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Measuring Dynamics in Energy Materials Using Functional Atomic Force Microscopy

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Atomic force microscopy (AFM) is a well-established tool for nanoscale imaging of surfaces for a wide range of materials of interest. In energy materials, such as photovoltaics or battery electrodes, the ability to combine *electrical* AFM with local optical illumination has enabled a wide range of novel electrical imaging methods that can correlate local structure with device function in realistic conditions. For example, it is possible to use electrical AFM techniques to measure important solar cell properties like local carrier injection barriers or processing effects on short-circuit photocurrent on *actual* solar cell device stacks [1].

In recent years, many researchers have turned to "big data" approaches to analyze AFM cantilever motion [2]. These data-aware methods have enabled new insight into *dynamic* processes at the nanoscale by applying time-frequency analysis to cantilever motion. The premise for these techniques is that changes in the AFM cantilever's oscillating motion reflect information about the sample, due to the electrostatic effects between the AFM tip and the substrate. Thus, by recording the cantilever position and then applying signal processing to the data, it is possible to extract new temporal insights from the measurement.

In this talk, we discuss how we measure dynamics in electrical AFM data with an emphasis on studying photovoltaic materials. Here, we focus on time-resolved electrostatic force microscopy (trEFM). trEFM measures dynamic information at sub-microsecond timescales by applying time-frequency analysis to the cantilever's motion in response to a transient stimulus such as photoexcitation of a solar cell [2-3]. This method allows us to extract dynamics from the AFM (Fig. 1A), which provides valuable insight into the transient phenomena that govern the behavior in many solar cells by imaging the local photovoltaic quantum efficiency [2].

We use trEFM to answer a key issue on hybrid organic-inorganic perovskites, a polycrystalline material at the forefront of thin film solar technologies [4]. In perovskites, one of the lingering questions is how carriers move at grain boundaries compared to grain centers. Our trEFM data on a model layered perovskite system show that grain centers exhibit both *faster* charging and *lower* charge density, implying a small density of trap states at grain boundaries (Fig. 1B-C). Interestingly, these data show timescales on the order of tens of microseconds, which are *far slower* than expected for pure charge motion. These data therefore reflect a different physical process, either ion motion or trap-mediated transport [4-5], previously overlooked in these materials. The trEFM results provide a powerful example of how electrical AFM dynamics can answer critical questions on energy materials.

In dynamic AFM methods like trEFM, the cantilever motion is a *nonstationary process* where the frequency changes with time. We can therefore apply newer signal processing and machine learning methods to AFM to further investigate the underlying physics in the surface materials of interest. We recently reported a new technique, non-stationary Fourier mode decomposition (NFMD), which combines stochastic gradient descent, Fourier mode decomposition, and knowledge of the AFM

cantilever physics to extracts the instantaneous frequency with significantly lower noise [6]. We apply NFMD to show improved measurements on our perovskite samples, with the goal of extracting hidden time constants from the trEFM signal.

Dynamic electrical AFM methods provide a powerful platform for analyzing functional materials. While we present these approaches in the context of analyzing photovoltaic materials, the general principle of measuring time constants in AFM is applicable to a wide range of candidate materials, from fast-motion in bio-active materials to ion diffusion in polymer electrolytes.

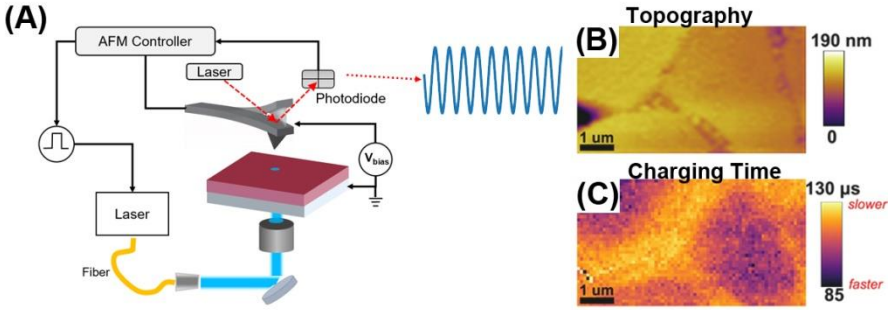

Figure 1. Example of applying time-resolved electrostatic force microscopy to a perovskite solar cell. (A) Experimental schematic where the photodiode signal is recorded at each point. (B) Topography (top) and charging time (bottom). Fig. 1B-C adapted with permission from Ref. 4. Copyright 2019 American Chemical Society.

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