Light-emitting diodes (LED) with different emission spectra are widely used in our daily life for a variety of applications. However, due to fundamental restrictions of light-emitting materials, the development of near-infrared LEDs (NIR-LEDs) is still modest. Recently, solution-processed tin-halide perovskites (THPs) have emerged as one of the most promising light-emitting materials for NIR-LED application. Electronic doping (p-type) is a unique property of THPs. To date, extensive efforts have been taken to reduce the p-doping concentration, with reference to their lead-based halide perovskites counterpart for a transition from a p-doped to an intrinsic semiconductor. This is mainly driven by the application of these materials in photovoltaic devices. However, in LED, where rather than charge extraction we want to maximize radiative charge recombination, carefully controlled p-doping becomes a favorable attribute of THPs for the successful creation of high-brightness devices. I will show how their electronic properties affect light emission efficiency, and I will present our efforts in material engineering to design and master the electronic properties of THP films in order to achieve bright and efficient LEDs.

8:30 AM EL04.14.02

Water- and Heat-Activated Dynamic Passivation for Perovskite Photovoltaics Wei-Ting Wang[1], Philippe J. Holzhey[2,3,4], Ning Zhou[1], Qiang Zhang[5], Suer Zhou[2], Elisabeth Duijnstee[2], Kevin Rietwyk[3], Jeng-Yu Lin[6], Yijie Mu[1], Yanfeng Zhang[5], Udo Bach[3], Chun-Guey Wu[7], Hin-Lap Yip[1], Henry Snaith[2] and Shien-Ping Feng[1]; [1]City University of Hong Kong, Hong Kong; [2]University of Oxford, United Kingdom; [3]Monash University, Australia; [4]Helmholtz-Zentrum Berlin, Germany; [5]Xi'an Jiaotong University, China; [6]Tunghai University, Taiwan; [7]National Central University, Taiwan

Further improvements in perovskite solar cells (PSCs) require better control of ionic defects in the perovskite photoactive layer during the manufacturing stage and their usage. Here, we report a living passivation strategy using a hindered urea/thiocarbamate bond Lewis acid-base material (HUBLA), where dynamic covalent bonds with water and heat-activated characteristics can dynamically heal the perovskite to ensure device performance and stability. Upon exposure to moisture or heat, HUBLA generates new agents and further passivates defects in the perovskite. Not only are the defects during the fabrication passivated, but new defects that evolve during the usage and operation of the device are passivated as well.

We prove the dynamic passivation ability of HUBLA, both chemically through X-ray photoelectron spectroscopy (XPS) and physically through photoluminescence (PL) maps of aged and pristine perovskite thin films. We determined the threshold for the water-activated passivation to be at 20% relative humidity, and for the heat-activated passivation, it is ≥ 55 °C. This dynamic passivation significantly improves the robustness of the treated perovskite thin films. For instance, at 85 °C in ambient air (~30% relative humidity), the perovskite thin film with HUBLA developed 2/3 less PbI_2 than the control film.

In devices, this passivation strategy achieved high-performance devices with a power conversion efficiency (PCE) of 25.1%. HUBLA devices retained 94% of their initial PCE for approximately 1500 hours of aging at 85 °C in N_2 under 1 sun illumination. Further devices with HUBLA maintained 88% of their initial PCE after 1000 hours of aging at 85 °C and 30% relative humidity (RH) in air under 1 sun. (1)

W.-T. Wang, P. Holzhey, N. Zhou, Q. Zhang et al., Water- and heat-activated dynamic passivation for perovskite photovoltaics. *Nature* (2024). https://doi.org/10.1038/s41586-024-07705-5

8:45 AM EL04.14.03

Understanding the Structural Dynamics of 2D/3D Perovskite Interfaces Alan Kaplan, Marko R. Ivancevic, Quinn C. Burlingame and Yueh-Lin Loo; Princeton University, United States

The incorporation of 2D perovskite capping layers has become common practice in high-performance lead halide perovskite solar cells to passivate 3D perovskite surface defects. However, recent work has shown these 2D/3D interfaces to be highly dynamic, undergoing structural transformation when subjected to thermal stress or illumination. Here, we study the structural dynamics of a series of commonly used alkylammonium-based Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phase 2D perovskites deposited on formamidinium lead iodide. By monitoring the grazing-incidence wide-angle x-ray scattering and photoluminescence of the 2D/3D perovskite heterostructures aged at 100°C or under 1 sun illumination, we observe that the 2D perovskite structures transform to progressively larger inorganic layer thickness (denoted by layer number n), eventually approaching a steady-state condition with only the 3D perovskite (n=∞) remaining. This transformation slows by a factor of two when increasing the size of the RP-forming ligand from butylammonium to dodecylammonium. Furthermore, substituting the RP-forming dodecylammonium with DJ-forming 1,12-dodecanediammonium of similar size, decelerates the structural transformation by a factor of 10. These findings suggest that the use of DJ 2D perovskite capping layers could be a promising pathway to form stable 2D/3D heterostructures.

9:00 AM EL04.14.04

Understanding Dynamic Titled Domains in Halide Perovskites with Big-Box Refinements of X-Ray Total Scattering Data Kieran W. Orr[1,2] and Samuel D. Stranks[2]; [1]Stanford University, United States; [2]University of Cambridge, United Kingdom

While solar cell and light-emitting devices based on halide perovskite materials have become significantly more efficient over the past decade,[1] much of this progress has been the result of empirical fabrication optimisation, and the community's structural materials understanding lags behind in comparison. For example, off the back of recent single crystal diffraction[2,3,4] and computational[5,6] studies, the field is only just beginning to appreciate that there are transient nano-domains where the lead halide octahedra are mutually tilted embedded in a higher symmetry average perovskite structure. Such dynamic domains are important for the properties of halide perovskites,[2] and functional materials more generally, where structural disorder is often property determining.[7]

Here I present our current work characterising these tilted domains in mixed-component halide perovskites using X-ray total scattering in the form of powder pair distribution function (PDF) analysis. By designing an advanced big-box refinement protocol that simultaneously considers the Bragg scattering and PDF data, where atomic positions in a supercell are unconstrained by crystal symmetry but obey local chemical rules, we produce atomic configurations which show a snapshot in time of the atomic halide perovskite crystal structure. Analysis of these supercells reveals pancake-shaped nanodomains where octahedra are locally tilted to lower symmetry in addition to Pb displacement from octahedral centres. Crucially, we perform these analyses on samples that have mixed compositions (like the highest-performance formulations) to understand the effects of ion substitution at different crystallographic sites on the size, shape, and density of the tilted nanodomains. Importantly, our big-box refinement approach uncovers evidence for these local domains using powder PDF measurements which are i) easier and higher throughput than single crystal diffraction studies, and ii) amenable for use on the most technologically relevant samples using either powders from scraped films or native thin films[8] as they would be found in devices. Our results inform device makers on how to best tune their perovskite formulations to realise more efficient and stable optoelectronics, and our approach can be applied to a variety of other materials systems where structural disorder is a key factor for material performance.

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9:15 AM EL04.14.05

Lead-Free Halide Double Perovskites—The Effects of Lanthanide Doping on Lattice Crystallinity and Related Photoluminescence Properties Simone Barbarossa[1], Salvatore Ferruggia Bonura[1], Valeria Demontis[2], Daniela Marongiu[2], Francesco Quochi[2], Michele Saba[2], Marco Cannas[1] and Simone Agnello[1]; [1]Università degli Studi di Palermo, Italy; [2]Università degli Studi di Cagliari, Italy

Over the past decade, considerable efforts have been directed towards enhancing the efficiency of solar cells and optoelectronic materials as part of the green transition. Within the latter, Perovskite materials have made an impact due to their attractive characteristics and promising potential.

Despite their impressive performance in lighting applications, such as achieving photoluminescence cutting quantum yields exceeding 100% in some cases[1], lead-halide materials still suffer from notable drawbacks including poor stability and lead toxicity[1]. As an alternative, an analogous class of materials, identified as double perovskites, has been introduced, which are characterized by the substitution of the Pb^{2+} ion of the octahedral structure with both M^{+} and M^{3+}metal ions in equal proportions (e.g. $Cs_2AgInCl_6$)[2]. Indeed, double perovskites present remarkable thermal stabilities (up to 500°C) and attractive emission spectra spanning across the entire visible region[3], ideal for a wide range of lighting applications.
Introducing suitable additives through doping has shown promise in enhancing their performance, notably leading to a sharp increase in Photoluminescence Quantum Yield (PLQY). This enhancement is believed to stem from improved lattice crystallinity and the creation of new parity-allowed radiative recombination pathways[4].
Nevertheless, substantial further research is necessary to fully comprehend these materials.
In this context, the current study aims to address these knowledge gaps by investigating various co-doped compositions of $Cs_2Na_{1-x}[X_xY_yZ_{1-y}]Cl_6$ halide double perovskites, by incorporating various elements such as Ag, Er, Yb, and Bi. The research employs Raman spectroscopy and photoluminescence measurements to evidence how changes in composition and crystallinity due to dopant addition correlate with variations in photoluminescence characteristics and QYs.
In this regard, a comprehensive Raman analysis spanning from IR to UV, coupled with micro-luminescence, provides detailed insights into the structural attributes of these perovskites and their relationship to emission properties.
This approach aims to advance our understanding of the underlying mechanisms governing the emission behavior of these innovative materials.

This study was developed in the framework of the research activities carried out within the Project “Network 4 Energy Sustainable Transition—NEST”, Spoke 1., Project code PE0000021, funded under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.3— Call for tender No. 1561 of 11.10.2022 of Ministero dell’Universita` e della Ricerca (MUR); funded by the European Union—NextGenerationEU.

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9:30 AM EL04.14.06
Surface Chemistry of Tin Halide Perovskites and Its Effects on Optoelectronic Properties Antonella Treglia, Mirko Prato, Chun-Sheng Wu, E Laine Wong, Isabella Poli and Annamaria Petrozza; Istituto Italiano di Tecnologia, Italy

Tin halide perovskites have recently garnered attention as low-bandgap materials for photovoltaic and light emitting applications.[1,2] They exhibit self-p doping, which significantly impacts the optoelectronic properties.[3,4] Additionally, the facile oxidation of Sn^{2+} to Sn^{4+} further enhances p-doping within the bulk and introduces non-radiative recombination centers on the surface.[5] Through a combination of photoemission optical spectroscopy and microscopy techniques, we investigate the chemical and optoelectronic heterogeneity, as well as the oxidation process, of tin perovskite processed without and with the addition of SnF_2.
We investigate the role of SnF_2 in determining the complex surface chemistry of tin halide perovskites. We show that oxygen is present on the surface of tin perovskite thin films even in the absence of exposure to ambient air. However, the presence of SnF_2 strongly affects the chemical nature of the found species. Specifically, fluorine acts as scavenger for Sn^{4+} species, effectively capturing available oxygen, which then preferentially binds to tin in the form of SnO_2 only when SnF_2 is added to the precursor solution. Conversely, without the additive, oxygen is mainly due to adventitious species. We thus highlight that the dominance of a single chemical state in the XPS Sn core level does not exclusively indicate Sn^{2+} species in the perovskite form but could also indicate the formation of superficial SnO_2. Through spatial mapping of both the local chemical environment with X-ray Photoemission Electron Microscopy (XPEEM) and photoluminescence mapping, we show that pristine films exhibit a higher accumulation of iodide at the grain boundaries. However, the addition of SnF_2 facilitates the preservation of the perovskite phase and reduces both chemical and optical heterogeneities. Furthermore, we show that exposing the films to ambient air results in analogous surface degradation, regardless of the presence of the additive. We distinguish the process of bulk oxidation and the impact on the optoelectronic properties: an initial increase in the doping density is observed, followed by the increase in long-lived deep defects.

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9:45 AM EL04.14.07
Predicting Organic-Inorganic Halide Perovskite Photovoltaic Performance from Optical Properties of Constituent Films Ruiqi Zhang, Moungi G. Bawendi and Vladimir Bulovic; Massachusetts Institute of Technology, United States

The photovoltaic performance of organic-inorganic halide perovskite solar cells largely depends on the perovskite composition and fabrication process. Most laboratory-scale fabrication methods are not transferable to industrial scale technologies such as slot-die coating or roll-to-roll coating, etc. Hence, it is advantageous to predict solar cell performance before completing the device. Most of the prevalent perovskite solar cell physical models aim to interpret devices’ interlayer recombination, band-bending, and charge injection, while the number of free parameters in these models require extensive measurements and fitting models that hinders their effectiveness as a prediction tool. Here, we present a machine learning (ML) method to take multiple measured device optical spectrums as input and directly predict the device JV curve output (Voc, Jsc and FF), thereby predicting the solar cell efficiency. These Blackbox models allow us to predict the performance of full devices with data that might contain many physical processes which could be too complex to predict accurately with a physics-based model. The model has achieved an averaged prediction percent error less than 5%. By analyzing the prediction weights of each parameter, we identify the optical transmission spectrum and photoluminescence spectral peak information are the most significant parameters that influence the algorithm results. This demonstrated work is the first work in the field to use ML to predict device photovoltaic properties solely from the optical properties of constituent materials and further establishes the potential of small-data-driven ML methods for guiding new designs of perovskite solar cell structures.

10:00 AM BREAK

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