

# Digging deeper for an in-depth understanding of energy materials

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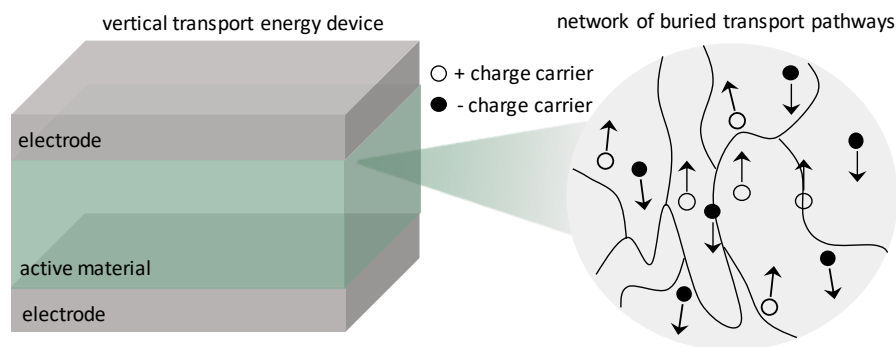
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**ABSTRACT** Oftentimes, advanced microscopy studies which measure the local performance of energy materials, are restricted to probing the surface. Yet, it is recognized that critical operational processes occur within these devices. In *Nature Communications* 11:3308 (2020), researchers dig deeper, by implementing tomographic atomic force microscopy to study local electrical transport pathways in a thin-film halide perovskite. From this yields a 3D, nanoscale spatial resolution map of the photoactive area, demonstrating how visualizing material interiors expands our understanding of next-generation energy devices.

We are in the midst of a global energy transition, where fossil-fuel based sources for energy generation are being replaced by renewable or low-carbon emission alternatives.<sup>1</sup> As such, the transition will induce a proliferation of new energy devices, such as solar cells, fuel cells, batteries, and light-emitting diodes (LEDs), incorporated into our society and onto our electrical grid. Uptake of these technologies is already happening, and in fact, there is a path forward that achieves 86% power generation from renewables by 2050.<sup>1</sup> Moreover, further adoption is essential for countries to reach their Paris Agreement nationally determined contributions.<sup>2</sup> In particular for solar cells, better performing devices can translate into lower cost,<sup>3,4</sup> which in turn accelerates deployment, providing a strong motive to continue improving efficiencies in energy technologies.

Most state-of-the-art energy devices are comprised of multiple thin film layers, see Figure 1. As depicted, the interior layers house the majority of a device's operational processes which ultimately govern its performance, while the exterior layers are used to ensure effective charge carrier extraction or injection. Therefore, revealing the pathways with which charge carriers are transported throughout the device operation cycle is critical to dictating a technology's efficacy.

Yet, the majority of characterization techniques that provide sufficient spatial resolution to image charge carrier transport pathways (i.e. nanoscale) are primarily capable of investigating only the top layer.<sup>5</sup> For this reason, much of the literature in this research area historically presents data performed on half-devices or thin films, rather than an entire device stack. Furthermore, when measuring the standalone active material, the characterization method often only probes the surface. While this is crucial for studying the portion of the active layer that will ultimately become an interface, it is insufficient for realizing the operative processes *within* the typically microscale-thick material. The three most common microscopy techniques used in energy device characterisation are: electron (or ion) beam, photon beam, or scanning probe, and while device cross-sectional studies are possible with all of these methods, often only a 2D picture of the materials in question is obtained.



**Figure 1. Energy device interiors are the backbone to the overall performance output.** This representative depiction of a vertical transport energy device highlights that the active area is the source where (i) most key operational interactions occur and (ii) buried interfaces are prevalent. Note: there are often additional layers in-between the active material and the electrodes to promote charge carrier extraction or injection, and the type of layers depends on the energy technology.

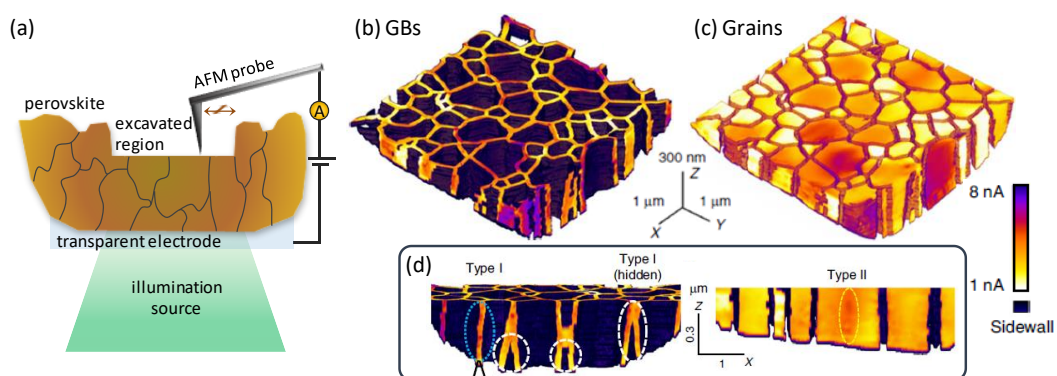
To address this blind spot, researchers developed a high spatial resolution characterization technique which images a material's electronic properties in 3D. In a recent article in *Nature Communications*, Song et al., implement photoconductive tomographic atomic force microscopy (T-AFM), realizing a 3D nanoscale carrier transport map for a halide perovskite thin film.<sup>6</sup> Briefly, halide perovskites are a promising polycrystalline material for next-generation solar cells, composed of an  $ABX_3$  crystal structure (A = organic/inorganic cation, B = cationic metal, X = anionic halide). This material class has

caused a huge stir in the photovoltaic (PV) community and despite their nascent discovery, are already serious contenders for on-market solar cells with many researchers investigating their scalability and commercialization prospects.<sup>7</sup> For example, the company Oxford PV is using a halide perovskite composition on top of the stable silicon (Si) device to deploy the first perovskite/Si multi-junction solar cell on the market.<sup>8</sup> Yet, as exciting as this material class is, due to its relatively recent usage as a solar energy material, there is much to understand about its operative processes.

The T-AFM technique presented in <sup>6</sup> and displayed in Figure 2, allows an unprecedented view of the charge carrier transport throughout the entire depth of the electrically active area within a halide perovskite material by implementing continuous in situ nanomachining with an AFM probe. Here, the tip gradually polishes the sample surface (Figure 2a), and uncovers buried microstructural features of interest. In the paper, the researchers mill away ~16 nm of halide perovskite with each sequential image frame to build up the 3D map. In addition to uncovering previously buried interfaces, this method also removes the ever-nagging susceptibility of scanning probe techniques to topographic artefacts. However, the technique is destructive by nature, requires long acquisition times, and questions about how the removed material influences the local response of the electrical properties is difficult to discern.

Note, this is not the first time this research lab has presented T-AFM, and the original work demonstrating the technique, published in *Nature Energy* in 2016, was performed on a CdTe solar cell material.<sup>9</sup> Similar to CdTe, halide perovskites are polycrystalline, meaning their active layer is comprised of grains and grain boundaries (GBs), and the contribution of these grain boundaries on the overall performance has been of notable debate in the PV community.<sup>10</sup> Not all GBs are at the surface, and therefore, to probe buried interfaces and understand how they also may influence carrier transport is of broad interest to the field.

Interestingly, in their recent paper <sup>6</sup> the researchers identify two different types of GBs in halide perovskite thin films, designated as Type I and Type II interfaces (see Figure 2b-d). For Type I the boundaries act as preferred channels for conduction through the film vertically, obstructing any lateral inter-grain carrier diffusion in a normal electric field, and also inhibiting carrier diffusion upon in-plane electric field application. While for Type II boundaries vertical conduction is benign and lateral carrier transport is uninhibited, resulting in ‘single-crystal-like’ behaviour. The authors hypothesise that the Type II boundaries may be twin GBs, however, more characterization is required to confirm.



**Figure 2. Tomographic Atomic Force Microscopy implementation and results.** (a) Schematic of the T-AFM technique. 3D maps of the photoconductivity in a halide perovskite thin film obtained via T-AFM displaying the distribution of (b) grain boundaries (GBs), (c) grains, and (d) the two types of GBs identified in ref <sup>6</sup>. [adapted from Figures 1 and 4 in Ref <sup>6</sup>]

The authors go a step further than the 3D map and use a montage of photoconductive images acquired at different biases (all taken ~100 nm below the original surface) to calculate the mobility using the photocurrent drift equation:

$$I_{ph} = \frac{qN_{ph}\mu AV}{L}$$

where  $q$  is the unit charge,  $N_{ph}$  is the photogenerated charge carrier density,  $\mu$  is mobility,  $A$  is tip-sample contact area,  $V$  is applied voltage, and  $L$  is the film thickness. Because of the “polishing” performed by T-AFM,  $A$  and  $L$  are set as constant. Therefore, obtaining an estimated value for the  $\mu N_{ph}$  product at the nanoscale is possible by calculating the slope of the linearly fit  $I_{ph}$ - $V$  curves at every pixel. The estimated  $\mu N_{ph}$  product map may then be interpreted as a nanoscale-resolved map of the relative photo-generated carrier mobility. This type of analysis reveals higher mobilities at the Type I GBs, suggesting they enhance charge carrier transport. This is exciting because it indicates that GBs in future perovskite solar cells could be engineered to optimize the device performance.

Importantly, the authors emphasize that there is no strict answer as to which GB type is preferred, and the desired type depends on the application. For instance, in devices that depend heavily on the lateral transport of carriers, inhibiting charge carriers at GBs will limit their diffusion. In such a configuration, a higher proportion of Type II GBs is favoured, as the single-crystal-like behaviour could enhance the performance. For vertical transport devices (e.g. photodetectors or standard solar cell designs), the device efficiency is dominated by vertical charge carrier transport, and as such, Type I GBs should be more populous, as is the case for the data presented in Figure 2.

Ideas for future characterisation investigations using T-AFM within halide perovskite solar cells could include 3D maps with both carrier-selective layers as well as the active region to obtain a complete picture of the electron and hole transport properties. Also, perovskites are highly susceptible to degradation, and the authors mention that T-AFM may help diagnose causes for the performance drop by imaging either migrating ions or degradation-inducing environmental elements during device operation. Moreover, to protect perovskites from degrading researchers implement various passivation techniques and T-AFM could directly probe the depth of the dopants (or another defect-passivating species).

Beyond solar cell materials, this type of characterization could be sought after in many different energy technology fields such as batteries, fuel cells, and LEDs. The disconnected and fragmented nature of the active regions in those devices is the source of fast and innovative carrier transport, but also a common root of material failure. Understanding the different reasons behind improved or inhibited transport by physically observing it, presents an intriguing perspective and has proven to provide a deeper knowledge with regards to the underlying operational mechanisms.

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## DECLARATION OF INTERESTS

The author declares no competing interests.

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