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Nanohalos: A manifestation of electron channelling in gold nanoparticles

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ABSTRACT

We discuss interesting haloing effects observed in experimental images of gold nanoparticles obtained using aberration-corrected scanning transmission electron microscopy (STEM) employing the low-angle annular dark-field (LAADF) imaging mode. The LAADF images contained bright rings of intensity (halos) with a diameter equal to or smaller than the diameter of the nanoparticle, the diameter varying as a function of the defocus of the STEM probe. Numerical simulations reveal that the halos are only present if the nanoparticles are imaged down a zone axis. Since the halos were observed in nearly all experimental images, this suggests that the nanoparticles become oriented along crystal zone axes during imaging.

1. Introduction

Scanning transmission electron microscopy (STEM) has been extensively used to image materials at atomic resolution, and in particular nanoparticles. The most widely used variant of STEM, Z-contrast imaging, is based on detecting electrons scattered to high angles after inelastic scattering during which a phonon is excited, a process also referred to as thermal diffuse scattering (TDS). Electron energy-loss spectroscopy (EELS) imaging has also been extensively developed [1]. Imaging using a low-angle annular dark-field (LAADF) detector is another possible mode of imaging which can potentially be used to detect buried layers [2].

The experimental geometry for STEM LAADF imaging is illustrated in Fig. 1(a). The LAADF imaging geometry employs a convergent electron probe with an annular detector in the diffraction plane whose inner aperture angle is only marginally greater than the probe forming aperture angle and hence is just outside the bright-field cone, similar to the proposal of Cowley and co-workers [3,4]. Electrons which have been scattered by the specimen, both elastically and inelastically (the latter mainly due to TDS) are then detected. It has recently been pointed out that this leads to enhancements in signal when the probe is on a column for probe defocus values Δf in the vicinity of interfaces, a phenomenon which is due to enhanced elastic scattering, TDS or a combination of both [2].

We have recently used the LAADF mode to image gold nanoparticles in the cytoplasm of a biological cell. The images were taken on the 200 kV Oxford-JEOL 2200MCO with third order spherical aberration correctors. Using a probe forming semi-angle of 24 mrad and with an annular detector aperture spanning a range of approximately 24–50 mrad, the images showed interesting bright rings (halos) of intensity when the probe was focussed away from the particles, as can be seen in Fig. 1(b). This is most evident in the topmost particle, where the periphery of the particle is clearly brighter than the centre. These halos disappear if the detector annulus is moved further away from the bright field cone, in other words for the medium angle annular dark-field (MAADF) imaging case (detector semi-angles approximately 30–64 mrad), as can be seen in Fig. 1(c). That image is qualitatively similar to that obtained by Z-contrast or high-angle annular dark-field (HAADF) imaging. Here we will explore the origin of the halos seen in the LAADF geometry and we show that they are essentially an electron channelling phenomenon. Furthermore, since the halos were observed in nearly all experimental images, this suggests that the nanoparticles become oriented along crystal zone axes during imaging.

2. Experiment and interpretation

To explore the occurrence of the halos shown in Fig. 1(b) we have obtained a focal series of STEM LAADF images using similar gold nanoparticles but now on the surface of an amorphous carbon film rather than in the cell. This provides a more controlled environment in which to explore this phenomenon since a given defocus of the STEM probe will be similar for all the particles being examined. The probe forming aperture was 19.5 mrad and the detector range was 21–34.7 mrad. Once again,

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halos were seen for almost all the particles with the size of the halo depending on the amount of defocus. The halo emerges from the centre of the image for large defocus (either under or over focus) values and becomes larger in diameter as the in focus condition is approached, eventually coinciding with the boundary of the particle profile at this focal position. The halo is less evident with the probe focussed within the particle. Halos on a number of nanoparticles can be seen in Fig. 2(a) and the corresponding (atomic resolution) images with the probe focussed near the top surfaces of the nanoparticles are shown in Fig. 2(b). Examination of Fig. 2(b) reveals that most of the nanoparticles are twinned, some exhibiting faceting. Recently Xu et al. [5] studied particles of similar size and shape to those discussed in this paper, which have diameters in the range of 10–20 nm. Such nanoparticles may exhibit a range of structures: decahedral, Ino decahedral, Marks' decahedral, truncated octahedral, and variations thereof [6,7]. High mobility of surface atoms, enhanced by energy from the focused electron probe, serves to round these particles, resulting in essentially two types of spheroidal particles; an fcc monocrystalline particle and a polycrystalline particle with typically five strained fcc segments joined at twinning planes. In particular, Xu et al. [5] studied the crystal structure of Marks'-decahedral gold nanoparticles of 20 nm mean diameter and found that the central axis lay along the [110] zone axis, consistent with our own observations.

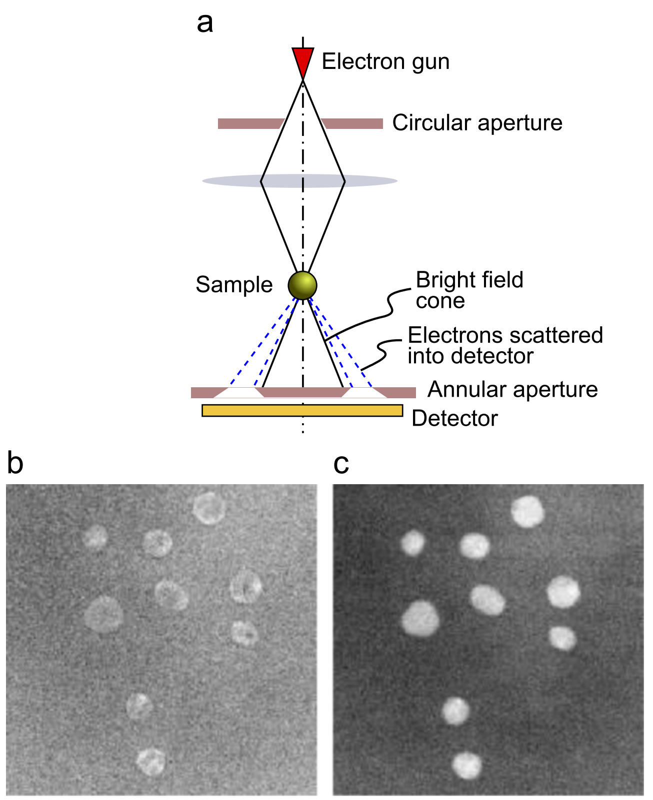

Fig. 1. (a) The LAADF geometry. (b) LAADF STEM image of gold nanoparticles within a biological cell showing the presence of bright rings (halos). (c) MAADF STEM images of the same nanoparticles.

However, some of the nanoparticles were observed to be monocrystalline and in Fig. 3(a)–(e) we show more detailed LAADF images of such a nanoparticle taken at the defocus values indicated. Defocus is defined relative to the centre of the nanoparticle with positive values corresponding to overfocus and negative values to underfocus. This case provides a good starting point for our modelling of the halo effect. We will return to multiply twinned nanoparticles later. The "in focus" image of the nanoparticle in Fig. 3(c) suggests that it is appropriate to approximate it by the spherically truncated monocrystalline structure shown in Fig. 4(a). We have carried out simulations which demonstrate that these halos rely on an electron channelling effect and, as we will show later, disappear if the particle is orientated away from a zone axis. Therefore the presence of the halos implies that the gold nanoparticles are oriented along a zone axis with respect to the beam during imaging. We consider propagation of the probe wave function through the specimen using the multislice absorptive model [8]. In this context the absorptive model gives results similar to the many-body quantum-mechanical model of [9] based on a Born–Oppenheimer approximation and which, in turn, yields numerically equivalent results to the well-known semi-classical frozen phonon (FPh) model [10,11].

The simulations in Fig. 3(f)–(j) show the same features as seen in the experimental data. The simulations were done assuming a diameter for the nanoparticle of 13.4 nm. The characteristic halos are particularly clear when line scans are extracted by averaging over a horizontal strip of pixels approximately 1.5 nm wide and symmetrically placed with respect to the centre of the particle, as shown in Fig. 3(k)–(o). We will now discuss the existence of halos and their size as a function of defocus. Our arguments will be based on Fig. 5, which schematically shows the STEM probe relative to the particle for a range of defocus values. Inspection of this figure shows that as the defocus of the probe varies across

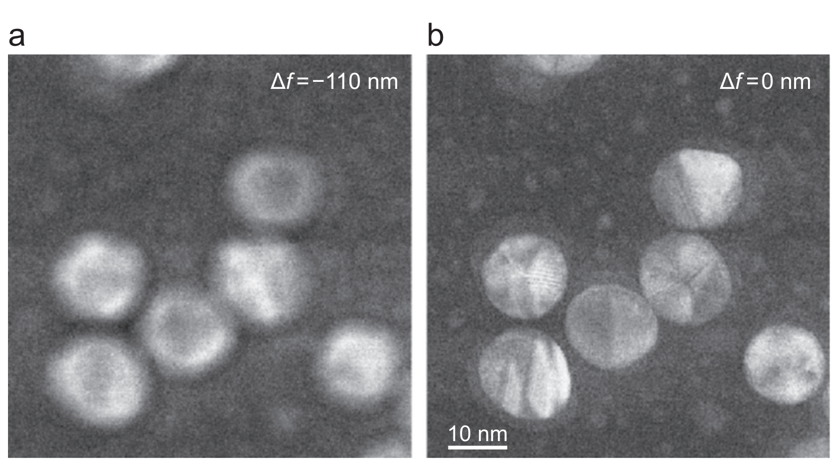

Fig. 2. LAADF STEM images of polycrystalline gold nanoparticles on an amorphous carbon film. (a) Images at an underfocus $\Delta f = -110$ nm showing the presence of halos. (b) In focus images of the same particles ($\Delta f \approx 0$ nm) show atomic columns and structure due to internal twinning planes is discernible.