Application Note

Poseidon Select™

Dynamic Imaging and Elemental Analysis of Nanostructures in Liquid

Problem Statement

Wet chemical processing provides a flexible and inexpensive means to synthesize a wide variety of nanocrystal structures, but controlling and predicting the shape and size-distributions of the resulting materials remains a challenge. Limited progress toward understanding liquid-phase nanocrystal growth mechanisms has been achieved due to the difficulty of probing dynamic processes occurring within liquids.

Background

Advances in semiconductor nanofabrication have enabled the development of liquid environmental-cell specimen holders for the TEM, allowing atomic resolution imaging of nanomaterials in liquid. Using such a system, dynamic observations of nanocrystals in liquids have provided new insights into complex phenomena like nanoparticle growth and coalescence, but complementary elemental mapping of liquid phase systems was thought to be impossible. Although EELS has proved effective for measuring the thickness of liquid layers and to give insights into dynamic processes, high sensitivity EELS can only be achieved when analyzing very small volumes of material. Elemental identification from core-loss EELS peaks is challenging in this environment and spatially resolved elemental spectrum imaging is impossible. XEDS suffers from a geometrical limitation — the physical design of the typical liquid cell holder prevents characteristic X-rays, emitted from the region of interest, from reaching the XEDS detector.

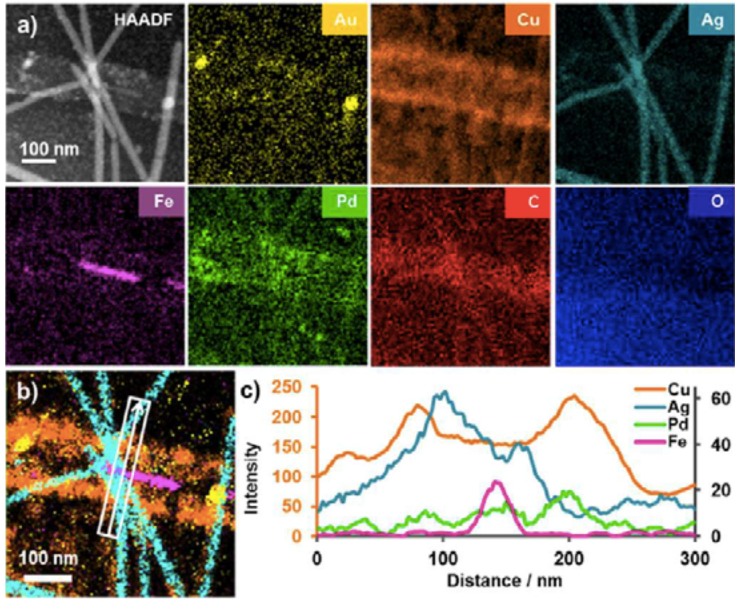

Figure 1: HAADF STEM image and XEDS hyperspectral images demonstrating simultaneous mapping of multiple elements at the nanoscale in liquid. The full range of nanostructures can be clearly differentiated. The HAADF image shown in (a) was taken before imaging, when little Cu deposition had occurred. The Cu deposition during XEDS acquisition is inhomogeneous, with elevated Cu concentration along the outer walls of the Pd-CNT as shown in the line scan (c) taken from the region indicated in (b).

Methods

Here, the holder design was modified and its performance studied with an aqueous solution containing copper ions and a mixture of engineered nanostructures to provide a chemically-rich environment. Liquid-phase spectral imaging was used to observe nanoscale Cu precipitation dynamically. *In situ* XEDS identified the precipitation of Cu-rich species upon a silver nanowire in liquid. Spectra show the presence of a large oxygen signal, verifying the presence of water, and line profiles across the Cu-coated Ag nanowire in liquid demonstrate a spatial resolution better than 15 nm. Until now, it has not been possible to identify or measure the composition of the resulting structures in solution. Here, the beam-induced growth of Cu nanoparticles was observed in the presence of other pre-synthesised nanostructures. An estimated areal growth rate of 550 nm2/s is calculated based on a sequence of scanned HAADF images, and it appears that the pre-existing nanostructures influence Cu growth. No deposition is observed for imaging of a similar dry Ag-NW, confirming that this reaction is a result of immersion in liquid containing Cu ions. The figure at right clearly demonstrates the effectiveness of elemental X-ray spectrum imaging during liquid e-cell experiments. This liquid-immersed region contains the complete compendium of structures from the nanoparticle “soup” solution: Ag-NW, Au-NP, and Pd-CNT as well as copper deposited by the action of the electron beam. All structures can be clearly identified using HAADF STEM and XEDS at high resolution

Conclusions

The first nanometer resolution elemental mapping of nanostructures in solution has been demonstrated. The compositional distribution of multiple elements was imaged during the liquid-phase synthesis of core-shell nanostructures. This technique can provide new insight into dynamic processes, such as lithiation/delithiation of battery cathodes.