Cryo-STEM for Energy Materials Research

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Transmission electron microscopy (TEM) enables atomic-scale studies of the structure and chemistry of energy related materials including catalysts and solid/solid interfaces in complex oxides. The processes at liquid/solid interfaces such as electrolyte/electrode interfaces, which are critical to the battery's performance, have, however, not been explored at high spatial resolution. Traditional TEM of these materials in their native environments is hampered by the liquid evaporating immediately after loading into the vacuum of the microscope column. The more recent electrochemical TEM liquid cells have enabled real-time structural and chemical studies of materials and devices during their operation, but with limited spatial resolution due to radiation damage.

Here, we use cryo-electron microscopy techniques to image these nanostructured materials stabilized by snap-freezing at low temperatures. Using cryo-immobilization techniques developed for electron microscopy of hydrated-biological specimens [1-5], we have prepared solid-liquid interfaces in energy related materials for subsequent structural and chemical characterization by cryo-TEM. Cryo-immobilization through vitrification, the transformation of the liquid into the glass state, provides structural preservation of the sample in its near-native state. Vitrification can be achieved by rapidly cooling the sample through its glass transition using plunge-freezing. For nanoparticles in aqueous solutions, plunge frozen samples can be directly imaged in the cryo-TEM. Using these techniques, we have imaged silica nanoparticles from hybrid electrolytes embedded in vitreous, ice revealing their arrangement and shape (Fig. 1).

A major challenge of imaging nanostructures in non-aqueous solutions, such as organic electrolytes, is the sample thickness after plunge-freezing, which prevents direct imaging in the cryo-TEM. Sample thinning techniques at cryogenic temperatures are therefore required. Using Cornell's cryo-focused ion beam (FIB), we have adapted thinning methods originally developed for thinning of biological specimens (Fig. 2) to prepare cryo-TEM samples for subsequent characterization in the cryo-TEM. Site-specific sample thinning is performed directly on a plunge-frozen TEM grid, which is then transferred into the cryo-STEM under liquid nitrogen. Studying liquid/solid interfaces in energy related systems, with the liquids preserved, is an important step to understanding their operation and failure mechanisms. [6]

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[6] The CCMR EM Facility is supported through the NSF MRSEC program (DMR-1120296). Additionally, this project was supported by the EMC^2, a DOE EFRC (DE-SC0001086).

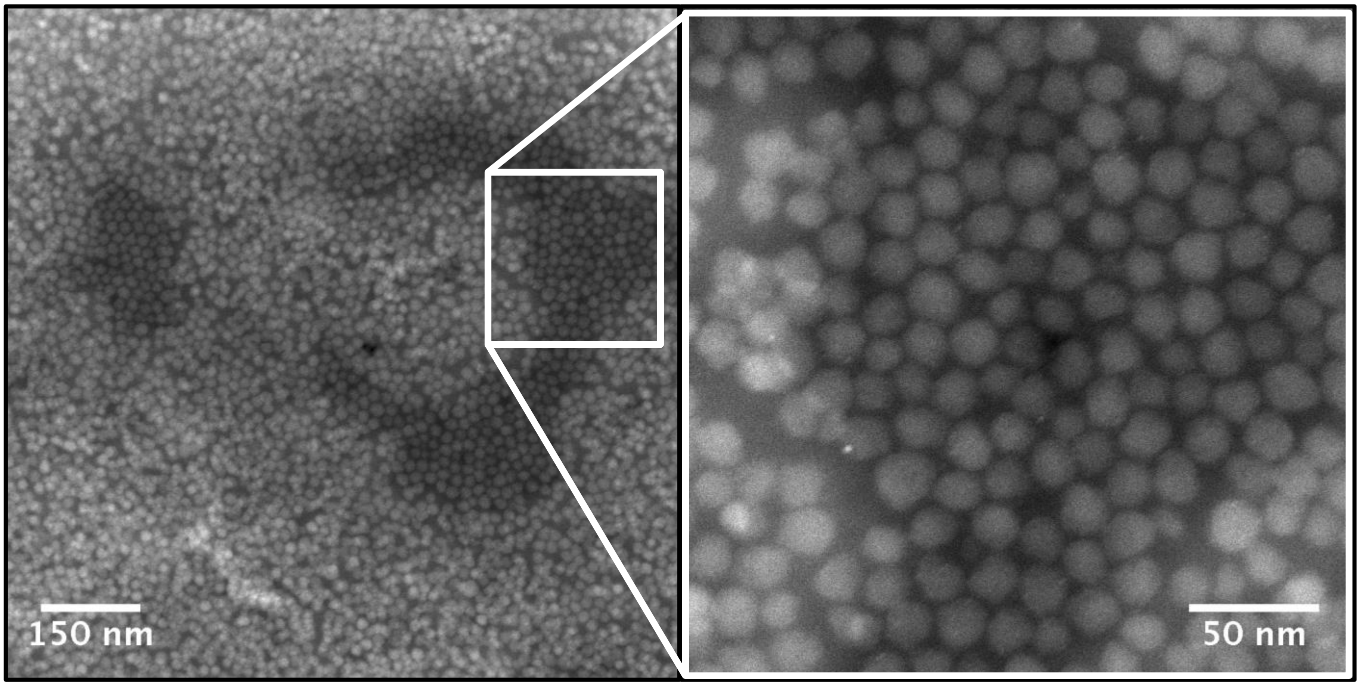

Figure 1. Cryo-immobilization of solid/liquid nanostructures by plunge freezing enables high-resolution characterization by cryo-STEM. Cryo-STEM imaging of silica nanoparticles from lithium metal battery hybrid electrolyte, embedded in vitreous ice.

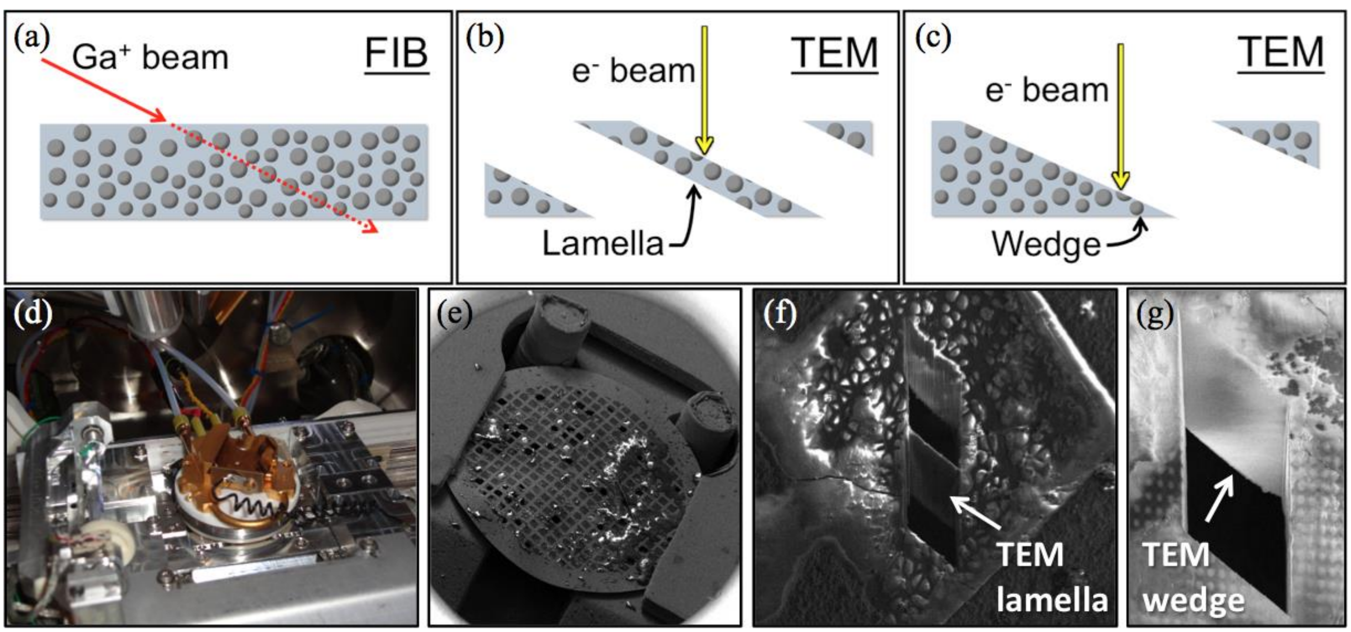

Figure 2. Cryo-focused ion beam (cryo-FIB) milling of thick samples in preparation for cryo-TEM analysis. **(a)** Cryo-FIB uses a focused gallium ion beam for site-specific milling of samples. This allows lamellas **(b, f)** and wedges **(c, g)** to be formed, producing regions thin enough for imaging in the TEM. A cryo-stage installed on a standard FIB **(d)** allows loading and thinning of snap-frozen samples directly on TEM grids **(e),** which can subsequently be loaded into the cryo-TEM for high-resolution characterization.