

Novel Synthesis and Multi-technique Characterisation of Au-Cu Nanoparticles

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Heterogenous catalysis are a critically important feature in many vital applications, including chemical reforming [1] and plastics fabrication [2]. In all applications, a common theme is the use of nanoparticles, and increasingly efforts are being turned to achieving tight control of the shape, composition and internal structure of such particles. This is the key to achieving significant gains in performance, as the catalyst function strongly correlates to such nano-scale features.

To produce novel catalytic materials thus requires both advanced methodologies, as well as the ability to examine the chemical and spatial structure with near atomic-scale resolution. For the latter, a number of previous studies have demonstrated the potential of Atom Probe Tomography (APT) to understand the detailed structure of nanoparticles. While these have significantly advanced this field, particularly when APT data is combined with catalytic testing results to understand the origins of improved performance [3], there are a number of issues limiting the impact of APT on catalytic nanoparticle research. These include producing suitable samples from nanoparticle powders, reconstruction accuracy, and ensuring representative sampling.

In this work, we use Inert Gas Condensation (IGC) to produce model nanoparticles with tightly controlled sizes and composition. A prior study has confirmed the validity of this method for producing pure Ag-particles [4], while in the current study we explore how preparation of binary alloys (Au-Cu and Au-Ni) can be carried out and examined using a combined approach of TEM, AFM, XPS and APT.

Substrates for TEM (holey carbon film coated grids), AFM/XPS (Si wafers) and APT (Si flat-top lift-out coupons) were introduced within a Mantis Deposition NanoGen TRIO instrument, which produces nanoparticles by magnetron sputtering metallic targets under ionized Ar gas. The resulting mixed ion gas was mass filtered before being condensed into particles through a flight tube/pressure drop and deposited onto the substrate materials. For APT samples, a magnetron coating of Ag was applied to the coupon to encapsulate both Si post and nanoparticles, before final samples were shaped by Focused Ion Beam (FIB), using a Zeiss NVision to produce needle-shaped tips with an apex diameter <40nm.

Fig. 1 shows TEM analysis of the Au-Cu system. A bimodal distribution is seen with peaks centered at 3 nm and 8 nm. The bright field images confirm uniform and reproducible sub-monolayer coverage of nanoparticles, matching the intended deposition density. Furthermore, the nearest neighbour distance ranges from ~10 to 40 nm, which is importantly within the range of the field of view of APT analyses. For the internal chemistry of the Au-Cu nanoparticles, HAADF image and EDX maps of Cu and Au (Fig. 2a)) confirm both elements and that in all 3 particles the Au and Cu are quite uniformly distributed

with no indication of local segregation. For the APT, Fig. 2b) shows a representative capture of a single Au-Cu nanoparticle within the analysis volume, and looking at this in closer detail, Fig. 2c), reveals subtle microstructural variations with non-uniform Au-Cu distributions. The combined analyses indicate tightly controlled binary nanoparticles can be prepared using IGC, and that there are further possible gains in refining their nanoscale structure to optimize catalytic performance. A full discussion of the synthesis and characterization of these and other model nanoparticles will be presented, highlighting the potential to nanoengineer catalytic nanoparticles for a wide range of applications.

References:

- [1] D Kim et al., Nat. Commun. **5** (2014), p. 1.
 [2] GJ Hutchings, J. Catal. **295** (1985), p. 292.
 [3] K Tedsree et al., Nat. Nanotechnol. **6** (2011), p. 302.
 [4] Q Yang et al., Catal. Struct. React. **1** (2015), p. 125.

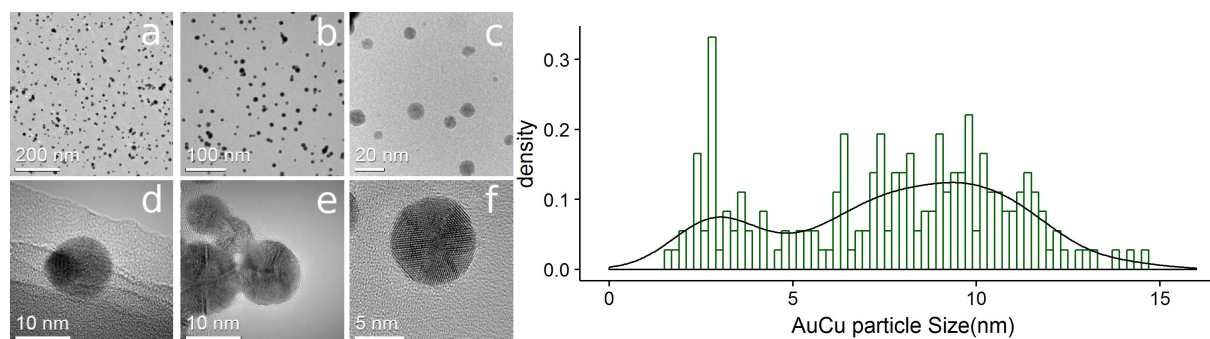


Figure 1. Bright Field images of Au-Cu nanoparticles, and size distribution measured from images

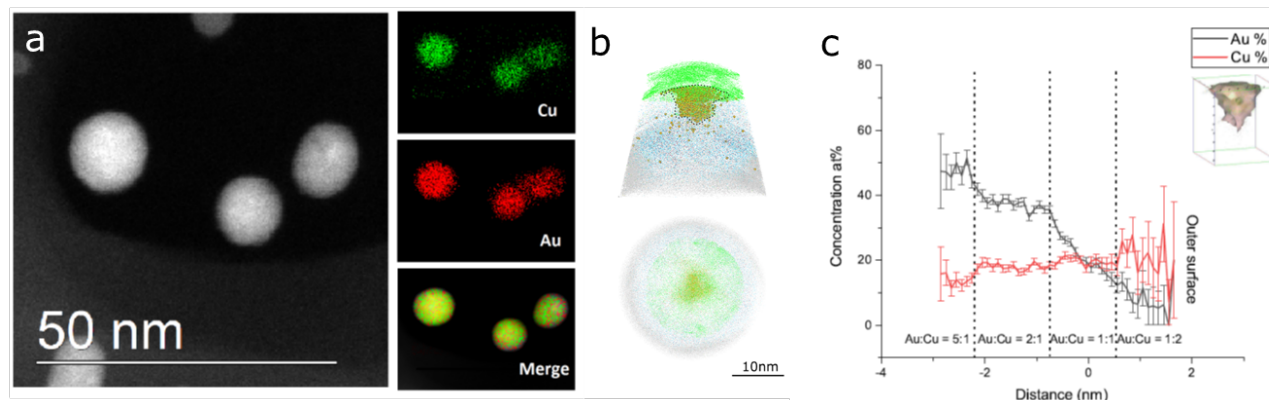


Figure 2. a) HAADF image/EDX maps of Au-Cu nanoparticles. b) APT map of single particle. c) Proximity histogram through isolated particle (shown inset), confirming Au-rich core and Cu-rich shell