Crystal Morphologies of Organolead Trihalide in Mesoscopic/Planar Perovskite Solar Cells

Yuanyuan Zhou,‡† Alexander L. Vasiliev,† Wenwen Wu,‡ Mengjin Yang,‡ Shuping Pang,§ Kai Zhu,‡ and Nitin P. Padture*‡†

†School of Engineering, Brown University, 184 Hope Street, Providence, Rhode Island 02912, United States
‡Chemical and Materials Science Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, Colorado 80401, United States
§Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Qingdao 266101, P.R. China

Supporting Information

ABSTRACT: The crystal morphology of organolead trihalide perovskite (OTP) light absorbers can have profound influence on the perovskite solar cells (PSCs) performance. Here we have used a combination of conventional transmission electron microscopy (TEM) and high-resolution TEM (HRTEM), in cross-section and plan-view, to characterize the morphologies of a solution-processed OTP (CH3NH3PbI3 or MAPbI3) within mesoporous TiO2 scaffolds and within capping and planar layers. Studies of TEM specimens prepared with and without the use of focused ion beam (FIB) show that FIBing is a viable method for preparing TEM specimens. HRTEM studies, in conjunction with quantitative X-ray diffraction, show that MAPbI3 perovskite within mesoporous TiO2 scaffolds has equiaxed grains of size 10–20 nm and relatively low crystallinity. In contrast, the grain size of MAPbI3 perovskite in the capping and the planar layers can be larger than 100 nm in our PSCs, and the grains can be elongated and textured, with relatively high crystallinity. The observed differences in the performance of planar and mesoscopic-planar hybrid PSCs can be attributed in part to the striking differences in their perovskite-grain morphologies.

Solar cells based on solution-processed organometallic trihalide perovskite (OTP) have emerged as a new “player” in the photovoltaics (PVs) field over the past few years.2–4 Since Miyasaka and coworkers5 first reported the use of methylammonium lead triiodide (CH3NH3PbI3 or MAPbI3) perovskite as light harvester, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has topped 20% within a short period of time.6 On the basis of the architecture of the photoactive OTP layer, the PSC embodiments are broadly classified as3–4,7 (i) mesoscopic, (ii) planar, and (iii) mesoscopic-planar hybrid. In the mesoscopic PSC the photoactive layer consists of a thick (typically 300 to 1000 nm) mesoporous oxide (TiO2, Al2O3) scaffold fully infiltrated by the OTP. The scaffold helps anchor the OTP, and in the case of TiO2 it provides electron-conduction pathways.8 The planar PSC is based on a thin film of OTP without the mesoporous oxide scaffold, and it has gained popularity due to the enhanced light absorption and simpler architecture; however, planar PSCs are generally prone to photocurrent (J)–voltage (V) hysteresis issues.9 The third emerging type of PSCs with mesoscopic-planar hybrid structure aspires to combine the two structures and their desirable attributes into one. These PSCs typically use a mesoporous oxide scaffold that is fully infiltrated by the OTP and then topped with a planar OTP “capping” layer, which enhances light absorption,10,11 resulting in PSCs with hysteresis-free PCE of >20%.12

There have been numerous studies on controlling the overall morphology/coverage (see, e.g., ref 13) and crystallinity (see e.g., ref 14) of OTP thin films in the different PSC embodiments and their effects on OTP properties and performance of the PSCs; however, there is paucity of detailed characterization studies of the OTP crystals (grains) themselves within those PSC embodiments. Because the OTP within the oxide-scaffold mesopores crystallizes under a 3-D constraint, which is absent for planar OTP or capping-layer OTP, the size and the morphology of the OTP crystals in those locations are different and thus have different properties. Scanning electron microscopy (SEM) is commonly used to study OTP films, but the SEM has significant limitations in terms of resolution and the ability to identify crystal phases. In this context, Petrozza and coworkers15 have characterized MAPbI3 and MAPbI3−xClx and then topped with a planar OTP "capping" layer, which enhances light absorption, resulting in PSCs with hysteresis-free PCE of >20%.

Received: May 12, 2015
Accepted: June 1, 2015
Published: June 4, 2015
in the form of planar films and inside mesoporous TiO₂ using Raman spectroscopy and X-ray diffraction (XRD). They highlight the differences in the way the OTP crystallizes in the two forms and how it affects the onset of optical absorption in OTPs and other properties such as texture. Most recently, Mora-Sero and coworkers have studied MAPbI₃-Cl in planar films, within mesoporous oxide scaffolds and in mesoscopic-planar hybrid PSCs, using quantitative XRD. They find that the grain size of the OTP within the mesoporous oxides is 25 to 26 nm, consistent with the size of the mesopores, and grain size in both the planar film and the capping layer is 134–150 nm, although that grain size is beyond the validity of quantitative XRD methods and no direct visual evidence is provided. Using photoluminescence (PL) spectroscopy, they observe dramatic differences in the electron diffusion lengths (L_D), with L_D values for planar, mesoscopic, and mesoscopic-planar hybrid PSCs of 400, 40, and 260 nm, respectively. They conclude that the OTP in the mesoporous oxide controls the contact properties, while the OTP capping layer controls the photovoltaic performance. Nanova et al. have studied mesoscopic-planar MAPbI₃-Cl films using transmission electron microscopy (TEM), in conjunction with electron energy loss spectroscopy (EELS), to overcome some of the limitations of SEM, Raman spectroscopy, and XRD. That study used energy-filtered EELS elemental mapping to deduce the OTP distribution within the TiO₂ mesopores and the capping layer, although there is no mention of OTP grain size and the perovskite phase is not identified as such. Nevertheless, these papers highlight the importance of studying the morphology of OTP grains within the different locations (planar, mesoscopic, capping layer), which can have a dramatic effect on the OTP properties. To that end, we have used a combination of TEM and quantitative XRD techniques, that complement each other, to study the site-specific morphology of MAPbI₃ perovskite in mesoscopic, planar, and capping-layer locations.

Figure 1A,B shows cross-sectional bright-field TEM images of mesoscopic-planar hybrid and planar PSCs specimens, respectively, prepared using focused ion beam (FIB), providing overall views of the PSCs. (See Supporting Information (SI) for all experimental details.) In the mesoscopic-planar hybrid PSC (Figure 1A), both the mesoscopic-TiO₂-MAPbI₃ and the MAPbI₃ capping layer can be seen clearly, although the capping layer is somewhat rough in this particular PSC. The energy-dispersive spectroscopy (EDS) elemental maps (Figure 1C) show significantly reduced Ti signal (noise) within the capping layer and strong presence of Pb and I in both layers. In the case of the planar PSC (Figure 1B), the ~300 nm planar MAPbI₃ layer, in addition to the fluorinated tin oxide (FTO) substrate, the compact-TiO₂ layer, the hole-transporting material (HTM) layer, and the metal contact, can be delineated clearly. This is confirmed by elemental (Ti, Pb, I) EDS mapping shown in Figure 1D, where the Pb and I signals are observed only within the planar layer. Note the dense nature of the planar MAPbI₃ layer in Figure 1A and the absence of HTM penetration into that layer, which is attributed to the efficacy of the sequential spin-coating/annealing (SSCA) method used to prepare these MAPbI₃ films (see SI).

To understand the detailed morphology of the MAPbI₃ perovskite, we performed HRTEM studies on the TEM specimens from Figure 1A,B. While great care was exercised in preparing these cross-section TEM specimens using FIB (nanomachining using a Ga-ion beam), including the use of very low beam current (~10 pA) during the final polishing steps (see SI), some damage to the soft MAPbI₃ organic–inorganic perovskite materials may occur during the FIBing process. To address this issue, we prepared additional TEM specimens without the use of FIB by depositing planar and mesoscopic-planar hybrid MAPbI₃ films directly onto TEM grids, and they were observed in plan-view. HRTEM results from FIBed (cross-section) and non-FIBed (plan-view) specimens are presented in Figures 2 and 3, respectively. It is noted that MAPbI₃ perovskites are also prone to electron-beam-induced damage and decomposition, and hence it is important to use low beam currents and short exposures times during TEM observation. Thus, unlike in the case of hard inorganic materials, this limits the number of techniques (selected area electron diffraction (SAED), EELS, EDS, etc.) within the TEM that can be applied for comprehensive studies of the same region of the TEM specimens of these soft organic–inorganic materials.

Figure 2A is cross-sectional HRTEM image of the MAPbI₃ capping layer in the mesoscopic-planar hybrid specimen (FIBed), showing large MAPbI₃ perovskite grains. Abrupt
change in the orientation or termination of lattice fringes is used to estimate the grain boundary locations (dashed lines in Figures 2 and 3). The nominal lattice-fringe spacings are consistent with (002) and (022) planes in MAPbI₃ perovskite, as denoted in Figure 2A. (Note that the interplanar-spacings differences between (002) and (110) planes and between (220) and (004) planes are extremely small, and they cannot be resolved in HRTEM.) In contrast, the MAPbI₃ perovskite grains within mesoporous TiO₂ are much smaller (10−20 nm), as seen in the cross-sectional HRTEM image in Figure 2B. Once again, the nominal lattice fringe spacing is consistent with (002) planes in MAPbI₃ perovskite. TiO₂ (anatase) nanograins are also observed in Figure 2B, with (101) lattice spacing resolved. Figure 2C is a cross-sectional HRTEM image from planar MAPbI₃ film (FIBed specimen), showing large defective MAPbI₃ grains. Nominal lattice fringes (002) and defects (arrows) could be resolved in Figure 2C. Extensive “streaking” of spots in SAED patterns from similar MAPbI₃ TEM specimens (non-FIBed planar) indicates that these defects are planar faults (see SI Figure S1), but the exact nature of these faults is not known at this time.

Figure 3A is a plan-view HRTEM image of a region containing both the capping layer and the mesoscopic MAPbI₃ perovskite (non-FIBed). Relatively large MAPbI₃ perovskite grains are observed in the capping layer. The mesoscopic region is not well-resolved in Figure 3A, but in the image (Figure 3B) from the mesoscopic region small MAPbI₃ perovskite grains are observed, with resolved (002) lattice spacings. Anatase TiO₂ nanograins are also discernible in Figure 3B. The HRTEM image of the planar MAPbI₃ film (non-FIBed) is presented in Figure 3C, showing large MAPbI₃ grains. (These grains are larger than those in the planar PSCs (FIBed), which is associated with the differences in the wetting behavior of the precursor solution on the holey-carbon TEM grid and the compact TiO₂ surfaces.) Indexed SAEDP from that grain is...
included in Figure 3C inset, confirming the MAPbI₃ perovskite phase.

Qualitatively, the HRTEM results in both Figures 2 and 3 show larger grains in the capping layer and the planar MAPbI₃ perovskite films, whereas the MAPbI₃ perovskite grains within the mesoporous TiO₂ are much smaller. These data could not be quantified due to the complex nature of the microstructures. Unlike hard inorganic materials, where crystal (grain) interiors are relatively defect-free, MAPbI₃ perovskite grains appear to be replete with lattice defects, making it difficult to demarcate grain boundaries. This appears to be a typical feature of these soft organic−inorganic hybrid materials.¹⁸−²⁰ Because the defects are observed in both FIBed and non-FIBed TEM specimens, they are not an artifact of the FIBing process. The absence of other discernible differences between the FIBed and the non-FIBed TEM specimens indicates that carefully performed FIBing does not damage the MAPbI₃ perovskite significantly, making FIBing a viable TEM-specimen-preparation method for the TEM characterization of PSCs.

Quantitative XRD analysis is used to corroborate the HRTEM results. XRD pattern (2θ range 23.75 to 25.75°) from the mesoscopic-planar hybrid film is shown in Figure 4A, containing the 022 reflection from MAPbI₃ perovskite (tetragonal, space group 14/mmm) and the 101 reflection from anatase TiO₂. Contributions from capping-MAPbI₃ mesoscopic-MAPbI₃, TiO₂, and the background are deconvoluted in Figure 4A. The signal is dominated by the relatively narrow 022 peak from the capping-MAPbI₃ perovskite, followed by a broad 022 peak from the mesoscopic-MAPbI₃ perovskite shifted to lower 2θ. To obtain XRD patterns from only the TiO₂-MAPbI₃ mesoscopic layer within the mesoscopic-planar hybrid films, we removed the capping layer by polishing it away gently. The XRD pattern in Figure 4B from that layer shows a similarly broad 022 MAPbI₃ perovskite peak, together with the broad 101 TiO₂ peak. Using calibrated Scherer equation (see SI)²¹ the mesoscopic-MAPbI₃ grain size is estimated to be ~20 nm, which is consistent with the size of TiO₂ mesopores. The size of the TiO₂ grains from the broadening of its 101 peak (anatase phase) is also estimated at ~20 nm, which is about the size of the particles in the paste used to prepare the mesoscopic TiO₂ scaffold. Thus, the quantitative XRD grain size of mesoscopic-MAPbI₃ is consistent with that observed in the TEM studies. Figure 4C is XRD pattern from planar-MAPbI₃, which is similar to that of the capping-MAPbI₃ (Figure 4A). The Scherer equation could not be used reliably to estimate the grain size of the MAPbI₃ perovskite in the capping and the planar layers as it can be larger than 100 nm and is beyond the validity of this quantitative XRD method.

The mesoscopic-MAPbI₃ and planar-MAPbI₃ peaks are marked by dashed lines in Figure 4, showing a shift to lower 2θ (by ~0.075°) for the mesoscopic-MAPbI₃. Such a shift is also reported by Mora-Sero and coworkers,¹⁶ but no explanation is provided. A shift to lower 2θ implies increase in lattice parameters, that is, a volume expansion of the lattice by ~1%, corresponding to peak shift of ~0.075°. This is consistent with isostatic tensile strain produced in crystals that are grown from liquid precursors inside pores.²² The genesis of this tensile strain is the constraint imposed on crystal shrinkage during crystallization by the attachment of the crystal to the pore walls. While the tensile strain in mesoscopic-MAPbI₃ remains to be quantified in detail, it could be responsible for the extended absorption in near-infrared region by mesoscopic-MAPbI₃, which is typically not observed in planar-MAPbI₃.

It has been shown that J−V responses of planar and mesoscopic-planar hybrid PSCs are significantly different,²³ which is confirmed in Figure 5. In the case of planar PSCs, hysteresis between forward (JSC → VOC) and reverse (VOC → JSC) scans is typical, as is observed in Figure 5: the forward (F) and reverse (R) scan PCEs are measured to be 8.1 and 12.1%,
respectively. In contrast, Figure 5 shows that the mesoscopic-planar hybrid PSC is free of hysteresis, with a PCE of 10.8% regardless of the scan direction. Several hypotheses have been proposed to explain the hysteresis in planar PSCs and its elimination with the addition of the mesoscopic perovskite layer. They include: (i) ferroelectric switching of domains in the perovskite, (ii) ion migration and charge buildup at interfaces, and (iii) crystallographic domain texture in the perovskite. It has been suggested that for MAPbI3 perovskite inside mesoporous TiO2 ferroelectric domain switching is constrained. Also, the presence of the rough interface between mesoporous TiO2 and MAPbI3 perovskite interface helps screen charge accumulation. Furthermore, unlike capping- and planar-MAPbI3, mesoscopic-MAPbI3 perovskite grains are less textured. A combination of these attributes is argued to be responsible for the absence of hysteresis when a mesoscopic-MAPbI3 layer is included in the PSC. While the overall PCEs of both cells are reasonable, the open-circuit voltage \( (V_{OC}) \) of planar PSCs is higher (1.12 V) than that of mesoscopic-planar PSC (0.91 V) (Figure 5), which has been frequently observed by others. It has been suggested that the high density of the planar perovskite film is more effective in preventing the HTM from making contact with TiO2. In contrast, the capping-MAPbI3 perovskite layer in the mesoscopic-planar hybrid PSC is generally less dense, as seen in Figure 1, and also the surface area of the mesoporous TiO2 layer is very high. These factors enhance the possibility of the formation of parallel HTM-TiO2 p-n junctions, thereby decreasing \( V_{OC} \) in the mesoscopic-planar PSCs. This is consistent with high \( V_{OC} \) recorded in our planar PSCs containing high-density MAPbI3 perovskite thin films. This indicates that the \( V_{OC} \) of mesoscopic-planar hybrid PSCs can be enhanced by making the OTP capping layer more dense.

In summary, we have used a combination of conventional TEM and HRTEM, in cross-section and plan-view, to characterize solution-processed MAPbI3 perovskite inside mesoporous TiO2 scaffolds and outside (capping and planar layers). We show that FIBing is a viable method for preparing TEM specimens without significant damage to the MAPbI3 perovskite. The TEM and HRTEM results are supported by quantitative XRD characterization. We show that MAPbI3 perovskite within mesoporous TiO2 scaffold has equiaxed grains of size 10–20 nm, which is governed by the size of the TiO2 mesopores, and they have relatively low crystallinity. In contrast, the grain size of MAPbI3 perovskite in the capping and the planar layers can be larger than 100 nm, and the grains can be elongated and textured, with relatively high crystallinity; however, this grain size may depend on the specific thicknesses of the capping and the planar layers in other PSCs. MAPbI3 perovskite crystals within the mesoscopic region appear to be under hydrostatic tensile strain (~1%), which could be the result of their constrained crystallization within the mesoporous TiO2 scaffold. The dramatic differences in the crystal morphology and the size of the MAPbI3 perovskites in planar and mesoscopic-planar hybrid PSCs contribute in part to the important differences in their PSCs performance characteristics. This study highlights the use of TEM and XRD in revealing the crystal morphology of MAPbI3 perovskites in PSCs, which is critical to future efforts aimed at understanding effects of OTP morphology on the PSCs behavior and OTP morphological tailoring for improved PSCs performance.

### REFERENCES

1. (1) Snait, H. J. Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. J. Phys. Chem. Lett. 2013, 4, 3623–3630.
2. (2) Grätzel, M. The Light and Shade of Perovskite Solar Cells. Nat. Mater. 2014, 13, 838–842.
3. (3) Green, M. A.; Ho-Baillie, A.; Snait, H. J. The Emergence of Perovskite Solar Cells. Nat. Photonics 2014, 8, 506–513.
4. (4) Jung, H. S.; Park, N.-G. Perovskite Solar Cells: From Materials to Devices. Small 2015, 11, 10–25.
5. (5) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halid Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131, 6050–6051.
6. (6) NREL. www.nrel.gov/ncpv/images/efficiency_chart.jpg, 2014.
7. (7) Zhao, Y.; Zhu, K. Solution-Chemistry Engineering toward High-Efficiency Perovskite Solar Cells. J. Phys. Chem. Lett. 2014, 5, 4175–4186.
8. (8) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphrey-Baker, R.; Yum, J.-H.; Moser, J. E.; et al. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. Sci. Rep. 2012, 2, 591.
9. (9) Snait, H. J.; Abate, A.; Ball, J. M.; Eperon, G. F.; Leijtens, T.; Noel, N. K.; Stranks, S. D.; Wang, J. T.-W.; Wojciechowski, K.; Zhang, W. Anomalous Hysteresis in Perovskite Solar Cells. J. Phys. Chem. Lett. 2014, 5, 1511–1515.
10. (10) Heo, J. H.; Im, S. H.; Noh, J. H.; Mandal, T. N.; Lim, C.-S.; Chang, J. A.; Lee, Y. H.; Kim, H.-J.; Sarkar, A.; Nazeeruddin, M. K.; et al. Efficient Inorganic-Organic Hybrid Heterojunction Solar Cells Containing Perovskite Compound and Polymeric Hole Conductors. Nat. Photonics 2013, 7, 486–491.
11. (11) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. Nature 2015, 517, 476–480.
12. (12) Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Deo, J.; Seok, S. I. High-Performance Photovoltaic Perovskite Layers
Fabricated through Intramolecular Exchange. Science 2015, 10.1126/science.aaa9272.

(13) Eperon, G. E.; Burlakov, V. M.; Docampo, P.; Goriely, A.; Snaith, H. J. Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells. Adv. Funct. Mater. 2014, 24, 151–157.

(14) Liang, P.-W.; Liao, V.-Y.; Chueh, C.-C.; Zuo, F.; Williams, S. T.; Xin, X.-K.; Lin, J.; Jen, A. K.-Y. Additive Enhanced Crystallization of Solution-Processed Perovskite for Highly Efficient Planar-Heterojunction Solar Cells. Adv. Funct. Mater. 2014, 24, 151−157.

(15) Grancini, G.; Marras, S.; Prato, M.; Giannini, C.; Quarti, C.; Angelis, F. D.; Bastiani, M. D.; Eperon, G. E.; Snaith, H. J.; Manna, L.; et al. The Impact of the Crystallization Process on the Structural and Optical Properties of Hybrid Perovskite Films for Photovoltaics. J. Phys. Chem. Lett. 2014, 5, 3836−3842.

(16) Listorti, A.; Juarez-Perez, E. J.; Frontera, C.; Roiat, V.; Garcia-Andrade, L.; Colella, S.; Rizzo, A.; Ortiz, P.; Mora-Sero, I. Effect of Mesostructured Layer Upon Crystalline Properties and Device Performance on Perovskite Solar Cells. J. Phys. Chem. Lett. 2015, 6, 1628–1637.

(17) Nanova, D.; Kast, A. K.; Pfannmoller, M.; Muller, C.; Veith, L.; Wacker, I.; Agari, M.; Hermes, W.; Erk, P.; Kowalsky, W.; Schroder, R. R.; Lovrincic, R. Unraveling the Nanoscale Morphologies of Mesoporous Perovskite Solar Cells and Their Correlation to Device Performance. Nano Lett. 2014, 14, 2735−2740.

(18) Zhou, Y.; Yang, M.; Vasilev, A. L.; Garces, H. F.; Zhao, Y.; Wang, D.; Pang, S.; Zhu, K.; Padture, N. P. Growth Control of Compact CH$_3$NH$_3$PbI$_3$ Thin Films Via Enhanced Solid-State Precursor Reaction for Efficient Planar Perovskite Solar Cells. J. Mater. Chem. A 2015, 3, 9249−9256.

(19) Cullity, B. D. Elements of X-Ray Diffraction, 2nd ed.; Addison-Wesley: Boston, MA, 1978.

(22) Scherer, G. W. Crystallization in Pores. Cem. Concr. Res. 1999, 29, 1347−1358.

(23) Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. I. Solvent Engineering for High-Performance Inorganic-Organic Hybrid Perovskite Solar Cells. Nat. Mater. 2014, 9, 897−903.

(24) Kim, H.-S.; Park, N.-G. Parameters Affecting I-V Hysteresis of CH$_3$NH$_3$PbI$_3$ Perovskite Solar Cells: Effect of Perovskite Crystal Size and Mesoporous TiO$_2$, Layer. J. Phys. Chem. Lett. 2014, 5, 2927−2934.

(25) Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; Schülgäarde, M. v. Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells. Nano Lett. 2014, 14, 2584−2591.

(26) Kutes, Y.; Ye, L.; Zhou, Y.; Pang, S.; Huey, B. D.; Padture, N. P. Direct Observation of Ferroelectric Domains in Solution-Processed CH$_3$NH$_3$PbI$_3$ Perovskite Thin Films. J. Phys. Chem. Lett. 2014, 5, 3335−3339.

(27) Chen, H.-W.; Sakai, N.; Ikegami, M.; Miyasaka, T. Emergence of Hysteresis and Transient Ferroelectric Response in Organo-Lead Halide Perovskite Solar Cells. J. Phys. Chem. Lett. 2015, 6, 164−169.

(28) Lv, S.; Pang, S.; Zhou, Y.; Padture, N. P.; Hu, H.; Wang, L.; Zhou, X.; Zhu, H.; Zhang, L.; Huang, C.; Cui, G. One-Step, Solution-Processed Formamidinium Lead Trihalide (FAPbI$_3$–x)Cl$_x$ for Mesoscopic Perovskite–Polymer Solar Cells. Phys. Chem. Chem. Phys. 2014, 16, 19206−19211.