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Growth of Transition Metal Oxides in Solution under Liquid Cell Electron Microscopy and Electron Beam Effects

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Liquid cell electron microscopy provides an unique platform for the study of nanomaterials growth and transformations in their working environment at the nanometer or atomic scale. Many unseen mechanisms of colloidal nanocrystal growth and self-assembly have been discovered; the electrochemical reactions including lithiation-delithiation of cathode materials and metal dendrite deposition are also visualized. Although numerous successful implements of liquid cell transmission electron microscopy (TEM) have been demonstrated, there is limited understanding of the complex chemistry between precursor, solvent and electron beam so far. Especially, the role of electron beam in the growth of nanocrystals in an organic solvent under TEM is still unclear. The study of nanocrystal growth in solution under the electron beam is not only important for the understanding of electron beam induced nanoparticle formation, but also crucial for managing the electron beam effects in the study of electrochemical processes and other chemical reactions using TEM.

We used the growth solution of 0.3 mole precursors (nickel(II) acetylacetonate and iron(III) acetylacetonate) dissolved in 1 ml of surfactant/solvent (oleylamine, oleic acid, and benzyl ether) then loaded several microliter solution in a closed liquid cell with SiN_x membranes (15nm on each side of window). The liquid cell was then sealed and loaded in JEOL in-situ 3010 LaB_6 TEM operating at 300 kV. During growth, the beam intensities were recorded at the order of 10^5 A/m^2. The movies were captured 10 fame per second using Gatan Orius 833 camera and analyzed by ImageJ software.

Under electron beam induction, directional dendritic growth is found (Figure 1). By tracing each branches, we summarized the growth kinetics in Figure 1b. In Figure 1c, the as-grown sample under high-angle annual dark field (HAADF) image shows a light contrast layer encapsulating the bright dendrite, where the contrast is attributed largely to thickness (Z number for Ni and Fe are similar). Energy dispersive X-ray spectroscopy (EDS) mapping provides us abundant information on elemental distribution. As shown in Figure 1d, the dendrite is shown as blue contour and surrounding area are green from the X-ray signal integration, suggesting more Fe can be found in surrounding. Crystal structure is identified under high-resolution TEM. It is worth noting that low dose imaging condition is employed in order to minimize the perturbation of electron beam also prevent solution drying during image. Figure 1e shows several lattice image captured during growth and the crystal structure of $Ni_{1+x}Fe_{2-x}O_4$ has been identified. The reaction mechanisms of precursor and solvent with the electron beam will be discussed in great details [1].

References:

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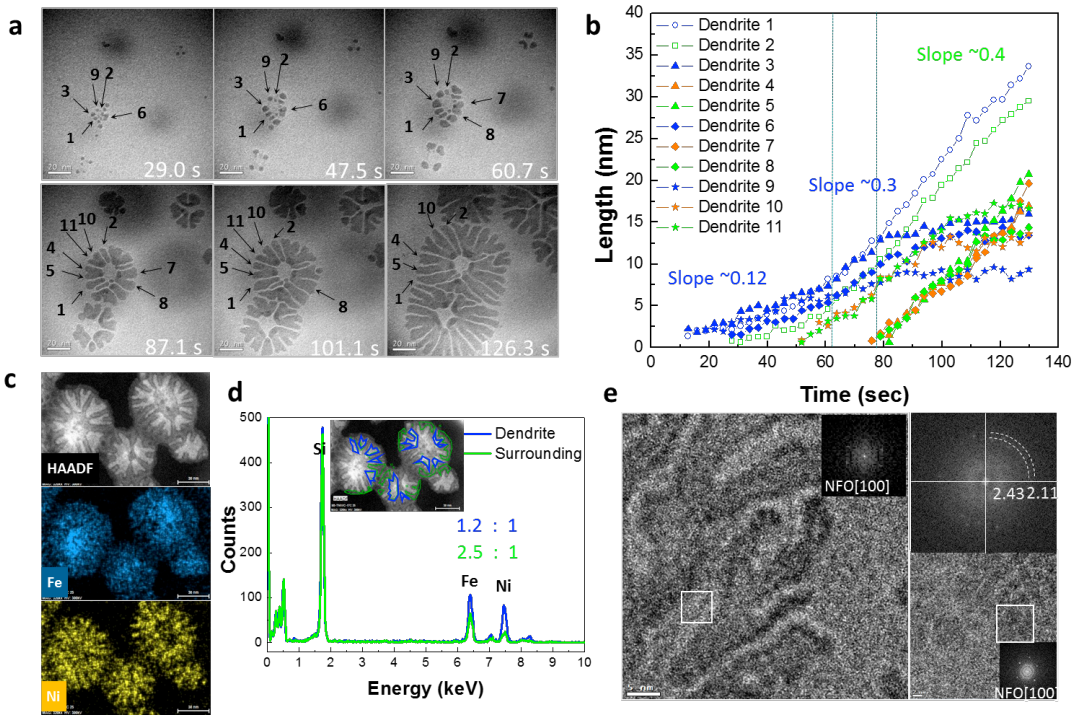

Figure 1. a: Time sequencial images of Ni-Fe-O dendritic growth in a liquid cell under TEM. Scale bars equal to 20nm. b. kinetic growth of each dendrite. c. EDS mapping, showing the elemental distribution. d. EDS spectrums acquired from dendrite (blue) and surrounding region (green). e. High-resolution TEM imaging captured during growth.