The application of spherical aberration correction and focal series restoration to high-resolution images of platinum nanocatalyst particles

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Abstract. A JEOL 2200FS transmission electron microscope equipped with a field emission gun, an objective lens spherical aberration corrector and an in-column energy filter has been used to acquire through focal series of high-resolution images of platinum nanocatalyst particles using a small value of the spherical aberration coefficient. The degree to which spherical aberration correction provides an improvement to image quality and interpretability for such particles is discussed, both with and without the use of through-focal series restoration.

1. Introduction
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]. Images of comparable spatial resolution to those taken on a $C_s$-corrected microscope can also be obtained using through-focus exit-wave function restoration (TF-EWR) [2,3]. It has been suggested that a particular strength of $C_s$ correction is its ability to resolve atomic structure in real time, and that TF-EWR can be used as a complementary technique. In this paper, preliminary results from the application of both techniques to the characterisation of platinum nanoparticles supported on graphitic carbon are presented.

2. $C_s$ correction
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. It has an uncorrected coefficient of spherical aberration of the objective lens $C_s$ of 0.5 mm (corresponding to a point resolution of 0.19 nm at Scherzer focus) and a coefficient of chromatic aberration $C_C$ of 1.1mm [4].

When performing electron microscopy with a FEG [4], because high spatial frequencies are present over a wider range of defocus than when using a LaB₆ source, and because of the formation of Fourier images, a particular set of lattice fringes may disappear and reappear.
repeatedly as the defocus is changed. For example, contrast reversals are predicted to occur in the present microscope every 42 nm in defocus for the 111 reflection in Pt.

When aligning a microscope equipped with a FEG electron source, it is difficult to assess the defocus and astigmatism of an image by eye. Instead, with the help of on-line processing, digital diffractograms can be acquired in the form of a Zemlin tableau. The aberration coefficients can then be measured and compensated [5]. All aberrations up to third order can be corrected and $C_s$ can be tuned to a desired value, which may be negative.

With computer assisted correction and alignment, a negative value for $C_s$ of -30 $\mu$m was used in the present experiment. The reason for choosing a non-zero value is twofold. First, at zero $C_s$, Scherzer focus corresponds to a defocus of zero and all phase contrast would then be expected to disappear. Second, it is not easy to compensate for spherical aberration exactly, and a small but finite value is easier to achieve (with an accuracy of $\sim$5-10$\mu$m) than a value of precisely zero. In addition, negative $C_s$ provides a new specimen-dependent imaging mode ($C_s$ is positive for convergent magnetic lenses), which may enhance desired contrast [6].

Figure 1 shows an example of the use of energy-filtered $C_s$-adjusted imaging to examine three Pt particles at two different defocus values. The lattice fringe contrast of the smaller particle, which is 2 nm in size, is high given that it is supported on carbon. Two of the particles are oriented close to the [1 10] zone axis.

![Figure 1. Energy-filtered HRTEM images of Pt nanoparticles, acquired at 200kV at two different defocus values, with $C_s$ adjusted to $-30 \mu$m.](image)

3. $C_s$ correction with exit-wavefunction restoration

TF-EWR, 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. The relative benefits of using aberration correction and focal series restoration remain to be assessed for different specimens.

Figure 2 shows a defocus series of energy-filtered images of a platinum nanoparticle oriented close to [1 10] acquired at 200kV using a 5 nm defocus step size. The images show high transparency through the particle to the carbon support.

![Figure 2. Defocus series of energy-filtered images of a platinum nanoparticle oriented close to [1 10] acquired at 200kV using a 5 nm defocus step size.](image)
Figure 2. Defocus series of images of a Pt particle, imaged at 200kV with $C_s$ adjusted to -30 µm. The defocus step size between successive images is 5 nm.

Figure 3a shows an HRTEM image of the Pt particle shown in figure 2, acquired with $C_s$ adjusted to -30 µm. Figure 3b shows a restored phase image of the same particle, calculated from a defocus series of 20 images acquired with a defocus step of 5 nm.

Figure 3. (a) HRTEM image of the Pt particle shown in figure 2, at an optimum defocus and with $C_s$ adjusted to –30 µm. (b) The same particle after applying TF-EWR. Below the images are power spectra.
The improvement in the information in the image is clear. The contrast from the carbon support film, which is at a different height to the particle, has been largely eliminated after TF-EWR, and the graphitic planes and carbon atoms close to the particle are now visible. Details of the surface atomic arrangement on the particle are also clear. Power spectra are displayed below each image. For the reconstructed image, higher spatial frequencies are present, and the contribution to the power spectrum from the amorphous carbon has decreased. Close to the edge of the particle, the phase image is expected to be proportional to the projected potential of each atomic column. However, preliminary multislice simulations (not shown here) suggest that the phase shift is in fact highly sensitive to the defocus of each atomic column, and hence the exact three-dimensional shape of the particle (the phase shift is recovered to a single defocus value using TF-EWR, and is sensitive to the defocus value chosen for the reconstruction). This effect, which may preclude quantification of the peak heights in the restored phase image, will be discussed in detail elsewhere.

Figure 4 shows a similar comparison. The improvement after reconstruction is again clear. The artefacts from the background are reduced, the surface atomic arrangement becomes clearer, and the graphitic planes and individual carbon atoms in the matrix are better defined in the post-processed image.

Figure 4. (a) Image of Pt particle acquired at 200kV at optimum defocus with $C_s$ adjusted to $-4 \, \mu m$. (b) restored phase image of the same particle obtained by applying TF-EWR to a defocus series of 20 images acquired at 200kV with $C_s$ adjusted to $-4 \, \mu m$.

4. Conclusions

It has been shown that $C_s$-correction gives rise to an improvement in the spatial resolution and visibility of Pt nanoparticles that are a few nanometers in size. After focal series restoration, 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. Future studies will involve the application of $C_s$ correction, focal series restoration and high-angle annular dark field tomography to the same particle, in order to characterise its three-dimensional atomic arrangement and shape fully, as well as its interaction with the carbon support.

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