Large-grain CH$_3$NH$_3$PbI$_3$ film by incorporation of urea in one-step solution process

Hadi Bazzazzadegan, Yadollah Mortazavi*, Abbasali Khodadadi, Maryam Mohagheghian

Nanoelectronics Centre of Excellence, School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11365-4563, Tehran, Iran

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ABSTRACT

The Lewis acid–base adduct is a comprehensive approach to modify crystallinity and surface morphology of perovskite, nevertheless, the key role of adduct in nucleation and growth mechanism is ambiguous. In our study, it was revealed that the size of perovskite colloidal clusters considerably increase when urea adds to the solution and this phenomenon controls the nucleation. In addition, the intermediate structures formed by urea govern the final perovskite morphology through retarding the perovskite crystal growth. Thus, large-grain CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) film with almost full surface coverage achieves by the incorporation of urea especially when antisolvent technique is applied during the spin coating. Finally, extremely large grains, larger than 100 micrometers, form via simultaneous use of dimethyl sulfoxide (DMSO) and urea in perovskite solution.

1. Introduction

The emergence of perovskite light harvester and the development of perovskite solar cells (PSCs) represents a great breakthrough in green energy production owing to low costs of materials and fabrication in comparison with established crystalline silicon solar cells. Nowadays, the conversion efficiencies of PSCs—based upon specific thin film fabrication technologies and innovative perovskite absorbers—have soared up to 22% [1]. Although these inorganic-organic perovskite materials have promisingly raised hope for PSCs industrial production, the commercialization of these devices have encountered serious challenges such as moisture and thermal stability [2–4] and photocurrent hysteresis [5].

With regard to the PSCs development, the architecture of PSCs has also developed from sensitized [6], meso-superstructure [7] and pillared [8] forms into planar heterojunction structures [9]. Generally, a mesoporous scaffold with a high surface area that provides many nucleation sites for perovskite formation, achieves a better surface coverage. By contrast, planar structures potentially assist to form larger perovskite grains [10]. Apart from the investigation into the PSCs’ architecture, researchers have made tremendous efforts to devise different methods for the deposition of perovskite film, including one-step [11] and two-step [12,13] solution processes, dual-source vapour deposition [14] and vapour-assisted solution [15] processes. Among these methods, one-step solution-based process utilizing spin coating technique is more popular due largely to their simplicity and fast implementation [16].

It has been proved that the performance of a PSC is mainly dependent on its quality of organohalide perovskite layer [17]. In this accordence, the layer of perovskite with a high degree of crystallinity, full surface coverage and large smooth grains without

* Corresponding author.
E-mail address: mortazav@ut.ac.ir (Y. Mortazavi).

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unconverted PbI₂, plays an essential role in accomplishing an eminently reasonable PSC [18]. Nevertheless, as a result of crystallization behavior of methylamine iodide (MAI)/PbI₂/dimethylformamide (DMF) solution, conventional one-step synthetic method forms needle-shaped crystals [17]. In fact, the type of intermediates [19] and also simultaneous nucleation and growth in a short processing time [20] result in incomplete surface coverage and non-uniformity of perovskite. Therefore, it is a great challenge to deposit a homogenous perovskite film with almost complete surface coverage and pinhole free via one-step processes [21]. In order to dominate the described challenges, researches have introduced some scientific techniques such as hot-casting [22], solvent engineering [11] and antisolvent [23] and more recently Lewis acid-base adduct approach [16,24,25]. Indeed, these methods are based upon two points of view, inducing rapid homogenous nucleation followed by crystal growth of perovskite (hot casting and antisolvent methods), and intermediate phases alteration in order to retard the crystallization of perovskite (solvent engineering and Lewis adduct approach). Consequently, providing proper conditions for rapid nucleation and by contrast, slowing down the growth rate of perovskite crystallization are thriving ways to fabricate a full coverage film with large grains of perovskite [20].

By the achieved results, adduct approach can hopefully improve the morphology of perovskite. Three main groups (O-, S- and N-donors) can be utilized as Lewis base adducts to modify perovskite [24]. However, it should be noted that the proposed components do not precipitate perovskite precursors; nor does it interfere in final perovskite structure. It is widely acknowledged that DMSO can effectively enhance perovskite morphology [25–27] and in subsequent researches, N-methyl-2-pyrrolidone (NMP) [28], dimethylacetamide (DMAC) [16] and thiourea [24] were applied with the aim of achieving a better perovskite film morphology. However, the key role of adduct in nucleation and growth of perovskite did not consider yet.

Herein, we select urea as a Lewis base molecule that has the potential to form adduct with PbI₂ [29]. It was observed that the incorporation of urea in standard MAPbI₃ solution causes to enlarge perovskite colloidal clusters. Moreover, due to the formation of new intermediate structures, the growth rate of perovskite is decreased and, in consequence, large-grain MAPbI₃ film is formed. Accordingly, through a significant retarding the perovskite crystal growth, a better surface coverage is obtained in one-step solution process. Fourier transform infrared spectroscopy (FTIR) results clearly confirm that the adduct intermediate(s) of urea and perovskite precursors forms and thoroughly governs the perovskite crystallization.

2. Experimental

2.1. Materials and device fabrication

Fluorine doped tin oxide (FTO)-coated glasses were first patterned by etching with zinc powder and hydrochloric acid (1 M). After that, the glasses were ultrasonically cleaned by a detergent, deionized water and a mixed solution of acetone and ethanol and finally were dried in air. The treated FTOs were heated at 300 °C on hotplate for 15 min and then cooled to ambient temperature. A compact layer of TiO₂ was deposited on the FTO glasses utilizing a solution of 0.15 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol by spin coating at 2000 rpm for 30 s. The substrates were subsequently heated at 125 °C on a hotplate for 5 min and then annealed at 500 °C for 30 min.

In order to fabricate perovskite layer, we prepared four solutions with 0.0, 0.5, 1.0 and 2.0 M ratios of urea to perovskite. In this accordance, a 1.0 M primary solution of perovskite in DMF was firstly prepared by dissolving 159 mg of MAI and 462 mg of PbI₂ in each 948 mL of DMF. Then the final solutions were obtained by dissolving relevant amounts of urea powder in samples derived from the main perovskite solution. The different perovskite solutions were spin coated at 4000 rpm for 25 s and were immediately heated at 50 °C for 5 min followed by heating at 100 °C for the next 5 min. In the case of antisolvent (diethyl ether) application, 200 μL of diethyl ether were dripped on the substrates 4 s after starting the spin coater. After that, for obtaining power conversion efficiency (PCE), the hole transport material (HTM) was deposited by spin coating at 4000 rpm for 30 s using a solution prepared by dissolving 72.3 mg of Spiro-OMeTAD, 28.8 μL of 4-tert-butylpyridine and 17.5 μL of a solution of lithium bis trifluoromethanesulfonimide (LiTFSI) in acetonitrile totally in 1.0 mL of chlorobenzene. The 80 nm of Au as back-contact electrode was deposited over Spiro layer by thermal evaporation in a vacuum chamber.

2.2. Characterization

The PbI₂ and perovskite films were characterized by UV−vis absorption spectroscopy (PG Instrument Ltd.) in a range from 400 to 900 nm. In addition, the photovoltaic properties of the PSCs were measured under one solar illumination (AM 1.5G, 100 mW/cm², Sharp solar, SIM-1000) and were recorded by an electroanalytical instrument (Palmens BV, the Netherlands), in a range of 0.0–1.0 V at a scan rate of 5 mV/s.

The surface images of lead iodide and perovskite film were analysed using a field emission scanning electron microscope (FE-SEM) at an acceleration voltage of 15–25 kV. The crystallographic structures of deposited films were characterized by X-ray diffraction (XRD) analysis using Cu Kα (λ = 1.54060 Å) radiation at 40 kV and 40 mA with a step size of 0.026°. The FTIR spectra (Bruker, Vector 22) were collected to examine MAI.PbI₂.yUrea adduct formation. The pellets used in FTIR, were prepared according to methodology reported elsewhere [24].

Dynamic light scattering (DLS) measurement (Particulate Systems, NanoPlus) was applied for the determination of the sizes of perovskite colloidal clusters in different solutions.
3. Results and discussion

We applied one-step solution process to fully elucidate the key role of a new adduct (i.e. urea) in the nucleation and growth of perovskite. Firstly, we examined the colloidal clusters of perovskite in DMF for the study of their size variations through the incorporation of urea as a base Lewis adduct molecule. Due to the fact that any colloidal clusters’ size increasing could lead to increase in the final size of perovskite grains [17,30], different perovskite solutions were analysed by DLS.

We clearly observed that the size of perovskite clusters increases when urea adds to the solution. The average size of colloidal clusters in (MAI + PbI2) solution was obtained ca. 364 nm while the value reaches 949 nm through incorporation of 1 M ratio of urea to PbI2 into the solution (see Fig. 1a and b).

Fig. 1c shows a schematic of our colloidal perovskite solution deposition. In fact, larger colloidal clusters in solution provide larger perovskite nuclei when the solution spreads over blocking layer. In this accordance, weak Van der Waals interactions between PbI2 crystal layers allows a guest molecule like urea to intercalate between the layers [30]. Therefore, new perovskite intermediates form and the size of clusters enlarge, in consequence, perovskite crystallization is retarded and large-grain MAPbI3 film is achieved.

The formation of adduct intermediates were confirmed by FTIR results (see Fig. 1d and e). The synthesis of PbI2.yUrea adduct was firstly published by Wharf et al. [29]; nevertheless, to the best of our knowledge, no article has reported the results of incorporation of urea into organo-lead halide perovskite yet.

Fig. 1d and e demonstrates the IR spectra for urea, PbI2.yUrea and MAI.PbI2.yUrea. The stretching frequency of the C=O bond at 1686 1/cm [31] has a minor downshift (see Fig. 1e), which clearly confirms the formation of oxygen-Pb bond between urea and PbI2.

The results are well consistent with other PbI2 adduct formation [24,25,32].

In order to investigate the impact of urea on perovskite crystal’s morphology, four perovskite solutions containing 0.0, 0.5, 1.0 and 2.0 M ratio of urea to MAPbI3 were prepared (for convenience, we use X as the representation of urea molar ratio to MAPbI3). It was observed that perovskite forms about 5 s after spinning the standard solution. In contrast, the addition of urea to perovskite solution resulted in a white coloured perovskite film that does not turn black during spin coating.

As shown in Fig. 2, the crystallization of perovskite is postponed by incorporation of urea, especially in case of X = 1.0. That is to say, the primary result of urea addition to the perovskite solution is to produce some new intermediate phases and thus the perovskite crystal growth is seriously retarded. It seems that the kinetic pathway to perovskite formation has completely changed in a similar way to what has been reported about Lewis acid-base adduct approach for perovskite crystals [24].

Fig. 3 shows the top view SEM images of perovskite crystals with different urea contents formed through conventional one-step deposition method. One-dimensional, needle shaped perovskite [17] with low surface coverage commonly obtains from MAI/PbI2/DMF solution through one-step deposition method (see Fig. 3, X = 0.0). It definitely demonstrates that the presence of urea in perovskite solution causes the needles to widen and, as the result, improves the perovskite surface coverage. It is interesting to note that by increasing urea content in perovskite solution, some perovskite aggregates appear and develop while the needles begin to fade. Although different crystal shapes are observed in Fig. 3, the XRD spectra (see Fig. 4) show the similar crystallinity of perovskite for samples with different urea contents. In this regard, the strong diffraction peaks at 14.1, 28.4 and 31.8 can be indexed to (110), (220) and (310) plane respectively which clearly prove the formation of perovskite tetragonal phase [33]. Nevertheless, a diffraction peak at 12.66 in the samples containing urea, corresponds to the presence of PbI2 [34]. This observation probably indicates that a stable PbI2.yUrea adduct structure forms when urea is added to the perovskite solution.
Indeed, similar XRD results for different morphologies obtained by perovskite solutions with different urea contents (see Fig. 4), shed light on the crucial role of intermediate phases in final perovskite morphology [19]. Furthermore, the Energy dispersive X-ray spectroscopy (EDS) measurements show that the Pb/I ratio for the sample with $X = 1.0$ is close to the stoichiometric ratio in the perovskite structure (Fig. S1†).

It is remarkable to note that through the addition of urea to the solution of MAPbI$_3$, two different base adduct molecules (urea and DMF) are ready to bond with PbI$_2$. Based upon the fact that PbI$_2$.DMF adduct yields needle shaped perovskite crystals [16], hence these authors propose that urea which is in competition with DMF for adduct formation, could essentially alter the crystal
morphology of perovskite (see Fig. 3). Moreover, the XRD pattern of PbI$_2$yUrea displays that the peak intensity of the peak concerning (001) plane of PbI$_2$ significantly has been increased (Fig. S2†) and obviously reflects the enhancement of PbI$_2$ crystallinity.

Furthermore, the full-width at half-maximum value of (001) plane of XRD spectra indicate an increase in PbI$_2$ crystal size up to ca. 3 times, from 23 to 74 nm calculated by Scherer’s equation. In addition, the SEM images of PbI$_2$-yUrea (Fig. S3†) show that the full surface coverage of PbI$_2$ film is achieved when urea adds to PbI$_2$ solution. As we discussed before, the incorporation of urea into perovskite precursors drastically declines the rate of perovskite growth and to a large extent determines how perovskite crystals develop. In fact, through the formation of some perovskite/urea intermediates, the path of perovskite crystallization is changed and as a result, in contrast to a urea-free perovskite deposited film, the perovskite containing urea film needs annealing at 100 °C for converting to final perovskite crystal (See Fig. 2, X = 1.0). This essential deceleration in perovskite growth rate provides valuable possibilities for controlling shape, size and morphology of perovskite crystal.

In according to fabricate a satisfactory solar cell, it is essential to deposit a perovskite film with an almost full surface coverage, while conventional one-step solution-processed approach generally results in non-continuous film with many pinholes. In this regard, a better perovskite film coverage is obtainable by applying an antisolvent during spin coating. In fact, antisolvent technique prepares a super saturation condition through the sudden extraction of DMF from the solution [23].

Here, we applied the antisolvent technique to investigate its effects on MAI.PbI$_2$-yUrea adduct formation and to achieve a satisfactory film coverage. In line with this examination, perovskite solutions with different contents of urea (X = 0, 0.5, 1.0 and 2.0) were prepared and spun at 4000 rpm for 25 s. During the spin coating, about 200 μL of diethyl ether were dripped on the centre of the substrates.

Fig. 5 demonstrates that utilizing diethyl ether as antisolvent can promisingly produce full-coverage, pinhole free film. Larger crystal grains are produced via increasing urea contents in perovskite precursors. It can be derived from SEM images (see Fig. 5), that the average size of grains increases from 300 nm for the standard solution (i.e. X = 0.0) to 720, 860 and 3870 nm for X = 0.5, 1.0 and 2.0 respectively. These results are well consistent with the sizes of colloidal clusters. Therefore, it confirms that the size of colloidal clusters demonstrates the final size of perovskite grains [30]. Moreover, this phenomenon could directly refer to the formation of adduct intermediates which retard the crystal growth rate. As the consequence, thermodynamic phenomena play the major role in perovskite crystal growth, such as Ostwald Ripening, resulting in the well-developed and larger crystal grains. However, it is observed that by increasing urea concentrations beyond a certain level, some pinholes appear on the surface owing to the three-dimensional crystal growth of MAI.PbI$_2$-yUrea adducts.

When a perovskite solution with X = 2.0 was used, an extraordinary crystal superstructure is established over the grains (see Fig. 5, X = 2.0). It seems that the excess urea is extracted from the film during annealing which makes the surface rough [35]. In this accordance, as it can be observed in Fig. 2, the rate of perovskite formation for the film with X = 2.0 is faster than the corresponding film with X = 1.0. This is probably due to the formation of some heterogeneous nucleation sites dispersing in the solution that boost the perovskite crystallization.

UV–vis absorption results show that light absorption enhances through the incorporation of urea, in which the perovskite film with X = 1.0 has higher absorption (see Fig. 5). We also examined the effect of urea on perovskite PCE and obtained a power conversion efficiency of ca. 8% with a short-circuit current density ($J_{SC}$) of 14.74 mA/cm$^2$, an open-circuit voltage ($V_{OC}$) of 0.87 V, and a fill factor (FF) of 62.8% for PSC with X = 1 (Fig. S4†). It means that the incorporation of urea has no negative effects on the performance of PSCs.

As a supplementary investigation in adduct approach, we decided to examine a second adduct along with urea in perovskite solution.

Park et al. [24] simultaneously tested two different Lewis base molecules (DMSO and thiourea) in perovskite solution to control the morphology of perovskite layer for the first time. Generally, DMSO is considered for its excellent ability to make intermediate with perovskite precursors enhancing film properties (e.g. film coverage and smoothness), and increasing the grain sizes [26,36]. Therefore, due to the satisfactory results obtained by DMSO, we decided to consider DMSO in combination with urea for adduct formation and final perovskite morphology modification. For this purpose, various amounts of DMSO were added to the perovskite solution. 

![Fig. 5. The SEM images (left) and the UV–vis absorption spectra of perovskite films formed through one-step process and treated by diethyl ether as antisolvent (right).](image-url)
solution with $X = 1.0$ to produce urea/perovskite solutions with $0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ M ratios of DMSO to perovskite. Fig. 6 shows the SEM images of perovskite films fabricated by perovskite solutions containing urea and DMSO. The images illustrate that by adding DMSO in precursors, the size of grains decreases drastically in comparison to the sample that has no DMSO. By contrast, the surface coverage improves effectively. In addition, by further increase in the amount of DMSO, the size of grains grows gradually. Finally, when this amount rises to $1.0$ M ratio to perovskite, grains with extraordinary size are appeared (larger than 100 micrometres). Therefore, employing several adducts in MAPbI$_3$ solution is a great approach to get peculiar morphology.
4. Conclusions

We investigated the possibility of forming Lewis acid-base adduct by the incorporation of urea into perovskite formulation. It was clearly observed that urea seriously increases perovskite clusters’ size, as well as it retards the perovskite crystallization. As the result, it thoroughly affects the perovskite film properties such as morphology, coverage and grains size. Finally, the addition of DMSO in perovskite/urea precursors produces very large grains of perovskite. Ultimately, it can hopefully depict a promising path to fabricate large perovskite grains with modified crystallinity and film morphology by employing the adduct approach in simple one-step deposition processes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.spnt.2018.07.041.

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