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Imaging Active Sites on Platinum Catalytic Nanoparticles Using Aberration-Corrected Electron Microscope

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The active components of industrial heterogeneous catalysts are often small metallic particles, whose reactivity and selectivity depend on the presence of steps and kinks on their surfaces [1]. The roles of different active sites on the extended surfaces of model catalysts can be identified using techniques such as scanning probe microscopy [2]. However, little is known about atomic arrangements on the surfaces of commercial catalyst nanoparticles, as highlighted by a recent study of ammonia synthesis in Ru-catalysed reactions [3].

High-resolution electron microscopy is a powerful technique to study the size and shape distributions of nanoparticles. However, such images suffer from aberrations introduced by the objective lens, and these images are generally not directly interpretable. Recent successful development of the aberration corrected microscopes [4] has greatly reduced the spherical aberration and hence reduced the delocalisation. The phase (of the specimen exit plane wavefunction) restored [5] from a series of differently aberrated images gives aberration free, complex specimen exit wave function. Here, the phase restoration from a focal series combined with aberration-corrected transmission electron microscopy is used to provide atomic resolution information about the local topologies of active sites on commercial nanoparticles.

We examined a powder of Pt nanoparticles on carbon black, which had been heated to 900 ºC in a N_2-rich atmosphere. These particles are used to both electro-oxidize H_2 and electroreduce O_2 at the anode and cathode, respectively, of a polymer electrolyte membrane fuel cell. Fig. 1a shows one member of the focal series images, and Fig. 1b shows the phase of the specimen exit plane wavefunction of a representative Pt nanoparticle, restored from a focal series of aberration-corrected images acquired using a JEM-2200FS TEM, viewed close to a <110> direction. Islands and steps on the surface of the nanoparticle are clearly visible in the restored phase shown in Fig 1b, with a sensitivity and spatial resolution that are improved greatly over that in a conventional high-resolution TEM image, as shown in Fig 1a. The monatomic steps that are visible are conventionally termed A- or B- type, with either {100} or {111} microfacet risers that have different catalytic properties. Fig. 1c shows the phase of the specimen exit plane wavefunction, simulated using Multislice method, from the model which is best fitted with the experimental restored phase shown in Fig.1b.

An important factor affecting the catalytic stability of nanoparticle clusters is the strength of their anchorage to their support. The restored phase also clearly shows the partially graphitized carbon surround the nanoparticles. The catalyst particles examined here were highly stable under the electron beam, indicating that they are anchored strongly to their carbon support, which is graphitized locally in the vicinity of each particle. The high density of kinks that we observe on (111) facets may provide an explanation for the strong anchoring of the particles to their support [6].

References

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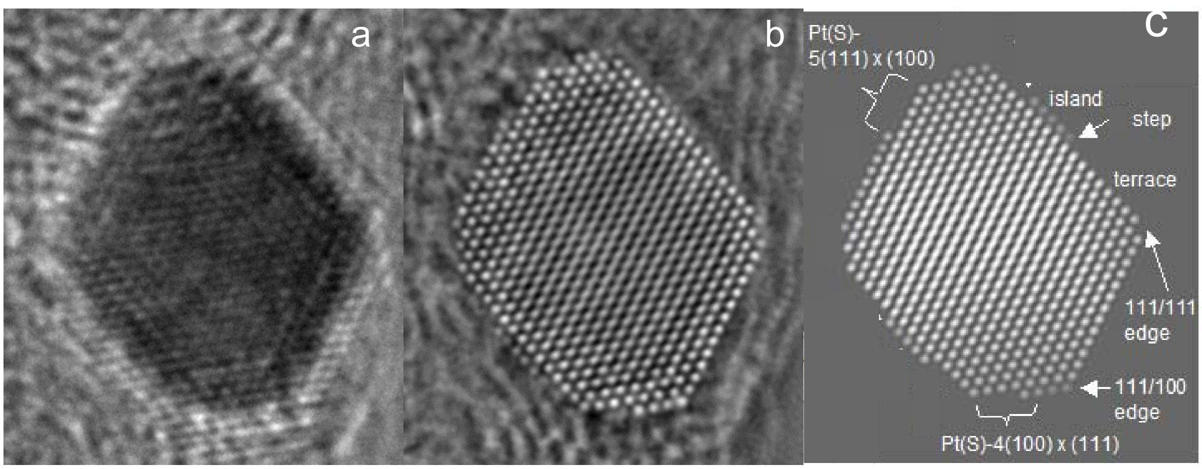

FIG. 1. (a) High-resolution image of a platinum particle supported on carbon in the [110] zone-axis. (b) Restored phase of exit plane wavefunction from a focal series of 20 images acquired at 200kV with C_s adjusted to – 4 μm. Islands and steps on the surface of the nanoparticles are clearly resolved. (c) Phase of exit plane wavefunction simulated using multislice method, from the model which is best fitted with the experimental restored phase shown in (b).