Anti-solvent Assisted Crystallization of $CH_3NH_3PbBr_3$ Perovskite Single Crystals by Inkjet Printing

Shiuan-Ying Peng and Ying-Chih Liao

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

ISCST-20180919AM-B-PD2

Presented at the 19th International Coating Science and Technology Symposium,
September 16-19, 2018, Long Beach, CA, USA[†].

Keywords: Inkjet printing, anti-solvent, perovskite, single crystal, large grain

Introduction

Photovoltaic conversion efficiency of organic-inorganic hybrid perovskite materials has rapidly increased from 3.8% [1] to 22.1%.[2] The perovskite materials have excellent absorption range and excellent long-distance transmission of carriers. These unique characteristics are suitable to solar cells, photodetectors, and LEDs.[3] Single crystals of perovskites have fewer grain boundaries, defects and longer diffusion length than the polycrystallines.[4] The common single crystal perovskite growth methods include: temperature rising crystallization, cooling crystallization, constant temperature crystallization, *etc*.[5] However, these methods are difficult to control the crystal growth position, and thus single crystal perovskites cannot be used easily in optoelectronic application.

In 2003, Cheng et.al first used lithography to pattern perovskites.[6] Su et.al controls the solution wetting to grow a single crystal array.[7] However, these methods require pre-patterns and the fabrication process is complicated, and rapid preparation of single crystal patterns is still a challenge. As a direct printing method, inkjet printing provides a feasible choice to grow single crystal perovskites with accurate patterns. One can directly printed perovskite solution on substrate, and finds crystals right after solvent evaporate. However, this type of crystallization solely relies on solvent evaporation, and the faster evaporation rate at the outer edge of printed droplets, or coffee-ring effect,[8] always leads to more perovskite crystals precipitate at the edges. To avoid this problem, Gu et.al utilized a lyophobic substrate with well-controlled temperature to create moving contact line in the evaporation/crysallization process, and successfully printed single crystal perovskite with a grain size about 20 μm.[9] However, although lyophobic substrates can help alleviate contact line pinning, fast evaporative crystallization at high perovskite concentrations can still leads to pinned contact lines. Thus, one can only print droplets with low perovskite concentration, and thus the crystalline size is still limited. To print single crystal with a larger size, or solution with saturated concentrations, one needs to seek for a different crystallization process other than evaporative method.

In this study, we used anti-solvent assisted method to overcome crystal grain size limitations on hydrophilic substrates. The anti-solvent is directly printed into the precursor solution to rapidly induce solute crystallization caused by solubility changes. Besides the faster crystallization rates, the anti-solvent spreads over the precursor droplets and thus can effectively suppress contact line pinning.[10] The wetting or dewetting of anti-solvents[11] after printed on the precursor sessile drops will be carefully examined to understand the instantaneous crystallization after drop impact. Moreover, the perovskite crystals growth mechanism in this dual liquid printing method will be also investigated to optimize the crystalline size.

Experiments

Lead(II) bromide (PbBr2), N,N-dimethylformamide (DMF), methylammonium bromide (MABr), n-Butyl Alcohol (NBA), Isopropyl alcohol (IPA), n-hexane and toluene (TL) were purchased from Sigma-Aldrich, and were used without further purification. The $CH_3NH_3PbBr_3$ inks were prepared by dissolving $PbBr_2$ (1M) and CH_3NH_3Br (1M) in DMF as the precursor ink. Indium tin oxide coated conducting glass (ITO, Solaronix SA, Rsh =7Ω$\square^{-1}$) was used as the substrates. The precursor inks and anti-solvent inks were deposited on the substrate by using a MicroFab JetLab4 system (MicroFab Technologies Inc.) with two

50 mm piezoelectric nozzles. The droplets size were carefully controlled around 80μm wtih an ejection velocity of 1.05 m/s.

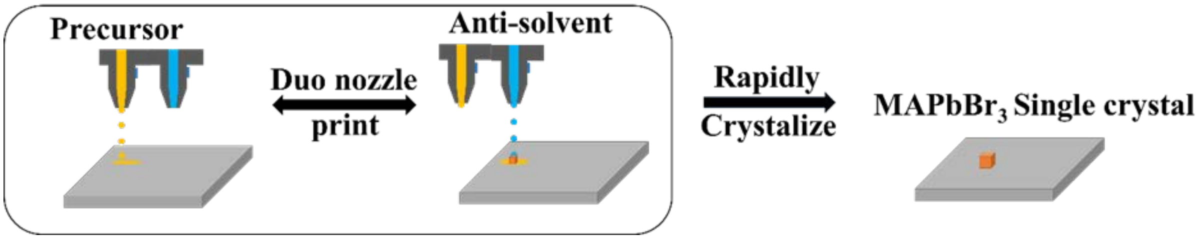

Figure1 Schematic of the dual nozzle printing process

Results and discussion

Figure 1 illustrates the fabrication procedure of perovskite single crystal by inkjet printing with dual nozzles. The droplet is ejected at a frequency of 500 Hz. $CH_3NH_3PbBr_3$ precursor dissolved in DMF is first printed on the ITO glass substrate. Then, the anti-solvent, which is miscible with DMF but cannot dissolve the precursor, is then printed on the precursor sessile drop. Right after drop impact, the miscible anti-solvent quickly mixes with DMF and reduces the precursor solubility. Thus, the crystallization occurs quickly and continues until both solvents evaporate. Four poor solvents for $CH_3NH_3PbBr_3$ precursor are selected: NBA, TL, IPA, and n-hexane. To examine the miscibility of these anti-solvents, a simple mixing experiment is conducted as shown in Figure 2 (a). Obviously, n-hexane is immiscible with DMF but the other three are miscible. To determine the miscibility among the three solvents with DMF, solubility parameter is used as a criteria. From literature, the solubility parameters of IPA (11.5), NBA (11.3), TL (8.91), and n-hexane (7.24) are all lower than that of DMF (12.14). When the difference in solubility parameters between two solvents is smaller, a better miscibility is expected and therefore TL has the least theoretical miscibility with DMF.

To further investigate the influence of anti-solvents, a tiny drop of anti-solvent (~ 60 pL) is deposited over a precursor ($CH_3NH_3PbBr_3$ in DMF) droplet by using the dual nozzle inkjet system. As shown in Figure 2 (b), conventional evaporation method after printing a precursor drop (W/O) results in scattered crystals surrounding in a ring shape, caused by the pinned contact line as shown previous in the literature. IPA, which has the best miscibility with DMF, results in small and densely scattered crystals in the circular area. On the other hand, toluene (TL), which has the worst miscibility among the three anti-solvents, results in a large cubic crystal of 50 um, which is larger than the reported values in the literature. These results indicate that the anti-solvent printed over precursor droplet can quickly yield in perovskite crystals. Moreover, by choosing an anti-solvent with suitable miscibility, this anti-solvent assisted crystallization can effectively grow large single-crystal perovskite on lyophillic substrates.

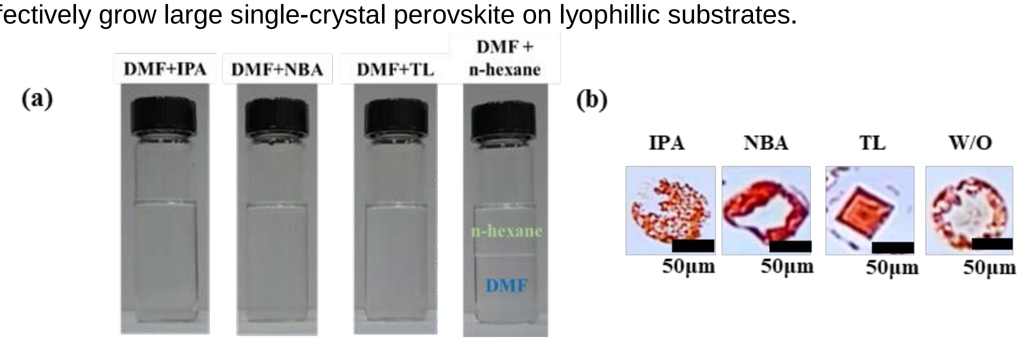

Figure 2 (a) Miscibility of different solvent and (b) crystal morphology of perovskite after dual drop collision with various anti-solvent.

---

*Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

To enlarge the crystal size, the precursor volume is increased to 6 nl. As previously shown, toluene has the best miscibility and is thus used as the anti-solvent in this experiment. By varying the precursor/anti-solvent ratio, as shown in Figure 3, the size of the printed single crystals can be adjusted. As expected, excess amount of anti-solvent, which quickly reduces the precursor solubility and yields in a faster crystallization rate, leads to smaller crystal sizes. When the anti-solvent amount is reduced, the crystal sizes increase possibly due to the slower crystal growth. A peak crystal size of ~180 μm was found when the ratio of 5P:1A is used. However, as the precursor increased to 6P:1A, the anti-solvent can't cover the whole precursor sessile drop and thus the crystal size decreases again. Similar printing parameters are thus used to print single crystal patterns. As shown in Figure 4 (a), perovskite single crystals can be precisely patterned into an array with an "NTU" word by this dual nozzle inkjet printing system. Besides, the average size of the perovskite single crystal can achieve ~ 90 μm (Figure 4 (b)).

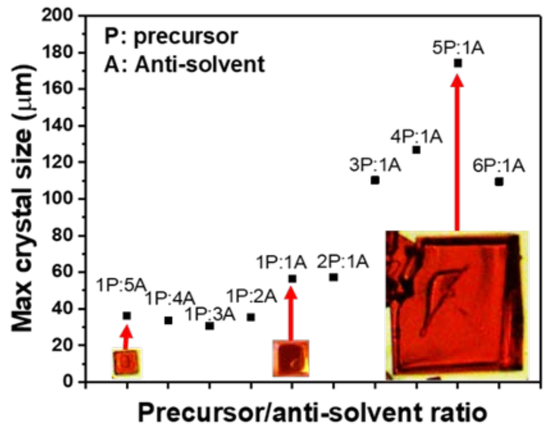

Figure 3 Variation in crystal size with different precursor/anti-solvent ratio.
(100 precursor drops were first printed on ITO surface to create a large precursor sessile drop with a volume of 6 nL, following by printing toluene droplet.)

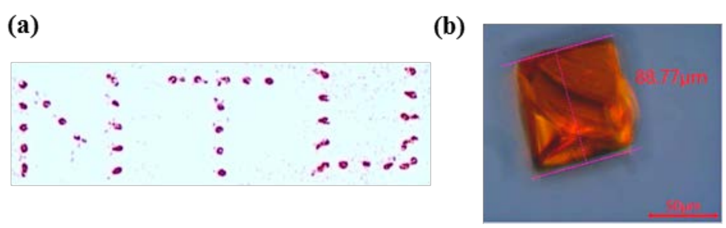

Figure 4 (a) Perovskite single crystal array pattern (b) Crystal size of array pattern

Conclusions

In this study, we developed an anti-solvent assisted crystallization process by using a dual nozzle inkjet printing method. To avoid coffee-ring effect in crystal growth process via solvent evaporation, anti-solvent is directly deposited onto perovskite precursor droplet. For the first time, sub-millimeter size (~200μm) single-crystal perovskite $CH_3NH_3PbBr_3$ are printed over lyophilic surfaces without any temperature control or heat treatments. Moreover, without any pre-pattern or transfer crystal, single perovskite crystals can be directly printed into precise patterns. The printed single-crystal perovskite shows low grain boundary and good light absorption, and can be used for photodetector or LED applications. This anti-solvent assisted inkjet printing method can be easily applied to other crystallization processes and paves the way to direct patterning of large single crystals.

References

1. *Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells*; J. Am. Chem. Soc., 2009, 131, 6050–6051
2. *High-Performance Photovoltaic Perovskite Layers Fabricated Through Intramolecular Exchange*; Science., 2015,348, 6240, 1234-1237
3. *Metal Halide Perovskite Nanomaterials: synthesis and applications*; Chem. Sci., 2017, 8, 2522-2536
4. *Single Crystal Formamidinium Lead Iodide ($FAPbI_3$): insight into the structural, optical, and electrical properties*; Adv. Mater., 2016, 28, 2253–2258
5. *Recent Progress in Single-Crystalline Perovskite Research Including Crystal Preparation, Property Evaluation, and Applications*; Adv. Sci., 2018, 5, 1700471
6. *Patterning and Photoluminescent Properties of Perovskite-Type Organic/ Inorganic Hybrid Luminescent Films by Soft Lithography*; Chem.Phys. Lett., 2003, 376, 481 − 486.
7. *"Liquid Knife" to Fabricate Patterning Single-Crystalline Perovskite Microplates toward High-Performance Laser Arrays*; Adv. Mater., 2016, 28, 3732.
8. *Patterned Photonic Crystals Fabricated by Inkjet Printing*; J. Mater. Chem. C, 2013, 1, 6048–6058
9. *Direct-Writing Multifunctional Perovskite Single Crystal Arrays by Inkjet Printing*; Small, 2017, 13, 1603217.
10. *Inkjet Printing of Single-Crystal Films*; Nature 2011, 475, 364-367
11. *Underlying Mechanism of Inkjet Printing of Uniform Organic Semiconductor Films Through Antisolvent Crystallization*; Adv. Funct. Mater. 2015, 25, 4022–4031