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On the Mechanism of Solvents Catalyzed Structural Transformation in Metal Halide Perovskites

Jun Xi, Junke Jiang, Herman Duim, Lijun Chen, Jiaxue You, Giuseppe Portale, Shengzhong (Frank) Liu, Shuxia Tao,* and Maria Antonietta Loi*

Metal halide perovskites show the capability of performing structural transformation, allowing the formation of functional heterostructures. Unfortunately, the elusive mechanism governing these transformations limits their technological application. Herein, the mechanism of 2D–3D structural transformation is unraveled as catalyzed by solvents. By combining a spatial-temporal cation interdiffusivity simulation with experimental findings, it is validated that, protic solvents foster the dissociation degree of formamidinium iodide (FAI) via dynamic hydrogen bond, then the stronger hydrogen bond of phenylethylamine (PEA) cation with selected solvents compared to dissociated FA cation facilitates 2D–3D transformation from (PEA)$_2$PbI$_4$ to FAPbI$_3$. It is discovered that, the energy barrier of PEA out-diffusion and the lateral transition barrier of inorganic slab are diminished. For 2D films the protic solvents catalyze grain centers (GCs) and grain boundaries (GBs) transform into 3D phases and quasi-2D phases, respectively. While in the solvent-free case, GCs transform into 2D–3D heterostructures along the direction perpendicular to the substrate, and most GBs evolve into 3D phases. Finally, memristor devices fabricated using the transformed films uncover that, GBs composed of 3D phases are more prone to ion migration. This work elucidates the fundamental mechanism of structural transformation in metal halide perovskites, allowing their use to fabricate complex heterostructures.

1. Introduction

Structural transformations of soft materials offer an important tool to tune their physical properties. In soft semiconductors, weakly bonded moieties can trigger structural transformation at the presence of external stimuli, thus altering the physical properties and functionalities of the system. Metal halide perovskites are emerging soft semiconductors, which have become popular in the optoelectronic community because of their simple fabrication procedure as well as their exceptional physical properties. The intrinsic high defect tolerance in both polycrystalline and single-crystalline states endow admirable merits to them, such as long charge-carrier diffusion range. Previous studies suggest that such properties are closely correlated to their soft lattices, with the formation of large polarons, which reduce the impact of charge scattering.

Their natural elasticity owes to the relatively lower formation energy of the ionic octahedral unit, where the metal-halide bond can not only stand high mechanical...
deformations but also tend to be switched upon chemical stimuli. In light of such chemical elasticity, intentional structural transformation can be foreseen. To date, the scientific community has taken advantage of structural transformation to artificially build thermodynamically metastable perovskites in bulk structures and in their nanostructures. Impressively, using the well-known ion exchange routes, researchers have gained access to metastable states that are hardly synthesized directly, such as black phases of CsPbI₃, FAPbI₃, etc., ordered alloyed compounds (FAPCs and PbSn), and even heterostructures (planar or gradient type).

2D perovskites-like systems, in particular the one in Ruddlesden–Popper configuration, are considered to be thermodynamically stable due to their high formation energy. Once the intercalated bulky cations are exchanged by smaller cations, the transformed 3D lattices inherit the ordered layer structure, as verified by our previous investigations. From thermodynamic point of view, during such transformation, the degree of configurational freedom, therefore entropy, increases, favoring the 2D–3D transformation. This is rather different from the 3D–2D surface reaction used for surface defect passivation in optoelectronic devices, the reaction degree of which is very limited.

In a 2D–3D transformation, except the entropy which is generally enhanced, the formation enthalpy would fluctuate. In this case, it remains difficult to assess the Gibbs free energy to judge the thermodynamics of the transformation. In principle, Le Chatelier’s principle can be followed, to obtain a clearer picture of the reaction processes involved in the transformation. However, at the moment, the understanding of the mechanism of the structural transformation remains elusive, limiting the optimization of structurally transformed materials and therefore their application in devices.

Here, we establish an understanding of the mechanism driving the 2D–3D transformation of metal halide perovskites. Taking the transformation from (PEA)₂PbI₄ to FAPbI₃ as an example, we found out that the use of protic solvents favors the dissociation degree of solvated FA moieties via hydrogen bond interactions, and then accelerate the exchange of PEA cations with dissociated FA cations via a notable stronger hydrogen bond of the solvent with PEA⁺ compared to FA⁺. Such interactions initialize the reaction and facilitate the out-diffusion of PEA⁺ from the 2D lattices, making room for the transformation from 2D to 3D of the inorganic framework as well as the intercalation of FA⁺. In addition, the simulated larger cation interdiffusivity rate of FA⁺ allows rationalizing the reaction dynamics of the structural transformation.

Interestingly, the 2D–3D transformation catalyzed by protic solvent is generally occurring in grain centers; however, grain boundaries (GBs) of the 2D phase transform into distinct quasi-2D phases. By comparing solvent catalyzed samples with the ones transformed from a solid–solid reaction, the latter case leads to a limited transformation of grain centers to 3D perovskites, but allows a majority of 3D phase forming at the GBs. Using the transformed films by the two 2D–3D reaction paths (solid–solid versus solid-solvent), we fabricate memristor devices, and reveal that the vertical ionic conductivity is dictated by 1D phase in GBs rather than in grain centers. The density of halide vacancies of the obtained 3D GBs (from solid–solid reaction) is 1–2 orders of magnitude higher than that of 3D grain centers.

2. Results and Discussion

First, since the state-of-art electronic devices prevalently adopt polycrystalline films of metal halide perovskites, we probe the 2D–3D transformation in polycrystalline films. Scheme 1 depicts a pair of 2D–3D transformation reactions using 2D PEA₂PbI₄ (PEA = 2-phenylethylammonium) and FAI as the starting reactants. The difference between the two routes lies in the reactive state of FAI: In the first reaction, there are no solvents involved, thus the reaction is proposed as a solid–solid system (Note that the little amount of solvent used to deposit FAI has negligible effect on PEA₂PbI₄, and a FAI solid film is successfully formed on PEA₂PbI₄ as confirmed by the SEM images and XRD patterns, Figure S1, Supporting Information); In the second reaction, FAI is dissociated in certain solvents for the whole reaction, resulting in a solid-solution system. In both reactions, the PEA₂PbI₄ film should be preserved in the solid state.

As for the solid–solid system, to guarantee that a FAI thin film is formed on PEA₂PbI₄, we heated the substrate to 80°C to completely remove IPA and forming a FAI layer on PEA₂PbI₄. In principle, a solid–solid reaction system has a limited reaction rate, which can be improved by increasing the temperature. To avoid thermal decomposition of chemicals and a too fast reaction time, we employed a relatively mild temperature (100 °C) to accelerate the solid–solid reaction. Here, we noticed that the reaction reaches its maximum at around 20 min from the start (Figure S2, Supporting Information).

In order to understand the role of solvents in the solid-solution reaction, we choose two kinds of solvents, namely protic and non-protic, with which FAI can be solvated via different intermolecular interactions. We first pay attention to the protic-based reaction. Figure 1a and Figure S3 (Supporting Information) provide the film morphologies of the pristine 2D template (PEA₂PbI₄) and the transformed samples catalyzed by the selected protic solvents. The sample fabricated using the solid–solid reaction is displayed as a reference. The insets of Figure 1a are the optical images of the reported films. As expected, the film color variation from yellow to brown suggests the transformation from 2D to 3D, as proved by the optical measurements in Figure S4 of the Supporting Information.

Here we need to highlight, that in view of Le Chatelier’s principle, without the end washing with a solvent such as the one used in the reaction, the 2D–3D transformation would give rise to an unstable result (immediate back reaction) (Figures S5 and S6, Supporting Information). When looking at the quality of the transformed samples, the one obtained from a FAI solution in isopropanol (IPA) leads to a homogeneous morphology with compact surface grain boundaries (SGBs), while the one

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Scheme 1. Reaction schemes for 2D–3D transformation when 2D (PEA₂PbI₄) bulks interact FAI solids (Reaction 1) and FAI solutions (Reaction 2). Here, for the equilibrium equation, s denotes solid state, and l denotes liquid state.

Figure 1. 2D–3D transformation for metal halide perovskite polycrystalline films. a) Film morphologies (SEM) of the pristine 2D (PEA₂PbI₄) polycrystalline film, and the transformed specimens in different conditions. Pictures of the samples are provided as insets. b) Schematic of the collection for the steady-state PL spectra and for the confocal laser scanning microscopy (CLSM). c) CLSM mapping of the pristine 2D (PEA₂PbI₄) polycrystalline film. d–f) CLSM mappings on the front-side (above panel), back-side (middle panel), and corresponding PL spectra of transformed specimens for d) isoopropanol (IPA), e) ethanol (EtOH) in solid-solution system, and f) solid–solid system. For the PL mappings, blue, green, and red channels correspond to phase pure 2D (515±30 nm), quasi-2D (590±50 nm), and 3D (>650 nm), respectively. Scale bar: 20 μm.

from ethanol (EtOH) coarsens the transformed morphology with needle-like crystals emerging at the SGBs. As for the solid–solid case, although the morphology seems perfect with negligible cracks formation, the displayed khaki color suggests a limited degree of 2D–3D transformation. By contrast, we noticed that the non-protic solvents fail to allow such transformation (Figure S7, Supporting Information).

To elucidate the heterogeneities of the transformation obtained with different reaction conditions, confocal laser scanning microscopy (CLSM) was conducted to investigate the local photoluminescence (PL) signal, which is a clear fingerprint of the presence of different phases (Figure 1b). Notably, the starting PEA, PbI2 film has a large variation of PL intensity (Figure S8, Supporting Information), where stronger PL intensity along SGBs than in the center of grains is clearly observed (Figure 1c). This we believe is determined by the heterogeneities of the sample composition especially at SGBs which correlated with halide vacancies.[19] Both the front- and back-side of the transformed samples were measured due to the distinct physical conditions of the exposed and buried surfaces. To unravel the relative phase heterogeneities, we plot a group of three PL spectra measured at random regions of the sample surface, both exciting the samples from the front- and the back-side (Figure 1d–f). Furthermore, the signal histograms of each channel corresponding to the CLSM mappings for different samples are summarized in Figure S9 of the Supporting Information. With respect to the transformed films, the PL heterogeneities appear to be distinct between the front- and back-side for all three samples (note: red, green, and blue channels correspond to 3D (>650 nm), quasi-2D phases (590±50 nm, where n ≥ 2), and phase pure 2D (515±30 nm, where n = 1)).

(1) For the IPA case, the dominant red PL emitting (≈810 nm) phases in the CLSM maps from both sides unveil a nearly complete 2D–3D transformation (see also Figure S10 of the Supporting Information). There are almost no deviations between the multiple PL emission measured in either the front-side or the back-side, indicating the relatively high homogeneity of the sample. Nonetheless, we realize an interesting phenomenon, namely that a little amount of quasi-2D phases emerges along the SGBs at front-side and in isolated domains at the back-side. (2) For the EtOH case, at the front-side, most red PL emitting regions are surrounded by green and blue regions in the SGBs. These regions, much larger than those of the IPA sample, are composed by both phase pure 2D and quasi-2D phases. The back-side of the sample has a similar heterogeneity but the quasi-2D domains appear much larger than the one in the front-side. We notice obvious deviations between the multiple PL spectra especially when measured from the front-side, revealing significant heterogeneity of 2D/quasi-2D phases. Furthermore, the enhanced PL intensity of the green channel from the back-side validates the massive presence of quasi-2D phases (Figure S10, Supporting Information). (3) For the solid–solid case, the front-side CLSM map is governed by the red emission: as most of the grain centers transform into 3D phases, and a minority to quasi-2D ones. While at the back-side, grain centers almost remain purely 2D. GBs at the front-side evolve into 3D phases, on the back-side except a considerable part of them which evolves to the 3D phases we also observe a little amount of disconnected quasi-2D phases (emission in the green range). Such a mixture of quasi-2D and 3D phases at the back-side could be a result of nonuniform downward penetration of FA along GBs. The deviations of the PL spectra emerge at both green and red domains especially from the back-side, showing the large vertical heterogeneities resulting in a totally different composition of the sample at the front- and the back-side. This intriguing 3D–2D heterojunction demonstrates that the 2D–3D transformation dynamics is limited in the grain centers without catalysis by protic-solvent.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements of the samples obtained with IPA and EtOH (Figure S11, Supporting Information) further evidence the spatial heterogeneities. Except for the obvious 3D diffraction features, dominant quasi-2D phases reflected by (0k0) spots are clearly observed, belonging to n = 2 phases for IPA, and n = 3 phases for EtOH. These results are in agreement with the CLSM study. The XRD analysis of the films (Figure S12, Supporting Information) validates that, films transformed by protic-solvent catalyzed reaction to single 3D structure (trigonal, P3m1 space group) with minor quasi-2D phases (below instrumental lowest limit), while the one obtained by solid–solid reaction appears more like a 2D (triclinic, P1 space group)-3D heterostructure.

The above findings demonstrate that solvent molecules interacting with FAI are fundamental in determining the 2D–3D transformation. Therefore, we turn to investigate the latent effects on FAI solutions determined by different solvents. Figure 2a illustrates the structures as well as the properties of the used solvents, including EtOH, IPA, acetonitrile (ACN), 2-methoxyethanol (2Mexy), and pyridine (PRD). A photograph of as-prepared FAI solutions in the different solvents is shown in Figure S13 of the Supporting Information. All the solutions are transparent without any precipitations, indicating that FAI is dissolved completely. As mentioned above, we classify these solvents into protic (EtOH, IPA, and 2Mexy) and nonprotic (ACN and PRD). Here, we like to stress the peculiarity of 2Mexy which is protic, but shows also high polarity similar to the nonprotic solvents.

To unravel the solvent effects on FAI dissociation, we conducted Fourier-transform infrared spectroscopy (FTIR) measurements on these solutions. The results are summarized in Figure 2b. As a reference, the FTIR data of FAI solid powders were also recorded (Figure S14, Supporting Information). Logically, the obtained FTIR curves of any FAI solutions are totally different with that of FAI solids, highlighting the role of solvent in the dissociation of FAI.

Four dominant regions labeled from (i) to (iv) are highlighted in the FTIR spectra. We discuss these features by underlining the specific modes associated with the protic solvents (EtOH, IPA, and 2Mexy)

1) In region (i), a strong contribution of NH2 stretching vibrations can be observed for all three protic solutions, which is absent in FAI solids (Figure S14, Supporting Information). We deduce that such feature originates from FAI dissociation interacting with the protic solvent molecules. Moreover, the peak shows a slight shift to lower wavenumbers from 3400 cm−1 in 2Mexy, to 3330 cm−1 in IPA, and to 3320 cm−1 in EtOH, accompanied by increasing peak intensity. We believe that the variation in the NH2 vibration is determined by
Figure 2. Solvents catalyzed 2D–3D transformation of metal halide perovskites. a) Molecular structures and properties of selected solvents dissolving FAI, including: ethanol (EtOH), isopropanol (IPA), acetonitrile (ACN), 2-methoxyethanol (2Mexy), and pyridine (PRD). b) Representative FTIR spectra of as-dissolved FAI solutions (20 mg mL\(^{-1}\)) in different solvents.

1. The polarity and proton donating ability of the protic solvents.

2. In region (ii), sharp C–H stretching modes belonging to the FA moiety are visible for both EtOH and IPA based samples. This is likely a result of coordination between FAI and solvents. However, this feature is absent for 2Mexy based one. In light of the electron-rich methoxy group in 2Mexy, additional interaction between 2Mexy and FAI may heavily undermine such C–H motion.

3. In region (iii), a series of continuous vibrations belonging to quaternary ammoniums (R\(_3\)N\(^+\), R = organic group) are observed for all protic samples. Because of the absence of R\(_3\)N\(^+\) moieties both in solvents or in FAI molecules, we hypothesize that this could be an indication of the formation of [FA\(^+\)·OH\(^-\)] complexes, where the delocalized –NH\(_2\)\(^+\) from FA cation interacts with hydroxyl groups (OH\(^-\)) from the solvents via hydrogen bonds. The fact that these peaks are absent for ACN and PRD (solvents without OH\(^-\) groups) verifies our hypothesis.

4. In region (iv), typical C=N stretching vibrations belonging to the FA cation are observed. Interestingly, as the solvent changes from EtOH to IPA, and to 2Mexy, this peak intensity variation shows an opposite trend compared to that in region (i). Accordingly, we deduce that the enhanced FAI dissociation can reduce C=N motions, agreeing well with what we found for the NH\(_2\) vibrations.

In summary, the selected protic solvents dictate the dissociation degree of FAI via dynamic hydrogen bonding: the more hydrogen bonding interactions, the higher dissociation degree for FAI is occurring. When PEA\(_2\)PbI\(_4\) solids are reacting with FAI protic solutions, the improved dissociation makes the interaction between FA and PEA\(_2\)PbI\(_4\) more efficient, which allows the reaction equilibrium to shift forward (reaction 2 in Scheme 1). In other words, the protic solvent molecules work as the catalytic agents by carrying FA to the surface of PEA\(_2\)PbI\(_4\).

With respect to the nonprotic solvent group, the collected FTIR spectra are totally different from what was previously described: for example the vibrations from NH\(_2\) as well as R\(_3\)N\(^+\) moieties do not appear. While the C=N stretching peaks shift, suggesting that FAI likely stays as strongly bound molecule rather than as dissociated cations. This suggest that the state of FAI in solution highly correlates with the solvent’s nature.

Here, density functional theory (DFT) calculations are used to understand the relevant interactions at the molecular scale to evaluate the solvent-catalytic effects. We calculate the interaction energies (IRE) of solvents with FA and PEA cations and compare their interaction strength by calculating the difference in the interaction energy (see Figure S15 of the Supporting Information). We find large positive value (>0.1 eV) of IRE for protic solvents, such as, IPA and EtOH, indicating stronger interaction of the solvents with PEA\(^+\) compared to FA\(^+\), a sign of favorable catalytic ability for the 2D–3D transition. This effect could be attributed to the stronger hydrogen bond of the –NH\(_2\) group in PEA\(^+\) (than –NH\(_3\) in FA\(^+\)) with the hydroxyl (–OH) group in the solvent molecule, as indicated by the larger Mayer bond order (see Figure S16 of the Supporting Information). The IRE is negligible in the protic 2Mexy and in the nonprotic ACN. One exception...
is the non-protic PRD, its interaction with PEA$^+$ is stronger than FA$^+$; however, a totally different type of bond, i.e., interaction with N atoms of PRD (C$_5$H$_5$N) makes the transformation fail.

To validate the simulated relative catalytic effect of the protic solvent, we designed an experiment employing 2D PEA$_2$PbI$_4$ single crystals (SCs) to induce 2D–3D transformation by dipping them into protic FAI solutions. Figure S17 of the Supporting Information, shows the relative variation of nuclear magnetic resonance (NMR) $^1$H spectra for FA dependent on reaction time of the transformed SCs. The normalized kinetics rate of 2D–3D transformation catalyzed by EtOH is $\approx$1.66 times higher than that of IPA, in line with the simulated favorable IRE of EtOH respect to IPA.

After understanding the molecular interactions, we investigate how the protic solvents impact the dynamical processes during the 2D–3D transition, by looking at how solvents interact with the 2D perovskite surface and their impact on the out-diffusion of PEA$^+$ cation from the 2D phase and the lateral transition of the inorganic framework into 3D structures. First, Irving equation is used to simulate the relative interdiffusivity (Figure S18, Supporting Information), where we can clearly see a pronounced interdiffusion kinetics ($\omega$ (PEA/FA) < 1%). Figure 3a illustrates ab Initio Molecular Dynamics (AIMD) simulation (20 ps) of

**Figure 3.** Dynamics of the 2D–3D transformation for metal halide perovskites. a) The dynamic interdiffusivity model for PEA cations assisted by different solvent molecules. From left to right are initial state and final state of systems after 20 ps AIMD simulation, respectively. b) Relative energies along the PEA diffusion path (see Figure S15 of the Supporting Information) for molecules without and with solvent IPA and EtOH. c) Schematic of the lateral transition and d) lateral transition barrier in PEA$_2$PbI$_4$ without and with protic solvents (IPA and EtOH).
how solvents interact with 2D perovskite surfaces: in protic solvents, in particular, the –OH groups tend to interact closely with PEA cations on the surface; while the nonprotic solvents are generally repelled further away from the surfaces. As a result, in Figure 3b, the diffusion barrier of PEA⁺ from the surface into the protic solvents is reduced by about 1 eV (see details in Figure S19 of the Supporting Information), facilitating their dissolution and initializing the phase transition from 2D to 3D in this way.

It is well known that in a Ruddlesden–Popper (RP) perovskite (Figure 3c), a 1/2 octahedral displacement can be found among adjacent inorganic [PbI₆]⁴⁻ layers. To transform the RP phases to 3D structure, this displacement should be eliminated (Figure 3c) and such process may involve a lateral energy barrier. Figure 3d summarizes the calculated lateral transition barrier as a function of step size of 1/6 octahedral displacement. At the initial stage of such transition (1/6), all transition barriers are slightly negative, indicating a spontaneous initialization irrespective of reaction conditions. As the step size increase to 1/3 and further to 1/2 octahedral displacement, the transition experiences an energy barrier of 0.05 and 0.15 eV without solvent, respectively. Interestingly, in presence of protic solvents, such as, IPA and EtOH, barriers are reduced by about 50%. This indicates that protic solvents promote a favorable lateral octahedral transition during 2D–3D transformation.

As mentioned earlier, in the perovskite films, the nature of GBs totally differs from that of grain centers. It is therefore important to understand the behavior of GBs especially when IPA is used. In a typical film, the top surface has the largest reaction area together with the highest density of SGBs. Hence, we deliberately sealed the top surface of the starting PEA,Πb₁ film by covering it with a layer of polymethyl methacrylate (PMMA) to manipulate the IPA-catalyzed transformation. Interestingly, the assumed transformation could not be observed even if the reaction duration is prolonged by 5 times (Figure S20a, Supporting Information). However, along the GBs, the yellow phases evolved into red ones. Absorption and PL spectra (Figure S20b,c, Supporting Information) unveil a new excitonic peak at 2.18 eV, implying that the obtained red GBs strongly correlate to the formation of quasi-2D phases (n = 2, PEA,Πb₆). Given that only the edge surfaces of the films can directly interact with solvated FAI, the overall delayed cation interdiffusion to the grain centers respect to the GBs is deemed as the main reason. In addition, the almost unchanged grain centers suggest that the obtained PEA,Πb₆ at GBs could not further induce the grain centers transformation to 3D phases in the thickness direction to the substrate. PEA,Πb₆ (n = 2) transformation failure is probably due to its lowest formation enthalpy compared to its adjacent phases (n = 1 and n = 3). Accordingly, despite the faster transformation into quasi-2D phases, GBs could not interfere with the established 2D–3D transformation of grain centers.

Hence, we can draw a clear roadmap of 2D–3D transformation in polycrystalline film catalyzed by protic-solvent as follows: (1) As the 2D film is firstly immersed into FAI protic solutions, except the buried surface, other surfaces interact with solvated FAI immediately. At exposed surface, due to the larger areas of SGBs than grain centers, the possibility of interaction with solvents should be higher. Hence, cation interdiffusion at SGBs precedes that of grain centers. Furthermore, concentrated halide vacancies along SGBs result in a peculiar transformation to quasi-2D phases instead of 3D ones,

$$n \text{PEA}_{2} \text{PbI}_{4} - \text{vac} + n \text{I} - \text{vac} + (n - 1) \text{FAI} \rightarrow (\text{PEA})_{2} \text{FA}_{n-1} \text{Pb}_{n} \text{I}_{3n+1} + 2(n - 1) \text{PEAI}, (\infty > n > 1)$$ (1)

where I - vac denotes iodide (halide) vacancies. (2) At this time, the stronger molecular interaction between perovskites and solvents would partially corrode and even collapse the freshly formed perovskite at SGBs on the exposed surface, the intensity of which depends on the solvent polarity. This is why coarsened SGBs are visualized in SEM. During the interdiffusion, EtOH with higher polarity can corrode SGBs penetrating until the buried surface, resulting in formation of quasi-2D phases at this surface; IPA with lower polarity has a slightly weaker corrosion effect, thus small cluster-like quasi-2D phases form at the buried surface. (3) The transformation of the grain centers follows after the reaction at GBs starts. Irrespective of the protic solvents, the original 2D phases in the grain centers can finally transform into 3D perovskites, complying with the previously proposed catalytic reaction dynamics.

After understanding the mechanism of 2D–3D structural transformation from theory and experiment, we attempted to further explore the natural ionic properties of these peculiar structures. In general, the ionic conductivity of 3D perovskites outperforms that of the 2D counterparts. It has been demonstrated that perovskites can be used in memristors to switch resistance states under bias and that this depends on the ion migration. However, an open question remains: whether GBs in a typical 3D perovskite film are the dominant channels for ion migration. Encouragingly, we find that the films made from 2D–3D transformation can be used to verify the degree of ion migration, due to the formed distinct spatial heterogeneities especially along GBs: the solid-solution system results in quasi-2D phases penetrating the GBs, while the solid–solid one allows the formation of 3D phases penetrating the GBs.

Hence, to elucidate the nature of ion conductivity in perovskites, we fabricated a series of memristor devices using the aforementioned films. Herein, a sandwiched structure was adopted for all the devices (Figure 4a), where ITO/PEDOT:PSS (poly(3,4-ethylendioxythiophene):polystyrene sulfonate) and Au serve as electrodes. To drive the device operation, a DC sweep voltage ranging from 0 V to ±2 V was applied, the direction of which is described in Figure 4b with labels from (1) to (4). We summarize the behavior of the representative I–V curves measured on different devices

1) The device using 2D film delivers an almost symmetric hysteresis and the lowest saturation current level (10⁻⁷–10⁻⁸ A). In particular, the limited ON/OFF ratio (≈10) (Figure 4c) and indefinite resistance transition further evidence the poor switching capacity of the material. This can be rationalized by the limited ion migration (here iodine anion) originating from the uninterrupted nonconducting PEA cations in the 2D system. Here, only GBs with localized iodine vacancies could allow for finite ionic conductivity.

2) As for the device employing the solid–solid transformed film (denoted as solid2), an abnormal asymmetric hysteresis
Figure 4. 2D–3D transformation for ion conductivity of metal halide perovskite polycrystalline films. a) Adopted memristor device structure using 2D–3D transformed polycrystalline films. b) I–V curves and On/Off ratios of the optimized memristors by applying a DC sweep voltage from 0 to ±2 V.

appears with slightly increased saturation current level (10⁻⁶–10⁻⁵ A), in line with the emergence of minor 3D phases. We note that in the positive sweep direction, the high resistive state (HRS) clearly switches to the low resistive one (LRS) at a threshold voltage of ≈1.26 V, corresponding to the “SET” regime for this device. As a result, a pronounced ON/OFF ratio of 10³–10⁴ is shown. We attribute this SET transition to the ion migration from the back- to front-side of the film, during which iodine vacancies redistribute from the 3D phases at the GBs of the buried surface to the 3D dominant phases in exposed surface. In other words, instead of the grain centers, the GBs penetrating the film dictate the conducting channels. Under negative bias, the device transits from LRS to HRS via a RESET process, in which the accumulated iodine vacancies at the perovskite/Au interface progressively fade and finally extinct at ITO/PEDOT:PSS electrode. Importantly, the measured synaptic conductance states indicate that these predicted channels are steady (Figure S21, Supporting Information).

3) For the device leveraging IPA-catalyzed 2D–3D transformation, a similar asymmetric hysteresis with an enhanced saturation current level up to 10⁻²–10⁻¹ A is measured. As the device transits from the HRS to LRS, a raised SET voltage of ≈1.95 V is shown with an ON/OFF ratio dropping to ≈10². These inferior memristor characteristics are reasonable: (i) Given the quasi-2D phases increasingly occupy or passivate GBs from the back- to the front-side of the film, the dominant GBs fail to allow efficient iodine vacancies redistribution. (ii) Instead, grain centers entirely occupied by 3D phases may work as another conducting medium. However, the density of iodine vacancies in native grain centers is much lower than that at the GBs, which ought to increase the activation energy of iodine redistribution through fewer migration channels. In response, the threshold voltage should increase. Again, filling these relatively low number of iodine vacancies should give rise to a low ON/OFF ratio. Accordingly, the density of iodine vacancies of grain centers is at least 10⁻¹⁰ times lower than that of GBs. Finally, the device undergoes a delayed RESET process to HRS under a negative bias.

4) For device using EtOH-catalyzed transformation, although the saturation current level reaches the highest level, typical memristor characteristics cannot be observed. Such poor performance strongly correlates to the almost “short-circuited” conducting pathways caused by seriously corroded GBs going throughout the film.

In summary, the above results show how to match the heterogeneities of our samples to the ion migration features in memristor device operation, providing the insight that 3D GBs are the dominant channels responsible for ion conductivity. Furthermore, they provide a clear demonstration of how complex heterostructures can be useful once they can be controlled.

3. Conclusion

We have elucidated with a systematic experimental and theoretical investigation the mechanism of a 2D–3D structural transformation for lead halide perovskites. Interestingly, mild
protic solvents (ethanol (EtOH), and isopropanol (IPA)) are validated to catalyze the 2D–3D transformation. The phenomena can be understood as follows: pronounced hydrogen bonds with molecules of protic solvent allow the dissociation of FAI, then the stronger interactions of these solvent molecules with PEA cation compared with dissociated FA cation (due to the stronger hydrogen bonds with hydroxy group from IPA or EtOH) allow for the catalytic substitution of the two cations. Such interaction also decreases the energy barrier of the out-diffusion of PEA$^+$ cations from the surface of the 2D perovskite into the solvents, and facilitates the lateral transformation of the inorganic framework from 2D–3D and the subsequent intercalation of FA$^+$ cation. Notably, all protic solvents reduce the transition barrier of the inorganic layer in a similar way. When polycrystalline films are used, we discover quasi-2D phases are formed especially along grain boundaries, differing from the newly transformed 3D phases in grain centers. Finally, we fabricated memristor devices by using the 2D–3D transformed films with and without protic solvents. Comparison of the conductivity measurements of these devices allow us to clearly identify the grain boundaries of 3D domains being the major channels for ionic conduction.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
cation interdiffusivity, heterostructures, metal halide perovskites, solvent catalysis, structural transformation

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