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Gas-Induced Formation/Transformation of Organic–Inorganic Halide Perovskites

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S Supporting Information

ABSTRACT: The recently discovered gas-induced formation/transformation (GIFT) of organic—inorganic halide perovskites (OIHPs) represents unprecedented phenomena. The GIFT phenomena have not only revealed surprising properties of the fascinating OIHP materials but also showed tremendous promise in various applications, including solar cells, optoelectronics, sensors, and beyond. After briefly reviewing recent progress in the exploration and understanding of GIFT, a perspective on the future research directions in this area is provided herein. Also provided is a discussion on the significance of future mechanistic studies in unraveling the rich chemistry and materials science underlying GIFT and in exploring more potential applications.

rganic-inorganic halide perovskites (OIHPs) are a family of hybrid crystalline materials with the general formula ABX₃, where A is an organic cation, such as $CH_3NH_3^+$ (methylammonium or MA⁺) or $HC(NH_2)_2^+$ (formamidinium or FA⁺), B is a metal cation such as Pb²⁺ or Sn²⁺, and X⁻ is a halide anion such as I⁻, Br⁻ or Cl^{-,1,2} Figure 1A illustrates the crystal structure of the most typical MAPbI₃ OIHP. Due to the wide tunability of properties in this amazing family of materials, OIHPs have shown great promise in various applications including solar cells, light-emitting devices, spintronics, sensors, and radiation detectors.^{2,3} In particular, the use of OIHPs as light-absorber materials in the emerging perovskite solar cells (PSCs) has been catalyzing a revolution in the photovoltaics (PVs) field.¹⁻⁴ The OIHP family has been expanded to embrace larger organic cations (e.g., butylammonium (BA^+) , phenylethylammonium (PEA^+)) and a variety of metal cations (e.g., Cu2+, Eu3+, Sb3+, Bi3+) in the perovskite structure, resulting in OIHPs with not only variation in structural dimensionality (3D, 2D, 1D, 0D, or fractional dimensionality) but also chemistry (e.g., A2BX4, A2B3X9, ABX4).^{2,5} Such vast compositional and structural space has been rarely seen in other material systems, endowing OIHPs with unprecedented chemical versatility and transformative behavior. It is in this context that the gas-induced formation/transformation (GIFT) phenomena in OIHPs were recently discovered and is being developed. The surprises and the new science emerging from the studies of GIFT phenomena so far are leading to the rise of a new research paradigm in chemistry and materials science with the potential for broad impact.

The crystal structure of OIHPs is based on an inorganic framework because the major bonds that hold the OIHP



Organic-inorganic perovskites are a family of materials that exhibit microstructural features of conventional polycrystalline "hard" materials but are also "soft" like polymers.

structure together result from the strong B-X ionic/covalent interactions, whereas the ionic/covalent/hydrogen bond between the organic A cations and X anions is relatively weak. Furthermore, there is no coordinate/covalent bonding between the metal (B) and the carbon within A-cation, and thus, OIHPs are not considered to be organometallic compounds.⁶ This inorganic-based framework of the OIHP structure is responsible for OIHPs having microstructures consisting of typical grains and grain boundaries (Figure 1D) that are similar to those of typical "hard" inorganic materials such as ceramics (e.g., Al₂O₃, SiC, TiO₂, etc.). For example, Figure 1E is a typical transmission electron microscope (TEM) image showing MAPbI₃ grains and grain boundaries, where a proliferation of defects is observed within the grains. The latter is due to the intrinsic low formation energy of the defects in OIHPs.⁷ Thus, the existence of these defects, as well as the ultrafast organic-ion rotation dynamics^{8,9} (Figure 1B) and ion mobility¹⁰ (Figure 1C), is likely responsible for the apparent "soft" nature of OIHPs. In fact, the low hardness and elastic modulus of OIHPs in the

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Figure 1. Schematic illustration showing (A) the crystal structure of the most typical MAPbI₃ OIHP (purple = I; green = Pb; center = MA) and (B) the rotation dynamics of the polar MA⁺ cation. (Adapted with permission from the Nature Publishing (ref 8.) (C) Schematic illustration showing ion-transport pathways in OIHPs. (Adapted with permission from the Nature Publishing (ref 10.) Typical (D) SEM and (E) TEM images of a MAPbI₃ OIHP thin film. (Adapted with permission from the Royal Society of Chemistry (refs 12 and 13.) (F) Results from nanoindentation experiments on MAPbI₃, MAPbBr₃, and MAPbCl₃ OIHP single crystals, showing Young's modulus values ranging from 10 to 20 GPa. (Adapted with permission from the Royal Society of Chemistry (ref 11.)

ranges of 0.3–0.5 and 10–20 GPa, respectively, relative to inorganic ceramics, confirm their relatively soft mechanical properties (Figure 1E).¹¹ All of these soft signatures endow OIHPs with high chemical reactivity, which is responsible for the GIFT phenomena. However, the hard microstructure of OIHPs also plays an important role in the GIFT phenomena. Thus, OIHPs represent a true, unprecedented bridge between the soft and hard materials from chemistry and materials science perspectives.

The discovery of methylamine gasinduced phase/morphology transformation behavior of OIHPs has invoked new thinking into this fascinating family of materials and the synthetic approaches for processing them.

It was in 2015 that the discovery of methylamine (CH₃NH₂ or MA⁰) induced phase/morphology transformation of the MAPbI₃ OIHP was first reported by Zhou et al.¹⁴ As shown in Figure 2A, when two MAPbI₃ single-crystals are exposed to MA⁰ gas at room temperature (RT), the crystals become liquefied through uptake of the MA⁰ gas molecules and, eventually, merge into one liquid sphere. It is also found that the as-formed liquid phase is metastable only under MA⁰ gas. Upon removal of the MA⁰ gas atmosphere, the intercalated MA⁰ molecules are released from the liquid, inducing recrystallization of the MAPbI₃ OIHP. In that study, a chemical formula of MAPbI₃·xCH₃NH₂ was used to describe the liquid intermediate.¹⁴ That is because the x value had not been accurately determined, and it can also be dependent on the exact MA⁰ partial pressure. Nevertheless, by simply comparing the weight of the raw MAPbI3 and as-formed MAPbI3. xCH₃NH₂ liquid, a rough x value of \sim 3 has been suggested in

order to form a MAPbI₃·xCH₃NH₂ phase in the liquid state.¹⁴ While the MA⁰-induced MAPbI₃ \rightarrow MAPbI₃·*x*CH₃NH₂ \rightarrow MAPbI₃ chemical conversion is slow (up to hours) in the case of millimeter-sized single crystals (Figure 2A), it is very rapid (seconds) in the case of thin films. This is due to the following two structural features of thin films that allow rapid ingress/ release of MA⁰ throughout the MAPbI₃ phase: (i) MAPbI₃ thin films have a nanoscale thickness and a large surface to volume ratio and (ii) typically, solution-processed MAPbI₃ thin films also contain numerous pinhole/void defects as well as a high-density grain-boundary network. In this context, a simple method involving MA⁰ gas treatment was then invented to create uniform, smooth MAPbI3 thin films, as shown schematically in Figure 2B. In this method, a MAPbI₃ thin film of poor quality (rough, incomplete coverage) is first deposited using a nominal solution-processing method, and it is subsequently exposed to MA⁰, converting it into a clear MAPbI₃. xCH_3NH_2 liquid film (optically bleached) within 2 s. It appears that once it forms, the MAPbI3:xCH3NH2 liquid spreads immediately due to surface tension. The film is then removed from the MA⁰ gas atmosphere, and a shiny (smooth, full coverage) MAPbI₃ thin film is readily crystallized. (See the Supporting Information for a video of this process.) Figure 2C compares the morphologies and microstructures of the MAPbI₃ thin film before and after the MA⁰ gas treatment, which shows the striking defect-healing effect of the MA⁰ gas treatment. Prior to this study, Zhao et al.¹⁵ reported their findings on the optical bleaching phenomenon of MAPbI₃ upon exposure to a different gas, NH₃, and they identified a MAPbI₃:xNH₃ intermediate that leads to this phenomenon. It was later revealed by Zhou et al.¹⁴ that the MAPbI₃·xNH₃ intermediate still exists in the solid state, and therefore, there is no significant morphology improvement (healing) that occurs in the MAPbI₃ thin film when NH₃ gas is used for the treatment. In parallel studies, it was shown that treating MAPbI₃ with other amine gases such as ethylamine $(C_2H_5NH_2)$ and butylamine $(C_4H_9NH_2)$ results in



Figure 2. (A) In situ optical microscope observation of MAPbI₃ single crystals interacting with MA⁰ gas at RT. (Adapted with permission from Wiley (ref 14). (B) Schematic illustration of the process of healing defects in the MAPbI₃ thin film using MA⁰ treatment. (Adapted with permission from Wiley (ref 14). (C) Comparison of the surface morphology of the MAPbI₃ thin film before and after MA⁰ gas treatment (Adapted with permission from Wiley (ref 14).

the formation of liquid intermediates, which heal the thin films, although the MAPbI₃ phase is not recovered upon removal of the amine gas atmosphere (discussed later).¹⁴ These observations highlight the key role of the liquid state of MAPbI₃. xCH₃NH₂ on the defect-healing behavior of the MAPbI₃ thin film and the subsequent recovery of phase-pure MAPbI₃ OIHP.

Later, Jen et al.¹⁶ studied the effect of MA⁰ vapor pressure $(P_{\rm MA})$ in the gas atmosphere on the phase/morphology transformation behavior of MAPbI₃ OIHP. It was shown that film healing can occur at high P_{MA} (Figure 3A), while at low P_{MA} , the morphology change is subtle (Figure 3B). It is clear that P_{MA} affects the x value in the MAPbI₃·xCH₃NH₂ as its formation is based on the MA⁰ equilibrium established at the gas-liquid interface. It is most likely that at low P_{MA} , the x value in MAPbI₃·xCH₃NH₂ is relatively small (<3), in which case the solid to liquid state change does not occur during the chemical conversion of MAPbI₃ to MAPbI₃·xCH₃NH₂. In another report, Jacobs et al.¹⁷ studied the phase transition of MAPbI₃ thin films under a constant MA⁰ gas atmosphere as a function of annealing temperature. It is revealed in Figure 3C that above 55 °C the liquid-to-solid transition of the MAPbI₃. xCH₃NH₂ thin film starts to occur under a constant MA⁰ gas atmosphere. This is actually consistent with the results from Jen et al.¹⁶ A higher annealing temperature will increase the vapor pressure of intercalated MA⁰ in the MAPbI₃·xCH₃NH₂ thin film, and in order to maintain the MA⁰ equilibrium at the

gas-liquid interface, some of the MA⁰ molecules inside of the MAPbI₃·xCH₃NH₂ thin film will be released, resulting in solid MAPbI₃·*x*CH₃NH₂ with a relatively small *x* value. Jacobs et al.¹⁷ have further proposed a 2D phase diagram that illustrates comprehensively the phase transition from MAPbI₃ to MAPbI₃. xCH₃NH₂ based on two variable parameters: annealing temperature and P_{MA} . However, this proposed 2D diagram is somewhat tentative because careful control over the exact parameters is needed to construct an accurate phase diagram. Nevertheless, the proposed scheme of the MAPbI₃-MAPbI₃. xCH₃NH₂ phase diagram provides clues for exploring the optimal processing routes of MA⁰ gas treatment to achieve the desired thin-film microstructures of MAPbI₃. Indeed, by employing the processing roadmap shown in Figure 3D, Jacobs et al.¹⁷ have successfully prepared full-coverage MAPbI₃ thin films with grain sizes up to several tens of micrometers (Figure 3E), compared to the ~100-nm grains in the MAPbI₃ using all-RT $MA^{\tilde{0}}$ gas treatment. In another successful effort, Jiang et al.¹⁸ performed MA⁰ gas treatment on a smooth raw MAbI₃ thin film at a constant elevated temperature and observed significant reduction in defects at grain boundaries as well as grain-boundary grooving (Figure 3E).

Because MA^0 is one building block of the MAPbI₃ OIHP, it is natural to think how MA^0 participates in the formation process of MAPbI₃ as a precursor phase. In order to meet the MAPbI₃ stoichiometry, Pang et al.¹⁹ have determined that the HPbI₃ compound can serve as the counterpart precursor phase of MA⁰ and studied the interaction behavior of a HPbI₃ crystal with MA⁰ gas at RT (Figure 4A). It is interesting, and somewhat surprising, that the first reaction product of HPbI₃ interaction with MA⁰ gas is the MAPbI₃·xCH₃NH₂ liquid, instead of the MAPbI₃ solid. Pang et al.¹⁹ proposed that excess MA⁰ molecules are taken up as soon as the MAPbI₃ forms via the combination reaction of HPbI₃ and MA⁰. This is reasonable considering that the as-nucleated MAPbI3 can be at the (sub)nanoscale, which enables extremely rapid MA⁰ ingression and induces direct conversion of HPbI₃ to MAPbI₃·xCH₃NH₂. To support this claim, Pang et al.¹⁹ further studied the interaction of HPbI3 with MA⁰ gas at an elevated temperature $(150 \ ^{\circ}C)$ when MAPbI₃ could uptake a negligible amount of MA⁰, as discussed above. The results in Figure 4B show the gradual conversion of HPbI₃ to MAPbI₃ with the original morphology well-preserved. In another experiment by Zong et al.,²⁰ NH₄PbI₃ compound was chosen as the precursor counterpart of MA⁰, instead of HPbI₃. The reaction between NH₄PbI₃ and MA⁰ is expected to produce MAPbI₃, as well as a byproduct, NH₃ gas. Here, Zong et al.²⁰ observed morphologypreserving conversion of NH₄PbI₃ to MAPbI₃ prior to the formation of the MAPbI₃·xCH₃NH₂ liquid (Figure 4C). Because NH₃ exhibits a higher vapor pressure than MA⁰, the simultaneously produced NH₃ gas resists the ingression of excess MA⁰ into the as-formed MAPbI₃ until the depletion of NH₄PbI₃ phases is complete. This effect is similar to the role of heat in the HPbI₃ to MAPbI₃ conversion at high temperatures. Another consistent finding is reported by Raga et al.,²¹ who monitored the formation process of MAPbI₃ by reacting a PbI₂ thin film with MA^0 in the presence of water (H_2O) or ethanol (C₂H₅OH). They observed a morphology-preserving conversion of PbI₂ to MAPbI₃ before the uptake of excess MA⁰, once again due to the byproducts associated with the MAPbI₃ formation reaction. On the basis of all of this evidence, the MA⁰-induced formation/transformation of MAPbI₃ from its precursor phases is illustrated in Figure 4D, which involves two



Figure 3. TEM images of MAPbI₃ thin films (on carbon-coated TEM grids) before and after (A) high-pressure MA⁰ gas exposure and (B) lowpressure MA⁰ gas exposure. (Adapted with permission from the Royal Society of Chemistry (ref 16.) (C) Photographs of MAPbI₃ thin films that are exposed to a N₂ or MA⁰ gas atmosphere for a period of time at constant temperature. Top row: images of films after 5 min in N₂. Middle row: image of the films immediately (<1s) after exposure to MA⁰. Bottom row: images of the films after 30 s in MA⁰ gas. The scheme at the bottom shows the proposed 1-D phase diagram of MAPbI₃ (solid)–MAPbI₃·CH₃NH₂ (liquid) under a constant MA⁰ gas atmosphere. (Adapted with permission from the Royal Society of Chemistry (ref 17.) (D) Proposed 2D phase diagram showing MAPbI₃–MAPbI₃· CH₃NH₂ interconversion according to the MA⁰ gas pressure and temperature conditions. (Adapted with permission from the Royal Society of Chemistry (ref 17.) (E) SEM images of a MAPbI₃ OIHP thin film before and after a designed MA⁰ gas treatment process. The processing route (1 \rightarrow 2 \rightarrow 3 \rightarrow 4) is shown in (D), and MAPbI₃ thin films with extra-large grains are formed. (Adapted with permission from the Royal Society of Chemistry (ref 17.) (F) SEM images of a MAPbI₃ thin film before and after MA⁰ gas treatment at a constant high temperature (150 °C). (Adapted with permission from the Royal Society of Chemistry (ref 18.)

chemical conversion steps. The first step is MAPbI₃ formation, which entails morphology-preserving conversion from the precursor phase (HPbI₃, NH₄PbI₃, or PbI₂) to MAPbI₃. In the second step, the reversible phase transition of MAPbI₃ \rightarrow MAPbI₃·*x*CH₃NH₂ \rightarrow MAPbI₃ occurs upon rapid response to the change in P_{MA} , which transforms the morphology to a more pristine state owing to the liquid intermediate. In the absence of any byproducts or heat that can resist the excess MA⁰ ingression in the first-step chemical reaction, these two steps can occur simultaneously, resulting in the appearance of direct conversion of the precursor phase to the MAPbI₃·*x*CH₃NH₂ liquid.

Such MA⁰-induced formation/transformation of MAPbI₃, either from raw, nominally processed MAPbI₃ thin films or from predeposited inorganic precursor thin films, opens up a new, versatile OIHP thin films processing concept, which is radically different from previous efforts that mainly focused on controlling crystallization for OIHP from solutions. Furthermore, protocols such as incorporating additives and manipulating the reaction byproducts can be promising for achieving desirable film structures and compositions through the MA⁰based process and, thus, unlocking a hitherto unexplored, rich research space.

Research efforts in OIHPs solution processing and microstructure tailoring in the past have primarily emphasized the MAPbI₃ composition. It has been recognized that the solution crystallization kinetics/mechanisms of OIHPs can be extremely sensitive to the composition of OIHPs.²² Thus, for OIHPs other than MAPbI₃, there is a need for reoptimizing processing



Figure 4. In situ optical microscope observation of HPbI₃ crystals interacting with MA⁰ gas at (A) RT and (B) 150 °C. (Adapted with permission from the American Chemical Society (ref 19.) (C) In situ optical microscope observation of the NH_4PbI_3 crystal interacting with MA⁰ gas at RT. (Adapted with permission from Wiley (ref 20.) (D) Schematic illustration showing the process of OIHP formation and transformation upon interaction of HPbI₃/NH₄PbI₃ precursor phases and MA⁰ gas. (Adapted with permission from Wiley (ref 20.)

Morphology-preserving composition switching of OIHPs induced by gases offers a way to synthesize new OIHP materials without having to reinvent specific synthetic methods.

parameters based on trial-and-error or even reinventing new synthetic methods, which can be time-consuming. In this context, the most typical example is that of formamidinium lead triiodide (FAPbI₃) OIHP, which is emerging as a more promising material owing to its more ideal bandgap and inherently superior thermal stability compared to MAPbI₃.²³⁻²⁵ However, synthesis of high-quality FAPbI₃ OIHP thin films is typically accompanied by formation of the nonperovskite polymorph (δ -FAPbI₃). To overcome this issue, as shown in Figure 5A, Zhou et al.²⁶ simply exposed MAPbI₃ thin films to formamidine (HC(=NH)NH₂ or FA⁰) gas at an elevated temperature (150 °C). The organic cation displacement reaction of MAPbI₃ with FA⁰ forms FAPbI₃ and MA⁰ gas. It is expected that the heat-treatment condition and MA⁰ gas byproduct both contribute to the resistance of the ingression of excess FA⁰ molecules into the as-formed FAPbI₃ OIHP. Accordingly, the original morphology of the starting MAPbI₃ thin film is perfectly preserved as the thin-film phase undergoes rapid transformation of MAPbI₃ to FAPbI₃ OIHP (Figure 5B,C). This is, in fact, consistent with the morphology-preserving features that are observed in the HPbI₃ to MAPbI₃ conversion at elevated

temperature (150 °C) and NH_4PbI_3 to $MAPbI_3$ at RT. Another key to the success of this approach is the redox nature of the reaction that involves the oxidation of FA^0 to FA^+ and the reduction of MA^+ to MA^0 , which enables rapid and robust conversion kinetics.

Similar to the A cation displacement, the X anion displacement is also possible with the use of halogen (X_2) gases. Solis-Ibarra et al.²⁷ showed that halogen gas can displace the halide ions in OIHPs at RT while maintaining the material's crystallinity. As expected, the X2 gas must possess a higher positive reduction potential than the halide in the OIHPs (Figure 5D) for redox-type conversion reactions to occur. Using this X₂ gas treatment, bromide and/or chloride OIHPs are easily obtained from iodide OIHPs. It is also interesting to see that the overall morphology of the iodide OIHPs is mimicked overall in the final bromide and/or chloride OIHPs (lower panel in Figure 5D), although there are variations in the grain sizes. We envision that by tuning the temperature of the X2-gas treatment the exact morphology-preserving feature of OIHP composition switching, akin to the case of the FA⁰ gas treatment, can be achieved. In that same study, the reactivity with X₂ gases was extended to the organic layers in these 2D OIHPs.²⁷ Figure 5E illustrates that the alkene groups of the BEA⁺ cations in the 2D (BEA)₂PbBr₄ OIHP can capture Br₂ gas molecules, reversibly forming dibromoalkanes, which modifies the organic cations in the 2D OIHP.²⁷

In another study, Chen et al.²⁸ demonstrated that the halide switching in OIHPs occurs with gaseous HX through ion-exchange reactions, as illustrated in Figure 5F. Here, owing to the



Figure 5. (A) Schematic illustration showing the morphology-preserving OIHP composition switching of MAPbI₃ to FAPbI₃ based on the cation displacement reaction of MAPbI₃ thin films with FA⁰ gas at an elevated temperature. (Adapted with permission from the America Chemical Society (ref 26.) (B) Comparison of the raw MAPbI₃ thin film and the as-converted FAPbI₃ thin film using the process in (A). (Adapted with permission from the America Chemical Society (ref 26.) (C) Evolution of XRD patterns and UV–vis spectra of thin films, along with the progression of MAPbI₃ to FAPbI₃ conversion. (Adapted with permission from the America Chemical Society (ref 26.) (D) Schematic illustration showing OIHP halide switching with halogen gases at RT. The lower panel shows the OIHP morphologies for corresponding compositions. (Adapted with permission from the Royal Society of Chemistry (ref 27.) (E) Schematic illustration showing composition switching of (BEA)₂PbBr₄ to (BEA–Br₂)₂PbBr₄ and (BEA–Br₂)₂PbCl₄ under Br₂ and Cl₂ gases at RT, respectively. (Adapted with permission from the Royal Society of Chemistry (ref 27.) (F) Interconversion of MAPbBr₃ and MAPbCl₃ OIHPs upon exposure to HX gases at RT. (Adapted with permission from the America Chemical Society (ref 28.)

nonredox nature of this reaction, mutual conversions among three MAPbX₃ (X = I, Br, and Cl) halides are realized; however, close-to-complete conversion requires much longer time (>100 h). It is interesting that this HX gas treatment approach can be used to achieve single-crystal to single-crystal transformation from bromide OIHP to its chloride counterpart.²⁸ Many of the GIFT phenomena have rarely been observed in other material systems, indicating the existence of unusual chemical/physical interactions between the gas phases and OIHPs owing to the unique compositions and materials structures/properties of OIHPs (Figure 1). In order to have a complete understanding of the GIFT phenomena, mechanistic

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Detailed understanding of the mechanisms underlying the GIFT phenomena is still lacking. It is important to understand whether and how established chemistry and materials science principles are at play. It is also likely that new science will evolve through mechanistic studies of GIFT.

studies at the atomic, molecular, and nanometer scales are called for, in particular focusing on the following topics.

Gas-Induced OIHP "Melting". Neutral $R-NH_2$ gas molecules (MA⁰, EA⁰, BA⁰, etc.) interact with OIHPs, forming intermediates in the liquid state. While the intercalation of neutral

species into a solid crystalline framework is common in the host-guest chemistry, it is remarkable that the R-NH₂ molecules disrupt the OIHP crystalline structures to a completely disordered state, that is, liquid. There are four common hostguest interactions: hydrogen bonding, van der Waals forces, ionic bonds, and hydrophobic interactions.²⁹ It remains to be determined which of these chemical forces play role(s) in the "melting" and whether there are any new dominant chemical forces in this process. As discussed earlier, a number of factors such as the nature of the R-group in R-NH₂, vapor pressure, temperature, and byproduct(s) will affect the OIHP melting. On the other hand, the bonding in the OIHP crystal is strongly dependent on its composition. While MAPbI₃ OIHP has been studied as a representative case, it is also interesting to explore the influence of the OIHP composition on the melting. By experimentally investigating these factors, a comprehensive map of the OIHP melting behavior can be obtained. Theoretical modeling also becomes important for providing insights into



Figure 6. (A) Preliminary theoretical modeling of the interaction of $MAPbI_3$ with MA^0 molecules forming possible new clusters based on molecular dynamics simulations. (Courtesy of Dr. M.-G. Ju, and Prof. X. C. Zeng of University of Nebraska—Lincoln.) (B) Nonclassical crystallization pathways of bulk crystals from ions, atoms, and molecules. (Adapted with permission from the American Association for the Advancement of Science (ref 32.) (C) Proposed mechanisms of the morphology-preserving composition switching of OIHPs induced by organic, halogen, and hydrogen-halide gases. (D) Vision for the scope of future GIFT phenomena research.

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the state change in the molecule—ion interaction during the melting process (see Figure 6A).

Nucleation and Grain Growth of OIHPs from Intermediate Liquids. The crystallization of OIHP from the intermediate liquids, most typically MAPbI₃·xCH₃NH₂, is unique compared with the crystallization OIHP in other routes. The uniformity, high crystallinity, and texture that are frequently observed in OIHP thin films in gas-based processes are not well understood. One can think of the metastable intermediate liquids in equilibrium with the R-NH₂ gas atmosphere as OIHP precursor "solutions". Removal of the R-NH₂ gas environment will result in the deintercalation (or self-degassing) of R-NH₂ molecules and induce supersaturation, which triggers nucleation of OIHPs.³⁰

In classical nucleation theory, the free energy for homogeneous and heterogeneous nucleation is given by, respectively 30,31

$$\Delta G_{\text{HOM}} = \frac{\pi \gamma_{\text{CL}}^3}{3} \left(\frac{4V_{\text{M}}}{RT \ln(S)} \right)^2 \tag{1}$$

and

$$\Delta G_{\rm HET} = \Delta G_{\rm HOM} f(\theta) \tag{2}$$

where γ_{CL} is the crystal/liquid (C/L) interface energy, V_M is the molar volume, R is the gas constant, T is the absolute temperature, and S is the supersaturation. The parameter $f(\theta)$ is given by

$$f(\theta) = \frac{1}{4} \{2 + \cos(\theta)\} \{1 - \cos(\theta)\}^2$$
(3)

where $\cos(\theta) = (\gamma_{SL} - \gamma_{SC})/\gamma_{CL}$ with γ_{SL} and γ_{SC} being the energies of the substrate/liquid (S/L) and the substrate/crystal (S/C) interfaces, respectively. The expression for the nucleation rate (I_{NUCL}) contains two exponential terms

$$I_{\rm NUCL} \propto \exp\left(\frac{-Q_{\rm D}}{RT}\right) \exp\left(\frac{-\Delta G^*}{RT}\right)$$
 (4)

where Q_D is the activation energy related to mass transport and ΔG^* is the activation energy related to homogeneous or heterogeneous nucleation, as described above.

For conventional OIHP crystallization, heterogeneous nucleation is expected to dominate considering the large-area surface area of the substrate. However, in the gas-based process, homogeneous nucleation may play a more crucial role as S becomes very large very rapidly due to rapid degassing. Thus, it becomes imperative to separate the contribution of homogeneous and heterogeneous nucleation in order to control I_{NUCL} in the gas-based OIHP crystallization process. Regarding the temperature dependence, the first and second exponential terms in I_{NUCL} (eq 4) increase and decrease with an increase in temperature, respectively. The net result is that the overall I_{NUCL} goes through a maximum as a function of temperature. Therefore, temperature is also a critical factor that determines the nucleation process and the resulting OIHP microstructures. This is consistent with the fact that OIHP microstructures can be engineered by tuning the annealing temperature, as demonstrated by Jacobs et al.¹⁷ It is also possible that nonclassical nucleation mechanisms may be at play in OIHPs. As shown in Figure 6C, in addition to the classical "monomerby-monomer" mechanisms, there are several alternative pathways toward crystal nuclei formation. 32 The determination of the exact nucleation mechanisms is seriously hampered by the rapid crystallization of OIHP thin films, and it awaits innovative in situ analytical microscopy at the atomic to micrometer length scales^{33,34} and theoretical modeling.³⁵

Gas-Induced Morphology-Preserving Composition Switching. Very limited mechanistic studies have been performed regarding the gas-induced morphology-preserving composition switching in OIHPs. In Figure 5B, Zhou et al.²⁶ have shown that MAPbI₃ and FAPbI₃ OIHPs coexist as separate phases in the FA⁰ gas-induced morphology-preserving process of MAPbI₃ to FAPbI₃ conversion. However, whether the composition switching occurs in a grain-to-grain manner has not been confirmed. If that is true, one hypothesis is that the FA⁰ gas molecules attack the MAPbI₃ perovskite structure at the OIHP surface and grain boundaries, resulting in local composition switching, and eventually, the whole film is converted, as depicted in Figure 6C. It is also hypothesized that the similarity in the structure of the OIHP before and after composition switching is equally important for facilitating the reaction kinetically. This may explain why the formation of the δ -FAPbI₃ nonperovskite polymorph is suppressed in the FA⁰ gas-induced MAPbI₃ to FAPbI₃ conversion. In addition, other thin-film microstructural features, such as grain size, grain orientation, and defects, can play a significant role in the transport of FA⁰ gas molecules into thin films and, thus, in the morphology development (preservation and/or transformation) of thin films. Furthermore, how the mechanisms of A-cation switching differ from those of the X-anion switching remains to be explored.

These GIFT phenomena and their mechanistic studies can be extended to a wide range of OIHPs, OIHP precursor phases, and gases. Figure 6D shows the possible pairs of solid-gas reactions. The "solid" category includes OIHPs and their precursor phases, and the "gas" category includes R-NH2, X2, and HX. A number of solid-gas reactions are possible between these two categories. Three key questions remain to be answered: (i) Does the phase convert? (ii) Are the morphologies of reagent solids preserved or transformed? (iii) Are these reactions reversible? The answers to these questions will form general rules that govern the GIFT phenomena and, by unraveling the mechanisms underlying the answers, will allow manipulation of GIFT for desired purposes. We envision vast research opportunities in this direction. In particular, innovative in situ characterization (transmission electron microscopy, atomic force microscopy, photoluminescence microscopy, infrared/ Raman spectroscopies, etc.),²² in combination with theoretical modeling, will be indispensable in achieving these goals.

Several promising applications of the GIFT phenomena have already been demonstrated. Exploring more functionalities of GIFT will lead to more important and surprising applications.

The GIFT phenomena exhibit unique, controllable features in terms of phase/morphology transitions in OIHPs. These phase/morphology transitions usually lead to striking changes in optical/electric properties in OHIPs. By combining these features and the intrinsic functionalities of OIHPs, various potential applications have been explored.



Figure 7. (A) Illustration of the PSC up-scaling based on the GIFT phenomena. (Adapted with permission from the America Chemical Society (ref 40.) (B) Observation of optical switching of solutions (containing MAPbBr₃ nanoparticles and MA⁰) upon response to heat. (Adapted with permission from Wiley (ref 47.) (C) Purification of I₂ gas based on GIFT reactions. (Adapted with permission from the Royal Society of Chemistry (ref 27.) (D) NH₃ gas sensor made based on the resistivity change of OIHP upon reversible intercalation/deintercalation of NH₃. (Adapted with permission from the Royal Society of Chemistry (ref 48.)

Solar Cells. The morphologies or microstructures of OIHP thin films play central roles in determining the performance of PSCs. Therefore, the MA⁰-induced morphology healing and microstructure reconstruction of MAPbI3 are very promising for fabricating high-quality OIHP layers for PSCs. For example, Conings et al.³⁶ have shown that MA⁰ gas treatment improves the MAPbI₃/TiO₂ interfaces and, therefore, electron injection into TiO₂. In particular, for mesoscopic PSCs, liquid intermediate formation also allows compact pore filling of HOIPs inside of the TiO_2 mesopores due to capillarity. Zhang et al.³⁷ have claimed that the texture in the MA⁰ gas-treated MAPbI₃ thin film contributes to better energy-level alignment with TiO₂ and significantly prolonged photocarrier diffusion lengths. There is also evidence showing that MAPbI₃ OIHP thin films prepared via this approach contain MA⁰-rich grain boundaries that could trigger moisture-induced degradation reactions and, thus, enhance the OIHP stability.^{38,39} The improvement of these properties in MAPbI₃ thin films has led to PSCs with much higher efficiency and more stable performance. Furthermore, as with any gas-based process, this GIFT-based OIHP synthetic approach is intrinsically scalable. The compatibility of this chemical approach with industrial thin-film coating technology such as slot-die coating and doctor-blading has also been demonstrated in some preliminary work (Figure 7A).^{14,40} Here, very large area nominal MAPbI₃ OIHP thin films are prepared using slot-die coating and are subsequently exposed to MA⁰ gas in a large chamber at RT. In another approach by

Moore et al.,⁴¹ the liquid intermediate can be further diluted using a low-boiling-point, low-velocity solvent such as acetonitrile, forming an OIHP precursor solution where uniform OIHP thin films can be "painted" very rapidly. It is worth noting that the past gas-based processing of PSCs has focused mostly on MAPbI₃, and thus, the versatility of this method needs to be extended. It is envisioned that more efforts will be devoted to synthesizing highquality OIHPs with new state-of-the-art compositions,⁴² such as $Cs_x(MA_{0.17}FA_{0.83})_{(1-x)}Pb-(I_{0.83}Br_{0.17})_3$,⁴³ $FA_{0.85}MA_{0.15}Pb-I_{2.55}Br_{0.45}$,⁴⁴ (Rb,FA,MA,Cs)PbI₃,⁴⁵ (FAPbI₃)_x(CsSnI₃)_{1-x},⁴⁶ and so forth, based on a combination of GIFT reactions.

Optical Switching. GIFT can cause vivid color/optical property transition in OIHPs. Inspired by this possibility, Nishikubo et al.⁴⁷ reported a low critical solution temperature for toluene solutions containing alkylamines and MAPbBr₃ OIHP nanocrystals (Figure 7B). The interaction of the alkylamines with MAPbBr₃ induces reversible formation and decomposition of MAPbBr₃ nanoparticles upon heating and cooling, respectively, accompanied by optical switching of green and blue photoemissions.

Gas Absorption/Purification. On the basis of the discovery of the interaction behavior of OIHPs with halogen gas, Solis-Ibarra et al.²⁷ have demonstrated the reversible iodination of alkene molecules in OIHPs as an intriguing example of gas capture through reversible chemisorption, and the equilibrium for iodine release can be tuned through OIHP crystal/molecule design. In their later study, it is further shown that the organic

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functionalities in 2D OIHPs can be designed for selective chemisorption to enable separation of halogen gases of similar molecular sizes.²⁷ Figure 7C shows that the alkene groups in 2D OIHPs can chemically absorb Br_2 gas, and the selectivity of this chemisorption for Br_2 over I_2 helps achieve I_2 gas with extreme purity.

Sensors. The striking, reversible change in the optical/electric properties of OIHPs due the intercalation/deintercalation of R-NH₃ can be used for detecting R-NH₃ gases with high sensitivity and selectivity (Figure 7D). In this context, Zhao et al.¹⁵ were the first to demonstrate a NH₃ gas sensor based on the optical response of the MAPbI₃ thin films to NH₃ gas. In another study, Bao et al.⁴⁸ observed that the resistance of MAPbI₃ thin films decreases significantly in seconds when the films are exposed to an NH₃ atmosphere at RT and recovers to its original value in seconds upon removal of the NH₃ environment. In this context, Bao et al.⁴⁸ have successfully fabricated a resistivity-based NH₃ gas sensor. Similar high-sensitivity sensors for other R-NH₃ gases with high selectivity can be achieved based on the GIFT phenomena in OIHP thin films.

In closing, the newly discovered GIFT phenomena are unprecedented in the fields of chemistry and materials science. The GIFT phenomena are made possible, over a large compositional and structural space, due to the unique structure of the OIHP materials and their hybrid soft and hard characteristics. The gas-based nature of GIFT makes it inherently scalable for the controlled synthetic processing of high-quality OIHPs with controlled microstructures, opening up the use of GIFT in fabricating a wide range of OIHP-based devices such as solar cells,¹⁴ light-emitting diodes,⁴⁹ and beyond. On the basis of the functionality of OIHPs and that of the GIFT phenomena themselves, we envision that more advanced, unprecedented applications of GIFT will emerge. This presents vast research opportunities for the mechanistic studies of the nascent OIHPs GIFT phenomena for not only discovery of new science but also broad technological impact.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00667.

Real-time video of healing of a dull MAPbI₃ thin film to a shiny MAPbI₃ thin film upon exposure to, and subsequent removal from, MA_0 gas atmosphere (AVI)

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Notes

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