**Mapping Copper on the Surface of Gold Nanocubes**

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The important properties of novel nanoparticles are directly related to their shape, size and composition, providing a parameter set that can be tuned to optimise properties for given applications. Despite advances in wet chemistry methods enabling the synthesis of nanoparticles with various shapes and sizes, the underlying growth mechanisms are still the subject of intense debate. Recent studies have indicated that metallic additives, such as $Ag^{+}$ and $Cu^{2+}$, play important roles in inducing anisotropic growth and affording control over shape, which is essential for controlling the exciting optical properties of metallic nanoparticles [1][2]. However, a critical question remains, - where is the metallic additive? Does it reside on or within the nanoparticle and, if so, where?

Efforts to address this question with conventional methods, such as quantitative scanning transmission electron microscopy (QSTEM) and energy dispersive x-ray (EDX) spectroscopy, can be limited, due to a lack of sensitivity, poor *information* (as opposed to image) resolution due to electron scattering onto adjacent atomic columns [3] and/or beam damage. Here we consider the important case of the role of copper in the growth of gold nanocubes. We develop and apply scanning convergent beam electron diffraction (SCBED) to investigate the distribution of copper in gold nanocubes and compare this to conventional QSTEM and EDX measurements.

QSTEM results suggest the presence of copper and copper alloys at the nanocube surface (Fig 1) but the results are equivocal due to the complex interplay between the parameters of composition, imperfection in shape and electron scattering effects at the surface. EDX mapping reveals the presence of copper on surface facets, with a slightly higher concentration on the {111} facets when compared with {100} facets, however, a high electron dose, with concomitant beam damage, is required to achieve good statistics. We therefore investigated a scanning CBED technique to enhance the sensitivity to copper location at and near the surface. In scanning CBED, a convergent probe is scanned across the particle and the corresponding CBED pattern is collected at each electron beam position using an ultra-fast camera (in this case, both CETA and EMPAD cameras were used in an aberration-corrected Titan$^3$ 80-300 FEG-TEM) [4]. CBED simulations (figure 2 below) show that it is possible to determine the presence and sequence of copper by looking at the relative intensity between and within specific diffraction discs in each CBED pattern. We will demonstrate this approach and compare it with conventional methods.

References:

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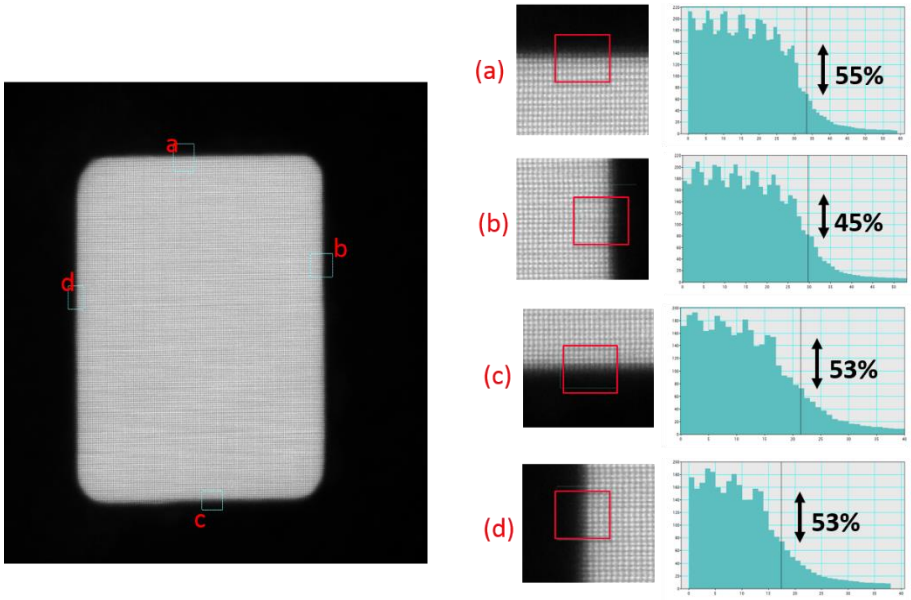


Figure 1: An ADF-STEM image of a gold nanocube. A quantitative analysis of the contrast at the surface is suggestive of the presence of copper but not conclusive.

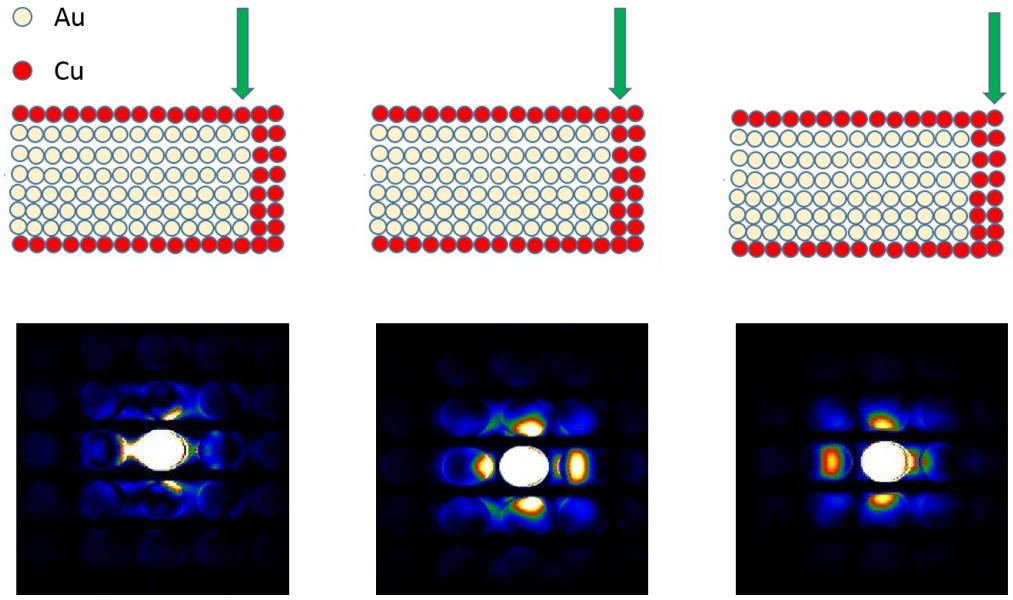


Figure 2: A specific example of the sensitivity of scanning CBED to Cu on the surface of a Au nanocube. The CBED pattern arising from a focussed electron probe positioned at different locations on the specimen surface. The relative intensity between and within certain locations on the pattern can uniquely identify the presence and sequence of copper on and near the surface.