Crystal size and shape analysis of Pt nanoparticles in two and three dimensions

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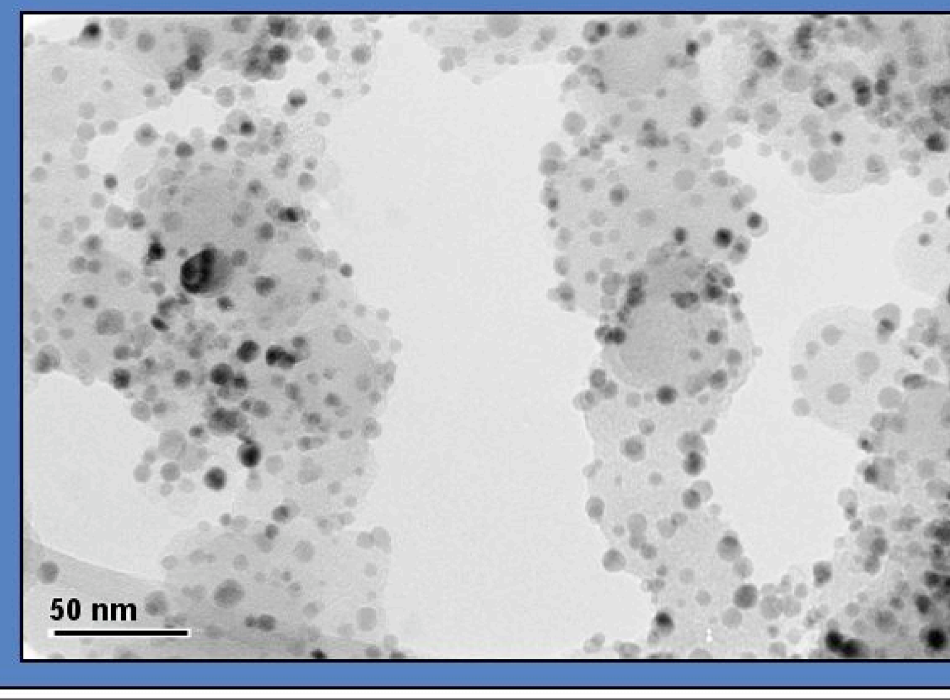
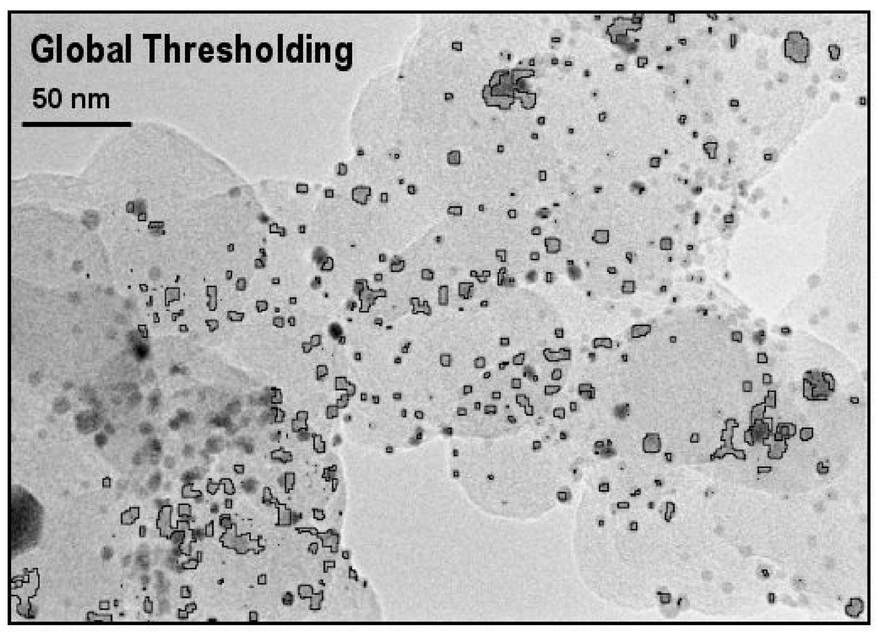
Abstract

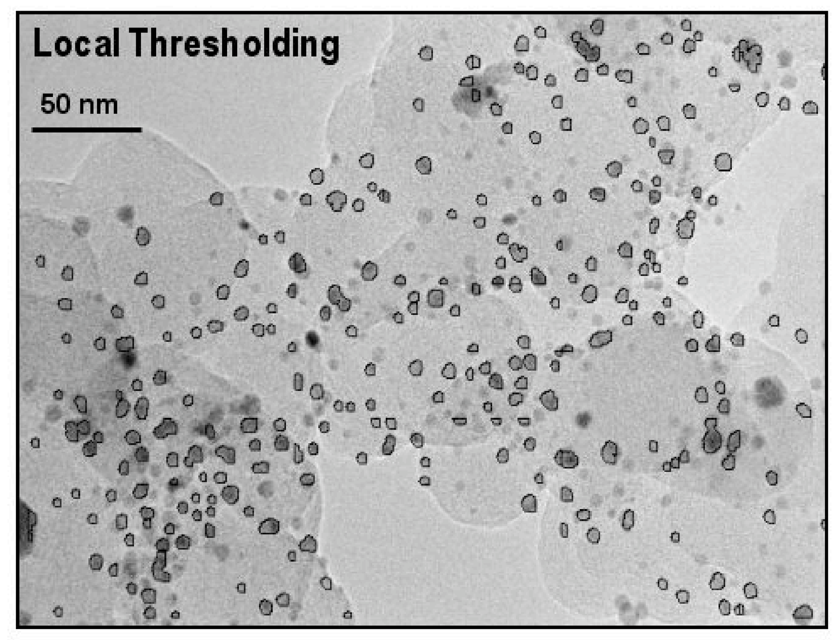
The majority of industrial catalysts are high-surface-area solids, onto which an active component is dispersed in the form of nanoparticles that have sizes of between 1 and 20 nm. In an industrial environment, the crystal size distributions of such particles are conventionally measured by using either bright-field transmission electron microscope (TEM) images or X-ray diffraction. However, the analysis of particle sizes and shapes from two-dimensional bright-field TEM images is affected by variations in image contrast between adjacent particles, by the difficulty of distinguishing the particles from their matrix, and by overlap between particles when they are imaged in projection. High-angle annular dark-field (HAADF) electron tomography provides a convenient technique for overcoming many of these problems, by allowing the three-dimensional shapes and sizes of high atomic number nanoparticles that are supported on a low atomic number support to be recorded. Here, we discuss the three-dimensional analysis of particle sizes and shapes from such tomographic data, and we assess whether such measurements provide different information from that obtained using two-dimensional TEM images and X-ray diffraction measurements.



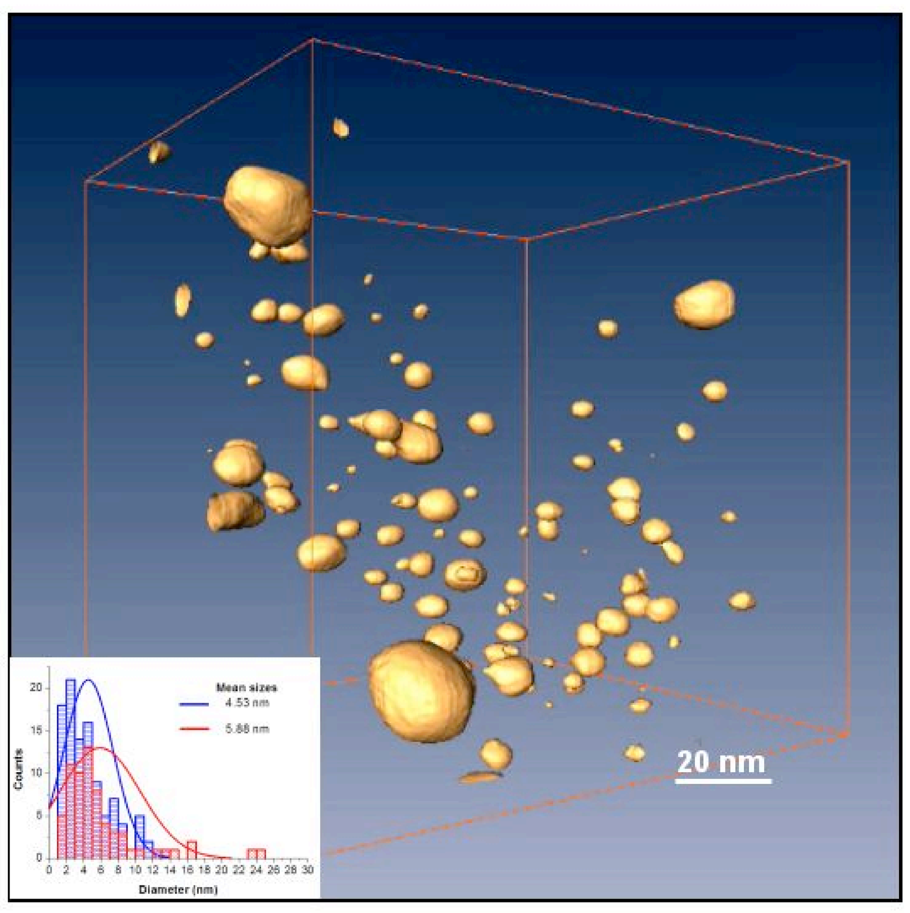
Local thresholding of TEM images



It is often challenging to measure the sizes of small particles from greyscale TEM images. Similar particles can have very different intensities as a result of diffraction contrast, while the carbon support has a thickness that changes locally and variable contrast that affects the mean intensity values of the particles. Conventionally, a greyscale image is converted into a binary image, such that pixels with a greyscale value higher than a chosen threshold are separated from those with values below the threshold. This transformation is applied to the whole picture, using a single threshold value. This procedure rarely works across an entire image. Here, we propose using an adaptative threshold that is automatically adjusted in different parts of an image. The figures on the left and right show a comparison between the two approaches for particle detection using global and local thresholding, respectively.



Tomography for the determination of crystal sizes and positions

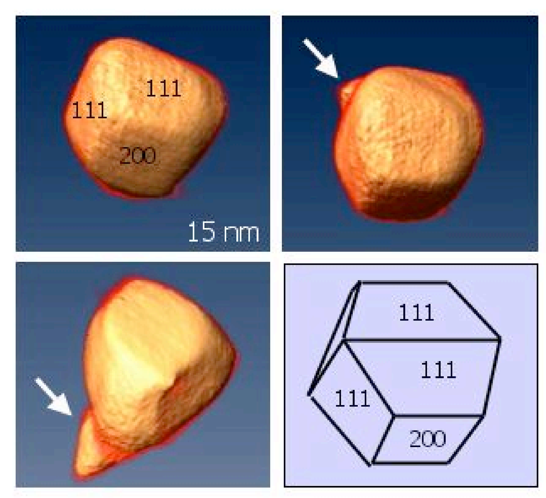


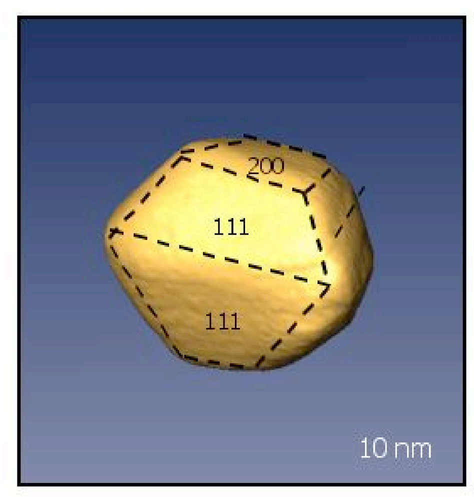
HAADF tomographic reconstruction of a distribution of PtCr nanoparticles.

The uncertainty of using two-dimensional images of three-dimensional crystals to infer their shapes can make conventional TEM, even with subsequent image processing, inconclusive. The application of HAADF tomography to the measurement of crystal size distributions (CSDs) may overcome the limitations of conventional TEM images. The figure on the left shows a three-dimensional HAADF reconstruction of a distribution of PtCr nanoparticles, obtained at 200 kV using a Tecnai F20 TEM equipped with a field emission gun (FEG). Images were acquired over a sample tilt range of –68 to +68 degrees in steps of 2 degrees, at a magnification of 640kx. Quantitative measurements of the volumes and spatial distributions of the particles in three dimensions are possible from such datasets. Alternatively, the reconstructed information can be reprojected in any direction, and the resulting CSDs measured conventionally. The inset to the figure on the left shows, the graphs that illustrate the danger of interpreting CSD measurements performed on small datasets consisting of two-dimensional projections of three-dimensional particles. The mean particle sizes differ by 20% when they are viwed from different directions

Tomography and particle shapes

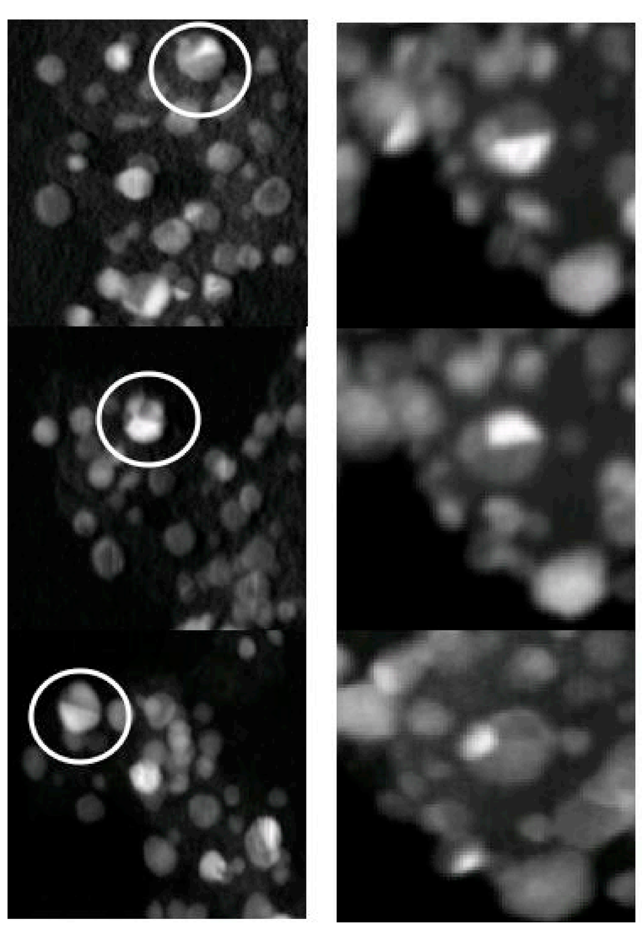
The figures below show examples of the application of HAADF tomography to obtain information about the shapes of Pt particles. Angles between certain planes in the reconstruction are consistent with the value of 129.5º expected between 111 and 200 planes in Pt, while the overall particle shape is a truncated octahedron.



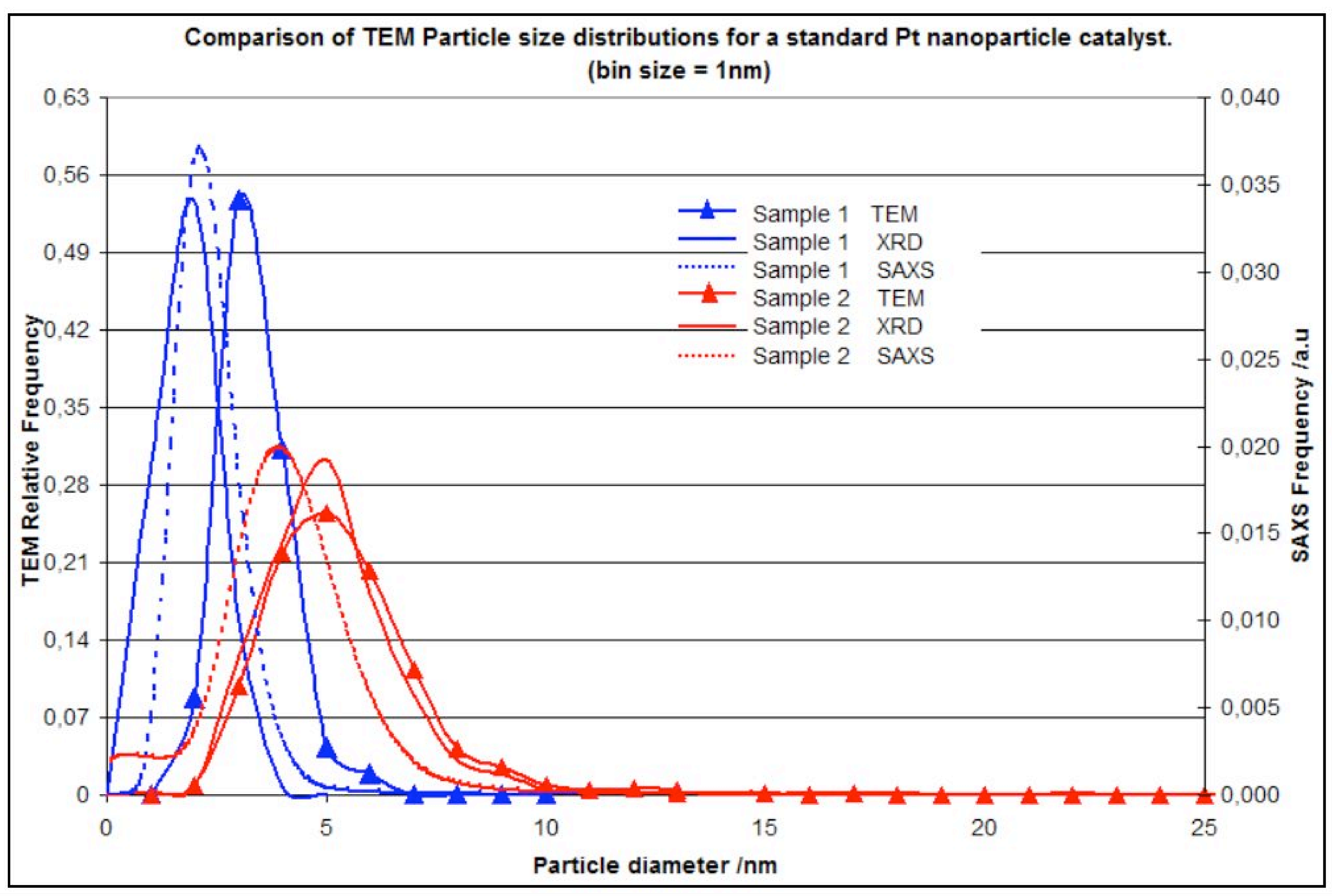


The quality of the reconstruction of an object from a series of projections is affected greatly by the tilt range used for acquisition. In the figures shown above, white arrows show artefacts that result from the limited tilt range. Future developments in tomographic acquisition and reconstruction, including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

CSD measurement by SAXS and TEM



CSD measurements from TEM images are usually performed on at least 1000 particles. However, larger particles are often deliberately omitted from the measurements. Small angle X-rays scattering (SAXS) and X-ray Diffraction (XRD), instead, provide information indiscriminately from much larger numbers of particles. The graphs on the right show CSD measurements obtained from two different samples, and illustrate the differences that result when using different techniques. In addition, SAXS and XRD reflect the average size of a scattering element, which may be smaller than the crystal that contains it. The figure on the left shows low-angle annular dark-field TEM images that illustrate qualitatively the presence of regions within individual Pt particles that diffract differently, and which would appear to be separate crystals when measured using SAXS or XRD.



References

Heinemann K and Soria F 1986 *Ultramicroscopy* **20** 1-14

Treacy M M J and Howie A 1980 *J. Catal.* **63** 265

Hÿtch M J and Gandais M 1995 *Phil. Mag. A* **72** 619-634

Weyland M, Midgley P A and Thomas J M 2001 *J. Phys. Chem. B* **105** 7882-788

Conclusions

An automated approach for particle detection from TEM images using local thresholding has been presented. This approach is based on adaptative thresholding. The application of HAADF electron tomography to crystal size distribution measurement for nanocatalysts supported in a low atomic number matrix is also illustrated. The use of a low-angle annular dark-field detector to examine the crystallinity of Pt nanoparticles is used to highlight a possible source of discrepancy between crystal size measurements made from TEM images and similar measurements made using small-angle X-ray scattering and X-ray diffraction.