Nanoscale liquid phase in situ observations of structural transformations of Au and Au-Cu nanostructures

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Metallic nanocrystal synthesis has been a focus of intense research activities in the past few years. This interest is mostly fuelled by the fascinating properties delivered at such size domains. Existing strategies usually employ liquid phase synthesis to formulate unique nanocrystal shapes. The underlying chemical reactions for such kind of syntheses are fairly simple however developing an understanding of the complex nucleation and growth mechanisms is altogether a different challenge. In this context liquid cell transmission electron microscopy (LCTEM) has emerged as a fairly powerful tool to visualize the relevant growth phenomenon at the nanoscale. Moreover radiolytic syntheses driven by the electron beam provides an ideal platform to finely tune the growth mode by means of applied electron dose rate.[1] We have employed LCTEM in this work to study in real time the dynamics of growth of Au and Au-Cu nanostructures.

LCTEM experiments were carried out on an aberration corrected JEOL ARM 200F microscope operating at 200KV. For liquid cell experiments we used a commercial liquid-cell holder provided by Protochips Inc. Electron dose rate measurements were diligently carried out in order to account for the effects of electron beam on growth dynamics.

Seed-mediated synthesis of symmetric Au nanostars (NSs) in methanol was followed by LCTEM in STEM mode (Fig. 1, 2).[2] We take advantage of high spatial and temporal resolution offered by LCTEM in order to unravel the key effects of growth speed, seed crystal morphology and dimethylamine functionalization on the formation mechanism, shape and stability of NSs enclosed by high-index facets. By establishing the relationship between the symmetry of grown NSs having 20 arms with the initial faceting of icosahedral seed crystals (Fig. 1), these *in situ* investigations clearly reveal the true potential of LCTEM for studying complex synthesis protocols involving seed and functionalization mediated strategies.

Beam induced phenomena were also utilized to understand the solution chemistry of the exposed solvent which is in turn responsible for driving reversible redox reactions in bimetallic nano-systems.[3] By studying the formation of Au@Cu core-shell nanostructures in methanol, it was revealed that depending upon the applied electron dose rate reversible cycles of growth/etching of Cu takes place on top of Au nanoparticles (Fig. 3). This observation highlights the ability of the electron beam to switch the oxidizing or reducing nature of the liquid solvent. At high electron dose rates growth of Cu was observed while at low electron dose rates dissolution of Cu takes place. In the absence of an external stimuli, the whole process is dictated by the relative concentrations of reducing and oxidizing species at particular electron dose rate. Nevertheless the role of additional factors such as complexing agents and bimetallic corrosion should be considered as well. It could be said with near certainty that LCTEM is well placed to explore exciting new avenues within the domain of nanomaterial growth, electrochemical processes and radiation physics.

[1] Zhang et al. Chem. Mater. 29, 24, 10518-10525 (2017).

[2] Ahmad et al. Nano Lett. 17, 7, 4194-4201 (2017).

[3] Ahmad et al. Journal of Microscopy. 269, 2, 127-133 (2017).

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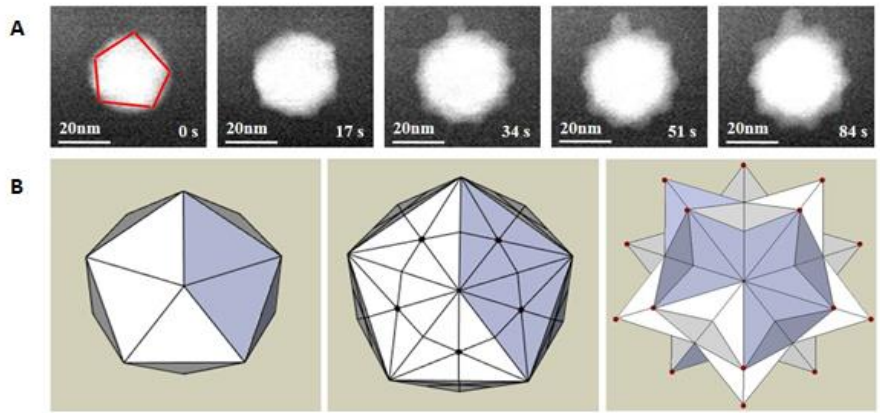

Fig 1: DMA-assisted transformation of an icosahedral seeds into a symmetric NS. **(A)** Time series of STEM-HAADF images acquired in methanol with DMA concentration of 0.06 mM and dose rate = 3.4 electrons/Å^{2}s The irradiation time of the observed area is indicated in the bottom right corner of each image **(B)** Geometric model elucidating the transformation process via the growth of hexagonal pyramids on each triangular facet of the icosahedral seed.

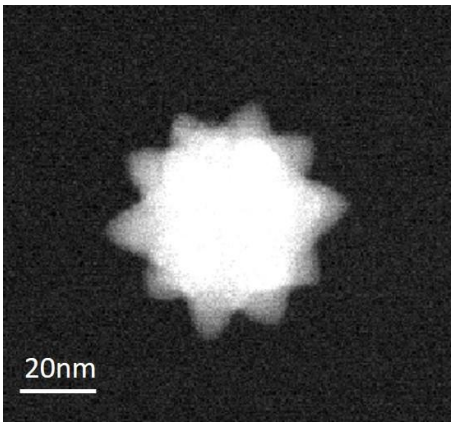

Fig 2: Fully formed Au NS with sharp symmetric arms observed at high magnification in STEM-HAADF mode.

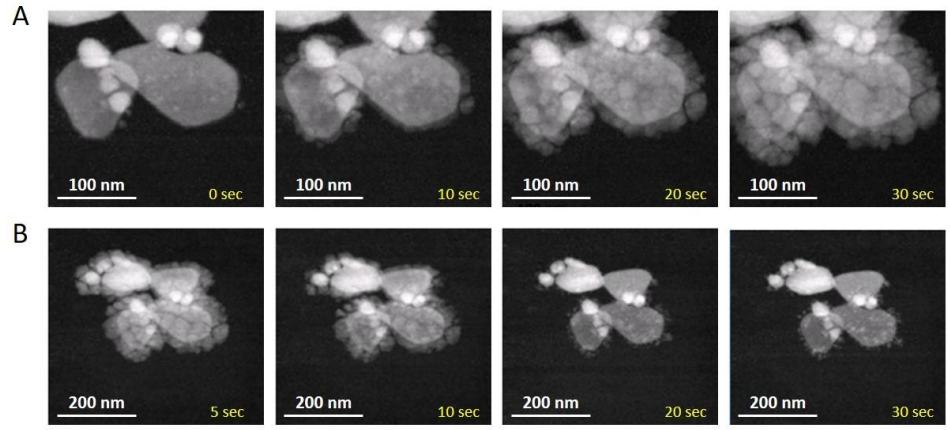

Fig 3: Cycle of deposition and dissolution of Cu nanoshell on gold nanoparticles in methanol. **(A)** Nucleation and growth of Cu nanoshells monitored by STEM HAADF with a magnification of 800 k (dose rate = 6.1 electrons/Å^{2}s). **(B)** Dissolution of Cu nanoshells monitored by STEM HAADF with a magnification of 400k (dose rate = 1.5 electrons/Å^{2}s). The irradiation time at a given magnification is indicated in the bottom right corner of each image.