

## Electron tomography of Pt nanocatalyst particles and their carbon support

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**Abstract.** Industrial nanocatalysts usually comprise crystalline particles of high atomic number that have sizes of between 1 and 20 nm and are supported or embedded in a lower atomic number matrix. The physical characterisation of the three-dimensional shapes and sizes of such particles can now be carried out using high-angle annular dark-field electron tomography. The spatial distribution of the particles with respect to their matrix is an issue of paramount importance for their performance as catalysts. Here, we show experimental electron tomography results from platinum particles dispersed in a carbon support. We show that both the high and the low atomic number regions of the same region of a sample can be characterised by using a combination of high and low angle annular dark field and bright field signals.

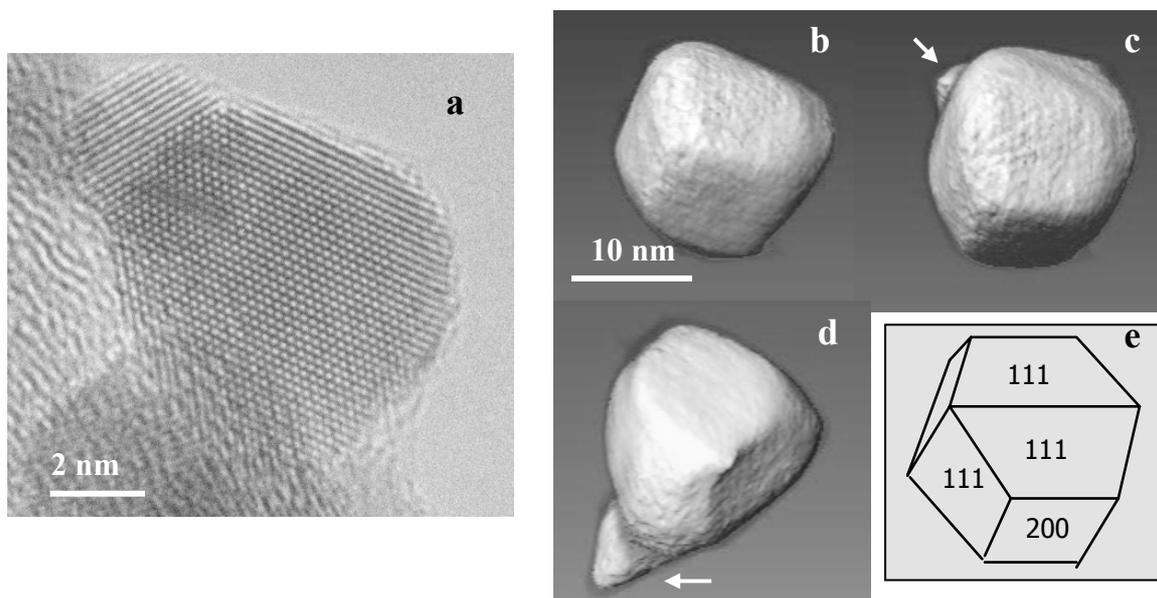
### 1. Introduction

Two important applications of platinum group metal heterogeneous catalysts are in fuel cells and car pollution converters. Characterisation is critical to the development of new catalysts, whose preparation is generally not well controlled. The full characterisation of Pt nanoparticles is challenging and requires the use of different microscopy techniques. The recent development of high-angle annular dark field (HAADF) electron tomography allows both qualitative and quantitative information about the shapes, volumes and three-dimensional spatial distributions of nanoscale particles to be obtained [1]. Here, HAADF tomography is used to study Pt nanoparticles. It is suggested that it is difficult to assess the locations of such particles in a carbon matrix using HAADF tomography, and that low-angle annular dark field and bright field measurements may be used to provide this information.

### 2. Characterisation of particle shape

It is important to be able to relate the geometrical shapes of Pt particles to their catalytic activity and selectivity, which depend on the exposed surfaces of the particles [2]. Historically, high-resolution transmission electron microscopy (HRTEM) has been the major contributor to the analysis of such particles and their supports. Figure 1a shows an HRTEM image of two overlapping Pt particles with sizes of 7.5 and 5 nm, acquired at 400kV using a JEOL 4000EX electron microscope. Although such images contain important information about crystalline structure and atomic arrangement, they are projections of a three-dimensional volume, and the true shape of a particle cannot be inferred from such an image unambiguously. In contrast, figures 1b-d show three different views of an HAADF tomographic reconstruction of a 15 nm Pt

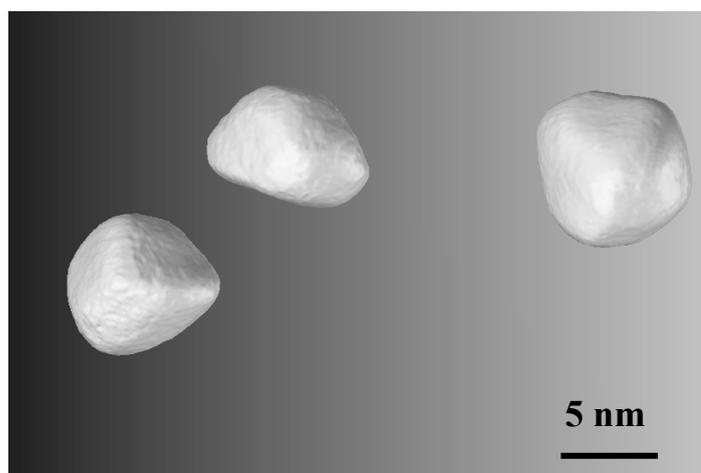
particle. Angles between certain planes in the reconstruction are consistent with the value of  $129.5^\circ$  expected between 111 and 200 planes in Pt, while the overall particle shape is a truncated octahedron.



**Figure 1.** (a) HRTEM image of a Pt particle acquired at 400kV. (b)-(d) Three different views of an HAADF tomographic reconstruction of a 15 nm Pt particle. Tomographic acquisition was performed at 200kV in a Tecnai F20 microscope at a magnification of 1.3Mx. 136 images were acquired from  $-70$  to  $+66$  degrees in steps of 1 degree. White arrows indicate an artefact of the reconstruction. Angles measured between planes matched those of a truncated octahedron, similar to that shown in (e).

The quality of the reconstruction of an object from a series of projections is affected greatly by the tilt range used for acquisition. In figures 1c-d, white arrows show artefacts that result from the limited tilt range. Future developments in tomographic acquisition and reconstruction, including dual-axis tomography, may allow such artefacts to be eliminated.

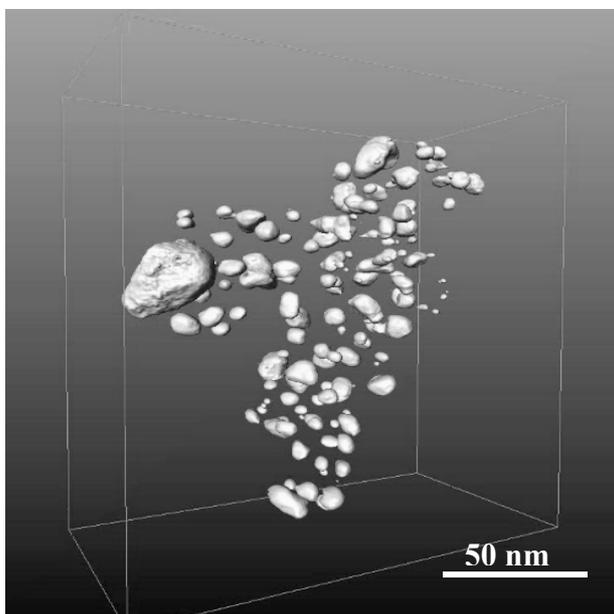
Figure 2 shows a similar tomographic reconstruction of Pt nanoparticles that have a mean size of 5 nm. It remains to be established whether the rounding of the particle edges in reconstructions of particles of this size is real, or whether it is an artefact of the reconstruction.



**Figure 2.** HAADF tomographic reconstruction of Pt particles with a mean size of 5 nm. 138 images were acquired at a magnification of 1.8Mx using a tilt range of  $-70$  to  $+68$  degrees and a tilt step of 1 degree.

### 3. Characterisation of the matrix

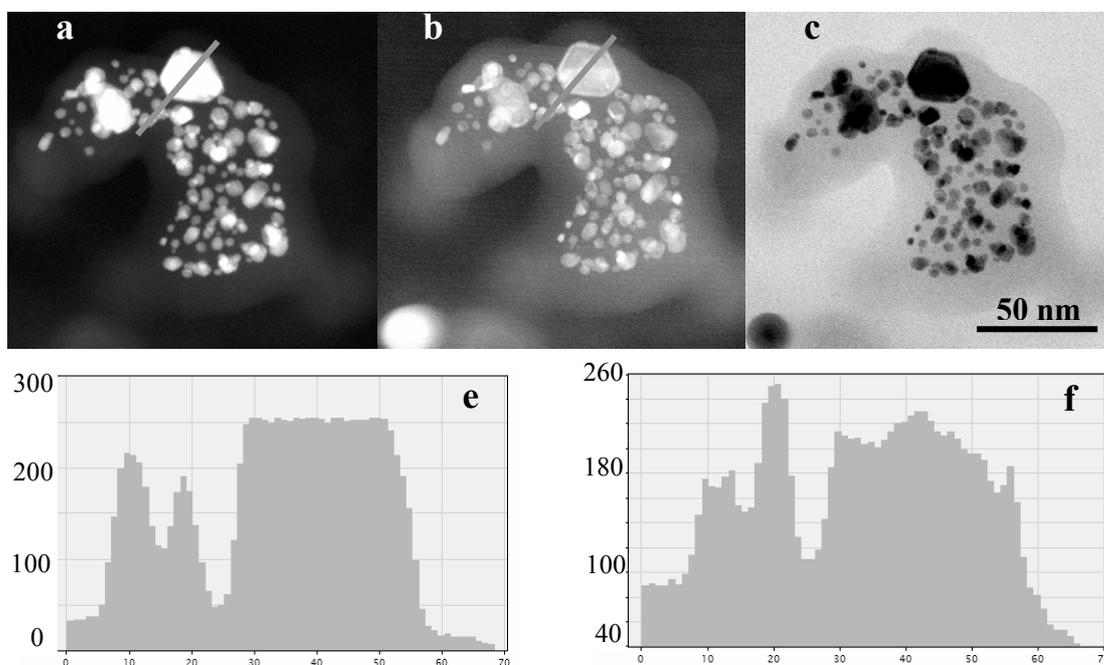
The distribution and orientation of the Pt particles with respect to the carbon matrix is important because the support helps to disperse the particles evenly and to keep them as small-



**Figure 3.** HAADF tomographic reconstruction of a distribution of Pt nanoparticles that have an average size of 5nm and are supported in carbon. The low atomic number of the carbon support makes its reconstruction and visualisation difficult.

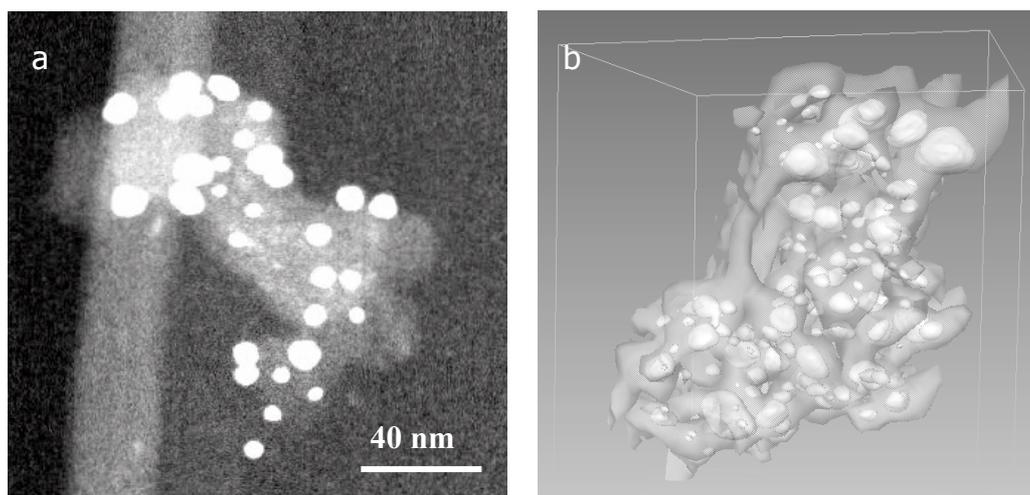
nanoparticles during activity [3-5]. Figure 3 shows the spatial distribution of a large number of Pt nanoparticles obtained using HAADF tomography from which the particle size distribution can be measured. The carbon matrix is not visible in the reconstruction. If a lower threshold level were set for visualising the result of the reconstruction, artifacts (streaking) from the Pt particles would affect the signal from the carbon matrix significantly.

Figure 4 shows a comparison of three images of the same distribution of Pt nanoparticles in a carbon matrix acquired using HAADF, low-angle annular dark field and bright field detectors in scanning mode. The HAADF signal does not show appreciable diffraction contrast, and is strongly dependent on atomic number density. As a result of the large difference in atomic number,  $Z$ , between the Pt particles ( $Z=78$ ) and the carbon



**Figure 4.** (a) HAADF, (b) low-angle annular dark field and (c) bright field images of a distribution of Pt particles, acquired at 200kV. (d) and (e) are profiles of the signal acquired along the grey lines drawn on images (a) and (b), illustrating the large difference in the signal level of the matrix with respect to that of the Pt nanoparticles.

matrix ( $Z=6$ ), as well as the approximately  $Z^2$  dependence of the recorded intensity, the contrast from the matrix is very low.



**Figure 5.** (a) HAADF image acquired after adjustment of the detector to visualise the carbon surrounding a distribution of Pt particles, which are themselves saturated in the recorded image. (b) Carbon matrix and particles after tomographic reconstruction

However, neither of these signals is suitable for tomographic reconstruction of the particles, and appreciably larger artefacts than for HAADF tomography would extend into the matrix if reconstruction of the particles were attempted.

Figure 5a shows an HAADF image, in which the detector was adjusted to enhance the signal from the carbon matrix. However, the Pt particles are then saturated, and tomographic reconstruction. Figure 5b results in artefacts in the reconstruction of the carbon matrix.

Two solutions to these issues are possible. The first is to use HAADF tomography to reconstruct the three-dimensional particle shapes and positions, but to infer the particle positions in the matrix qualitatively by observing a low-angle dark field ultra-high tilt series of images visually. The second is to use digital image processing techniques to remove the Pt particles from each image in a tilt series, to interpolate the matrix across the positions of these particles, and then to reconstruct the shape of the matrix alone, for comparison with the particle positions. Both of these approaches are being developed and assessed.

#### 4. Conclusions

It has been shown that information about Pt nanoparticles in a carbon support can be obtained using high-angle annular dark field electron tomography. The three-dimensional shapes and sizes of catalyst particles with sizes of 5 nm have been determined, and the shape of a 15 nm particle has been demonstrated to be similar to that of a truncated octahedron. Three-dimensional characterisation of the carbon matrix that surrounds the Pt particles is difficult using HAADF tomography. We suggest two possible solutions that may be used to overcome the limitation of imaging the low atomic number matrix, by using a combination of high and low angle annular dark field and bright field signals.

#### References

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