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The Value of Watching How Materials Grow: A Multimodal Case Study on Halide Perovskites

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Abstract

Material synthesis is one of the most important aspect in human kinds endeavor to discover and create new materials for energy applications. One strategy to tailor materials with desired functions in a rational way is by knowing how functions relate to structure, synthetic variables, arrangement of atoms and molecules, and how functions evolve during synthesis. In order to accelerate materials synthesis, discovery, and optimization by 10 times it is the right time now to integrate computational tools, synthesis and characterization. One particular gap realizing this concept is to understand when and how phases form in real time during synthesis which is challenging to asses by existing theoretical frameworks. In addition, transient or metastable phases with positive free energy above the lowest-free energy ground state can be revealed by such real time (*in situ*) measurements. Metastable materials are ubiquitous in condensed matter and can show superior properties compared to their equilibrium form. This essay discusses the value of emerging multimodal *in situ* characterizations exemplified on hybrid halide perovskites. Finally, it is discussed how the implementation of *in situ* measurements can advance the materials science synthesis field as well as their role to enable close-loop feedback control and autonomous synthesis.

[1]

Introduction

Successful synthesis of functional materials is a major engine of the technological advancement of society. This relation is expressed in the fact that historians have named whole periods of time according to the predominant material that was used to advance humankind e.g. bronze or silicon age. The discovery of novel materials however, has historically been based on serendipitous approaches including trial and error experimentation which are costly and time-intensive.[1] Materials by design approaches that tightly integrate computation, synthesis, and characterization are a new paradigm that is gradually developing to rationally design innovative functional materials by predicting and controlling the placement of atoms into larger macroscopic assemblies with desired properties.[2]–[4] Close integration of machine learning on the fly during synthesis to allow for autonomous screening of combinatorial parameter spaces and real time control can change the way we are used to do material synthesis. Realizing this paradigm would not only speed up new materials discovery, shorten the development and optimization time of deploying new materials in commercial products by 10 times,[5] but also make better use of research resources. Towards this goal, further developments spanning new computational tools, materials databases, and synthesis and characterization techniques, need to converge. One approach to rationally synthesize materials, is to leverage in depth understanding of how complex materials assemble, how their properties evolve over time, and how this affects the overall physiochemical macroscopic properties. In this regard, the mission innovation report recently identified the lack of structure-property relationships as one significant gap towards accelerated materials discovery using data-driven approaches.[6]

Much of today's experiments are conducted by measuring single properties one by one *ex situ*, mostly near equilibrium. *Ex situ* measurements (referred to as "black box" synthesis) describe materials or device characterization post fabrication and do for example not allow for insights into crystallization pathways, chemical transformations, as well as the evolution or reciprocal correlation of functional properties that are happening dynamically over time during synthesis and device operation (Figure 1). Some experiments are conducted as break-off experiments where the synthesis is interrupted at different points during the reaction to conduct *ex situ* measurements and to capture snapshots of the reaction. More recently, *in situ* measurements are performed in real time as the material is synthesized i.e. measurements are

conducted during synthesis and one can monitor the possibly intricate interplay between thermodynamic and kinetically driven formation pathways. As an example, *in situ* diffraction measurements during synthesis that span several processing steps can reveal metastable crystalline phases that form as intermediates and then disappear at the end of the reaction.[7]–[9]

With the beginning of modern science there has been a relationship between scientific discovery and innovative tools. Fast data collection was enabled by detector developments with integration times on the order of ~ms and increasing X-ray fluxes available at synchrotron facilities.[10] These developments allow now to follow growth kinetics, structural transformations, and transient changes in soft materials and thin films. Driven by the hypothesis that unveiling reaction pathways and establishing correlations between functional properties will provide new insights into synthesis but requires transformative experimental tools.[11] These new tools are defined by their ability to enable finer observation (including dynamic processes and heterogeneous systems) as well as manipulation on multiple time, length, and energy scales. In this regard, one next stepping stone towards materials by design, discovery of new materials, and real time adaptive control during synthesis are multimodal *in situ* platforms. Such platforms enable monitoring of materials formation, chemical transformations, as well as evolution and interrelation of functional properties by correlative *in situ* measurements. In a next step, this knowledge can be used to deliberately tailor structure and physicochemical properties. On the device level, when performance parameters are monitored simultaneously with material properties such as structure,[12] spin state,[13] and elemental stoichiometry[14] one typically refers to *operando* measurements.
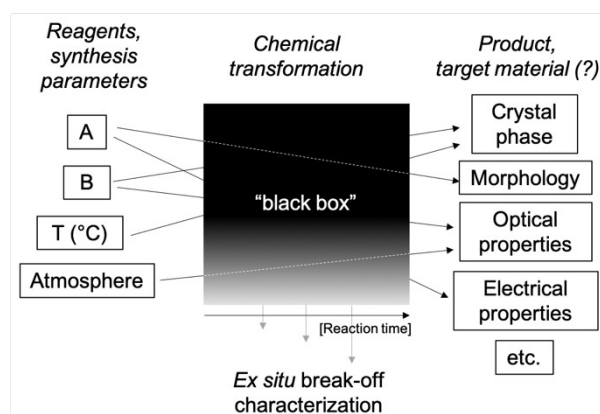
Figure 1. In a black box synthesis, correlations between properties get lost during the chemical transformation of reagents (precursors) to final products. *Ex situ* break-off characterization can provide snapshots at certain times during precursor transformation.

In this Essay, the focus will be on physicochemical evolution of properties that occur on different time and length scales during chemical and structural transformations which can take place during material synthesis and device operation. The term multimodal is used to describe the simultaneous data collection from complementary techniques, also referred to as multi-probe and correlative characterizations. While these measurements are applicable to many research domains including soft matter, polymers, organic and inorganic semiconductors,[15]–[18] halide perovskites are chosen as a model system to delineate advances in synthesis science and establishing relationships by coupling functional properties.

Metal halide perovskites with formula ABX_3 and the most studied prototype material being methylammonium lead iodide ($CH_3NH_3PbI_3$, in short, MAPbI) are typically grown by chemical solution synthesis followed by post-annealing.[19][20] Most approaches either use a one-step or two-step synthesis, where in the former case all elements are mixed together in one pot while in the latter case a PbI_2 film (step 1) is reacted with organic cations and halides (step 2), respectively. Modifications to synthetic routes involve dropping of an orthogonal solvent (antisolvent) during synthesis[21][22] and post-fabrication surface passivation treatments. [23] Most of these synthetic approaches are accompanied by fast precursor transformation or surface reconstruction happening on the ~sub-seconds to few minutes time scales. In general, fast reactions require short acquisition times. Being able to capture these transformations for example via *in situ* X-ray diffraction (XRD) necessitates the use of high brilliance synchrotron light sources for reasonable signal to noise. Many *in situ* XRD measurements have been performed recently to provide mechanistic insights in synthesis and degradation processes of halide perovskites.[24]–[30] Beyond synchrotron-assisted characterization, light, including monochromatic or certain parts of the spectrum, has been successfully used to probe optical properties such as absorption and photoluminescence (PL) during synthesis.[31]–[35] To this end, *in situ* measurements have proven powerful in revealing crystallization pathways, unveiling metastable phases, formation kinetics, and to determine the time window between co-presence of precursor residues with perovskite phase and its decomposition. However, single probe *in situ* measurements do not allow for drawing relationships between for example crystal phase-

[4]

optical properties or crystal phase-morphology as it can be done by more complex *in situ* multimodal studies where multiple probe beams are used simultaneously (Figure 2). While it is not the intention to provide a full review on multimodal *in situ* studies the goal is rather to provide an overview of the depth of scientific insights that can be gained from these correlated measurements. In this regard, this Essay describes several recent works mostly focusing on the synthesis aspect including one example that directly connects synthesis optimization with device output, followed by a brief summary of a few multimodal and *operando* device degradation studies. At the end, a short discussion on future needs, prospects of multimodal *in situ* characterizations, and the perspective of the author is given.
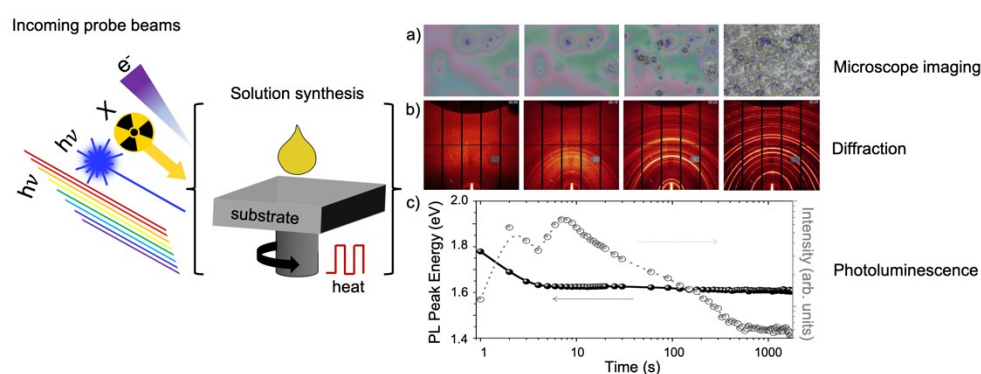

Figure 2. Use of multiple probe beams during synthesis via solution deposition. Evolution of *in situ* a) optical microscope images, b) 2D diffraction, and c) PL signal over time. c) Adapted with permission.[36] Copyright, 2020, Wiley VCH.

1. *In situ* multimodal studies during chemical solution synthesis

In a study by Song et al. the physicochemical evolution of MAPbI with the Pb-salt as a variable was revealed by combined *in situ* XRD, optical imaging, and PL measurements.[36] The multimodal nature of the experiment allowed to correlate structure-morphology and structure-PL emission. Depending on the Pb-salt, different formation kinetics and crystallization pathways can be observed. Use of Pb halide precursors lead to kinetically-driven formation of crystalline precursor phases $(MA)_2(DMF)_2Pb_3I_8$[36] and $(MA)_2PbI_3Cl$[29] when PbI_2 and $PbCl_2$ were deployed, respectively. Presence of the latter precursor phase together with MACl leads to a slow precursor conversion to MAPbI and explains the need for longer heat treatments. In contrast, $PbAc_2$ (Ac = CH_3COO^-) promotes direct halide perovskite

[5]

formation from the colloidal perovskite precursor.[36] Correlating *in situ* diffraction and microscope imaging, it was found that the precursor phase $(MA)_2(DMF)_2Pb_3I_8$ forms during spin coating at room temperature and its microstructure patterns final film morphology. The needle-like microstructure stemming from the fast formation of $(MA)_2(DMF)_2Pb_3I_8$ is undesirable for photovoltaic (PV) applications. Identifying this structure-morphology relationship provides guidance how to suppress it by interfering in the crystallization pathway. One way to do so is the use of an antisolvent which will prevent formation of $(MA)_2(DMF)_2Pb_3I_8$ by inducing the direct formation of MAPbI with homogeneous pinhole free microstructure, provided that the timing of the antisolvent dropping is optimized.[32] Lastly, *in situ* PL measurements during post annealing of MAPbI films were related to diffraction measurements.[36] This correlation revealed that PL measurements are very sensitive to subtle changes appearing during chemical precursor transformation including nucleation, growth and coalescence of MAPbI crystals as well as its decomposition if over annealed. Correlating structure with PL emission allows to reduce the need for precious synchrotron beamtime and consequently paves the way for the use of PL as *in situ* process control.

The majority of synthetic routes to form halide perovskites involves a post-thermal annealing treatment in order to remove excess solvent and enhance grain growth. To reduce processing cost, and limit interface reaction during device fabrication, it is desirable to use room temperature (i.e. no heating) crystallization processes. One possibility to obtain high quality MAPbI films with micron-sized grains and long carrier lifetimes is via additive engineering at room temperature which was demonstrated to result in solar cells with reduced current-voltage hysteresis.[37] Specifically, methylammonium thiocyanate (MASCN) and excess PbI_2 were successfully employed.[37] To understand the effect of additive-assisted perovskite thin film formation Abdelsamie et al. combined *in situ* grazing incidence wide-angle X-ray scattering (GIWAXS) and PL during spin coating and subsequent N_2-drying at room temperature.[38] This study confirmed that MASCN is responsible for the formation of larger aggregates in the precursor solution, it promotes crystallization of perovskite phase, and it leads to a lower nucleation density with larger nuclei size. Further it was shown that nucleation and growth of the perovskite phase is determined by the kinetics and stability of the intermediate phases. Presence of MASCN helps to destabilize the intermediate phases and

thus increases the yield of perovskite phase. These mechanistic findings will benefit further additive engineered process developments.
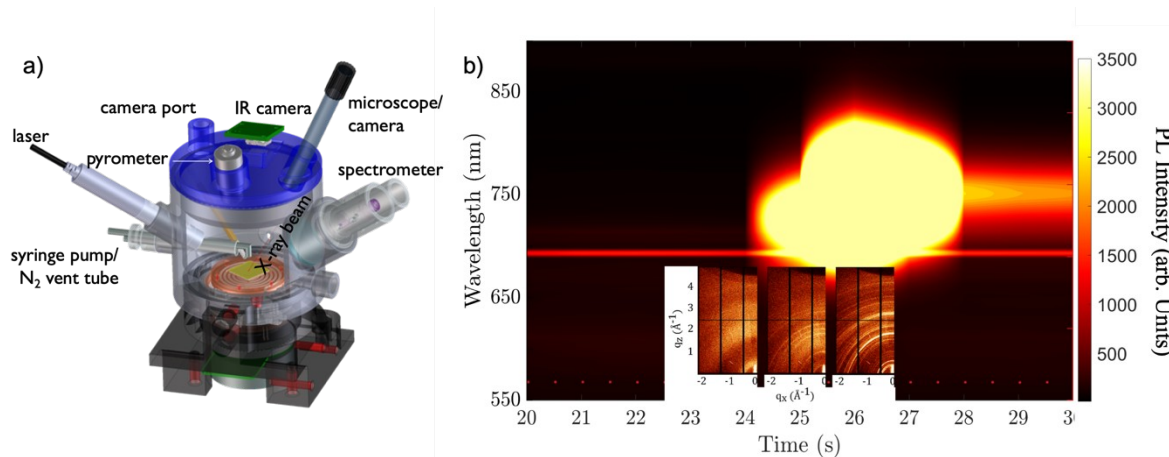

Figure 3. (a) Multimodal *in situ* analytical cell that is attached to a synchrotron source. Reproduced with permission.[39] Copyright 2019, IUCr Journals. (b) Combined PL and 2D GIWAXS data (lower part) capturing the event of the antisolvent dropping, before, during, and afterwards.[40]

The recent work by Pratap et al.,[39][40] made use of an advanced analytical cell (Figure 3a) attached to the Advanced Light Source to conduct multimodal measurements. Similar to the study by Abdelsamie et al.,[38] *in situ* XRD was combined with PL measurements (Figure 3b). The use of a novel analytical cell however, allowed to collect both simultaneously during spin coating and subsequent heating. Interestingly, immediately upon dropping of the antisolvent, the diffuse halos transform into low intensity but distinct diffraction rings corresponding to cubic MAPbI phase. Only one second later, diffraction rings corresponding to the orthorhombic solvent complex ($(MA)_2Pb_3I_8.2DMSO$) appear. Although MAPbI phase is weakly visible in diffraction, complementary PL shows very intense emission signal and a red shift upon antisolvent dropping. This PL signature can be interpreted as initial stages of quantum confined MAPbI nucleation (high PL emission energy), increase in nucleation density, growth, and coalescence.[32][41]

Suchan et al. investigated the effect of Cl-derived MAPbI(Cl) during thin film processing and revealed formation kinetics as well as evolution of optoelectronic properties combining *in situ*

optical UV/Vis reflectance and calibrated PL (Figure 4) together with *ex situ* break-off diffraction, X-ray fluorescence, and time resolved PL.[42] An advantage of these optical *in situ* measurements is the possibility to directly implement the optical probes in the glovebox meaning in the real fabrication environment (Figure 4a). The collection of *in situ* PL and *ex situ* XRD led to the postulation of the existence of $MAPbI_{3-x}Cl_x$ nuclei at the beginning of the growth process which is accompanied by strong PL emission at 1.7 eV. Initial nucleation is followed by a delay time before $MAPbI_{3-x}Cl_x$ films form. From the combination of PL and UV/Vis measurements, the PL quantum yield (PLQY) during drying and annealing was calculated. The PLQY can be directly related to the open-circuit voltage (V_{oc}), an important PV figure of merit. It was found that it reaches a maximum of 1.2 V after 38 min of annealing before it drops monotonically. This example illustrates how *in situ* optical characterization can be applied for process monitoring and engineering to determine an optimized combination of annealing time(s), duration, and atmosphere.

Similarly, Buchhorn et al. built a multimodal setup to follow PL and absorption during solution processing of organic semiconductors including the spin coating and heating steps.[33] Again, absorption and PL data were used to extract the process-step dependent PLQY. In this study a substantial redshift of the PL emission happening before the aggregation process was found and explained by a conjugation length increase of the disordered chains. Following this observation, the important aspect of chain planarization before the aggregation process was highlighted. It is emphasized that the latter two studies solely make use of optical probes and demonstrate the great potential to provide novel insights on fundamental film formation processes without the need of synchrotron facilities.
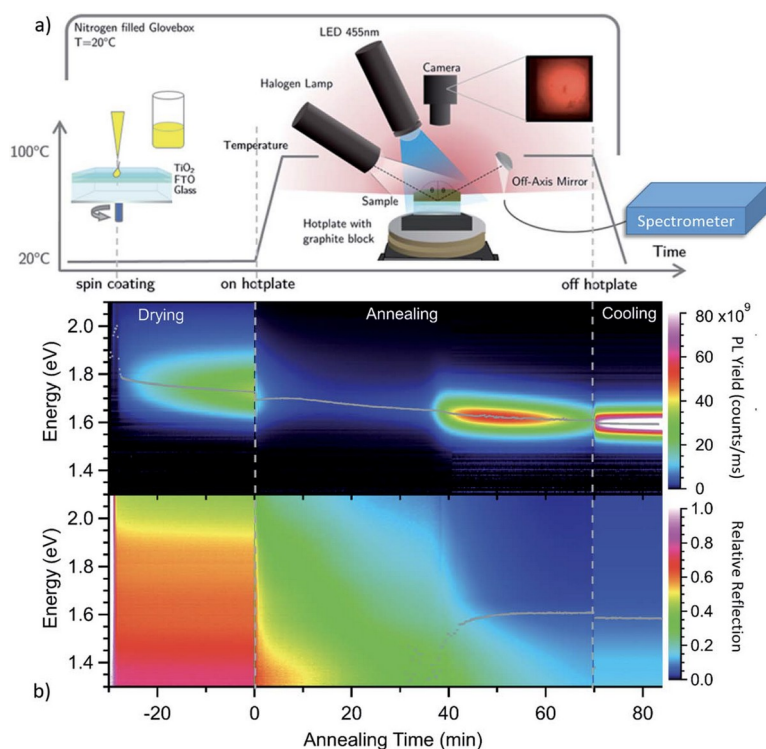
Figure 4. a) Schematic illustrating optical characterization during synthesis performed in the glovebox. b) *In situ* PL Yield and reflection data as a function of processing step. Reproduced with permission.[42] Copyright 2020, Royal Society of Chemistry.

Going one step further, Alsari et al. performed a multimodal study to establish a direct relationship between structure evolution during synthesis and PV device performance.[43] The authors combine simultaneous synchrotron XRD with *operando* current-voltage measurements while perovskite films (MAPbI and mixed cation and mixed halide perovskite compositions) are grown on interdigitated back contact structures. It was found that semiconducting properties evidenced by high V_{oc} set in at the very early stages of perovskite formation from the solution precursor. In addition, the maximum V_{oc}'s were found before the full precursor conversion to perovskite phase and was explained by a self-passivation of defects in the presence of amorphous precursor material. In contrast, the short-circuit current (J_{sc}) develops a maximum when the precursor is fully converted to perovskite phase such that there is an uninterrupted path for charge carriers to reach the contacts. Both, *in situ* structural and optical information obtained at different reaction temperatures can be used to assess formation kinetics of materials under study (e.g. Ref. [42][43]).

2. Multimodal *operando* studies during device characterization

Multimodal studies are highly relevant to provide mechanistic insights during halide perovskite device degradation. The understanding of failure mechanisms in halide perovskite devices presents one of the current bottlenecks towards long-term stability and commercialization. As a side note, degradation/decomposition can to some extend be regarded as the opposite of synthesis/formation and thus, several of the above mentioned and recently established experimental capabilities can be applied to tackle this challenge. For example, Schelhas et al. were interested in how the tetragonal-to-cubic phase transition, which likely occurs in MAPbI solar cells under operating conditions (~54 °C[44]), affect device function.[12] Combining temperature-dependent XRD with device performance measurements a decoupling of long-range crystalline order from device parameters was found. This indicates that optoelectronic properties are mostly governed by the local structure which continues to be characterized by uncorrelated and dynamic rotations of the PbI_6 octahedra. In a different multimodal study, Schelhas et al. provide insights into operational stability of mixed cation perovskites in order to correlate phase segregation as well as loss of crystallinity with device performance.[45] The major findings suggest that stability at ~50% relative humidity is related to device architecture, chemical composition of the active perovskite layer and importantly, the processing temperature of the perovskite layer to ensure ideal cation mixing. A gradual transformation of the photoactive perovskite ☐-phase to the non-perovskite hexagonal ☐-phase was correlated to a drop in PV performance and particularly the J_{sc}, due to the wide bandgap of the ☐-phase.
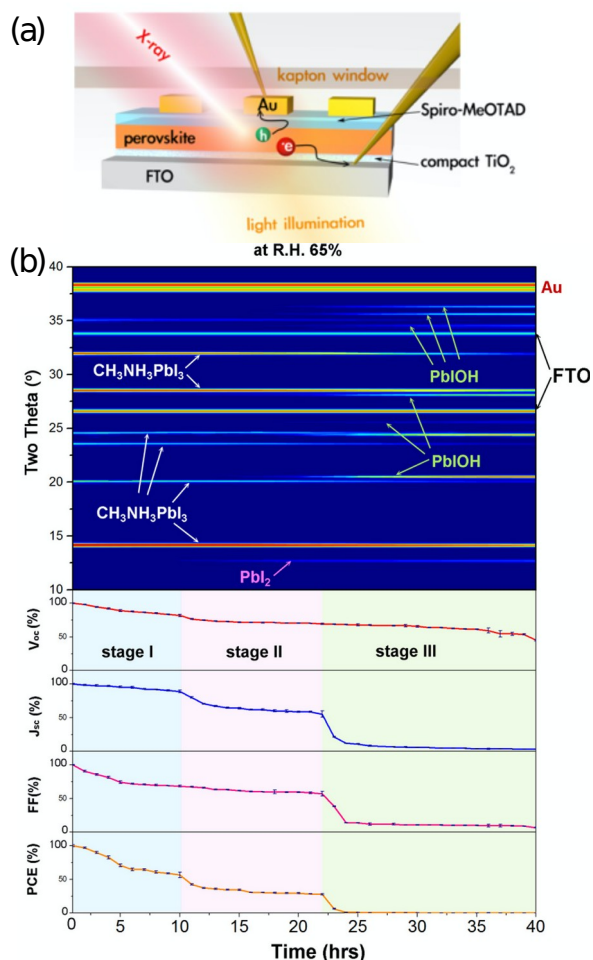
Figure 5. a) Schematic illustration of the *in situ* cell allowing for simultaneous XRD and device measurements. b) Correlation of XRD data (top) with device parameters (FF = fill factor, PCE = power conversion efficiency) measured over time at 65% relative humidity and 25 °C. Modified with permission. [46]. Copyright 2017, American Chemical Society.

Using *in situ* XRD and ellipsometry, Leguy et al. were able to measure the reversible hydration of MAPbI films, single crystals, and full devices.[47] Upon exposure to water vapor, colorless monohydrate MAPbI·H_2O forms which has a bandgap of 3.1 eV and leads to a >90% reduction in J_{sc} as well as a ~20% loss in V_{oc}. By keeping the device in dry N_2 for several hours this process is reversible and device losses fully recover.

As a last example in this section to demonstrate how multimodal *operando* measurements can inform device degradation mechanisms, Chen et al. performed *in situ* XRD and X-ray absorption spectroscopy while measuring perovskite device performance.[46] Figure 5a illustrates the setup, and Figure 5b the correlation between the evolution of XRD patterns and

[11]

PV parameters. The authors distinguished three different degradation stages. In the first stage, the power conversion efficiency (PEC) gradually dropped by > 25% although no significant change in the diffraction signal was observed. In the second stage, PbI_2 was observed as a decomposition product of MAPbI mostly affecting J_{sc} (and V_{oc}). After 23 h, in stage three, the PCE suddenly dropped to ~2% accompanied by major losses in fill factor (FF) and J_{sc}. *In situ* diffraction showed appearance of PbIOH phase which possibly triggered significant device deterioration. In addition, formation of PbIOH was only found in devices where spiro-MeOTAD was present but not if PTAA or P3HT were used as hole selective layers.

3. Perspective and Outlook

Understanding synthesis, tailoring material properties for certain functions, discovery of new materials, and ultimately, autonomous synthesis with adaptive control, would greatly benefit from the development of advanced correlative tools that allow to follow synthetic reactions in real time. As exemplified above, *in situ* multimodal measurements can help to establish composition-structure-property-performance relationships, follow their trajectory from initial to final state, and simultaneously reveal metastable phases. Such results from *in situ* studies can add value when integrated into computationally driven efforts predicting synthesis to test and further develop theoretical frameworks.

Bringing together synthesis and characterization to happen at the same time at the same place provides opportunities to advance our knowledge of underlying physicochemical processes. An important challenge to consider for experimental design at a synchrotron is the building of deposition and synthesis capabilities that are comparable to state-of-the-art lab tools or commercial tools. The synthesis environment for example can play a significant role on the experimental outcome. Solution synthesis is often conducted in dedicated gloveboxes or fume hoods with controlled environments which need to be mimicked in customized setups operated at beamlines to collect meaningful data.

Although the high spatiotemporal resolution characterization at synchrotron sources allows for real-time insights over multiple time and length scales it is enabled by high X-ray fluxes (number of photons per second per unit area) which can damage the structure under study and thus, need to be considered in the experimental design steps. Clearly, there are unique advantages of synchrotron-based characterization[10][48] but such large-scale facilities are not

readily available on a day-to-day basis for most researchers. In the context of this Essay with emphasis on multimodal characterization of synthesis and device behavior, one strategy can be for example the correlation of synchrotron-based diffraction with optical measurements such as PL or UV/Vis. The latter can be conducted in the lab and the information from these correlations can be used in follow-up studies by the broader community. Alternatively, *in situ* optical measurements can be combined with *ex situ* break-off diffraction measurements conducted on lab instruments as nicely demonstrated in Ref. [42]. Optical, lab-based measurements provide the opportunity to be conducted during synthesis in the typical fabrication environment such as a glovebox.[32][42] Ideally, these *in situ* optical measurements conducted in controlled environment can be cross-checked with the same measurements performed at the beamline.

An imperative requirement for *in situ* and *operando* studies is the awareness of potential probe-induced modifications. Probe beam exposure can lead to a significant accumulation of energy onto a comparably small spot on the sample which can interfere with the processes under study. The extend of interference depends on the beam energy, flux, and exposure time. X-ray beam damage for example is often accompanied by a decrease in scattering intensity[49] while exposure to visible light can result in reversible and irreversible changes due to a complex interplay between excitation energy and duration, ion migration, and sample damage from local thermal effects.[31][50] Careful experimental design and cross checks are needed for each individual system under study.

Certainly, *in situ* multimodal capabilities are powerful but represent (only) one piece towards materials by design, autonomous synthesis with adaptive control, and discovery of metastable materials. As necessary next steps, synthesis, characterization, and computation, have to be closely connected by an interface that translates data into the respective algorithm-conform data format. Similarly, the output of the algorithm has to be translated to be readable by a particular instrument in order to create a closed feedback loop to explore synthesis variables and functions thereof (i.e. experimental outcomes). The tuples of synthesis variables and experimental outcomes can be fed into a Gaussian process regression (GPR) algorithm for example to build a surrogate model with associated uncertainties. Both are then used to find optimal new synthesis variables in order to explore the space efficiently or to focus on a specified target, such as a desired material characteristic.[51]–[53] GPR is a Bayesian technique that learns a prior probability density function over functions. The training can be based solely

[13]

on data (physics-agnostic) or can take advantage of many kinds of physics and general domain knowledge on the particular synthesis to inform the next experiments. Another approach that had been recently shown to be successful in controlling materials self-assembly is evolutionary reinforcement learning which was used to training neural networks.[54] Realizing the opportunities along the way towards materials by design, several studies were recently published in the field of halide perovskites combining high throughput synthesis and machine-learning (ML)-assisted data analysis to identify novel functional materials.[55]–[58] Moving to the next level in accelerating synthesis and fully exploiting the advancements of automated and autonomous synthesis it can be advantageous to implement *in situ* diagnostics in ML-assisted high throughput experiments that will allow for real-time monitoring and data-driven stirring of the experiment. The advancement of characterization techniques and computational frameworks together with implementation of automated workflows can change the way we are doing synthesis at the moment. Such a paradigm shift can accelerate synthesis science and open new research directions.

Conflict of Interest

The authors declare no conflict of interest.

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