doi:10.1017/S1431927620018115
Microsc. Microanal. 26 (Suppl 2), 2020

A New Pathway for the Formation of Co-aligned Hierarchical Mesocrystals

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In-situ liquid phase TEM is an emerging technique, that can provide new insights into fundamental physicochemical process. [1] It has proven especially useful in the field of crystallization, where it has revealed complex new crystallization pathways. [2-4] Recently, crystallization by particle attachment (CPA) has been recognized as a common mechanism of crystal growth that can result in complex morphologies and which has been exploited to create hierarchical nanomaterials with unique, emergent properties. [5] Oriented attachment (OA) [3] is a form of CPA in which the primary particles align and attach along specific crystallographic directions. OA can produce mesocrystals: structures that diffract like single crystals, even though the constituent primary particle domains are still discernable [6]. The conventional view of OA is that nucleation and particle assembly are separate events. That is, nucleation provides a supply of primary particles, which encounter other primary particles or particle aggregates via Brownian motion biased locally by attractive interparticle potentials. However, many mesocrystals exhibit highly regular morphologies and uniform size distributions, with shapes that appear similar regardless of size or location. It is challenging to explain how a random nucleation, diffusion and aggregation process can underlie the formation of these highly regular structures.

Here we focus on the crystallization of hematite (hm, Fe_2O_3) mesocrystals from ferrihydrite (fh) nanoparticles. In oxalate-free solutions, the resulting hm crystals are well faceted rhombohedron, while in the presence of oxalate, hm forms nanoporous spindle-shaped mesocrystals. We applied in-situ liquid-phase TEM with controlled temperatures of 80 °C to investigate mesocrystal formation in both TEM mode and STEM mode. We directly observed the dissolution of fh and the nucleation of new hm particles, which formed within close proximity (~ 1 nm) of the hm/solution interface. Immediately after nucleation, the hm particles attached to the nearby seed to form a hm mesocrystal. We carefully disassembled the liquid cell and performed ex-situ EDX mapping and electron diffraction to future confirm the growth of spindle-shaped hematite during the liquid phase TEM experiments. Furthermore, we utilized a quasi in-situ approach with indexed TEM grids to cycle samples between the growth reactor and the TEM to track their growth pathway. The hematite is only observed to grow on existing fh aggregates, and consistently grows into the surrounding solution. This is consistent with our liquid cell TEM observation that hm grows by nucleation of new particles near the hematite-solution interface and then aggregation. This represents a new paradigm for mesocrystal formation by OA, in which the presence of an interface biases the nucleation of primary particles to occur near that interface, leading to a more deterministic growth process [7].

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[7] The authors thank the support by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, Geosciences Program at Pacific Northwest National Laboratory (PNNL).