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Visualizing the Invisibles in Perovskites

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Abstract

Halide perovskites are a class of soft crystalline materials for numerous energy applications such as high-performance photovoltaics and large-area displays. Decisive and accurate characterizations of microstructures and defects in halide perovskites are critical but generally restricted due to their instabilities under electron microscopes. Recently, Rothmann *et al*. employed a low-dose low-angle annular dark field scanning transmission electron microscopy imaging method to realize a direct, atomic-scale examination of perovskite thin films, unravelling key structural details that are invisible to previous observations. This study opens the door to comprehensively revealing microscopic structure-property-performance relationships in perovskites and beyond, which will fundamentally guide the re-invention and optimization of energy devices.

The increasing energy consumption of the modern society drives an urgent demand for clean and renewable energy generation exceeding fossil fuels. Amongst a spectrum of alternative energy sources including wind, hydro, solar, and nuclear powers, photovoltaics (PVs) have been considered one top technology candidate, because they could potentially capture solar energy of about ten thousand exajoules annually into electricity that will be conveniently distributed for everyday activities of human beings. Therefore, since 1990s there has been a continuous, vast effort developing high-efficiency and low-cost PVs in numerous countries such as United States, China, Australia, and so on. While silicon (Si) is proven able to serve in PV panels efficiently and they are robust in the real-world applications, the energy payback time of Si PVs can be more than 2 years, and their production involves high-temperature synthesis and hazardous purification process, inevitably imposing adverse effects on the environment. In this regard, the field of solar energy is intensively searching for new-generation PV materials that not only exhibit high device performance, but also are easy and cheap for industrial fabrication. One most significant step that meets this demand is the intriguing discovery of halide perovskites (HPs) based PV materials, drawing phenomenal attention across the academia, industry, and governmental sectors.

The first perovskite solar cell (PSC) was reported by Miyasaka and coworkers with only 3.8 %,[1] but in the following decade the PV field has witnessed an unprecedented growth and expanding of this emerging research area, leading to a swift evolution in device efficiency to 25.5 %.[2] This progress is largely driven the innovation and

optimization of device fabrication processes.[3] Nevertheless, it now appears that the efficiency progress of PSCs has become relatively saturated, and the long-term stability of PSCs is raised as a significant concern. To address these critical issues, in parallel to the device development, there is ongoing effort resolving the fundamental structure-property-performance relationship at multiple scales in HPs, results from which is expected to guide the materials and device engineering to improve PSCs.[3] At the center of this research effort is the decisive, accurate characterization of microstructure and defect in HP thin films, because numerous studies have shown microstructure and defects play a significant role in influencing both the carrier dynamics and ionic/molecular transport in HP thin films, determining the efficiency and stability of PSCs, respectively.[4] In this regard, it becomes an urgent need to develop reliable, powerful characterization techniques. While common tools like scanning electron microscope (SEM) and atomic-force microscope (AFM) have been commonly used for morphological determination of HPs, they are generally limited to probing the sample surface without revealing details of materials interior. It is well-known that transmission electron microscopy (TEM) is capable of imaging at a much higher resolution, which is actually well-established for characterizing conventional materials. However, as a class of 'soft' semiconductors, HPs are prone to degradation upon exposure to electron irradiation, presenting an obstacle for high-quality TEM imaging.[5] While there are a handful of promising, recent studies that involve high-resolution TEM of HPs based on specific methods such as cryo-TEM and low dose imaging,[6] atomic-scale structures of HPs, in particular in their most important thin-film form, have rarely revealed, and thus the true mechanisms for the PSC performance and stability are still much obscured.

Now a remarkable progress has been made by Rothmann *et al*.[7], which was published in a recent issue of *Science*, demonstrating imaging of the HP microstructures in thin films at the atomic spatial scale (~10^{-10} m) using aberration-corrected scanning-TEM (AC-STEM). STEM is a typical mode of TEM working with a focused electron probe instead of a parallel electron beam in conventional TEM. With the recent development of aberration corrector, the electron probe can be focused down to the sub-atomic scale to observe structural details. The pixel scanning probe mechanism makes STEM able to directly reflect the accurate real-space position of atoms. Furthermore, STEM annular dark field (ADF) imaging has a contrast in proportion to atomic number (Z), distinguishing different types of atoms. Although STEM is widely used in characterizing functional materials include oxide perovskites, it has been rarely applied to HPs. In that study, Rothmann *et al*.[7] chose a thin film sample of formamidinium lead iodide ($FAPbI_3$) perovskite, which is the most typical HP in state-of-the-art PSCs.[8] They rationally selected the low-dose low-angle annular dark field (LAADF) STEM imaging, a technique that not only maintains the sensitivity to Z variations, but also collects a higher fraction of the scattered electrons for low dose imaging than conventional high-angle annular dark field (HAADF) STEM. With this technical development, several intriguing materials-science findings on the HP microstructures were demonstrated.

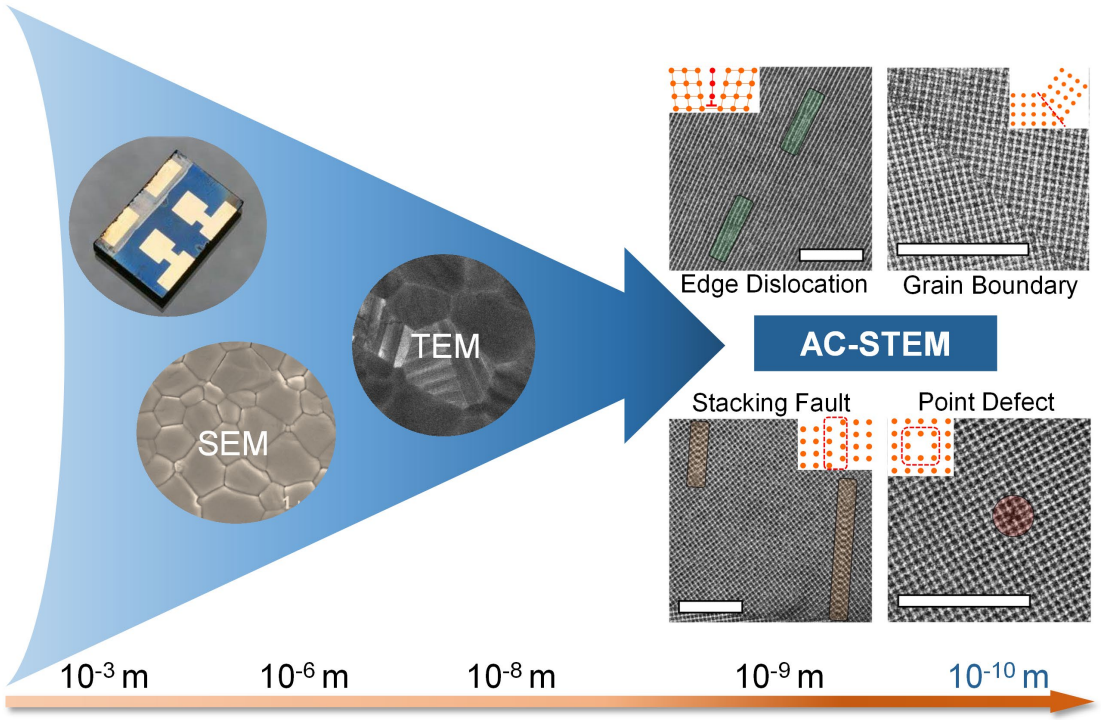

Figure 1. Schematic illustration showing the resolution of structures of halide perovskite semiconductors from macroscopic, to microscopic, to atomic scales based on the progression of characterization technique. Adopted from Ref. [7] with permission from the American Association for the Advancement of Science (AAAS).

Rothmann *et al*. showed the direct atomic-scale imaging of various crystal defects in the $FAPbI_3$ HP thin film with dimensions from 0D to 3D (**Figure 1**). For 3D defects, surprisingly, a coherent transition boundary with low lattice misfit and strain was found between the remnant PbI_2 (a precursor phase) and $FAPbI_3$ lattice. This may suggest that the epitaxial-like PbI_2 nanodomain could serve as seeds during the HP solution growth and such structural coherence may explain why a small amount of excess PbI_2 doesn't negatively affect the PSC performance. For 2D defects, grain boundaries and stacking faults are prominently observed. The authors show a well-defined crystallographically continuous grain boundary structure with a sharp interface and minimal lattice distortion. The near-120° triple boundaries represent the majority of observed grain boundaries in $FAPbI_3$. For the stacking faults, they exhibit a shift of half a unit cell and connecting Pb-I columns with I^- columns. 1D defects of edge dislocations are also revealed and they are dissociated in a direction perpendicular to their glide planes. Furthermore, the authors provide a preliminary identification on the atomic structure of aligned 0D defects of vacancies on the Pb-I sublattice. They also show an intermediate structure forms with the partially loss of FA^+ ions before the $FAPbI_3$ completely deteriorates to PbI_2, suggesting that the ordered FA^+-deficient intermediate structure may be formed as a result of facile ion migration.

With such comprehensive imaging of defect structures, the mechanistic investigations of optoelectronic properties and chemical stability of HPs can be facilitated. For

example, while grain boundaries have been known to affect the PSC performance,[3] we are now setting out to resolve how the grain boundary character influences their effects on PSCs. The influences of stacking faults and dislocations on the PSC performance have been less explored due to the difficulty in identifying their existence and locations, but now this important, exciting research direction become possible. Also, the acquisition of accurate atomic structure of HPs based on TEM will also benefit first-principles modeling and calculations, enable more reliable coupled theory-structure studies.

This inspiring step represents the possibility of atomic-scale characterization of HPs through regular S/TEM systems without specific high-end facilities. Rothmann *et al*. pointed out that the cryogenic conditions provide little noticeable contribution to reduce the beam sensitivity of the $FAPbI_3$ thin films, consistent with recent studies.[9] The authors further claimed that low electron accelerating voltage (80 kV) will lead to faster damage of HPs rather than high accelerating voltage (200 and 300 kV), which suggests that the sacrifice on resolution for a structural stability during TEM observation with reduced electron energy may not be necessary. A succinct conclusion can be thus drawn that the decisive factor for successful atomic scale STEM imaging of HPs is the dose rate. This finding points out a valuable research direction to perform in-depth STEM investigations of HPs and PSCs. For example, differential phase contrast imaging may help reveal the details of light atoms for the determination of accurate loss and migration of FA^+ ions which remains unclear in this work. Electron energy loss spectroscopy can be used to explore the physical properties of grain boundaries, stacking faults, dislocations, and point defects. Furthermore, *in situ* measurements may be feasible for direct, atomic-scale observation of structural evolution of HPs under external stimuli.[4,10] The adoption of higher efficiency detectors with better signal-to-noise ratio is also likely to improve the STEM imaging quality for HPs.

Seeing is believing. The direct observation of atomic-scale structures and defects under TEM will lay a solid foundation for future exploring emerging materials and energy sciences amongst HPs, and open the door to discussing the true relationships between materials properties, device performance, and those 'invisible' key structures. This will no doubt benefit the technological development of PSCs and other perovskite electronics. In a boarder context, soft crystalline materials like perovskites are finding prominent applications to energy technologies due to the combination of high structural flexibility and tunable electronic/ionic properties. The research methodology demonstrated by Rothmann *et al*. should be generic to studying all these promising materials, showing far-reaching impacts on the developments of variable energy technologies and potentially influencing the renewable energy landscape of the future.

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