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Understanding the limitations of the Super-X energy dispersive x-ray spectrometer as a function of specimen tilt angle for tomographic data acquisition in the S/TEM

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Abstract. We have investigated the use of x-ray energy dispersive spectroscopy during tomographic hyperspectral imaging experiments in the scanning transmission electron microscope. In this work, we have found that for an analytical system employing a commercial high-tilt tomography holder the measured x-ray signal is limited by shadowing caused by the penumbra of the holder relative to the x-ray detector system. This limits the ability to perform quantitative, elemental tomographic analysis.

1. Introduction

Electron tomography is one of the more powerful techniques for retrieving nanoscale three-dimensional information, deduced from a series of two-dimensional projections. Tomographic reconstruction requires that the input data satisfies the projection requirement, which is that the signal intensity is a monotonic function of the quantity to be reconstructed. High angle annular dark field (HAADF) scanning transmission electron microscope (STEM) imaging satisfies the projection requirement and has thus far been one of the preferred imaging modes for crystalline materials specimens [1]. In cases where regions of the sample are sufficiently different in atomic number (Z), HAADF STEM tomography is readily able to distinguish between features via Z-contrast mechanisms. Elemental imaging is a useful augmentation to tomographic reconstruction and involves the use of complementary spectroscopic characterization using either electron energy loss (EEL) [2] or energy dispersive x-ray (EDX) [3] spectroscopic imaging. In the latter case, it is well known that detector/specimen holder geometry can limit successful data acquisition and analysis. This is due to the fact that, in some instrument configurations, x-ray signals may only be confidently acquired for specific ranges of specimen holder orientations. Newer generation analytical microscopes, such as the FEI Titan G2 80-200 S/TEM with ChemiSTEM™ technology have been designed to minimize such limitations by incorporating multiple silicon drift detectors (SDDs), positioned symmetrically about the tomographic axis [4]. While successful qualitative tomographic reconstructions using EDX data sets have recently been reported [5,6], some such studies have ignored the effects of x-ray detector



shadowing introduced by some designs of tomographic stages. This shadowing, when it is present, compromises the ability of the EDX signal to provide quantitative three-dimensional information.

In this paper, we report on the magnitude of the shadowing observed when using a Fischione high-tilt tomography specimen holder for two different x-ray detector geometries. The spectrometers positions are compared in Figure 1d (SuperX EDX spectrometer on an FEI Titan G2 S/TEM microscope) and Figure 1e (Oxford Instruments X-Max 80 EDX spectrometer on an FEI Tecnai F30 S/TEM).

2. Experimental Method

The specimen chosen for this study was a single Au/Ag nanoparticle (NP) with a diameter of ~ 30 nm and a hollow geometry (Figure 1a) which was supported on a holey carbon +200 mesh Cu support film. The sample was synthesized as reported in reference [6] and has recently shown high efficiency as a catalyst in the conversion of 4-nitrophenol to 4-aminophenol. The nanoparticle selected for measurement was carefully chosen to be near the center of any support grid, so as to minimize the effects of grid bars. The same specimen and stage was used for all measurements reported in this work, but a different nanoparticle had to be used for each tilt series as relocating the same nanoparticle was problematic.

We have compared EDX detectors measurements as a function of tilt angle from two microscopes with different EDX detector geometries. Microscope 1 is the FEI Titan G2 80-200 which is fitted with an X-FEG high brightness source, and is probe-side aberration corrected to 3rd order. The instrument was operated at an accelerating voltage of 200 kV and with a beam current of 0.3 nA. STEM HAADF data were acquired with a convergence angle of 26.2 mrad and a HAADF inner angle of 52 mrad. Microscope 1 has the ChemiSTEM™ Super-X EDX detector whose geometry consists of two pairs of silicon drift EDX detectors (SDD) either side of the tomography holder primary tilt axis, as illustrated in Figure 1d. These pairs of detectors (1+2) and (3+4) are rotated about the optic axis symmetrically by $\pm 45^\circ$ in the eucentric plane tilt axis. Data from these detectors were recorded as pairs of spectrum images so as to allow assessment of any shadowing created by the penumbra of the tomography stage as the holder is tilted. Microscope 2 is the FEI Tecnai F30 S/TEM equipped with an Oxford Instruments X-Max 80 SDD EDX system. It was operated at 300kV using a beam current of ~ 1 nA. Microscope 2 has the traditional EDX system geometry in which a single x-ray detector is located perpendicular to the tomographic tilt axis (Figure 1e).

The EDX spectrum image data sets (512 x 512 pixels) were acquired every 10° between $\pm 70^\circ$ using a Fischione 2020 single tilt tomography holder. Drift correction was applied to ensure that the nanoparticle remained central within the field of view. The specimen pixel size used was the same for both microscopes and the live acquisition time per spectral image was chosen such that the total beam current was also the same (300 s for Microscope 1 and 108 s for Microscope 2). Spectrum images were exported from either Bruker Esprit or Oxford Aztec software and processed in Gatan DigitalMicrograph™. Total x-ray counts from the whole spectrum image were summed without background subtraction using a 400eV energy window centred on the energy of interest.

3. Results and Discussion

Theoretically, because the nanoparticle is small and of constant volume, one would expect negligible variation in the detected x-ray intensity (counts) as a function of holder tilt. The crystalline structure of the nanoparticle means that strong electron channelling at specific crystallographic orientations could perturb results at a single tilt angle but will not affect the general trend of behaviour observed for the whole tilt range [8]. Figure 1c compares the experimentally observed Au $L\alpha$ x-ray counts for Microscope 1 using the full Super-X detector (4 SDDs) with that obtained by reading out two pairs of SDDs separately. Reference spectra acquired on a nearby region of carbon film contained no gold signal so that these counts are considered to result entirely from the specimen.

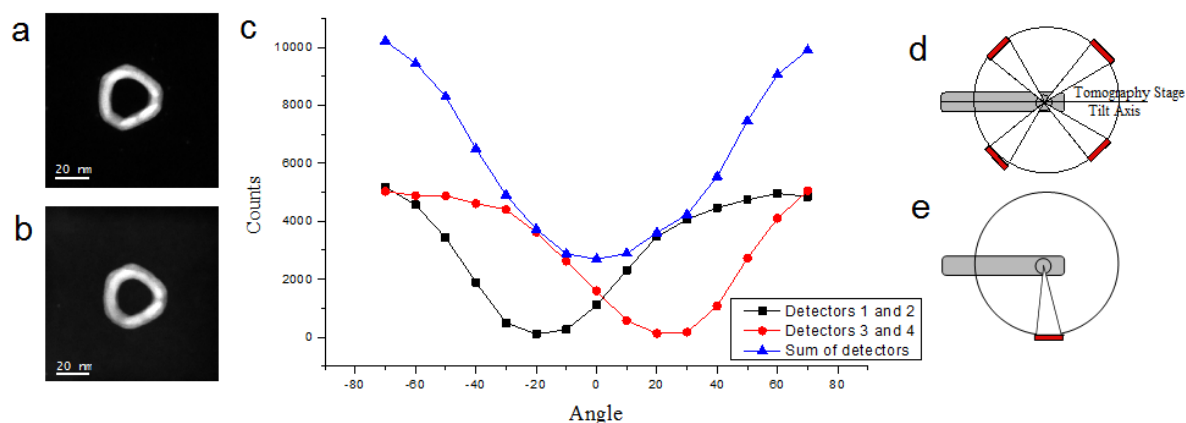


Figure 1. HAADF STEM images from Microscope 1 for a single NP (a) before and (b) after tilt series acquisition. (c) Au L α x-ray counts from the NP shown in (a) as a function of holder tilt for Microscope 1 (Titan ChemiSTEMTM/Super-X). SDDs to the right (1 and 2) and left (3 and 4) of the holder tilt axis are compared with the sum found for all four detectors the geometry of which is illustrated in (d). (e) Traditional EDX detector geometry of Microscope 2 (Tecnai/Xmax).

The variation of the x-ray counts when the signal from all of the Super-X detectors is summed (Figure 1c) demonstrates qualitatively that whilst signal counts are maintained above zero for the full angular range, there is a significant variation in the measured intensity with tilt angle. This intensity variation can be directly attributed to absorption of the NP x-rays by any intervening material along the line of sight path between the NP region of interest and the active area of the x-ray detector being used. The principal culprit in this regard is the tomographic stage side walls and support structures, with the maximum absorption (minimum signal) occurring when the tomography holder is oriented perpendicular to a given detector pair. This is most succinctly illustrated by studying the holder tilt-dependent signals for the two pairs of detectors, 1+2 and 3+4. These mirror each other, reflecting the symmetry of the tomographic stage and x-ray detector geometry on either side of the holder tilt axis. The minima in these latter two curves (at approximately $\pm 20^\circ$) is indicative of the elevation angle of the Super-X detectors.

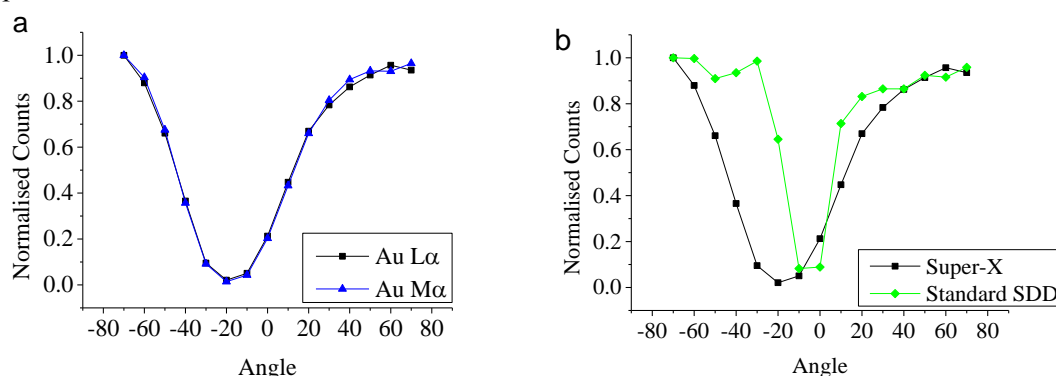


Figure 2. (a) Signal variation with tilt angle for Microscope 1 (Titan/Super-X) using a pair of detectors (1+2). Normalized x-ray counts are compared for Au L α (9.7 keV) and Au M α (2.1 keV) x-rays. (b) Comparison of the variation with tilt angle for the Au L α x-ray signal for a pair of detectors (1+2) from Microscope 1 with the single SDD detector of Microscope 2.

To ascertain whether shadowing effects varied as a function of x-ray energy we have also compared the normalized signal counts for one pair (1+2) of the Super-X detectors signal counts as a function of tilt angle for different energy x-rays from the same element (Figure 2a). The tilt dependent variation of the Au $L\alpha$ (9.7keV) signal and Au $M\alpha$ (2.1keV) signal is identical in the absence of background subtraction suggesting that shadowing is independent of x-ray energy for the tomographic holder used. This is indicative of massive absorption effects as the energies of these two lines are significantly different.

Figure 2b compares the normalized Au $L\alpha$ x-ray counts for one pair of detectors from Microscope 1, with similar measurements made using the single detector geometry of Microscope 2 (Tecnai/X-max). The minimum signal for the pair of detectors on Microscope 1 occurs at a larger tilt angle than that the single X-max detector of Microscope 2 from which one can directly conclude that the elevation angle of the Super-X SDD detectors is greater than that of the single X-max80 SDD detector. The detector pair of Microscope 1(Titan/Super-X) is also shadowed for a wider angular range than the conventional geometry of Microscope 2 (Tecnai/Xmax), due to its larger solid collection angle [9].

4. Conclusions

In this study we have shown that for a nanoparticle sample the measured signal varies significantly with tilt angle when using a Fischione 2020 high tilt tomography holder. This variation is sufficient that it is likely to compromise the reconstruction of quantitative tomographic x-ray spectroscopy data.

There are several approaches that could be used to improve the ability of the EDX signal to satisfy the projection requirement. The first is *a posteriori* compensation of shadowing for EDX tilt data obtained with a uniform acquisition time by applying a weighting factor. The risk of this method is that it could increase noise levels in the EDX maps and thereby lead to false data in the reconstruction. An alternative approach is to redesign the tomographic holder geometry so as to minimize shadowing of the detector during EDX measurements, which is work in progress. It is our expectation that different designs of tomographic holder will perform differently, as their construction varies. This work emphasizes the necessity of testing tomographic holders as to their suitability for tomographic hyperspectral imaging using x-ray spectroscopy.

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