

Directed Radiolytic Synthesis of Nanostructured Materials using in situ Liquid Cell Microscopy

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There are a wide range of solution-based strategies available for the size- and shape-controlled synthesis of functional nanomaterials for applications in catalysis, energy storage, biomedical, optical, and electronics.¹ To elucidate growth mechanisms, *in situ* liquid scanning transmission electron microscopy (STEM) plays a role for directly imaging and quantifying growth dynamics of nanoparticles from liquid-phase precursors.^{2,3} In this work, we report several strategies for the *active* controlled synthesis of metallic and bimetallic nanoscale architectures using the concept of radiolytic synthesis.^{4,5} In one approach, we developed a direct-write, template-free method to fabricate self-supporting, hollow, metallic nanostructures, and we interpret the formation mechanisms based on direct observations of nucleation and growth. The electron beam used for imaging stimulates radiolysis, promoting the dissociation of water (H₂O) molecules and the formation of complex radical species such as aqueous electrons (e_{aq}⁻) and other reducing and oxidizing species. The highly reducing radiolytic species assist in the chemical reduction of metal ions from the precursor solution, resulting in the formation of a metallic nanocrystal seed, which then acts as a catalyst for H₂ gas generation forming a metal encapsulated hollow nanobubble. In another approach, a custom-built electron beam nanopositioning and scan-generator system is used to precisely control the position and electron dose of the focused electron beam to fabricate metallic and bimetallic nanostructured materials.^{6,7} These strategies enable fundamental electron beam interaction studies and open a new pathway for direct-write nanolithography from liquid-phase solutions.

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