Structural quantification of nanoparticles by HAADF STEM

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Abstract. A new method of quantifying the HAADF STEM signal on absolute scale, building on the z-contrast nature of the technique, has been developed to address the problem of characterising nanoparticles to an atomic scale. Experimental images are scaled to a fraction of the incident beam intensity from a detector map. The integrated intensity of each individual atomic column is multiplied by the pixel area yielding a more imaging-parameter robust quantity, termed a scattering cross-section. Using this cross-section approach, and simulated reference data we show how it is possible to count the number of atoms in individual columns, in order to compare against theoretical 3-dimensional structures. All this is with the aim of trying to obtain as much information as possible from a single image of these beam sensitive samples.

1. Introduction

Platinum nanoparticles are used for catalysing a wide range of reactions however their high cost has driven research into reducing particle size and trying to optimise active sites by controlling particle shape. Further improvement of these systems can only be made by careful investigation of the atomic structure of these particles, including surface facets and steps. These catalysts nanoparticles provide a severe characterisation challenge due to their minute size and beam sensitivity. The necessary aim, therefore, is to extract as much information from one image as possible.

Much quantification work has been previously carried out on more large scale bulk materials or model systems. The new scattering cross-section technique [1] for high angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) quantification shows real promise for analysing nanoscale objects where statistical counting [2] and unit cell averaging are less applicable [3] due to the low total number of atomic columns within an image and therefore poor column statistics.

2. Method

The samples investigated were platinum supported on an amorphous 3-dimensional carbon support; received in powder form which was dusted onto a copper holey carbon grid. All experimental images were taken on an FEI Titan³ G2 60-300 (S)TEM operating at 300kV with convergence angle of 20.2mrad and a camera length of 145mm giving detector collection angles of 34.9-190mrad.
Experimental images were taken and converted to an absolute scale through a detector calibration, Figure 1. [4] The accuracy of this approach was further refined by taking into account the variation in detector sensitivity as a function of scattering angle leading to an up-scaling of the experimental results. A peak finding routine was then carried out on the images. Once the location of peaks are known it was then possible to carry out a locally varying background subtraction behind the particle. This is carried out using the remainder of the image which contains no peaks carrying out iterative inpainting over the remainder of the image. The image was then subsequently segmented into Voronoi polygons; each pixel was assigned to its nearest peak up to a maximum value, to prevent excessive expansion at the surface. Conversion to scattering cross-sections was carried out by integrating within each Voronoi cell and then multiplying by the pixel area. The results were then constructed into a cross-section map, Figure 1, allowing the cross-section of each atomic column to be related back to its location within the particle structure. A program for automated processing of the images as outlined here is freely available online. [5]

A library of scattering cross-sections was obtained by simulating a platinum crystal oriented down the <110> crystallographic direction with increasing number of atoms in the z-direction. These simulations were carried out using a full frozen phonon calculation (QUEP) with 8 phonon configurations. The simulations were carried out to match those experimental conditions used for imaging; voltage of 300kv, Cs of 1.84μm, C5 of -1.25mm, convergence angle of 20.2mrad and detector collection angles of 34.9-190mrad. A ‘super-cell’ was constructed in CrystalMaker™ with a cross-section of 30 atoms and vacuum around the edge to act as a buffer. The cross-section of each of the central 12 atomic columns were averaged to give the tabulated result. For the calculated probe it was estimated that the intensity had fallen to 1% of the maximum value by a radius value of 0.85Å or by 1.58Å at 8.5nm depth into a crystal due to simple geometrical broadening of the probe, this will be slightly larger with a sample due to scattering. For the Pt crystal structure this means that the cross-section of each column can be evaluated independently.

Using the simulated library, Figure 2, each atomic column in the image was assigned to its nearest integer number of atoms. We can then check consistency of proposed nanoparticle models with the atom counting.

3. Results and Discussion

From the library simulations, Figure 2, it is possible to see the strength of the scattering cross-section technique as the channelling effects are much less strong than those presented by the peak intensity with increasing number of atoms. The peak intensity measurement will also be affected by the pixel sampling and whether or not this is coincident with the maximum intensity of the 2-dimensional Gaussian profile. It is still, however, vital to carry out direct comparison with simulation due to the non-linearity of the cross-section value with increasing thickness.

Figure 3, demonstrates a 3-dimensional reconstruction which is in agreement with the atom counting results. From this information it would then be possible to extract important catalytic information such as what surface planes predominate and the distribution of surface atoms with low coordination, which are thought to be the more catalytically active.
Figure 1. Left: The greyscale HAADF image of a Pt nanoparticle viewed down the <110> direction, scaled as a fraction of the incident beam intensity. Right: A scattering cross-section map of the same particle where each coloured region represents the Voronoi polygons over which the cross-section for that atomic column was integrated.

Figure 2. The scattering cross-section and peak intensity plotted against number of atoms in the column, along the <110> direction. This is the library used to assign columns for the reconstruction.
Figure 3. Shows a 3-dimensional image of an example final reconstructed Pt nanoparticle based on the atom counting results.

4. Conclusion

The scattering cross-section technique produces a much more reliable method for direct comparison with simulations, producing a library which varies monotonically with thickness. Using the new scattering cross-section technique it is now possible to estimate the atomic structure of a single element nanoparticle from one HAADF image. This has particular advantages for samples of high beam sensitivity, such as nanoparticles, where a tomographic series is not feasible.

5. References

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