oc-2022-003854.R1

Name: Peer Review Information for "Solvent gaming chemistry to control the quality of halide perovskite thin films for photovoltaics"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

In this work, Huang et al. reveal the mechanism of the solvent gaming chemistry in perovskite materials growth, which guides prepare defect-less α-FAPbI3 via sidestepping the break of strong coordination bonds. This work is interesting, and I believe it will attract broad audience of ACS Central Science. Therefore, I recommend publishing this work after a minor revision. Some minor comments:

1. The authors mentioned that when $\beta \geq DN^*$ ($DN^*=DN/38.8$), solvents integrate with FA+ cations to form hydrogen bonds within the (FA···solvent)PbI3 lattice; when $\beta < DN^*$, solvents coordinate with Pb2+ to form the PbI2-solvent. Is it possible that two different interactions co-exist?

2. The NMR measurements are very helpful to further reveal the interactions between the ions in perovskite precursor and the solvent. NMRs for (1) FAI in solvent and (2) PbI2 in solvent compared with pure solvent should be conducted, which will help to determine are the two kinds of interactions co-exist and which shift the peak most.

3. For the FTIR results in Figure S7, it should be also helpful to check the wavenumber around 3400 cm-1 to see if hydrogen bonding is also co-exist.

Reviewer: 2

Comments to the Author

Unlike the covalent compounds, halide perovskites are interesting ionic materials with advantages of solution processability for many photonic and optoelectronic applications. There is no doubt that controlling the crystallization process is of vital importance in fabricating high performance perovskite devices. Although there are a few works concerning on the solvent effects on the crystallization, the understanding is far from a well-established phsycal chemistry model. In this manucript, Zheng et al. report the solvent-contained intermediate structures, and intermediate-to-perovskite α-FAPbI3 evolutions. They illustrate the hydrogen-bond-favorable kind solvent could form defect-less α FAPbI3 via sidestepping the break of strong coordination bonds. I was reading the whole manuscript with great interstes. The manuscript is strongly recommended for the publication in ACS Central Science after minor revisions.

(1) The authors compared the device performance of the PSC fabricated with using DMSO and NMP. In principle, the solvents should affect he grain size of resulting films. Although the authors show the SEM images in the SI, I would like to recommend the authors to describe the grain size before the device analysis.

(2) Except for the consideration of Lewis basic solvent binding with perovskite precursors, there are also works discuss the coordinated and non-corrdinated solvents (10.1021/acs.chemmater.7b01100; 10.1002/adom.201900774). Please discuss the relationshipwith Gutmann Donor Number (DN) and Kamlet-Taft β value.

(2) In

Author's Response to Peer Review Comments:

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June 23, 2022

Prof. Editor
Senior Editor
ACS Central Science

Dear Prof. Editor,

Submitted is a revised manuscript (oc-2022-003854) entitled “Solvent gaming chemistry to control the quality of halide perovskite thin films for photovoltaics” for your consideration as an article in *ACS Central Science.*

Thank you very much for providing us the opportunity to further revise the manuscript. We wish to express our deep appreciation to both reviewers for their comments and suggestions to enhance the quality of our manuscript. We have now carefully revised the manuscript accordingly. Our detailed responses to the reviewers are loaded as a separated file.

We have considered that all concerns raised from the reviewers have been addressed in our revised manuscript. A copy of the manuscript with major revisions highlighted in yellow background was also uploaded for your reference.

Hope that you will find the current version suitable for publication in *ACS Central Science.*

With best regards,

Nanfeng
On behalf of all authors

Reply to Referee #1

We appreciate the reviewer for the publication suggestion. Following the comments, we have revised our manuscript as follows:

Comment 1: The authors mentioned that when $\beta \geq DN^*$ ($DN^*=DN/38.8$), solvents integrate with FA^+ cations to form hydrogen bonds within the $(FA\cdots solvent)PbI_3$ lattice; when $\beta < DN^*$, solvents coordinate with Pb^{2+} to form the PbI_2-solvent. Is it possible that two different interactions co-exist?

Comment 2: The NMR measurements are very helpful to further reveal the interactions between the ions in perovskite precursor and the solvent. NMRs for (1) FAI in solvent and (2) PbI_2 in solvent compared with pure solvent should be conducted, which will help to determine are the two kinds of interactions co-exist and which shift the peak most.

Response: Thank the reviewer for the helpful advices. We would like to address **Comment 1** and **2** together because they are related to each other. Yes. Due to the possible existence of Lewis acid-base interaction between FA^+/Pb^{2+} and oxygen-containing solvent molecules (i.e., OXRs in this work) in the precursor solutions containing FAI, PbI_2 and solvent, the $FA^+\cdots$solvent and Pb^{2+}-solvent interactions would co-exist in the solution phase in a dynamic equilibrium. These two interactions can be intuitively reflected by the NMR measurements of FAI/PbI_2 precursors in solvents. NMP and DMSO solvents are used as the examples for the demonstration. As shown in the ^{16}O NMR (Figure S3a,b), both ^{16}O signals of NMP in FAI+NMP and PbI_2+NMP samples were shifted to low field compared with that of pure NMP solvent, suggesting that the interactions of $FA^+\cdots$NMP and Pb^{2+}-NMP decreased the electron cloudy density of O element in NMP molecule. In addition, the difference in the ^{16}O signal shift indicated that the stronger $FA^+\cdots$NMP interaction than Pb^{2+}-NMP interaction. The similar ^{16}O shift of DMSO in PbI_2+DMSO and FAI+DMSO samples were observed. However, the ^{16}O shift in PbI_2+DMSO sample was more apparent than that of FAI+DMSO sample. Furthermore, as revealed by the

^{1}H NMR (Figure S3c,d), the FA$^+$···DMSO interaction was relatively weaker than the Pb^{2+}-DMSO interaction, which was consistent with the ^{16}O NMR results. So the NMR measurements did demonstrate that two kinds of interactions (i.e., FA$^+$···solvent and Pb^{2+}-solvent) coexisted in precursor solutions. However, during the process of crystal growth from solutions, the dynamic equilibrium between two interactions would be broken, resulting in the final crystal structures with thermodynamically most stable state, either (FA···solvent)PbI_3 lattice or PbI_2-solvent + FAI. In our work or previous reported works, the co-presence of two different interactions was not observed in the $FAPbI_3$-based intermediates grown in the crystal form. More discussion on both FA$^+$···solvent and Pb^{2+}-solvent interactions is provided in the revised manuscript.

Comment 3: For the FTIR results in Figure S7, it should be also helpful to check the wavenumber around 3400 cm^{-1} to see if hydrogen bonding is also co-exist.

Response: Thanks for the suggestion. The hydrogen bonds of FA$^+$···NMP couples in the (FA···NMP)PbI_3 intermediate structure resulted in the shift of C=N signal in FA$^+$ cations and C=O in NMP molecules (Figure S7a). Consequently, the hydrogen-bond-induced change of -N-H signal was observed. The -N-H signal around 3260 cm^{-1} from the (FA···NMP)PbI_3 sample became broader as compared to δ-$FAPbI_3$ (Figure S7b), demonstrating the formation of hydrogen bonds in FA$^+$···NMP couples.

Reply to Referee #2

We thank the reviewer for the publication recommendation and constructive comments. These comments are very helpful for us to improve the manuscript. Following the comments, we have carefully revised our manuscript as follows:

Comment 1: The authors compared the device performance of the PSC fabricated with using DMSO and NMP. In principle, the solvents should affect he grain size of resulting films. Although the authors show the SEM images in the SI, I would like to recommend the authors to describe the grain size before the device analysis.

Respond: Yes. Solvent-binding intermediate structures have been demonstrated to affect film quality, particularly in grain sizes. As shown in Figure S15, the intermediate film of (FA···NMP)PbI_3 exhibited a more even and larger grain size than that from PbI_2-2DMSO (with FAI addition). The crystallinity of as-deposited (FA···NMP)PbI_3 intermediate film was higher than PbI_2-2DMSO (with FAI addition) film too. Similarly, the as-annealed (FA···NMP)PbI_3 intermediate film exhibited larger grain size and better crystallinity than that from PbI_2-2DMSO (with FAI addition). More discussion about solvent-effected grain sizes in films is added in the revised manuscript.

Comment 2: Except for the consideration of Lewis basic solvent binding with perovskite precursors, there are also works discuss the coordinated and non-coordinated solvents (10.1021/acs.chemmater.7b01100; 10.1002/adom.201900774). Please discuss the relationship with Gutmann Donor Number (DN) and Kamlet-Taft β value.

Response: Thank the reviewer for the suggestion. In this work, we mainly discuss the relationship between binding solvents, intermediate structures and film quality. It is true that there have been good works discussing the critical function of solvent on high-quality perovskite synthesis. For example, non-coordinated solvent (e.g., ACN) would effectively decrease nanocrystal defects compared with that from commonly used coordinated solvent (e.g., DMF). Due to the ionic property of halide perovskites, many perovskite-involved intermediate structures have been grown and explored. Taking $FAPbI_3$ as example, the Lewis acidic Pb^{2+} cations have a strong binding ability with Lewis-basic oxygen-contained molecules (i.e., OXR in this work). The Gutmann Donor number, one of Lewis-basic indicator, has been used to evaluate the binding strengthen of Pb^{2+}-OXR. Actually, another kind of $(FA\cdots OXR)PbI_3$ intermediate structures have also been observed in the process of film-formation and crystal growth. But they have not caught much attention yet. We found that the β value can reflect the formation capacity of hydrogen bonds between solvent and Lewis-basic species, which is a great indicator to evaluate the interaction of $FA^+\cdots OXR$ couples. While there is positive relationship among DN and β values, the different measurement methods limit the direct comparison of these two properties of Lewis basicity. For comparison, we choose HMPA (DN = 38.8 kcal/mol, $\beta = 1$) as the reference to obtain normalized DN^* value ($DN^*=DN/38.8$). Thus we can use DN^* and β values of solvents to directly compare the Pb^{2+}-OXR and FA^+-OXR interactions.