline core of element A and an amorphous shell of element B would be detected by both modes. Structural modes would include some sensitivity to atomic number (Z-contrast or scattering contrast), but would integrate all elements in projection in case of a composite, while chemical imaging modes in this sense image uniquely one chemical element (or a molecule/unit cell in case of more advanced chemical fingerprinting modes).
(iii) geometric versus computed tomography (GT vs. CT). This purely mathematical classification separates modes that measure metrological parameters (e.g. diameters or supports of objects) from methods that use full projections by Radon transform. Its applicability is closely related to the class (i) above, as CT would reveal the 3D bulk density, while GT is often ideal for 3D surface tracking. GT subdivides into many disciplines, of which we have introduced shape-from-silhouette [3, 4] using a binarised projection, and shape-from-contour [4] using an edge-enhanced projection. These techniques are principally applicable for objects of a minimum convexity, subject to exceptions [4].

(iv) low-resolution vs high-resolution tomography: a hybrid combination of this type would only be meaningful in conjunction with (ii), as the low-resolution information must be valuable (e.g. chemical) and complementary to the high-resolution information (e.g. atomic resolution imaging).

(v.a) thin specimen versus thick specimen tomography, and closely related:

(v.b) linear versus non-linear tomography:
Different TEM modes (or different settings within one mode) can be used to record per tilt angle a pair of images, one optimized for best definition of the thin areas and one for most reliable projection of the (difficult) thick areas. A hybrid reconstruction requires segmentation and/or superposition depending on the orientation of thin/thick areas relative to the rotation axis. This type of combination of two tomograms was perhaps the first hybrid CT application in the field of x-ray tomography of materials [5].

(vi) reconstructive versus destructive tomography. We add an instructive further combination of two modes, the first one “reconstructive” comprising all tomography modes considered so far, whether CT or GT, in the sense that a line integral (a ray of light or an “x-ray” along a line I) produces either the density projection (case of CT) of $P_{CT} = \int \rho(x,y,z) \, dl$ or (case of GT) a binary response ($P = 1$ if at least one voxel $>0$, $P = 0$ if all voxels $= 0$, i.e. outside the object O). To introduce a destructive tomography mode (DT) within the context of particle beam based nanofabrication we have to set the response to $P_{DT} (x, y, x_0, y_0) = I(t) \ast P_{CT}$, with $x_0,y_0 = x_0(t,\Theta),y_0(t,\Theta)$ indicating the beam position during a processing sequence $r_n(t)$, as a function of time and tilt angle. The drilling power intensity $I(t)$ is assumed binary and delivers $P=0$ for $x=x_0, y=y_0$ and $I>0$, while $P=P_{CT}$ for either $x\neq x_0, y\neq y_0$ for any I, or for $I=0$ for any $x,y$. The integration along the beam paths has to be understood as iterated over the tilt angular range, such that each new destructive exposure operates on the previous object $O_{n-1} = \rho(\Theta_{n-1}; x,y,z)$, with N counting the $n^{th}$ tilt angle $\Theta_N$ or the $n^{th}$ destructive modification rather than using the original object for $N=0$. The combination of voxels at different $\Theta_N$ then follows a logical NOR. This latter mode of operation has been shown topologically identical to the GT mode of (iii) [6].

3. Applications

We illustrate the concept of hybrid tomography with highlights of recent work, reinterpreted within the concept of section 2, and extended by a specifically selected application on core-shell particles.

3.1. Hybrid Spectrum Imaging (SI) tomography combined with ADF-STEM.
A primary example of hybrid TEM is the definition of a spectrum image region of interest (linescan or 2D scan) on an ADF STEM image, whether for EDX mapping or EELS-SI. The STEM image provides sharp details on the object shape and size, while the analytical signal in the SI adds internal chemistry. The latter is not only blurred due to delocalization of inelastic processes, but mostly limited in resolution to the spot increment in the scan, typically at least one order of magnitude worse than STEM resolution. In an earlier demonstration of combining a tomographic EDX line scan with an ADF-tomogram we added a sharp contour to a low-resolution multi-element RGB-tomogram [7]. Here we present the combination of an ADF-tomogram with a tomographic set of EELS-SI linescans of a glass-nanocomposite with a CeO$_2$ particle (Fig 1a), with a tilt series over 120° in 10° increment (JEM 2010F).

Suppression of star artefacts, noise and improved contour-resolution result from the multiplication of a binarised ADF-reconstruction (Fig 1b) with the Ce-M-edge slice (the 3D chemical map) of the SI tomogram (Fig 1c), see [8] for details. The dominating artefacts in 1c are due to the
large tilt increment and missing wedge, especially the false bright “corners” of the glass, while the poor particle definition is due to the coarse SI step size.

**Figure 1.** Spectrum Imaging (SI) tomography of a glass fragment: (a) ADF STEM image, member of ADF-tilt series; (b) binarised contour of cross-sectional ADF-reconstruction along dashed line of (a); (c) EELS-linescan reconstruction at around 900 eV loss (Ce-M-edge) with one precipitate arrowed in (a) and (c). The hybrid tomogram results from multiplication or application of logical OR.

### 3.2. Dual-Energy EFTEM of core-shell objects.

Core-shell nanoparticles (or their agglomerates) are another promising field for hybrid tomography, as illustrated by Al particles surrounded by amorphous oxide shell and embedded in carbon. Reconstruction (from a 120° tilt series in 5° increment) of the crystalline core via CT from the Al-plasmon at 15eV loss is combined with a projection at 20-25eV plasmon loss, including both amorphous Al$_2$O$_3$ and carbon. The resulting tomograms can be superimposed into a multi-segmented combined tomogram.

**Figure 2.** EFTEM tomography of Al nanoparticles: (a,b) 15eV plasmon loss image and 3D reconstruction; (c,d) 20-25eV plasmon loss image and 3D reconstruction (JEM 2010F)

### 3.3. Hybrid HREM tomography

Tomographic reconstruction of 2 or 3 zone axis patterns from a nanoparticle can result in a basic solution of unit cell geometry according to the principle of lattice-fringe based “goniometry” [9]. However, the information about the extent of the nanocrystal (its shape) is lost as the fringes are
backprojected to infinity. A multiplication with a complementary geometric tomogram from a full fine-increment tilt series can therefore deliver particle morphology in both external shape and internal crystal structure (if single-grained) \[10\]. The second tomogram could either be from low-resolution BF-TEM or ADF-STEM modes or from a binarized extract of the support of the particle from a full HREM tilt series. The latter is demonstrated for a CeO$_2$ nanoparticle in Fig 3 using a 130° tilt series with 10° increment \[11\].

3.4. Tomographic nanofabrication (destructive combined with reconstructive tomography)
A nickel nanotip is cut and drilled by a FEG-beam at 200kV in three viewing directions to generate a perforated binary structure of homogeneous Ni metal (Fig 4). A subsequent tomographic reconstruction from binarised bright-field images then exactly inverses the fabrication process and leads to a 3D model of the as-fabricated nanostructure. During the fabrication process, extrusions of metal are partially observed, see \[6,12\] for more details.

4. Conclusions
The examples of combining two tomograms acquired with different TEM modes or different data registration, serve to demonstrate that the resulting multi-mode tomogram can exceed in its information content any of the single-mode tomograms. Hybrid tomography is a promising research field in early stage of development with many more opportunities to be explored.

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References
[1] Weyland M, Midgley P A 2004 Materials Today 7 32-40
[2] Möbus G, Inkson B J 2007 Materials Today 10 18
[3] Xu X, Saghi Z, Gay R, Möbus G 2007 Nanotechnology 18 225501
[4] Saghi Z, Xu X and Möbus G 2008 J Microsc. 232 p186.
[5] Tam KC 1987, J nondestructive evaluation, 6 189.
[6] Saghi Z, Gnanavel T, Peng Y, Inkson B J, Cullis A G, Gibbs M R, Möbus G 2008 Appl Phys Lett 93 153102
[7] Saghi Z, Xu X, Peng Y, Inkson B J, Möbus G 2007 Appl Phys Lett 91 251906
[8] Saghi Z, Xu X, Möbus G 2008 Proceed. 14th EMSC, Aachen, 1 427
[9] Qin W, Fraundorf P 2003 Ultramicroscopy 94 245
[10] Saghi Z, Xu X, Möbus G 2009 J.Appl.Phys 106 024304
[11] Saghi Z, Gnanavel T, Xu X, Möbus G 2009 Mater.Res.Soc.Symp.Proc. 1184 HH02-03
[12] Gnanavel T 2010 J Phys Conf Ser, Proceed. EMAG2009, this volume