Imaging single atoms and atomic clusters in complex media by aberration corrected STEM

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Aberration correction has enabled the routine imaging of single atoms both in conventional TEM and in STEM mode though each mode is suited to different sample geometries and compositions. Indeed, in STEM mode, the imaging of single gold atoms has become a part of most acceptance tests for aberration corrected electron microscopes. Here we explore the imaging of single heavy atoms and small clusters in STEM in a variety of environments from the relatively beam insensitive to the relatively beam sensitive. Pushing the technique towards more beam sensitive samples is essential to include an ever growing variety of samples and hence scientific problems. In particular there is pre-existing widely used technology for attaching gold nano-particles as markers to specific proteins in biological tissue.

A humble but key problem that needs to be addressed for all samples but particularly for samples containing soft materials and samples that have a wet chemical processing route is that of the build-up of amorphous carbon contamination under the electron beam during analysis. For us this has been the cause of more lost beam time than any other problem. Our experience has been that it can be overcome by pre-baking the sample and holder at about 400K for a few hours. Unfortunately this is often not possible without significantly altering the sample; in which case, scrupulous cleanliness and careful purification of the sample has proved effective. As a last resort pre-irradiating the sample with a broad electron beam can buy short periods of contamination free analysis.

The first images of single atoms in the STEM were obtained by Crewe *et al.* in 1970[1]. However, the atoms needed to be separated as the probe size was at the 500picometre rather than 100picometer scale. Subsequently single heavy dopant atoms in silicon were imaged by Voyles *et al*.[2] but Batson *et al*. [3] were the first to image gold atoms with a dedicated STEM aberration corrector with 0.1nm resolution. This ability is now being applied to materials problems such as whether the optoelectronic performance of silicon nano-wires is impaired by single gold atom dopants [4], where platinum group metal atoms are in catalysts and the position of the included ions in endofullerene nano-peapod structures. What has become clear is that we need to work at accelerating voltages of 80kV or less for many of these systems and so resolution at 80kV and 60kV becomes the relevant specification of the instrument.

The imaging of nano-clusters raises its own set of specific problems. An important justification for the need for imaging and for extracting the maximum information from an individual particle is that generally in the physical sciences, nanoparticles are not identical replicates for which the average properties of an ensemble of particles are essentially representative of the individual particles. This also means that image averaging techniques such as single particle analysis as used by biological microscopists to reconstruct nanometre sized bio-molecules are of limited value (see [5] for one counter example of the application

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of single particle analysis to non-identical particles). The ultimate goal remains to image at atomic resolution a single nano-particle at atomic resolution.

Two specific examples of the imaging of nano-clusters together with soft media will be presented. The first shows, in Figure 1, the ability of chemists to dock a gold nano-particle into a metal ion containing enzyme[6]. The second example is of gold nano-clusters associated with an agarose gel[7].

The combination of single atom sensitivity together with careful control of the sample and choice of accelerating voltage is allowing an ever wider range of materials problems to be addressed by direct imaging at the 0.1nm scale.

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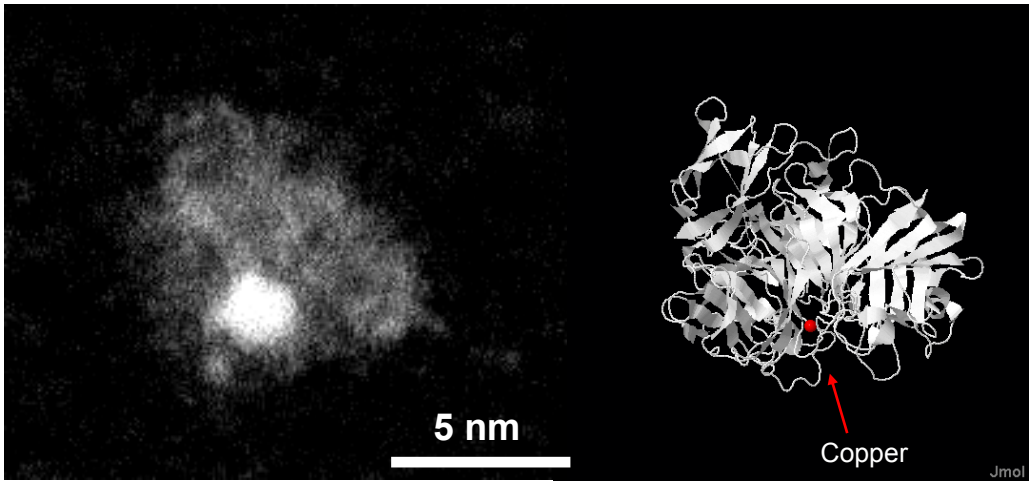

Figure 1. A thioctic acid-protected gold nanoparticle docked in the metalloenzyme GOase (D-galactose: oxygen-6-oxidoreductase, EC 1.1.3.9, 68 kDa). The STEM HAADF image is on the left and an inferred projection of the published structure of the enzyme (without the gold) is on the right (from [6]).

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