The application of novel TEM techniques to the study of Pt catalyst particles

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Abstract

Industrial catalysts 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. Electron microscopy is an important tool for the physical characterisation of their shapes, sizes and crystalline structures, which are, in turn, important for understanding their catalytic properties. Here, developments in transmission electron microscopy (TEM) such as spherical aberration (C_s) correctors and in scanning transmission electron microscopy (STEM) such as high-angle annular dark field (HAADF) electron tomography are applied to the study of 5-10 nm platinum nanoparticles supported on carbon. Indirect methods are used to remove lens aberrations using through-focal series exit-wavefunction restoration (TF-EWR).

1. Combination of spherical aberration correction and through-focus exit-wave restoration

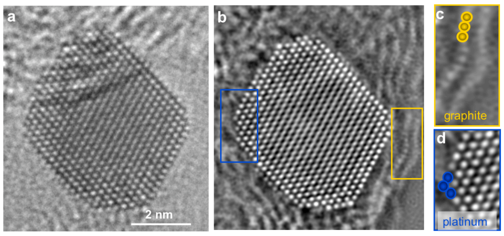


Figure 1. Image of Pt particle acquired at 200kV at optimum defocus with C_s adjusted to – 4 μm. (b) restored phase image of the same particle obtained by applying TF-EWR to a defocus series of 20 images acquired at 200kV. (c-d) Details of the graphitic C and Pt particle shown in (b).

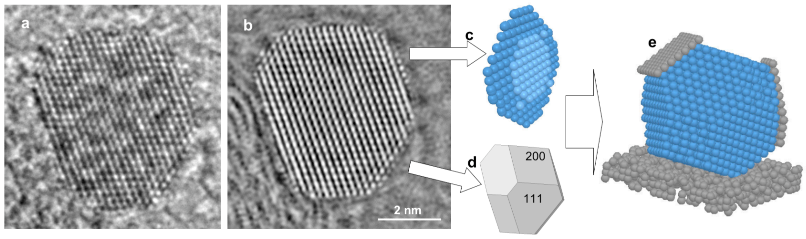
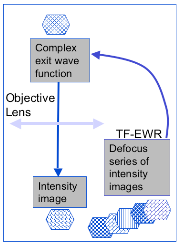


Figure 2. (a) HRTEM image of a Pt particle acquired at optimum defocus with C_s adjusted to –30 μm. (b) Phase of the exit-wave-function of the same particle after applying TF-EWR. (c) Atomic model of an incomplete surface layer. (d) Wulff-type model of the particle. (e) Atomic model of Pt particle with semi-filled surface layers (blue=Pt; grey=C).



The interpretation of conventional high-resolution transmission electron microscope (HRTEM) images is complicated by the effects on image contrast of aberrations of the microscope objective lens. Spherical aberration (C_s) correction allows imaging artefacts due to delocalisation to be reduced to a great extent [1] (**Figure 1a** and **2a**). Through-focus exit-wave function restoration (TF-EWR) [2,3] and other indirect image restoration techniques, allow phase distortions that have been introduced by aberrations of the electron microscope objective lens to be removed. They also allow both the phase and the modulus of the exit plane wavefunction to be recovered, with an increase in interpretable resolution that can approach the information limit of the microscope.

HRTEM images of Pt nanoparticles were acquired using a JEOL 2200FS microscope, equipped with a field emission gun (FEG) and operated at 200kV. This instrument incorporates aberration correctors in both its imaging and its probe forming lenses, as well as an in-column omega-type energy filter [4].

Figure 1 shows the improved visibility of the platinum particles when TF-EWR is used. Atoms of carbon in the graphite layers, and platinum atoms at the edges of the particle, can be resolved clearly. **Figure 2** shows an example that demonstrates that the surfaces of small particles are not completely filled. This information is important for catalysis, providing a better understanding of the nature of the active sites (i.e., the atomic coordination of the atoms on the surface of the particle).

2. Combination of HAADF Tomography and HRTEM with C_s-correction on the same particle

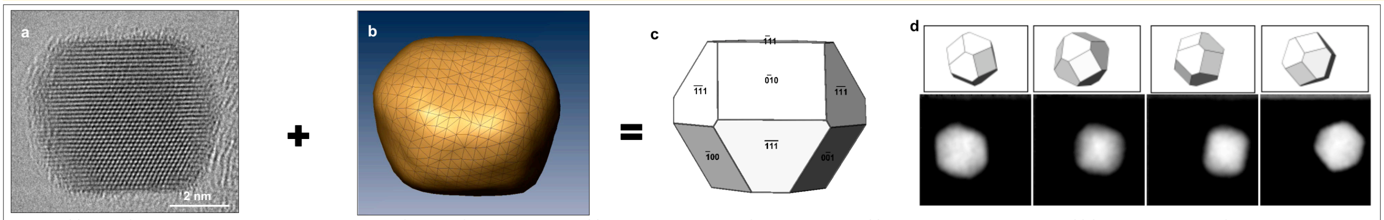


Figure 1. (a) Image of 8 nm Pt particle acquired at 200kV at optimum defocus with C_s adjusted to – 20 μm. (b) Three-dimensional shape of the particle shown in (a) obtained using HAADF tomography. (c) Crystallographic details of the Pt particle, combining the information in (a) and (b). (d) Selection of four HAADF images, acquired at different tilt angles (part of a series of 61 images) of the particle shown in (b) and the corresponding Wulff shapes (top) .

We have characterised the *same particle* in *two different microscopes,* in order to complement the two-dimensional high-resolution atomic information obtained in a JEOL 2200 FS microscope equipped with a C_s-corrector (**Figure 1a**), with the three-dimensional shape information from HAADF tomography [5] in a Tecnai F20 (**Figure 1b**). In HAADF imaging, for the signal collected at high angles in the electron microscope suitable for doing tomography because, to a first approximation, the intensity is proportional to Z^2. In order to minimise diffraction contrast from the particles and to maximise the signal-to-noise ratio (SNR), a the camera lenght of 150 mm was used. For obtaining the three-dimensional shapes of nanoparticles with adequate spatial resolution we used magnification values of between 910Kx and 1.3Mx, and acquired images using tilt ranges of ±65 degrees wih a tilt step of 1 degree. Alignment of the datasets was performed using Inspect3D software, and reconstruction was carried out using the simultaneous iterative reconstruction technique (SIRT) algorithm (15 iterations proved to be enough for convergence)

3. HAADF Tomography and the shapes of twinned nanoparticles

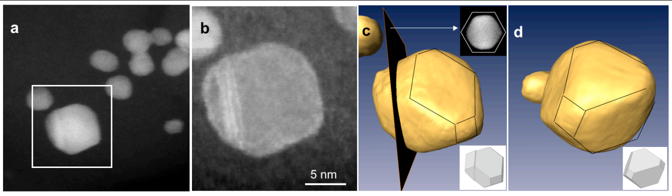


Figure 1. (a) HAADF STEM image of Pt particles acquired at 200kV. (b) ADF STEM image of the Pt particle shown in (a) acquired with higher magnification and higher camera lenght. Bright lines across the particle are an indication of lamellar twinning. (c-d) Two different views of the three-dimensional shape of the particle shown in (a) and (b). The corresponding Wulff construction is shown in the insets.

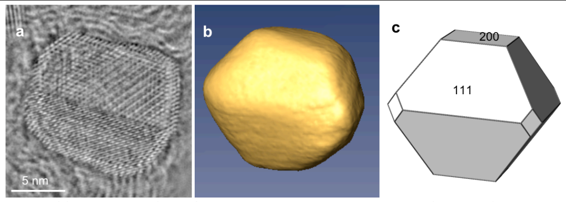


Figure 2. (a) Phase Image of a Pt_3Co particle acquired at 200kV at optimum defocus with C_s adjusted to –20 μm, after apliying TF-EWR to a defocus series of 20 images. (b) Three dimensional shape obtained from a HAADF tomographic series of 70 images of the same particle, acquired at a magnification of 910 kx. (c) Wulff model of the particle.

Ino showed first results of HRTEM of nanoparticles, built up of inhomogeneously strained single crystal units [6]. Small particles with FCC structures, often form in non-crystallographic shapes, multi-twinned-particles (MTP's), composed of five units yielding a decahedral structure or twenty units an icosahedral structure. Other types of twinned particles contain planar twin boundaries dividing the crystal into two sections, either symmetrically or asymmetrically; these are called "lamellar twinned particles" and can have several parallel twin boundaries. HAADF tomography is used here to determine the shape of an asymetrically twinned (**Figure 1**) and a symmetrical particle (**Figure 2**).

References

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Conclusions

It has been shown that C_s -correction and exit-wave restoration gives rise to an improvement in the spatial resolution and the visibility of Pt nanoparticles that are a few nanometers in size. After focal series restoration, the atomic surface arrangement on the particles can be seen. In addition, the signal to noise ratio is improved significantly, and details of the graphitic carbon support surrounding the particles become visible. Preliminary results of the application of C_s correction, and high-angle annular dark field tomography to the same particle have been shown. The aim of the work is to characterise three three-dimensional atomic arrangement and the shapes of such particles.