

Towards quantitative analysis of core-shell catalyst nano-particles by aberration corrected high angle annular dark field STEM and EDX

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Abstract. Core-shell structured heterogeneous catalyst nano-particles offer the promise of more efficient precious metal usage and also novel functionalities but are as yet poorly characterised due to large compositional variations over short ranges. High angle annular dark field detector in a scanning transmission electron microscope is frequently used to image at high resolution because of its Z-contrast and incoherent imaging process, but generally little attention is paid to quantification. Energy dispersive X-ray analysis provides information on thickness and chemical composition and, used in conjunction with HAADF-STEM, aids interpretation of imaged nano-particles. We present important calibrations and initial data for truly quantitative high resolution analysis.

1. Introduction

Core-shell structured nano-particles offer the promise of more efficient precious metal usage and also novel functionalities for heterogeneous catalyst applications. Characterisation of individual nano-particles is vital for understanding their catalytic properties. However, mapping such short range compositional variations in nano-particles is challenging.

Using a high angle annular dark field (HAADF) detector in the scanning transmission microscope (STEM), it is possible to directly image the atomic configuration of small nano-particles. This technique has often been chosen for heavy elements on light supports for the strong correlation between atomic number and imaged intensity, known as Z contrast. The major advantage of HAADF STEM over conventional high resolution transmission electron microscopes (HRTEM) is its incoherence; there are no contrast reversals often seen in HRTEM due to the phase contrast nature of the imaging [1].

However, though it offers many advantages, meaningful quantitative compositional information is less than straight-forward to extract from HAADF images because intensities are dependent on both composition and thickness. Some information on the composition and thickness of the sample is necessary before interpretation of an image can be made. Energy dispersive X-ray (EDX) analysis can map composition over a broad range of atomic numbers but is often not favoured as a high resolution analysis technique due to its poor spatial resolution and long acquisition times. Recent developments in aberration correction microscopy allowing for smaller, higher intensity probes have increased to atomic resolution both imaging and chemical mapping [2].

2. Towards Quantification in HAADF Images

Though much work has been done comparing simulations to experimental data, rigorous quantification is still not standard. LeBeau and Stemmer noted that it is essential to properly calibrate the ADF detector for quantitative analysis of HAADF images [3]. Here we determine the response efficiency of our ADF detector and the behaviour in gain and offset of its related analogue to digital convertors with incident beam currents to allow for a complete interpretation of images.

2.1. Detector Mapping

We mapped the scintillator efficiency of the upper ADF detector of the Oxford-JEOL 2200MCO double aberration corrected S/TEM. The probe was scanned across the detector (see Figure 1). It can be seen that there are variations across the detector, especially at low angles and including the shadow of the electron pipe around the central hole. Thus all HAADF simulations should include a detector efficiency weighting factor to allow for accurate comparison between simulated images and experimental data.

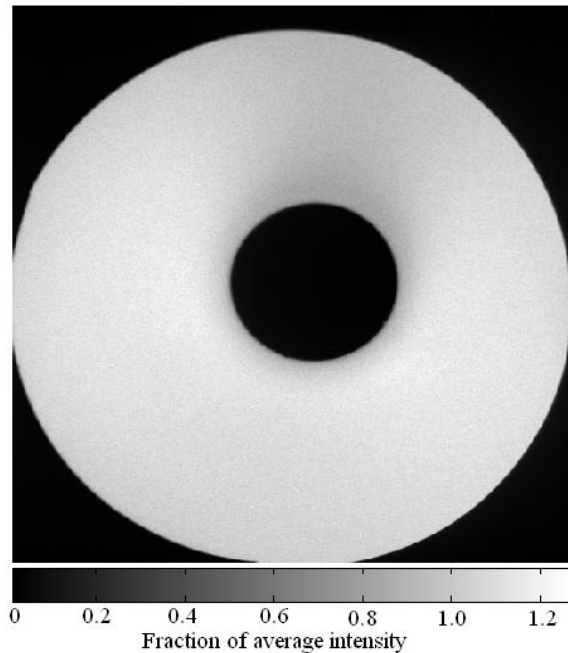


Figure 1: The detector scintillator efficiency as a function of probe position across the detector surface, scaled to mean value across detector. Variations in efficiency are seen across the detector surface, in particular at low angles.

2.2. Gain and Offset

The gain and offset (contrast and brightness) of the amplifiers which convert the signal on the detector to digital values were measured. By adjusting the settings with a beam of constant current, we found that the analogue to digital convertor behaviour varied linearly with offset but the gain behaved non-linearly over a short range of contrast values (See Figure 2).

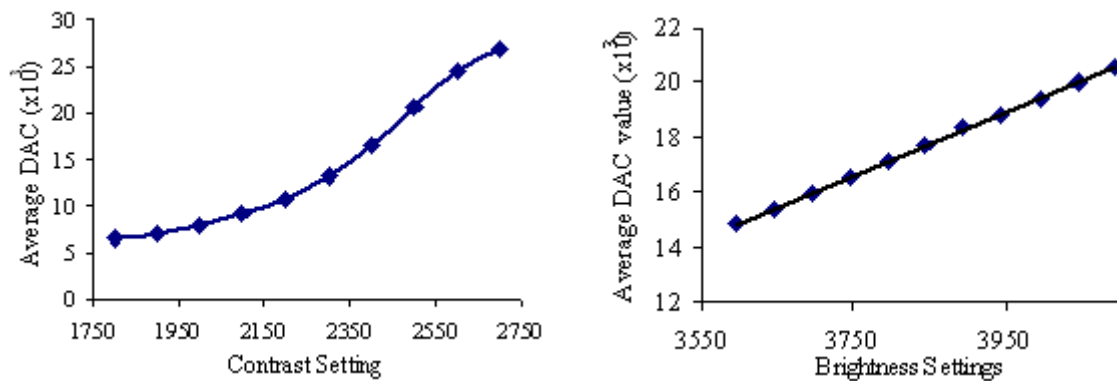


Figure 2 a) Non-linear response of the analogue to digital convertor with contrast (gain) **b)** Linear behaviour of the analogue to digital convertor with brightness (offset).

2.3. Variation of Detector Response to Incident Probe Current

The incident probe current for three spot sizes were measured using a Faraday Cup. Apertures of known size were used to systematically decrease the incident probe current, while brightness and

contrast settings were optimised for the highest beam current. The response of the detector to variations in incident probe current is linear (See Figure 3). The intensity of HAADF images can be directly compared with simulation.

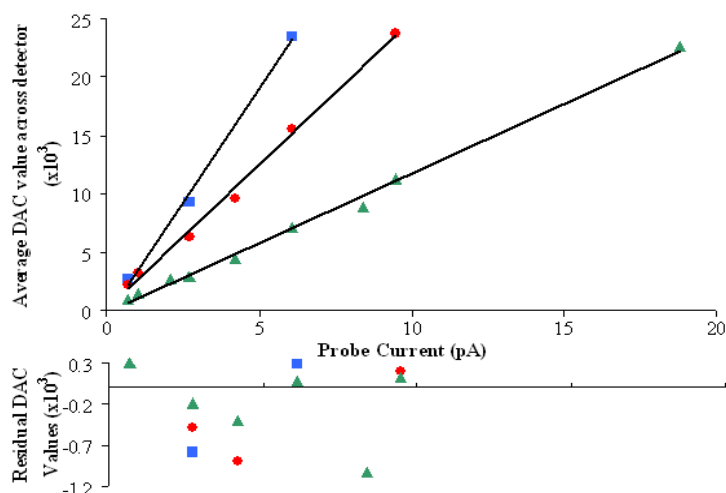


Figure 3 Brightness and contrast settings were optimised for the highest beam current and then kept constant as spot size and apertures were changed to vary the incident current. Three maximum beam currents were used (from spot size 8, 9 and 10 to give 9, 6 and 3 points respectively) to verify detector response across three brightness and contrast settings. The residual is from a linear fit. Variation of detector response to incident probe current is linear.

3. HAADF Imaging

Core-shell nano-particles of palladium core and platinum shell on porous carbon support were deposited onto a TEM grid with lacy carbon film support. The sample was then baked on a bulb for 30 minutes in vacuum at 115°C to remove possibilities of contamination when exposed to the electron beam. High resolution HAADF-STEM images were acquired using the Oxford JEOL 2200MCO. A map of the detector was taken so that the image of the nano-particle could be normalised to a known current.

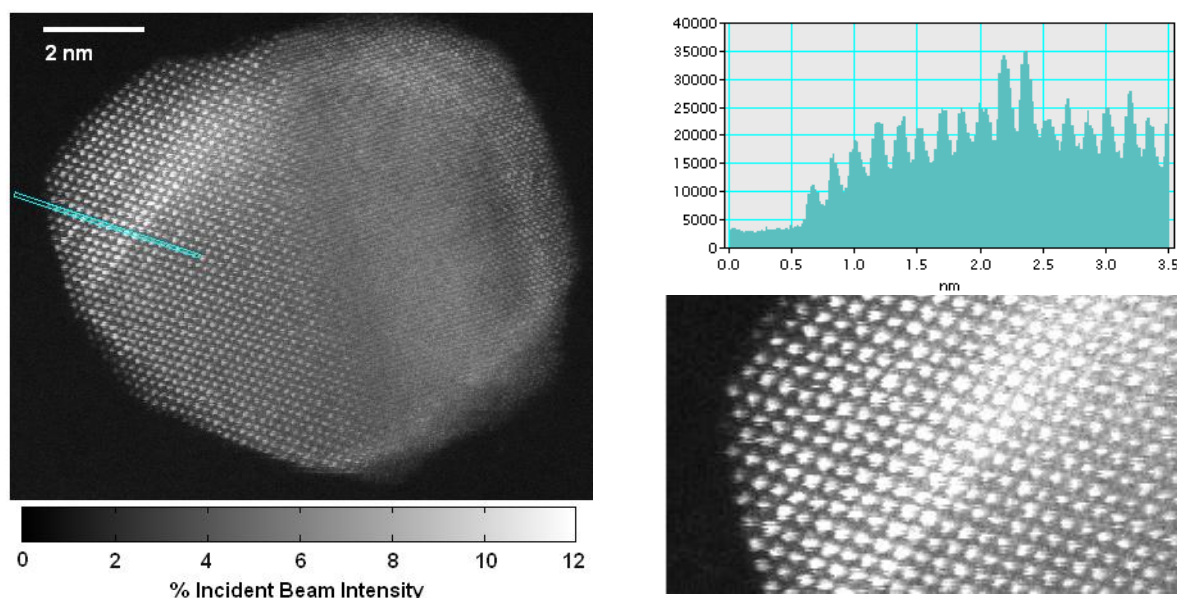


Figure 4 Twinned platinum and palladium nano-particle imaged using the Oxford-JEOL 2200MCO **a)** ADF image normalised to percentage of incident beam intensity. The particle is viewed down $\langle 110 \rangle$ zone axis. A twin boundary can be clearly seen down the centre of the particle and atomically sharp terminated edges on the left side. **b)** Line profile of intensity with integration width 3. Sharp increases in intensity indicate presence of heavier platinum as a dramatic increase in local thickness is unlikely. **c)** Detail of left corner of nano-particle.

A local approximation multi-slice simulation method is in development for the specific case of nano-particles, based on the Melbourne STEM program developed by L J Allen, S D Findlay and M P Oxley [4].

4. EDX

Composition and thickness information can be achieved with EDX line scans and mapping (See Figure 5), showing clearly the core-shell structure of the nano-particles. Though EDX by itself does not offer atomic resolution mapping, in combination with high resolution HAADF imaging, exact structures could be determined.

EDX spectra simulation techniques for compositional analysis often do not use accurate self-absorption corrections. We aim to compare the traditional Cliff-Lorimer approach with a composition-independent and mass-thickness-independent zeta-factor method [5].

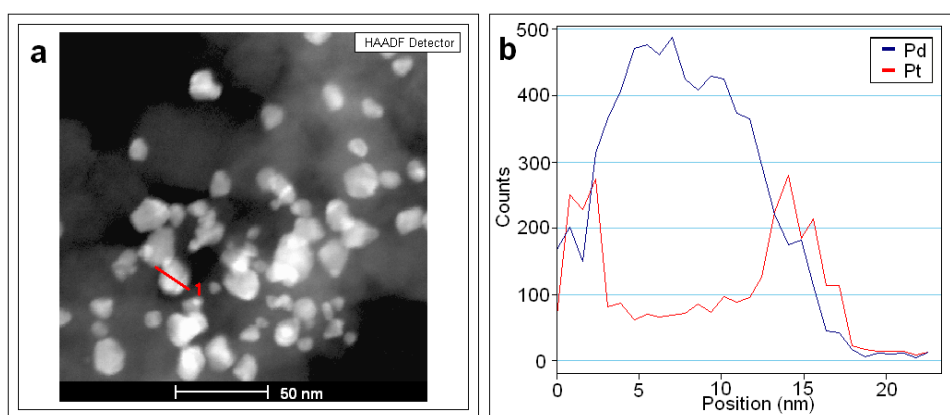


Figure 5 a) HAADF image of a cluster of nano-particles. b) EDX line profile taken across a nano-particle (see HAADF image in a), showing clear core-shell structure. (Acquired on a Tecnai F20)

5. Conclusions and Future Work

Calibrations of the Oxford-JEOL 2200MCO are completed so that true quantitative information could be extracted from HAADF images. We show that the detector responds linearly with incident probe current but that care is needed with the contrast settings as the analogue to digital conversion is non-linear with respect to changing gain. Nano-particles were imaged and intensities normalised to incident probe current so that they can be compared to simulation without free scaling parameters.

Simulation techniques for both HAADF images and EDX spectra are under development. Further work is planned towards achieving truly quantitative measurements of shell thickness, proportional coverage and information about facial orientations with a combination of these techniques.

6. Acknowledgements

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