Effects of ITO Substrate Hydrophobicity on Crystallization and Properties of MAPbBr₃ Single-Crystal Thin Films

Haipeng Di, Wei Jiang, Hao Sun, Chen Zhao, Feiyi Liao, and Yiying Zhao*

ABSTRACT: Fabricating perovskite single-crystal thin films (SCTFs) in controllable manner is the major challenge for the promising potential applications in optoelectronic devices. Although modifying the substrate surface is frequently used to realize the controlled growth of perovskite SCTFs, it is still unclear how the substrate condition affects the crystallization process. In this work, we systematically investigated the effects of the substrate hydrophobicity of indium tin oxide (ITO) substrates on the crystallization process of MAPbBr₃ SCTFs prepared by the space-confined method. Comprehensive characterizations show that the surface morphology and crystallinity of SCTFs are improved, and the defect density is reduced when increasing the substrate hydrophobicity. The best MAPbBr₃ thin film obtained has a full width at half-height of the rocking curve of the (001) crystal plane of 0.044°. The mechanism of the substrate hydrophobicity on the crystal growth is also discussed. These results will provide guidance to the controllable growth of high-quality SCTFs for perovskite SCTF devices.

INTRODUCTION

Organometal trihalide perovskites have been extensively studied as promising materials for a broad range of potential applications such as solar cells, light-emitting diodes, lasers, photodetectors, betavoltaic cells, and field-effect transistors. Recently, perovskite single-crystal thin films (SCTFs) attracted intensive attention for unique applications of photodetection and X-ray detection because of their superior properties resulting from the elimination of grain boundaries and the accompanied carrier recombination.1−12 Now, fabricating perovskite SCTFs in controllable manners is the main challenge for the future commercialization of high-performance optoelectronic devices.13

Many methods such as top-down growth, vapor-phase epitaxial growth, and solution-based lateral crystal growth have been developed to prepare perovskite SCTFs. Top-down growth such as mechanical exfoliation is simple but has low reproducibility and difficulties in fabrication of large-area SCTFs. Vapor-phase epitaxial growth can be applied to prepare all-inorganic SCTFs but requires high growth temperature and a high degree of lattice matching between substrates and samples, which is incompatible with most of the perovskite device fabrication processes. Solution-based lateral crystal growth is widely suitable and of low cost but with less control in the crystal geometry because of the isotropic growth rate in solution. The space-confined method is developed to improve the aspect ratio of SCTFs and has become the most promising one for realizing the controllable growth of high-quality SCTFs and device fabrications.

A great amount of effort has been carried out toward high performance and controllable growth of perovskite SCTFs using the space-confined method, such as increasing the crystal size via improving the mass transport of precursor solution and controlling of nucleation position. Chen et al. introduced a hydrophobic hole-transport layer PTAA on indium tin oxide (ITO) substrates to improve the mass transport, leading to perovskite SCTFs solar cells with an efficiency of 17.8%. Rao et al. employed a peristaltic pump to improve mass transportation and built a temperature gradient to control nucleation positions and nuclei numbers in the space-confined system, resulting in an enlarged MAPbBr₃ SCTF with a lateral size of 6 mm × 8 mm. Yang et al. demonstrated the selective growth of MAPbBr₃ SCTFs on hydrophilic substrates because of the reduced nucleation energy and also modulated the thickness of SCTFs ranging from 100 nm to 20 μm via changing the force applied on substrates, that is, the gap between two slides of substrates. Lee et al. developed a facile roll-printing method to fabricate patterned CH₃NH₃PbI₃ SCTFs with a high carrier mobility of 45.64 cm² V⁻¹ s⁻¹, where the lateral crystal growth control of SCTFs was realized by geometrically confining the ink spread area using the patterned mould and also the unidirectional growth caused by the instant crystallization of the precursor ink. Gu et al. successfully fabricated arrays of multifunctional perovskite SCTFs using the seed-assisted inkjet printing method, where...
the nucleation sites were determined by the seed position.\textsuperscript{33} Substrate surface condition such as the hydrophobicity and the chemical bonds state is frequently used to control the perovskite nucleation position,\textsuperscript{34} however, it is still unclear how the substrate surface condition affects the nucleation and crystal growth of perovskite SCTFs.

Herein, we systemically investigated effects of the surface hydrophobicity of ITO substrates on the crystallization process of MAPbBr\textsubscript{3} SCTFs for the applications of high-performance devices. MAPbBr\textsubscript{3} SCTFs were prepared on ITO substrates with different hydrophobicities using the space-confined method. We found that the crystallinity and the quality of SCTFs improved with the increase of the hydrophobicity of ITO substrates. The best MAPbBr\textsubscript{3} SCTF was obtained in square shape with a homogeneous and smooth morphology and a full width at half-height (fwhh) of 0.044°. The mechanism of how the hydrophobicity of ITO substrates affects the crystallization process and crystal quality was discussed. These results will provide guidance for the controllable growth of high-quality SCTFs and inspire further exploration of fabrication of high-performance perovskite SCTF devices.

## RESULTS AND DISCUSSION

MAPbBr\textsubscript{3} thin films were grown on substrates with different hydrophobicities using the space-confined method assisted with solvent evaporation at a constant temperature of 50 °C. The schematic diagram and the photo of experimental setup are shown in Figure 1a. The MAPbBr\textsubscript{3} precursor solution was dropped on the edge of ITO glass substrates and then solution migrated into thin films with the increasing amount of solvent evaporated. Photograph of the MAPbBr\textsubscript{3} SCTF prepared by the space-confined method; inset: optical photo of MAPbBr\textsubscript{3} SCTF with a scale.

![Figure 1. Illustration and photo of the experimental setup, morphology, and structural characterizations of MAPbBr\textsubscript{3} SCTFs.](image)

 dropped on the edge of ITO glass substrates and then solution migrated into the narrow gap between two glass slides driven by the capillarity force. Nuclei formed between the gap and grew into thin films with the increasing amount of solvent evaporated. Photograph of the MAPbBr\textsubscript{3} SCTF prepared by this method is shown as the inset of Figure 1b, with an area approximately 1 mm × 2 mm and a thickness of 7.78 μm determined by step-profiler. X-ray diffraction (XRD) patterns of the thin film in Figure 1b show four sharp diffraction peaks from a single-plane family, indicating a SCTF grown along the (001) orientation.\textsuperscript{35}

Effects of the surface hydrophobicity of ITO substrates on the nucleation and crystallization process of MAPbBr\textsubscript{3} SCTFs were systematically investigated in this work. ITO substrates with different surface hydrophobicities are obtained via varying the duration of the ultraviolet–ozone (UVO) treatment. As shown in Figure 2, contact angles of deionized water on ITO substrates decreases with the increase of the UVO treatment time, that is, the decrease of the hydrophobicity of ITO substrates. The contact angle of substrates treated with UVO for 40 min is only 6.2°. The decreased hydrophobicity of ITO substrates indicates the increase of the surface free energy and the decrease of the surface tension, which is attributed to the increased oxygen content and dangling bonds density on the ITO surface during the UVO treatment.\textsuperscript{36,37} Therefore, it can be concluded that the UVO treatment can effectively modify the hydrophobicity and the surface free energy of ITO substrates.

![Figure 2. Contact angles of deionized water on ITO glass substrates with different UVO treatment duration and photographs of MAPbBr\textsubscript{3} thin films at different growth times prepared on ITO glass substrates with different UVO treatment.](image)

Photos of MAPbBr\textsubscript{3} SCTFs at different growth times prepared on ITO substrates with different UVO treatments are shown in Figure 2. It can be seen that MAPbBr\textsubscript{3} crystals appear earlier on the ITO substrates with longer UVO treatment, and the number of crystals is correspondingly larger. This indicates that the nucleation of MAPbBr\textsubscript{3} is lower on the ITO substrate surface with longer UVO treatment because of the increased surface free energy of ITO substrates.

The number of MAPbBr\textsubscript{3} crystals on ITO glass substrates with different UVO treatments (denoted as UVO-treatment time) is plotted as a function of the growth time in Figure 3a. The number of crystals first increases and then remains constant with increasing the growth time. The MAPbBr\textsubscript{3} nucleation process is finished in the first 2 h in all samples. Meanwhile, the number of MAPbBr\textsubscript{3} crystals increases with the increase of the UVO treatment time. These results can be explained using the heterogeneous nucleation model. The work of heterogeneous nucleation can be expressed as

$$
\Delta G_{het} = \left[ \frac{16\pi L_S^2}{3\Delta g_{s}^2} \right] \times \left[ 1 - \cos \theta \right] \left( 2 + \cos \theta \right)
$$

where $\gamma_{LS}$ is the embryos/liquid phase specific interface energy, $\Delta g_{s}$ is the free energy difference per unit volume of the solid and liquid phase, and $\theta$ is the apparent wetting angle between the embryo and the substrate. Critical nuclear radius $R^*$ can be written as

$$
R^* = \left( 2\gamma_{LS} / \Delta g_{s} \right)
$$

From eqs 1 and 2, it can be seen that the increasing of $\theta$ (or substrate hydrophobicity) will lead to the increase of the nucleation work but will not affect the critical nuclear radius.
It means that there is fewer MAPbBr₃ crystals formed on the hydrophobic substrates where the nuclei are difficult to form. Correspondingly, more MAPbBr₃ crystals are observed on the hydrophilic substrates, which is consistent with our experimental results in Figure 3a.

The total area of MAPbBr₃ crystals on each type substrate is plotted as a function of the growth time as shown in Figure 3b. The crystal area is defined as the total number of all the pixels of MAPbBr₃ crystals in photographs, which can be calculated using the function library of MATLAB software. It can be seen that the area of the MAPbBr₃ single crystals first increases and then remains constant with the increase of growth time. The growth time of MAPbBr₃ crystals is longer on the hydrophobic substrates. The average area of MAPbBr₃ crystals is plotted as a function of growth time, as shown in Figure 3c. The crystal area of the UVO-40 sample in Figure 3c is plotted as 8 times the real area to show the trend clearly; (d) lateral crystal size of MAPbBr₃ crystals on different ITO substrates as a function of growth time fitted by $r^{0.5}$.

The photos, optical micrographs, and scanning electron microscopy (SEM) photos of MAPbBr₃ thin films prepared on ITO substrates with different UVO treatments are shown in Figure 4. It can be seen that MAPbBr₃ thin films exhibited larger crystal size and fewer crystal numbers with the decrease of UVO treatment time, that is, increasing the hydrophobicity of the substrate surface. Thin films grown on the untreated ITO substrates are homogeneous, and when decreasing the substrate hydrophobicity, thin films exhibit oriented growth featuring with steps. Overall, MAPbBr₃ thin films prepared on hydrophobic substrates exhibited the smaller effective growth area, less crystals, and the larger crystal size. The thickness of films is in micrometers. It can be concluded that the hydrophobic surface is better for the growth of MAPbBr₃ SCTFs.

ITO substrates with higher hydrophobicity correspondingly have the decreased surface free energy and the increased surface tension, which have significant impacts on the nucleation and crystal growth of MAPbBr₃ thin films. As shown in Figure 5, when a drop of MAPbBr₃ precursor solution is inserted at the end of two regular glass substrates, the solution migration on the high hydrophilic surface is very effective growth area of precursor solution, which can be explained by the fast solute diffusion. The average size of the MAPbBr₃ crystals on ITO substrates with longer UVO treatments is smaller because of the limit of the total amount of the MAPbBr₃ solute.

The lateral crystal size of MAPbBr₃ crystals at different growth times fits well with the function of $r^{1/2}$, as shown in Figure 3d, indicating that the process is the diffusion-controlled growth. The lateral crystal size $\lambda$ can be written as

$$\lambda = (2D\tau)^{1/2} \quad (3)$$

where $D$ is the diffusion coefficient, $\tau$ is the growth time. The fitting parameter which is proportional to the diffusion coefficients of solutes can be obtained by fitting the growth curves, which are, respectively, 0.00319 (UVO-0), 0.0366 (UVO-10), 0.194 (UVO-20), 0.458 (UVO-30), and 0.827 (UVO-40). It can be concluded that the MAPbBr₃ solute diffuses quickly on the hydrophilic substrate surface (substrates with longer UVO treatment time).

Figure 3. (a) Crystal number and (b) total crystal area of MAPbBr₃ crystals on different ITO substrates as a function of growth time; (c) crystal average area of MAPbBr₃ crystals on different ITO substrates as a function of growth time, where the crystal area of UVO-40 is 8 times the real area to show the trend clearly; (d) lateral crystal size of MAPbBr₃ crystals on different ITO substrates as a function of growth time fitted by $r^{0.5}$.

Figure 4. (a) Photographs of MAPbBr₃ crystals on air-laid wipe; (b) optical micrographs of MAPbBr₃ crystals labeled with thickness; and (c) SEM photos of MAPbBr₃ thin films grown on different ITO substrates.

Figure 5. XRD patterns of MAPbBr₃ thin films grown on ITO substrates with different UVO treatments.
substrates with a contact angle smaller than 6.2°, indicating the existence of multiple crystal grains. The XRD rocking curves of the (001) crystal plane is shown in Figure 6b, and the fwhh decreases with the increase of the hydrophobicity of the substrate surface. It can be concluded that the crystallinity of MAPbBr₃ thin films improves when increasing the substrate hydrophobicity.

Figure 6. (a) XRD patterns and (b) XRD rocking curves of the (001) crystal plane of MAPbBr₃ thin films grown on different ITO substrates; (c) steady-state PL spectra of MAPbBr₃ thin films on different ITO substrates; (d) PL main peak emission wavelength, PL secondary peak emission wavelength, and peak height ratio of MAPbBr₃ SCTFs, as a function of contact angle of deionized water on ITO substrates; inset: demonstration of peak-differentiating and imitating method; (e) fwhh of the rocking curve of the (001) crystal plane and fwhh of the PL emission peak as a function of the contact angle of deionized water on ITO substrates; (f) lattice constant, optical band gap, and photon energy of the PL emission peak as a function of the contact angle of deionized water on ITO substrates.

The steady-state photoluminescence (PL) spectra of MAPbBr₃ SCTFs are shown in Figure 6c to investigate the effects of substrate hydrophobicity on the crystallinity of the MAPbBr₃ SCTFs. It can be seen that the peak emission wavelength exhibits a blueshift from 560 to 540 nm, and the fwhh of the emission peak decreases with the increase of the substrate hydrophobicity. The blueshift of PL peak emission wavelength is resulted from the lower trap density in MAPbBr₃ SCTFs and the broader emission peak is mainly resulted from sub-band gap traps formed by MA⁺ vacancy. Therefore, the two emission peak wavelengths of the steady-state PL spectra of MAPbBr₃ SCTFs can be obtained using the peak-differentiating and imitating method as shown in the inset of Figure 6d. Peak wavelength and peak height ratio as a function of contact angles are shown in Figure 6d. It can be seen that the main PL peak wavelength blueshifts and the secondary peak wavelength redshifts with the increase of the substrate surface hydrophobicity (contact angles). The height ratio of the secondary peak over the main peak decreases when...
increasing the surface hydrophobicity of ITO substrates. It can be concluded from Figure 6c,d that the defect density of MAPbBr₃ thin films decreases when increasing the substrate hydrophobicity.

The fwhh of XRD rocking curves and the fwhh of PL emission peaks were plotted as a function of contact angles in Figure 6e. A similar trend can be observed that both fwhh of the XRD and PL decrease with the increase of the substrate surface hydrophobicity, which indicates the improved crystallinity and the reduced trap density. Correspondingly, the band gap calculated from UV–vis absorption spectra also becomes narrower with the increase of the substrate hydrophobicity, which exhibits the same trend as that of the band gap calculated from the PL peak emission wavelength, as shown in Figure 6f. It can also be seen that the lattice constant calculated from the XRD increases with the increase of the substrate hydrophobicity because of the decrease of the number of vacancies, which form sub-band gap traps and narrow the band gap. Overall, results of both the XRD and PL measurement show that the crystallinity of MAPbBr₃ SCTFs improves and the trap density decreases with the increased hydrophobicity of ITO substrates.

Photograph of MAPbBr₃ SCTF grown on untreated ITO glass is shown in the Figure 1b inset. From the optical microscope photo in Figure 7a and SEM image in Figure 7c, it can be seen that the SCTF is semitransparent with a homogeneous and smooth morphology. From the atomic force microscopy (AFM) image (Figure 7b), the mean roughness of MAPbBr₃ SCTF is 2.370 nm. It can be further confirmed by the XRD rocking curve of (001) plane, as shown in the Figure 7d. The fwhh is 0.044°, which is superior to the best reported work (fwhh = 0.05)⁹, indicating a pretty good crystalline quality and a small residual stress in the obtained SCTF. The optical properties of the MAPbBr₃ SCTF were investigated using the UV–vis absorption spectrometer and the steady-state PL measurement. As shown in Figure 7e, the MAPbBr₃ SCTF shows a clear band edge cutoff with no excitonic signature, which suggests a minimal number of in-gap defect states. A narrow emission peak of PL spectroscopy locates at 541 nm in line very well with the absorption onset (~543 nm) of the thin film. The band gap is 2.28 eV; it is calculated from the extracted data from the Tauc plot (Figure 7f) of the UV–vis absorption spectra.

The space charge limited current (SCLC) method was used to investigate transport properties of MAPbBr₃ SCTFs. The I–V curve of the device under dark was measured to derive the trap density (nTrap) and the carrier mobility (μ). As shown in Figure 7g, the linear I–V section at low voltage is the ohmic region (green). As the bias increases, the I–V curve shows a steep increase, indicating the presence of a trap-filling region (blue) starting at trap-filled limit voltage (VTFL). The nTrap calculated from VTFL = enTrapL²/2kT is 9.8 × 10¹³ cm⁻³, greatly lower than polycrystalline films. In the Child’s regime (orange), the μ is deduced to be 11.2 cm²V⁻¹s⁻¹ by fitting the curve with the Mott–Gurney law J = 9ε₀εrμV²/8L³, indicating pretty good transport properties.

■ CONCLUSIONS

Effects of surface hydrophobicity of ITO substrates on the crystallization process and properties of MAPbBr₃ SCTFs prepared using the space-confined method were systematically investigated. The hydrophobicity of ITO substrates can be varied from a wide range by carefully controlling the UVO treatment duration. Comprehensive investigations show that the increased substrate hydrophobicity will strongly improve the crystal size, the surface morphology, and crystal quality, resulting from the slow solution diffusion on the surface and the reduced oxygen dangling bonds on the high hydrophobicity surface. MAPbBr₃ SCTFs of best quality was grown on untreated ITO substrates at 50 °C. The SCTF is in square shape with a thickness of 7.78 μm and a fwhh of 0.044° of the rocking curve of the (100) crystal plane, which is the best result reported so far. These results might inspire further explorations of fabricating high-performance PSCs and other optoelectronic devices with hybrid perovskite SCTFs.

■ EXPERIMENT SECTION

Materials. Lead bromide (PbBr₂, 99%), methylammonium bromide (MABr, ≥99%), N,N-dimethylformamide (DMF, 99.9%) purchased from Aladdin. All materials were used without further purification. Substrates were ITO glasses (1.5 cm × 1.5 cm, thickness: 1.1 mm), bought commercially from HT technology.

Substrate Preparation. ITO substrates were sequentially ultrasonic-cleaned with glass cleaning liquid, deionized water, acetone and ethanol for 20 min, and finally dried with N₂. Then, the substrates were treated with UVO for different times.
SCFT Growth. PbBr₃ and MAPbBr₃ (1:1 by molar, 1.5 M) were dissolved in DMF and stirred overnight at room temperature to prepare the precursor solution. MAPbBr₃ precursor solution of 5 μL was dropped onto the edge of a treated substrate covered with another substrate, as shown in Figure 1a, and then, the precursor solution migrated into the narrow gap between two substrates because of the capillarity force. Then, the sample was placed on a hotplate for the crystal film growth at a constant temperature of 50 °C. After the completion of film growth, the samples on conductive ITO substrates were directly characterized by simply taking off the cover ITO glass substrate.

Materials Characterization. Optical images were taken using 10 XB-PC metallographic microscopy. SEM images were obtained on a Hitachi S4300N SEM. AFM images were performed on a Bruker Dimension Edge. The steady-state PL spectrum was measured on a Perkin Elmer LS55 spectrophotometer. The absorption spectra were collected on a Perkin Elmer Lambda 950 UV-Vis spectrophotometer.

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Notes
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