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IT-6-O-1684 in situ Nanoscale Hyperspectral XEDS Elemental Mapping in Liquids

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Recent years have seen an explosion of interest in *in situ* (scanning) transmission electron microscope (S/TEM) studies of solution-phase processes. Work employing silicon nitride windowed environmental cells (e-cells) to study nanostructures in liquid has yielded important insights into mechanisms of nanoparticle growth.[1,2] One of the great strengths of the S/TEM platform is the potential to combine high resolution imaging with local analytical information obtained using electron energy loss spectroscopy (EELS) and X-ray energy dispersive spectroscopy (XEDS). However, both EELS and XEDS face challenges when applied to specimens in liquid e-cells and elemental mapping has proved impossible until now.[3,4] In this work we show that by rational redesign of an e-cell holder we are able to dramatically increase the collection efficiency of characteristic X-rays,[5] in order to achieve elemental mapping of nanostructures in liquid. Improved X-ray detection is obtained using an analytical XEDS version of the Protochips Poseidon 200 holder in a FEI Titan ChemiSTEM operated at 200 kV. Wet specimens were encapsulated between a pair of 50 nm thick SiN_x windows in a Si e-cell with 150 nm spacers separating the windows.

As a proof of principle we have studied a sample consisting of a mixture of pre-synthesised nanostructures immersed in a Cu containing aqueous solution. Beam-induced interactions with the solution result in dynamic Cu nanoparticle growth processes (Fig. 1).[2] Simultaneous XEDS spectrum imaging of nanostructures in liquid facilitates interpretation of the dynamic processes occurring in this complex multicomponent system (Fig. 2). A beam-induced copper plating reaction occurs in the liquid-phase, (fig 2a and 2b) while similar growth is not seen in dry reference samples. The resulting spectrum image (Fig. 2c) reveals that Cu ions from the surrounding liquid are plating the pre-synthesised silver nanowires and gold nanoparticles producing bimetallic, core-shell, structures.

We have shown that it is possible to use XEDS to simultaneously map multiple elements in liquid with a spatial resolution approaching 10 nm. This new technique allows direct observation of nanoscale changes in composition and elemental distribution during solution-phase processes and has great potential in the field of nanoscience, to provide insights to aid the synthesis of mixed metallic nanostructures, as well for corrosion and biological studies.

1. Zheng H et al 2009 *Science* **324** 1309-1312.
2. Liao H et al 2013 *Chem. Commun.* **49** 11720-11727.
3. Jungjohann K L et al 2012 *Microsc. Microanal.* **18** 621-627
4. Holtz M E et al 2013 *Microsc. Microanal.* **19** 1027-1035
5. Zaluzec N J et al 2014 *Microsc. Microanal*. (in press) **20**

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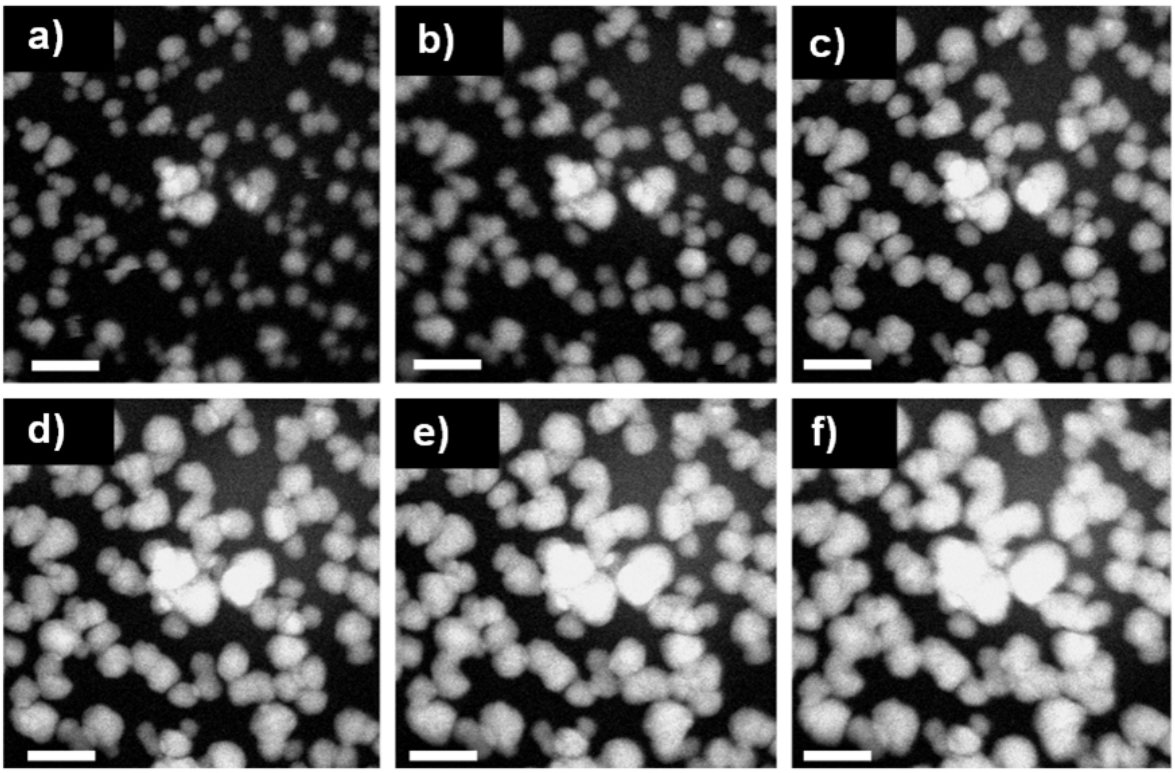

Fig. 1: Selected HAADF STEM images from a video sequence showing the beam-induced growth of Cu nanoparticles from an aqueous solution containing Cu ions. Images taken at time = 0s (a), 6.3s (b), 13.1s (c), 19.9s (d), 26.2s (e), and 31.4s (f). Scale bar = 80 nm.

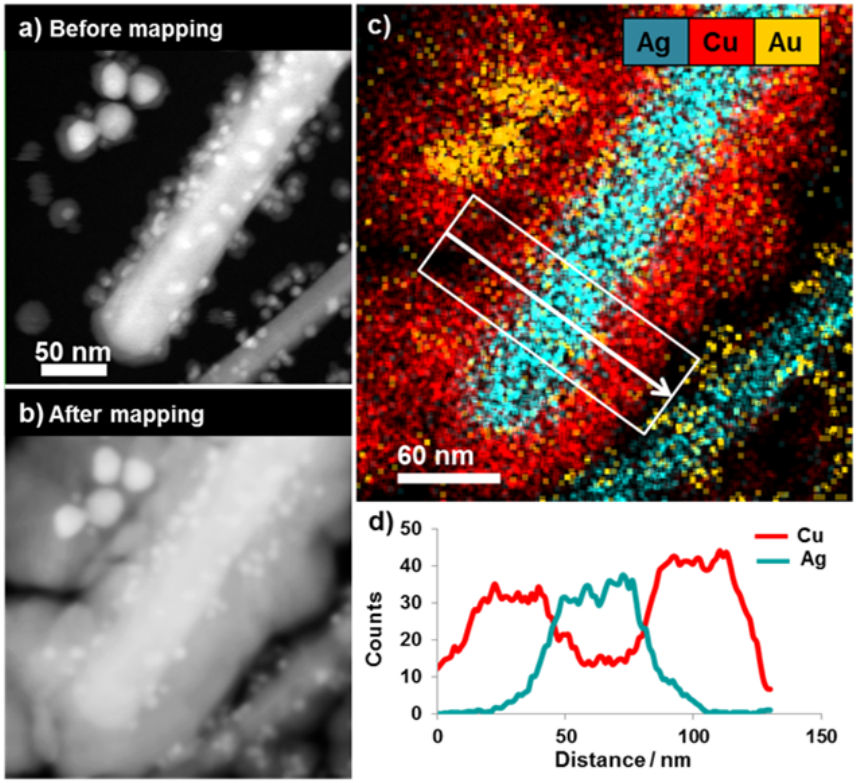

Fig. 2: Beam-induced growth of Cu nanostructures occurs during extended spectrum imaging, as observed by comparison of the HAADF images before and after (a and b). XEDS data facilitates simultaneous mapping of multiple elements in liquid (c) with a spatial resolution of the order of 10 nm.