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Chemical Conversion of Functional Nanostructures Studied by Liquid Phase Transmission Electron Microscopy

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Metallic and metal compound nanostructures show novel electronic, optical, and catalytic properties, comparing to their bulk counterparts [1, 2], and these physical and chemical properties can be tuned by controlling the structural and composition parameters, such as size, morphology, and elemental ratio. Among different nanostructure synthesis methods, solution phase route possesses obvious advantages, including low in energy consumption and equipment costs, easy for large scale production, and most importantly, the geometrical and chemical parameters of the nanostructures can be tailored by adjusting the nucleation and growth during the solution reaction.

Hollow or porous nanostructures have low mass density and large specific surface area, which are favorable for reducing the usage of materials, increasing contact area with the surrounding reaction medium, accelerating mass and ion transportation, and accommodating local strain and stress in the working conditions [3]. Therefore, hollow and porous nanostructures show a wide range of applications in sensors, biomedicine, catalysis, and batteries. It is of significance to understand the formation process and synthesize functional nanostructures with hollow or porous morphology.

By quenching the solution reaction at a given time and characterizing the resulting samples, *ex-situ* works provide useful information about the possible formation process of the nanostructures in liquid. Nevertheless, direct evidence requires real-time observation of the morphological evolution, and preferably reactions at a single-particle level. Recently, liquid phase transmission electron microscopy (LPTEM) has been employed to study different liquid processes, such as nucleation and growth, chemical transformations of nanocrystals with subnanometer scale spatial resolution [4, 5].

In this work, we use LPTEM for real time monitoring of the chemical conversion processes of solid nanostructures into hollowed ones, including the galvanic replacement reaction between Ag nanowires and gold(III) chloride trihydrate (Figure 1), the transformation from solid Cu_2O nanoparticles to hollow Cu_2S structures in a solution of Na_2S (20 mM, Figure 2). In these LPTEM experiments, no chelating ligands were added in the liquid cell, as these may change the possible solution reaction process. Instead, continuous flow of reagent solution into the liquid cell was employed and the electron flux was carefully controlled to a level that did not significantly influence the processes. In the end, real time observation and quantitative analysis of the chemical conversion processes were achieved. The results were compared with the *ex-situ* control experiments and previous *in-situ* works [6-9]. The detailed reaction progresses are quantitatively analyzed, and compared with the existing models. The obtained LPTEM results provide new insights in the chemical conversion processes in liquid that would be difficult to achieve by other methods, but also shed light on the synthesis of a wide range of functional nanostructures with novel properties. [10]

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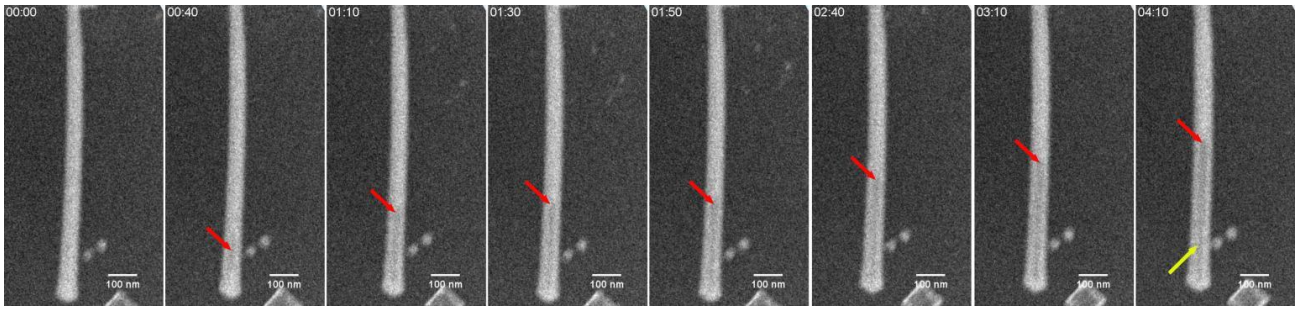

Figure 1. Timelapse series of HAADF-STEM images showing the conversion from Ag nanowire to AgAu nanotube. The red and yellow arrows indicate two different galvanic replacement reaction fronts as the Ag core is etched and a shell of an AgAu alloy is deposited.

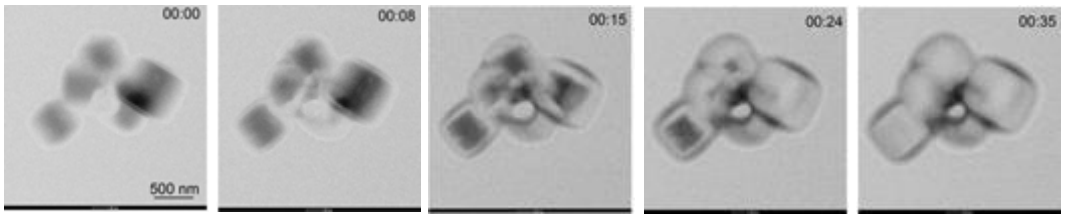

Figure 2. Timelapse series of HAADF-STEM images showing the conversion from solid Cu_2O nanoparticles to hollow Cu_2S structures in a solution of Na_2S (20 mM).

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