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In situ Template Assisted Growth of Ag@Au Bimetallic Nanostructures

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Recent years have seen an exponential increase in the use of liquid cell transmission electron microscopy (LCTEM) to analyze dynamic phenomenon in materials sciences, life sciences and electrochemistry. The technique is proving particularly very useful from the perspective of colloidal nanoparticle synthesis. It has been extensively employed to study the nucleation and growth mechanisms of inorganic nanoparticles. The main hurdle however remains in terms of accounting for the electron beam irradiation effects as they form an inherent part of most LCTEM studies. We have utilized the electron beam to radiolytically synthesize bimetallic nanoparticles of Ag@Au. These heterogeneous nanostructures have unique plasmonic surface properties and mechanistic observations of their growth dynamics can prove to be very useful for precisely tailoring synthesis strategies of bimetallic nanocrystals through wet chemical route. [1]

Liquid cell experiments were performed in STEM mode on a probe corrected Titan microscope at an acceleration voltage of 300 kV using commercial liquid cell holder from Protochips Inc. Ag nanoplates (0.02mg/mL) washed with deionized water to remove excess PVP from solution were then deposited on small e-chip with 150 nm flow spacer. After sealing the liquid cell, the entire assembly was inserted in the microscope. Electron dose rates ranging from 0.8 electrons/$Å^2$s to 6.2 electrons/$Å^2$s were used to deposit Au on the surface of nanoplates by flowing a precursor solution of 100µM $HAuCl_4$.

At these dose rates, it was observed that Au deposits on Ag nanoplates in a kinetically controlled fashion under constant flow of Au precursor solution. Interestingly the distribution of deposited Au on Ag nanoplates varied with the applied electron dose rate. At low electron dose rates of 0.8 electrons/$Å^2$s conformal deposition of Au over Ag took place (Fig. 1a). Increasing this dose rate to 2.8 electrons/$Å^2$s resulted in accelerated deposition of Au at the corner sites leading to concave nanocrystal morphology (Fig. 1b). Furthermore these *in situ* studies shed light on the critical role of surface diffusion on the nanocrystal morphology as the atoms at the corners tend to diffuse towards the edges leading to a more rounded profile with growth time. [2, 3]

The role of flow is also critical since under static conditions, the growth behaviour abruptly changes. We demonstrate this by irradiating a pristine area containing Ag nanoplates without any flow of precursor solution. At first the nanoplates grow under similar dose conditions as used for conformal growth of Au, however once the Au precursor is depleted in the surrounding area of the nanoplates, they tend to reshape and subsequently etch away into the solution (Fig 2). While the etching of nanoparticles under beam is not a new phenomenon in itself, however the systematic reformation of new facets at the expense of old ones offers an intriguing insight into beam induced etching of nanocrystals. We believe that such *in situ* studies are critically required for understanding the complex processes at play in order to re-evaluate existing growth models for bimetallic nanocrystal synthesis. [4]

References:

[1] Sutter *et al*, Nanoscale **9** (2017), 1271.
[2] Wu *et al*, Nano Lett **15** (2015), 2711.
[3] Ahmad *et al*, Nano Lett **17 (7)** (2017), 4194.
[4] This project has received funding from ERC under EU's Horizon 2020 program (Grant No. 681312).

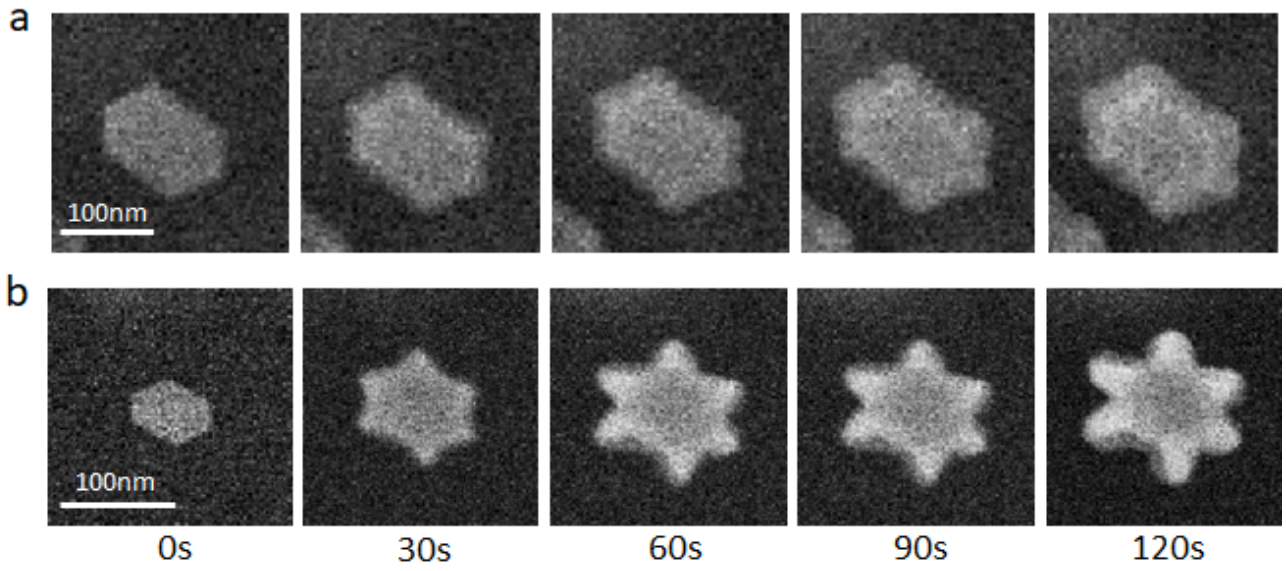

Figure 1. HAADF-STEM series of images showing deposition of Au on hexagonal Ag nanoplates. **(a)** Conformal deposition of Au equally over the edges and corners showing layer-by-layer growth at low electron dose rate of 0.8 electrons/Å^{2}s. **(b)** Star-like bimetallic nanocrystal evolution at dose rate of 2.8 electrons/Å^{2}s due to different deposition rate of Au at the corners and edges of similar hexagonal Ag nanoplate as in **(a)**.

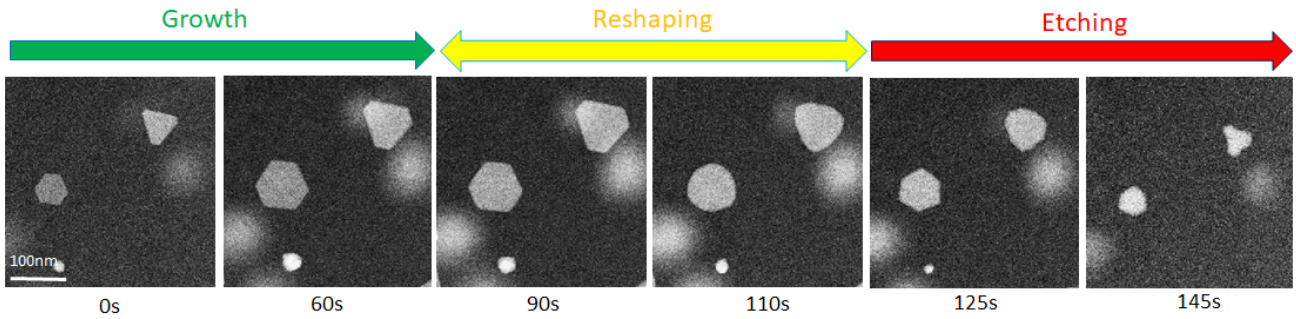

Figure 2. HAADF-STEM series of images showing the growth and subsequent etching of hexagonal and truncated triangular Ag nanoprism at 0.8 electrons/Å^{2}s. The particles reshape by growing new facets at the expense of old ones and subsequently etch away in a systematic manner in the absence of Au precursor flow.

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