Ex situ and *in situ* Scanning Transmission Electron Microscopy Studies of Functional Perovskite Materials and Devices

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Functional perovskite materials, especially oxide-based and halide-based perovskites, offer abundant physical properties for the development of information and energy conversion devices. Characterization techniques such as aberration-corrected scanning transmission electron microscopy (STEM) and differential phase contrast (DPC) provide crucial insights into the atomic structures and various physical information of materials, playing an important role in material and device development. To investigate the bending-related phenomena in ultrathin freestanding oxide perovskites, advanced STEM approaches were adopted to characterizing the cross-sectional atomic structures of wrinkled $BiFeO_3$ (BFO) and $SrTiO_3$ (STO) membranes. Our results show that both membranes can accommodate extremely high strain gradients up to 10^7/m. Moreover, the maximum polarization reached approximately 146.6 μC/cm^2 and 35.3 μC/cm^2 in BFO and STO, respectively, contributed by flexoelectricity. Additionally, we discovered a substantial change in membrane thickness in bent BFO, implying an unusual flexural deformation in ferroelectric membranes.

The polarization switching behaviors in ferroelectric materials play a significant role in information storage. Here, we present an *in situ* biasing approach for the direct atomic-scale STEM observations of domain nucleation and sideways motion in ferroelectric capacitors with uniform electric field. At lower electric field, the motion of ferroelectric domain walls exhibited creeping characteristics accompanied by continuous deformations. Atomic-resolution imaging of creeping domain wall also revealed concurrent variations in both the magnitude and orientation of polarization during the ferroelectric polarization switching process.

As emerging optoelectronic materials, halide perovskites have been widely applied in devices such as solar cells. However, their sensitivity to high-energy electrons still poses challenges for the study of atomic structure and dynamic behaviors. To realize the high-resolution characterizations of halide perovskites, post-protection treatment with ultra-thin carbon film was adopted to enhance the structural stability of perovskite solar cell cross-sectional specimens, optimizing the imaging conditions for STEM characterization. Low-dose STEM imaging revealed the atomic structures of grain boundaries, stacking faults, and twin boundaries within halide perovskite grains, corresponding theoretical calculations indicated that the interaction between point defects and intragrain interfaces could have detrimental influences on device performance. Furthermore, to investigate the photo-induced structural evolution and degradation

process of halide perovskites, an *in situ* chip-based platform and sample preparation techniques were developed for *in situ* and *ex situ* S/TEM observations under light illumination. During the photo-induced degradation process, nanoscale halide particles first appeared within the halide perovskite grains, then gradually expanding with accumulated illumination time. The generation of halide particles also introduced significant intragrain strain, which could accelerate the performance degradation of solar cell devices.

Key words: oxide perovskite thin films; perovskite solar cell; scanning transmission electron microscopy; *in situ* TEM