

Structural Transformations of Au and Au-Cu Nanoparticles during Liquid-Phase Synthesis and Redox Reactions in Gaseous Environment

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Liquid and gas-cell transmission electron microscopy (LCTEM and GCTEM) have rapidly emerged as potent tools for understanding dynamical processes taking place at solid / liquid and solid/gas interfaces. On the one hand, imaging the growth of nanostructures in solution with the high temporal and spatial resolutions of TEM enables understanding the kinetic and thermodynamic effects that control the final morphology of nanoparticles (NPs).[1-2] On the other hand, TEM analyses at high temperature in gaseous environments allow studying nanomaterial transformations during chemical or catalytic reactions.[3-4] Here, we exploited both LCTEM and GCTEM to provide mechanistic insights into the liquid-phase synthesis of Au and AuCu NPs and their oxidation/reduction processes under O₂/H₂.

LCTEM and GCTEM experiments were carried out in an aberration-corrected JEOL ARM 200F microscope equipped with a cold-FEG by using an acceleration voltage of 200 kV and 80 kV, respectively. We used *in situ* TEM holders marketed by Protochips Inc. The electron dose-rate were carefully measured for each experiment to take into account the beam effect on the dynamical processes under study.

The growth of Au and Au-Cu NPs *via* the radiolysis of methanol was followed by LCTEM. The electron dose rate provides a straightforward control of the concentration of reducing agents (solvated electron) and consequently allows controlling the growth rate of the NPs, an essential prerequisite for controlling their shape. By revealing the transformation processes of icosahedral seeds into symmetric nanostars with 20 arms (Figure 1), we highlighted the potential of LCTEM for studying sophisticated synthesis protocol, combining both seed and functionalization-mediated strategies. We showed that the shape and long-term stability of these stellated nanocrystals arise from the initial faceting of the seeds and the concentration-dependent stabilization of high-index facets ensured by dimethylamine functionalization. By studying the synthesis of Au@Cu core-shell nanostructures, we revealed that the electron beam can be used to drive reversible deposition / dissolution cycles of copper shells over gold NPs (Figure 2). This study of nanostructure behavior as a function of the dose rate highlights the possibility to switch the oxidizing or reducing nature of liquid environment only with the electron beam. High dose rates create reducing media leading to the growth of metallic nanostructures, whereas low dose rates reinforce oxidizing media favoring metal etching. In this case, Cu dissolution is made possible by bimetallic corrosion processes that favour the dissolution of the less noble metal.[5]

The morphological transformations of Au and AuCu NPs under O₂ and H₂ were monitored by GCTEM. In line with theoretical predictions,[6] we showed that the faceting of sub-10 nm Au NPs along the [001], [111] and [110] directions depends on the temperature and the pressure of O₂ in the gas-cell. Moreover, we also revealed that the reversible behaviour of CuAu NPs during redox cycles is size-dependant since sub-10 nm NPs exhibit different facets under O₂ and H₂, while the Kirkendall effect reversibly transforms larger bimetallic NPs into hollow Au/Cu₂O NPs.

References:

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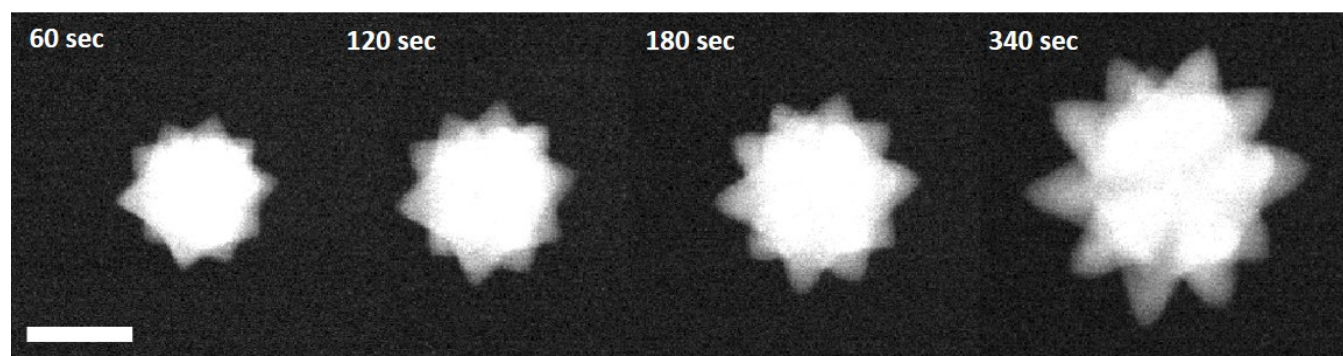


Figure 1. Growth of a Au nanostar in methanol monitored by STEM-HAADF. The transformation of an icosahedral seed into a stellated structure with 20 arms growing out from each of the triangular faces is driven by dimethylamine functionalization (we observe only 10 arms on projected images). Scale bar corresponds to 50 nm.

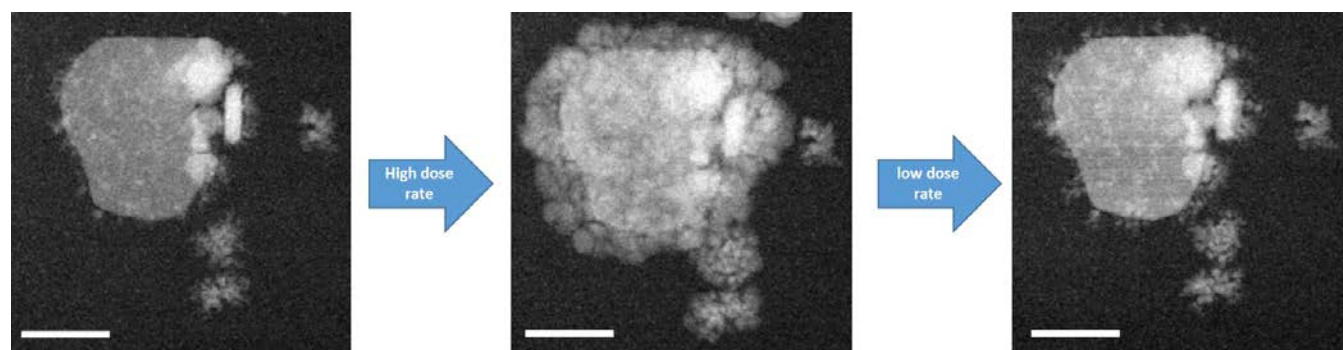


Figure 2. Cycle of deposition and dissolution of Cu nanoshell on gold nanoparticles in methanol monitored by STEM HAADF. The growth of Cu nanoshells occurs for high dose rates (≥ 6.1 electrons/ $\text{\AA}^2\text{s}$), whereas the dissolution of Cu nanoshells occurs for low dose rates (≤ 1.5 electrons/ $\text{\AA}^2\text{s}$). Scale bars correspond to 100 nm.