Crystallization of 2D Hybrid Organic-Inorganic Perovskites **Templated by Conductive Substrates**

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2D hybrid organic-inorganic perovskites are valued in optoelectronic applications for their tunable bandgap and excellent moisture and irradiation stability. These properties stem from both the chemical composition and crystallinity of the layer formed. Defects in the lattice, impurities, and crystal grain boundaries generally introduce trap states and surface energy pinning, limiting the ultimate performance of the perovskite; hence, an in-depth understanding of the crystallization process is indispensable. Here, a kinetic and thermodynamic study of 2D perovskite layer crystallization on transparent conductive substrates are provided-fluorine-doped tin oxide and graphene. Due to markedly different surface structure and chemistry, the two substrates interact differently with the perovskite layer. A time-resolved grazing-incidence wide-angle X-ray scattering (GIWAXS) is used to monitor the crystallization on the two substrates. Molecular dynamics simulations are employed to explain the experimental data and to rationalize the perovskite layer formation. The findings assist substrate selection based on the required film morphology, revealing the structural dynamics during the crystallization process, thus helping to tackle the technological challenges of structure formation of 2D perovskites for optoelectronic devices.

1. Introduction

Hybrid organic-inorganic perovskites are an emerging novel class of optoelectronic materials.^[1-3] The relationship between their composition and structure and their properties have been the focus of many investigations in the last decade, identifying

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materials more suitable for photovoltaics (PV) or light-emitting diodes (LEDs).^[4-6] However, recent works^[7,8] have somewhat smeared the boundaries between different classes of hybrid perovskites in terms of their suitability for a particular application and instead highlighted the importance of crystallinity and crystal orientation over structure dimensionality. 2D hybrid perovskites contain organic ammonium cations exceeding the Goldschmidt's tolerance factor^[9] and leading to layered structures of alternating inorganic metal halide sheets (octahedral PbI₆ coordination) separated by charge-balancing organics.

The epitomical, so-called 3D, methylammonium hybrid perovskite suffers from very low water and oxygen tolerance, limiting PV-cell manufacturing to a vacuum or glove-box environment.[10] In contrast, 2D hybrid perovskites have been proven to be remarkably stable under a broad range of applied conditions,[11-15]

and recently, the Ruddlesden-Popper type perovskites have been shown to combine the benefits of the two but are difficult to control in terms of crystallographic orientation.^[16]

Due to their multi-quantum well character and anticipated low exciton dissociation cross-section, 2D perovskites have not been considered feasible materials for PVs.^[17,18]

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However, it has been shown that irradiation almost exclusively leads to direct generation of free charge carriers, as in the 3D perovskites (methylammonium, formamidinium, etc.). Instead, the mean charge carrier diffusion length has been identified as the limiting factor.^[7,8] The breakthrough came with the ability to fine-tune the crystallographic orientation of 2D perovskites layers so that a continuous electrical conduction pathway for electrons and holes was formed. Many publications have used this technique to demonstrate comparably high power conversion efficiencies for 2D perovskite solar cells.^[16,19–31] The origin of the 2D perovskite layer orientation and the crystallization kinetics were thus intensely studied using grazing-incidence wide-angle X-ray scattering (GIWAXS).^[32–36]

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The design of perovskite-based PV and LED devices typically features either planar or bulk heterojunctions, making the crystal orientation essential in the former case and the crystal size critical in the latter case.^[37] The substrate effect has been studied in great detail, particularly the aspects of charge collection properties,^[38,39] induced elemental separation,^[40,41] and film morphology.^[42] However, the templating effects on the orientation of 2D perovskite layers induced by 2D materials, including graphene or related 2D monolayers, have not been studied in detail.

The crystal nucleation is generally understood to start at surface defects and corrugations on the substrate, making it one of the key aspects determining the properties of the final device. Simplified PV and particularly LED devices also employ active layer assembly (perovskite in the present case) directly on a conductive surface without the charge-guiding semiconducting interlayer.^[43] Thus, it is important to investigate conductive surfaces for hybrid 2D perovskite assembly to evaluate their effect and potential for optoelectronic devices such as LEDs or PV cells.

The chemical nature of the 2D perovskites precursors limits the solvent choice to polar aprotic solvents, most commonly N,N-dimethylformamide (DMF), with boiling point of about 150 °C. The necessary crystallization is therefore induced by the addition of an antisolvent or by solvent evaporation at elevated temperatures, requiring either prolonged drying times or rapid heat pulse to induce crystallization. Only the latter seems feasible for industrial applications.

In our work, we investigate the most commonly used conductive surfaces, FTO, and graphene, for their effect on 2D perovskite crystallization. We were specifically interested in: a) the overall crystallography, that is, phase and crystal orientation, of the film formed on different substrates, b) the kinetics of hybrid perovskite formation, and c) the supramolecular phenomena that dictate the assembly on surfaces. We have employed flash infrared annealing (FIRA)^[44] in situ monitored by GIWAXS using synchrotron radiation with 25 ms temporal resolution and corroborated the experimental data with molecular dynamics (MD) simulations. Our findings show that the substrate plays a key role in the crystallization process and thus dictates the suitability of the whole device for particular applications. Most importantly, a single atomic layer of graphene was shown to template the orientation of the 2D perovskite layer.

2. Results and Discussion

The in situ and real-time GIWAXS is commonly used to track the crystallization of thin perovskite films during spin-coating and following annealing.^[45–51] The experimental GIWAXS data can be used to reconstruct the unit cell's parameters and crystal orientation with respect to the underlying substrate. In this study, two conductive substrates have been investigated: commercial FTO on glass and graphene transferred onto Si/SiO₂ wafers (see Supporting Information for details). The precursor solutions of PbI₂ and piperonylammonium (3,4-(methylenedioxy)benzylammonium) iodide in DMF were spin-coated on the substrates, and GIWAXS was performed during the annealing process. The final GIWAXS patterns of 2D perovskite layers after FIRA heat treatment for graphene and FTO substrates are shown in **Figures 1**a,b, respectively.

After FIRA of the 2D perovskite precursor on graphene, when the temperature of the substrate approached the boiling



Figure 1. GIWAXS patterns of FIRA-processed 2D perovskite films on a) graphene and b) FTO substrates. On graphene, the diffraction spots confirm an orthorhombic (001) horizontally-oriented A_2BX_4 type 2D perovskite film formed from piperonylammonium iodide and PbI₂. The splitting of the diffraction points is due to spatial film inhomogeneities, which are particularly visible in GIWAXS geometry at larger exit angles. Please note that the l-index is 11 for the 1111 diffraction. c) Schematic structure of the 2D perovskite layer with chemical formula $(C_8H_{10}NO_2)_2PbI_4$. The parallel orientation of the (002) planes and the graphene substrate is highlighted.

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point of DMF, a clear diffraction pattern started to emerge. The GIWAXS pattern of 2D perovskite film on graphene displays diffraction spots that can be indexed utilizing the orthorhombic space group (Pbca) with (001) planes parallel to the substrate.^[52] The in-plane sample rotation verified the uniaxial anisotropy of the crystalline film. The *c*-axis of this textured 2D perovskite film is aligned normal to the surface. The most intense signal was recorded for the 002 diffraction spot. The presence of higher diffraction order signals are clear evidence of the layered structure assembled by alternating PbI₆ connected octahedra sheet, and the organic ammonium cations packed antiparallel to compensate the charge. The piperonyl moiety can partially π - π stack, however, this interaction is somewhat weakened by the sterically demanding dioxomethylene bridge.

However, the GIWAXS pattern of the perovskite film spincoated and annealed on the FTO substrate does not show the low-q diffractions typical for the large unit cells of 2D perovskite. Instead, it displays the 001 diffraction peak at $q \approx 0.9$ Å⁻¹ characteristic of PbI₂. These findings are further supported by SEM micrographs, AFM images, and XRD patterns (see Figure S3–S5, Supporting Information), which show largely different surface morphology and topography of the perovskite film on FTO substrate compared to that on graphene.

A distinct crystal preferential orientation observed on graphene as compared with FTO stems from the different nature of interactions at the interface (summarized in Table 1). Numerous examples have shown that aromatic hydrocarbons (typically derivatives of pyrene) feature a strong adsorption enthalpy on graphene, leading to the so-called "non-covalent functionalization" of the honeycomb lattice.^[53,54] This interaction combines the π - π overlap and London dispersion forces and preassembles the organic moiety in parallel to the graphene layer. This, in turn, exposes the protonated aminomethyl group into the liquid phase and this planar assembly of amines consequently forces the 2D perovskite crystallization to proceed parallel to the surface. Like other very smooth surfaces, graphene can act as a template for the directed growth of 2D perovskite films on arbitrary substrates.^[12] The high optical transmissivity and electrical conductivity of graphene, combined with the possibility of doping towards n- or p-type,^[55] enables its application in optoelectronics, including solar cells, photodetectors, and light-emitting diodes.

FTO is a very polar surface that can be terminated by a variety of chemical species: hydroxyl- or oxo-groups are dominant after oxidative annealing, low-valent tin is found under reducing conditions, and in addition, the doping can expose some fluorine atoms on the surface.^[58–60] Although hydrogen bonding between the ammonium salt and the FTO surface is theoretically expected, it is not very likely to contribute strongly in polar solvents such as DMF due to strong hydrogen bonding to solvent molecules.^[61] Instead, covalent bonds can readily

Table 1. Summary of water contact angle (WCA) and surface energy σ (including $\sigma^{\rm p}$ polar and $\sigma^{\rm d}$ dispersive component) data for the perovskite growth substrates used in this study. a) Data reported by Briand and Eslamian.^[56] b) Data reported by Annamalai et al.^[57]

Substrate	WCA [°]	σ [mN m ⁻¹]	σ ^ρ [mN m ⁻¹]	σ^{d} [mN m ⁻¹]
UV-cured FTO ^a	3.3ª	80.1ª	33.7ª	48.2ª
Graphene on SiO ₂	79.7	37.7 ^b	1.53 ^b	33.2 ^b

occur either a) between Pb^{2+} ions in the solution and hydroxyl, oxo, or fluoride groups on the surface or b) iodide anions in the solution and the coordinatively unsaturated Sn atoms of the surface.^[62–64] Both of these scenarios monodently bind PbI_5X (X is the surface atom) directly to the surface, and the Pb-I sheet crystallization can proceed at any other vertex of the octahedron. This weak, omnidirectional preorganization combined with irreversible covalent bond formation is considered responsible for the isotropic microcrystal orientation in the final film as evidenced by the GIWAXS, SEM, AFM, and XRD (see Figure S3–S5, Supporting Information).

To conclusively confirm the templating effect of graphene on the oriented growth of 2D perovskite films, we employed time-resolved GIWAXS. This method enables in situ and real-time investigation of crystallization kinetics during the annealing process (FIRA) with a millisecond temporal resolution. Figure 2a shows the temporal evolution of the intensity of the precursor diffraction ring^[48,65] located at $q \approx 0.4$ Å⁻¹ and the intensity of three selected diffraction peaks of the converted 2D perovskite film. The FIRA heating pulse started at 5 s and lasted for another 15 s. During the annealing period (including the ambient temperature phase), we observe a gradual decrease of the peak intensity of the precursor material over approximately 17 s, after which it rapidly vanished and instead peaks assigned to the 2D perovskite phase emerged. At the initial stage of 2D perovskite crystallization (approx. 2 s), a much steeper onset of the intensity increase was observed for the 111 and 108 peaks when compared to the 002 peak.

After switching off the FIRA heating pulse, the intensities of 111 and 108 stayed almost constant, while the limited exponential function can approximate the temporal evolution of the intensity of the 002 peak. After the fast initial nucleation and crystal growth, this suggests a secondary crystallization phase, which can be attributed to a delayed growth of perovskite crystals in the *c*-axis direction, that is, along the surface normal. Additionally, a more pronounced shift of the 002 diffraction spot than the 111 and 108 spots is primarily due to a significantly larger thermal expansion coefficient^[66,67] along the c-axis direction compared to the a- and b-axis directions. To follow the texture evolution of 2D perovskite films during FIRA, we plotted the cuts of 1111 pole figures along the χ azimuthal angle^[68] as a function of time (Figure 2b). This particular diffraction plot was chosen to enhance the tracking of lattice parameter changes, both in-plane and out-of-plane, of the perovskite film. The angular intensity distribution is unchanged over time, confirming a directed growth of 2D perovskite film along the surface normal from the very beginning. The magnitudes of momentum transfer values q were fitted using flat-top Gaussian function and are shown in Figure 2c. The largest changes in the q values are observed during the first two seconds following crystallization initiation. In the cool-down period, the observed shifts are predominantly due to thermal relaxation. Additionally, we can observe oscillations, especially well resolved for the 002 and 111 diffraction spots. The observed fringes are experimental artifacts presumably due to the mechanical mounting instabilities of the FIRA chamber during the cool-down period.

The orthorhombic crystal system has three independent lattice parameters *a*, *b*, and *c*, which can be unambiguously determined using three different non-coplanar diffraction spots. For







Figure 2. Evolution of GIWAXS patterns during annealing. a) The intensity of the precursor peak along with the intensities of 002, 111, and 108 diffractions of converted 2D perovskite. b) The azimuthal cuts across the 1111 diffraction as a function of time. c) The fitted positions of 002, 111, and 108 diffractions. (For the origin of the oscillations of the signal see main text).

this purpose, we selected the 002, 111, and 108 spots, the most intense complete set, marked in Figure 1a. The calculated lattice parameters are plotted in **Figure 3** as a function of time. The a and b lattice parameters exhibit insignificant variations within their confidence intervals during annealing and the subsequent

cool-down period. In contrast, the *c* lattice parameter, which corresponds to the interlayer spacing of the 2D Pb–I sheets, shows a large variation of almost 0.7 Å. This variation represents an increase of more than 2%, indicating that during the crystallization process, the sheets grow further apart. The comparably



Figure 3. The lattice parameters of 2D perovskite film during annealing and in the cool-down period showing the delayed crystallization along the *c*-axis (time axis is in log scale). The inset shows a simplified view of the unit cell.

smaller increase of the lattice parameter in the cool-down phase (t > 17 s) can be attributed to the ongoing thermal expansion of the crystal lattice. However, the large observed dilatation of the unit cell along the *c*-axis during the FIRA processing is counterintuitive and cannot be explained by thermal relaxation of the system. Furthermore, under identical crystallization conditions, a methylammonium lead triiodide (MAPI) 3D perovskite layer did not exhibit any changes of lattice parameters during or after the FIRA treatment (see Supporting Information for experimental trace). We suggest that the observed lattice expansion during crystallization was due to a relatively slow molecular alignment of the piperonyl spacers within the van der Waals gap of 2D perovskite film.

To support our hypothesis, we have performed a classical MDs simulation of the perovskite layer (parameters and details of the MD calculation are provided in the Supporting Information). The system was modeled as a slab of two perovskite layers. As the modeling of hybrid perovskites by empirical force fields is at an early stage,^[69] the organic moiety was simplified to a butylammonium cation. At first, a stable periodic crystal structure was obtained, then the periodic restrictions were removed and crystal grain boundaries were reconstructed by maintaining a null total charge. This system was then allowed to relax with open boundary conditions, representing an inverse process to crystallization.

The results (shown in **Figure 4**) indicate highly disordered organic moieties at the grain boundary, as expected. However, the surprising consequence of this disorder is a significantly shorter distance between Pb edge atoms of two adjacent layers. In Figure 4c, the histogram of Pb atoms interlayer spacing is plotted with respect to the distance of the atom from the edge

(see Supporting Information for evaluation details). Extreme disorder is characteristic of the very edge atoms, covering a wide spacing range, however, the nearest to the edge set of Pb atoms (i.e., those 2.8 Å from the edge) show spacing of 12.9 Å, while the second nearest set of atoms (*cca* 4.2 Å from the edge) are separated by 13.6 Å. This difference in interlayer spacing of 0.7 Å coincides well with the experimentally observed change in the *c* lattice parameter during crystallization. The further from the edge of the crystal grain, the more the interlayer spacing approaches the equilibrium value of the bulk crystal.

The following scenario can be proposed from the MD results: FIRA induces fast and dense crystal nucleation with a small number of repeating units in the $a \times b$ plane and highly disordered organic ammonium groups. The nuclei are forced to coalesce at their boundaries during the heating pulse, which forces the organic moieties to align with respect to the *c* axis leading to increased interlayer spacing. The nucleation occurs isotropically (at least in the $a \times b$ plane), and hence spatial reorientation of the whole crystal nucleus is required for it to merge with the neighboring nucleus constructively. This reorientation is fairly slow (compared to molecular motion) and requires a significant amount of energy to proceed. Therefore the steep expansion of the unit cell volume basically ceases when the FIRA ends.

3. Conclusion

We have studied the 2D hybrid perovskite crystallization by employing time-resolved synchrotron-based GIWAXS on two different substrates focusing on the preferential crystal orientation and crystallization kinetics. On the FTO substrate,



Figure 4. Results of the MD simulation results. a) Side-view of two layers of PbI₆ sheets showing significant disorder of the heavy atoms at the grain boundary (organic ammonium omitted for clarity). b) Top-view on a single layer of Pb atoms, the edge atoms are depicted in blue and exhibit large disorder. c) Histogram of the interlayer distance as a function of distance from the crystallite edge. The trend shows smaller interlayer distance at the edge, which converges to the equilibrium bulk value within 10 Å. d) Histogram of organic cation disorder defined as the cosine of the angle between Pb-layer normal and the vector between $C\alpha$ – $C\omega$ of the organic cation. The data reveal that the organic cation at the grain boundary is tilted outwards from the 2D perovskite structure, giving the Pb–I sheet no other choice than to contract and decrease the interlayer spacing.



isotropic crystallization using a FIRA annealing pulse takes place. In contrast, graphene induces a strong preferential orientation with the *c* axis normal to the surface. We attribute this effect to the interactions provided by the substrate-the FTO surface termination and defects preferably bond to the Pb or I atoms of the PbI₆ layer corrugations, while graphene provides a π - π interaction with the piperonyl moiety, which in turn leads to the observed preferential orientation. The preferential orientation propagates the templating effect of graphene through the perovskite layer, which shows markedly smoother surface topography than the layer grown on FTO. The kinetic data show significant lattice expansion during the rapid crystallization induced by FIRA. MD simulations explained this observation based on crystal nuclei fusion and corresponding forced alignment of the piperonyl species, which leads to a larger *c* lattice parameter. Since the properties of perovskite devices depend on the structure of the crystalline layer, an understanding of the processes occurring during layer formation is essential to optimize devices. The presented data rationalize the choice of substrate and annealing step to obtain the desired perovskite film morphology for specific optoelectronic devices.

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.

Keywords

2D perovskite, crystallization, GIWAXS, graphene, heterostructures

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