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Combining Spatial and Temporal Resolution in Cryo-TEM of Device Materials

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Cryogenic transmission electron microscopy (cryo-TEM) has been instrumental to reducing the effects of electron-beam sample interactions and enabling higher spatial resolution studies of beam sensitive materials. However, the process of thinning and freezing samples for cryo-TEM characterization is often complex and frequently requires removing materials from their environment or stimuli of interest for extended times, hindering characterization of transient or active states. For a device material such as a battery electrode, techniques involve disassembling the battery post-cycling and either liberating electrode particles, depositing them onto a TEM grid, and plunge freezing [1] or removing the entire electrode or electrode stacks and transferring to a cryo-focused ion beam for thinning [2,3]. Additional time is needed to protect the materials from air exposure, necessary to preserve their chemical structures akin to the original sealed battery.

While these methods enable ex-situ characterization of device materials at high spatial resolution, they sacrifice temporal resolution by leaving time for structural relaxation, diffusion, and other dynamic processes to occur between device operation and final characterization of the material or interfaces. Therefore, it is difficult to precisely correlate the imaged structure with native structures that evolve in situ during device processing, operation, or aging. One strategy to combat this is through the development of novel sample preparation techniques that freeze samples in situ during these critical processes in the relevant device lifetimes. This mirrors innovations that have taken place in structural biology, to move beyond preparing samples from aqueous suspensions of isolated biomolecules to freezing them within their cellular environments to understand their native, in-situ structures [4,5].

Our previous work has begun to incorporate this principle of preserving specimens in their native context of interest into the study of device materials [6]. By vitrifying inks used to cast metal-halide perovskite films, we are able to characterize the structural evolution of precursors during solution processing of perovskite optoelectronics. In particular, we identify nanoscale colloids consisting of a crystalline perovskite precursor phase that has only been observed out of solution for certain chemistries [7], as shown in Fig. 1. This demonstrates the value of developing techniques to characterize in-situ structures that arise at different points in processing, as these may be transient and distinct from the structure of the final film or device.

Further sample preparation innovations are required to capture the many dynamic structures that evolve in materials throughout the fabrication and use of a device. To extend these principles from device processing to operation, and to demonstrate their applicability to diverse materials, we present progress integrating plunge freezing with electrochemical cycling of batteries to enable characterization of electrode interfaces with high fidelity to their native, in-situ structures. This method offers a new pathway to improve the temporal resolution of cryo-TEM, while still exploiting its ability to achieve

high spatial resolution for characterizing beam sensitive materials [8].

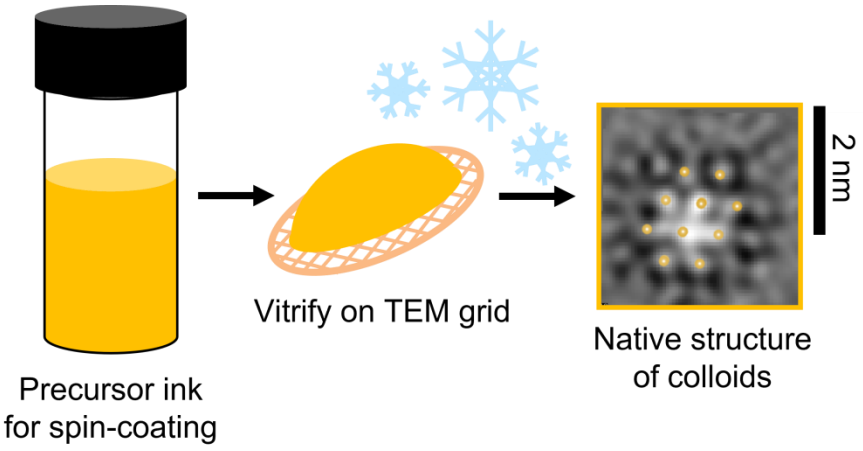

Figure 1. Schematic of cryo-TEM characterization of metal-halide perovskite precursor inks. A droplet of ink is flash frozen onto a TEM grid, enabling study of native colloid structure. Yellow overlays on colloid image produced through single particle analysis show locations of lead atoms indexed to crystal structure characterized by Stone *et al.* [7]. Micrograph reprinted with permission from Dutta *et al.* [6].

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