nature portfolio

Peer Review File

Moisture tolerant solar cells by encapsulating 3D perovskite with long-chain alkylammonium cation-based 2D perovskite

Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality.

3rd Mar 21

Dear Dr Gardner,

Thank you for submitting your manuscript, "Moisture Tolerant Perovskite Solar Cells: Alloying Stable 2D and Efficient 3D Perovskite Materials", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that while they find your work of potential interest, they have raised substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but are interested in considering a revised version that addresses these concerns.

You will see in particular that Reviewer 2 is questioning why the stability tests did not focus on high relative humidity, rather than the 25-80% range used, and asks for data on thermal stability, and under the sun. Reviewer 3 is also requesting additional data to confirm the presence of a 2D layer, and is questioning the analysis of the PL data.

Should further data and analysis allow you to address these criticisms, we would be happy to look at a revised manuscript. If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type ‘Revised Manuscript - Marked Up’ when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type ‘Article File’.

-An updated Editorial Policy checklist, uploaded as a ‘Related Manuscript File’ type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic ‘smart pdf’ and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

-Solar Cells: Reporting checklist for solar cell manuscripts

Please use the following link to submit your revised manuscript files:

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** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors apply for the first time a long-chain-based 2D material on a perovskite solar cell in order to prolong the shelf-life of the devices. Although they are any relevant new aspects in the work with respect the existence literature, the paper is well presented and the results undoubtedly support the claim. However, in order to improve the cite ability of the paper, I suggest to give a spreader landscape on the issue the paper wants to address (the moisture in PSCs). For example, in our recent paper (https://doi.org/10.1038/s43246-020-00104-z) we gave an innovative point of view on how solving the problem of the humidity for PSCs: in my humble opinion, I think this paper can be cited in the introduction of the manuscript.

Furthermore, there are some minor points to be fixed before final acceptance:

- typos: consider merging the references when submitting (ex. line 73)
- are you sure that the PbI2 is not present when 2D are used? In my opinion lead iodide can be present in amorphous phase, transparent to XRD. the authors are asked to discuss this point
- EIS measurements are not completely convincing. despite in table S3 the fitted results are presented, the parameters used are not proper: for example, in the 3D semicircle a constant phase element (CPE) must be used instead of simple capacitance. On the other hand, for removing any doubts, the authors should include the error values (in %) with respect to the fitting model used
- authors spent a lot of energy in trying convincing themselves and the reader that the Jsc drop when using 3D is due to inefficient light harvesting. However, EQE measurements are not in agreement with statistical analysis reported in fig. 2d where 21.5 vs 19.5 mAcm-2 can be extrapolated as

average (with respect to 20 - 19.7 mAcm for EQE, line 227).

Francesco Lamberti, PhD

Reviewer #2 (Remarks to the Author):

Gardner et al. reported the improved stability of 3D@2D perovskites, where three different alkyl chain length organic spacers were used in 2D perovskites. It is found that the 3D@2D perovskites show significant improvement in solar cell stability with limited compromise in solar cell efficiency. It is very impressive that the 3D@2D perovskite film could sustain over 1 minute in water. The finding in this work helps the community with a deep understand the 3D@2D perovskite solar cell. Moreover, the fabrication of 2D perovskite film using precursor solution of 2D perovskite crystals in THF also represents a novel approach. I recommend that it be published after they address my concerns below.

1. The authors prepare the 2D perovskite solution in THF using 2D perovskite crystals. The detailed preparation method and characterization of 2D perovskite crystals should be included in the manuscript or supporting information.
2. There are two absorption peaks between 450 to 500 nm for the absorption spectrum of C18 2D perovskite (Fig. S4). Typically, only one peak near 500 nm for 2D perovskite with n value of 1 and this peak could be assigned to n=1 peak of 2D perovskite. Why there are two peaks here?
3. Page 10, “Whereas under illumination the conductivity values of 3D@2D devices are one order of magnitude lower compared to 3D only devices.” Why?
4. It is strange that the device stability was measured under ambient atmosphere with RH at a wide range of 25-80%. As this work mainly focus on the improved moisture stability of 3D@2D PSCs, how about the device stability in high RH ~80%?
5. How about the thermal stability of the devices? Could 3D@2D perovskite improve the thermal stability? Could 3D@2D perovskite improve the stability of PSCs under continues light (1 Sun) soaking? The authors are suggested give some come comments or experiments results as the readers would be very interested in it.

Reviewer #3 (Remarks to the Author):

In this work, the authors have used 2D cations based on highly moisture resistive alkylammonium cation. They show long term stability due to the encapsulation effects of the 2D and a maximum efficiency of 17%.
Despite a lot of attention has been recently focused on such systems, the manuscript does not include enough novelty: the idea of the 2D/3D encapsulation has been widely explored in literature and the results obtained (PCE=17%) below most recent literature on that demonstrating 20-21% efficiency or above - as the authors correctly mentioned. In addition, there is a lack of a solid evidence of the presence of such 2D layer. The XRD in Figure S1 and the absorption spectra reported in the SI denote a bizarre behaviour. What is the number of layer of this 2D? Why it is not seen in the PL in Fig. 1e? Moreover, the performances are lower than the controller, indicating that the use of these cations is not beneficial and should not be considered for future device optimisation. This can be expected given the possibly lower mobility in this compounds. The analysis on the transient PL is

also poor, how can the author conclude that carrier lifetime is longer without analysing the data (normalisation of PL, Intensity dependance to check the density of carriers generated). Also, the stability is only checked for 200h which does not meet the general stability criteria. For the above mentioned reasons I think this manuscript cannot be published.

Manuscript ID: COMMSMAT-21-0026-T

Manuscript title: Moisture Tolerant Perovskite Solar Cells: Alloying Stable 2D and Efficient 3D Perovskite Materials

We would like to thank all the reviewers for spending their time to review our manuscript. The suggestions of the reviewers help us to improve the quality of the manuscript. We considered most of the comments while revising this manuscript. Our point-by-point responses to those comments/ suggestions are described in the followings and highlighted in blue italic text.

Reviewers' comments:
Reviewer #1 (Remarks to the Author):
The authors apply for the first time a long-chain-based 2D material on a perovskite solar cell in order to prolong the shelf-life of the devices. Although they are any relevant new aspects in the work with respect the existence literature, the paper is well presented and the results undoubtedly support the claim. However, in order to improve the cite ability of the paper, I suggest to give a spreader landscape on the issue the paper wants to address (the moisture in PSCs). For example, in our recent paper (https://doi.org/10.1038/s43246-020-00104-z) we gave an innovative point of view on how solving the problem of the humidity for PSCs: in my humble opinion, I think this paper can be cited in the introduction of the manuscript.

Response: We would like to thank the reviewer for finding our work interesting and acceptable in Communications Materials. The reference suggested by reviewer is now cited in the manuscript.

1. Furthermore, there are some minor points to be fixed before final acceptance:

- typos: consider merging the references when submitting (ex. line 73)

Response: We used endnote for managing the references but with Nature Comm. reference style we are not able to merge these references.

2. are you sure that the PbI2 is not present when 2D are used? In my opinion lead iodide can be present in amorphous phase, transparent to XRD. the authors are asked to discuss this point

Response: The reviewer is correct, some quantity of amorphous PbI_2 is probably present after coating 3D perovskite films with the 2D perovskite. There is not a way of knowing exactly how much would be present and the article makes no claims that after coating the thin film with 2D perovskite that PbI_2 is removed entirely. However, after coating with the 2D perovskite a significant portion of the crystalline PbI_2 phase was removed as shown in Figure 1b and Figure 1 below. To make it more visible we plotted the diffraction intensity in logarithmic scale and compared the XRD patterns of 3D only and 2D perovskite coated films specifically in the 2Θ= 12.45 region, see Figure 1. It is clear from these figures that the coating of 2D perovskite supresses the PbI_2 impurity, but it is difficult to get rid of PbI_2 phase completely. One would imagine that if the crystalline PbI_2 phase is suppressed that the

amorphous phase would be suppressed even more, since the lattice energy of the PbI_2 crystals should to some extent inhibit reactivity.

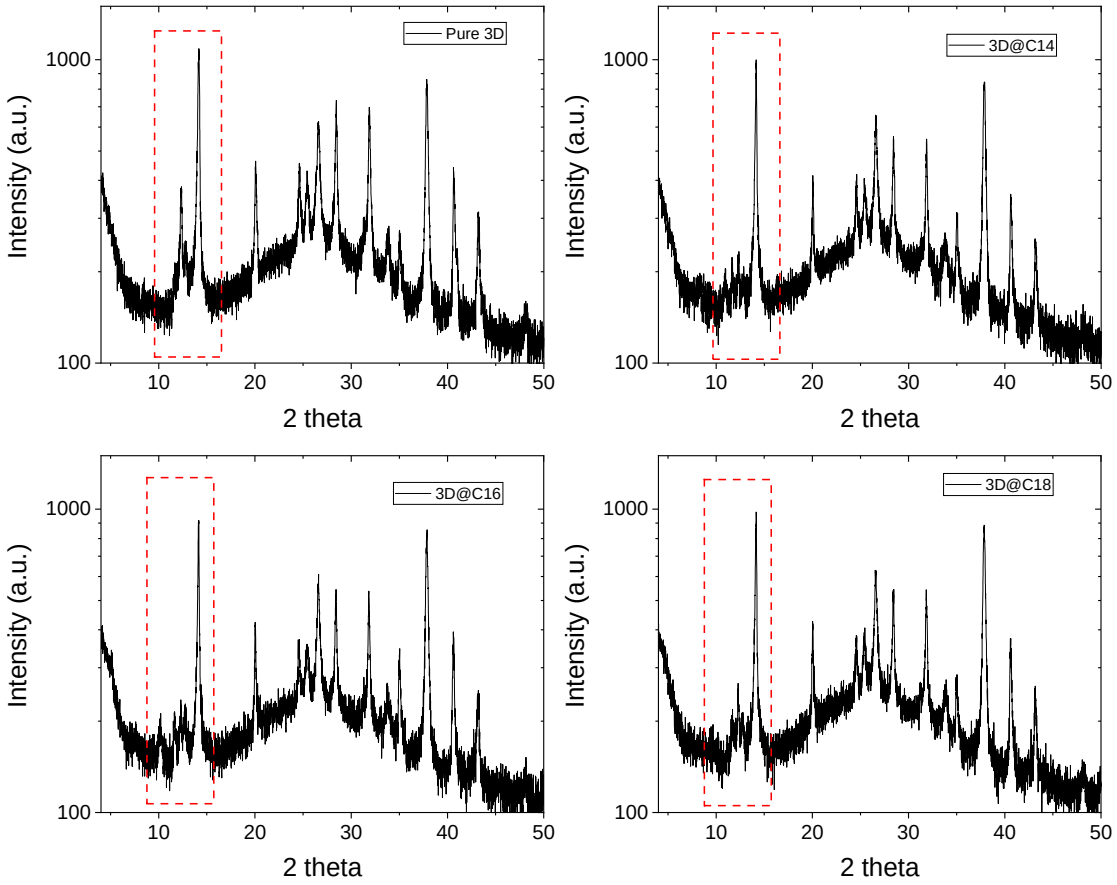

Figure 1. XRD patterns of 3D only and 2D perovskite coated thin films.

3. EIS measurements are not completely convincing. despite in table S3 the fitted results are presented, the parameters used are not proper: for example, in the 3D semicircle a constant phase element (CPE) must be used instead of simple capacitance. On the other hand, for removing any doubts, the authors should include the error values (in %) with respect to the fitting model used.

Response: As suggested by reviewer we fitted the EIS curves by considering CPE instead of simple capacitance. The inclusion of CPE results in slightly better fitting compared to simple capacitance based equivalent circuit, as shown in Figure 2 below. But, the error involved in the R_{rec} values is doubled when the EIS curves fitted using CPE model, see Table 2. Overall, the values of R_s, R_{ct} and R_{rec} extracted using both the equivalent circuit model are comparable and there is no significant change when considering the CPE into the EIS fitting, except in few cases, as given in Tables 1 and 2 below. Therefore, the conclusion drawn from the EIS analysis remain unchanged even after considering the CPE instead of simple capacitance in EIS fitting.

Table 1. Impedance curves fitted using a simple capacitance model

Samples	R_s (Ω)	R_{ct} (Ω)	C_{ct} (F)	R_{rec} (Ω)	C_{rec} (F)
3D only	12 (18%)	27548 (11%)	2.8×10^{-8} (7%)	1.05×10^{6} (18%)	7.43×10^{-7} (10%)
3D@C14	9.7 (18%)	3730 (12%)	4.8×10^{-8} (9%)	1.30×10^{6} (21%)	8.40×10^{-7} (8%)
3D@C16	10.5 (17%)	2983 (13%)	4.7×10^{-8} (9%)	2.20×10^{6} (23%)	6.58×10^{-7} (7%)
3D@C18	10.4 (18%)	3014 (12%)	4.7×10^{-8} (9%)	2.20×10^{6} (26%)	7.68×10^{-7} (8%)

Table 2. Impedance curves fitted using a constant phase element (CPE) model

Samples	R_s (Ω)	R_{ct} (Ω)	CPE_{ct} (Mho)	R_{rec} (Ω)	CPE_{rec} (Mho)
3D only	12 (18%)	27696 (14%)	2.17×10^{-8} (32%)	7.53×10^{5} (28%)	1.24×10^{-6} (18%)
3D@C14	10 (17%)	2794 (15%)	2.6×10^{-8} (50%)	2.23×10^{6} (44%)	1.11×10^{-7} (12%)
3D@C16	10.8 (16%)	2242 (15%)	2.75×10^{-8} (51%)	3.80×10^{6} (51%)	8.47×10^{-7} (11%)
3D@C18	10.8 (16%)	2242 (15%)	2.72×10^{-8} (51%)	4.65×10^{6} (71%)	9.99×10^{-7} (11%)

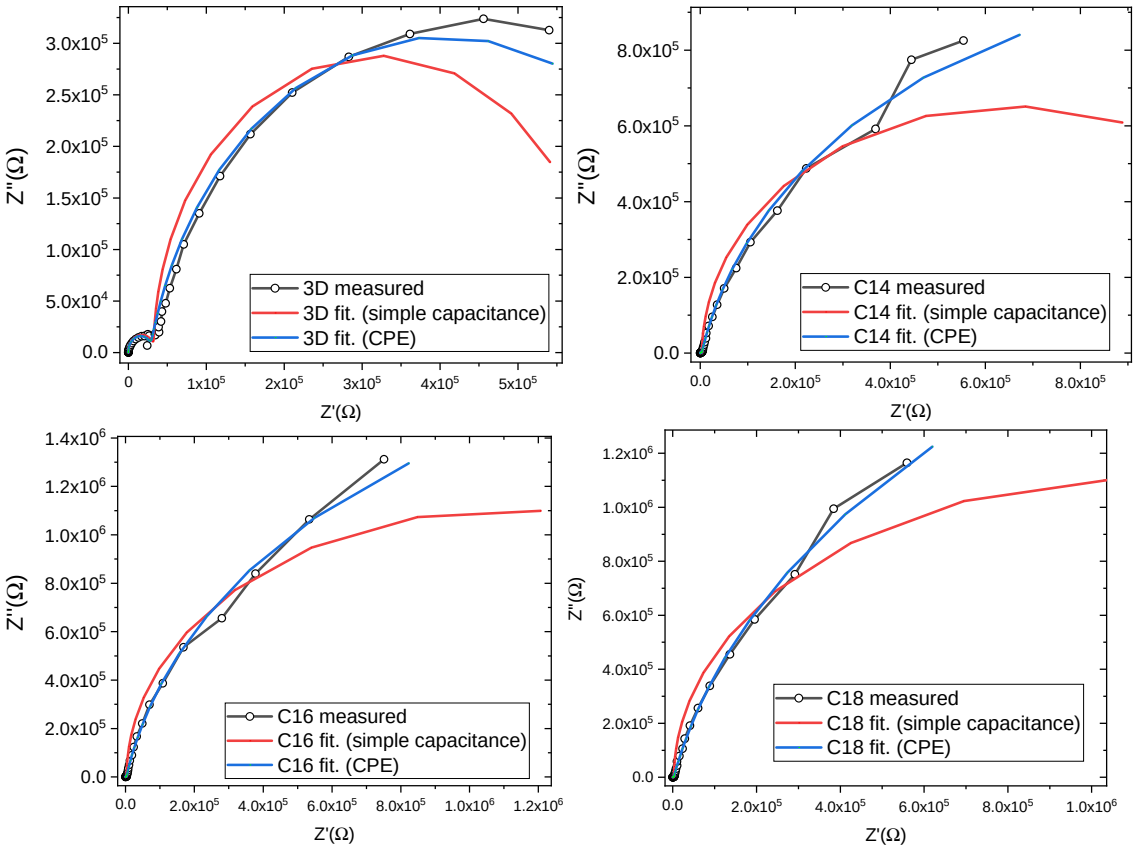

Figure 2. Impedance data fitting using simple capacitance and CPE model.

4. authors spent a lot of energy in trying convincing themselves and the reader that the Jsc drop when using 3D is due to inefficient light harvesting. However, EQE measurements are not in agreement with statistical analysis reported in fig. 2d where 21.5 vs 19.5 mAcm-2 can be extrapolated as average (with respect to 20 - 19.7 mAcm for EQE, line 227).

Francesco Lamberti, PhD

Response: Yes, we agree that the Jsc values extracted by integrating the IPCE spectra of 3D only and 3D@2D devices are quite similar, but by looking at the shape of the IPCE spectra of 3D only and 3D@2D coated devices there is a clear difference in the photon conversion efficiency of these two types of devices. For sure there is a drop in the Jsc values when the 3D perovskite is coated with 2D perovskite at least from the JV measurements. This difference between Jsc values of 3D only and 3D@2D perovskite coated solar cells is small in IPCE measurements but this does not imply that the photon conversion efficiencies in these two types of solar cells are similar. The IPCE spectra shows a clear difference in the photon conversion efficiencies of 3D only and 3D@2D devices. To give a clear picture please see Figure 3 below which show this difference persist in all the devices on which we carried out the IPCE measurements.

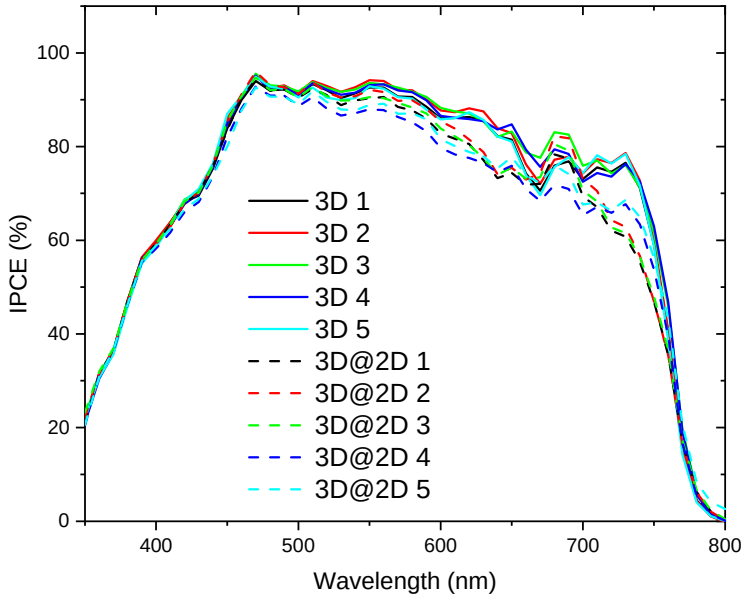

Figure 3. IPCE spectra of 3D only and 2D perovskite coated perovskite solar cells.

Reviewer #2 (Remarks to the Author):

Gardner et al. reported the improved stability of 3D@2D perovskites, where three different alkyl chain length organic spacers were used in 2D perovskites. It is found that the 3D@2D perovskites show significant improvement in solar cell stability with limited compromise in solar cell efficiency. It is very impressive that the 3D@2D perovskite film could sustain over 1 minute in water. The finding in this work helps the community with a deep understand the 3D@2D perovskite solar cell. Moreover, the fabrication of 2D perovskite film using precursor solution of 2D perovskite crystals in THF also represents a novel approach. I recommend that it be published after they address my concerns below.

We would like to thank the reviewer for finding our work interesting and suitable for publication in Communications Materials.

1. The authors prepare the 2D perovskite solution in THF using 2D perovskite crystals. The detailed preparation method and characterization of 2D perovskite crystals should be included in the manuscript or supporting information.

Response: The preparation of the 2D perovskite crystals have already been published in our previous study (https://pubs.rsc.org/en/content/articlehtml/2020/ma/d0ma00577k, Mater.

Adv., 2020, 1, 2395-2400). However, we have included a brief description about the synthesis of the 2D perovskite crystals and 2D perovskite thin film fabrication in supporting information.

2. There are two absorption peaks between 450 to 500 nm for the absorption spectrum of C18 2D perovskite (Fig. S4). Typically, only one peak near 500 nm for 2D perovskite with n value of 1 and this peak could be assigned to n=1 peak of 2D perovskite. Why there are two peaks here?

Response: The two peaks in the absorption spectra are due to the presence of two crystallographic phases in these 2D perovskite. When these 2D perovskite samples are annealed above their phases transition temperatures, then even after cooling to room temperature the presence of high temperature phase can be observed. This was examined in detail in our previous study. The 2D perovskite investigated here inhibit this unique property. Again this has already been reported in our previous work (https://pubs.rsc.org/en/content/articlehtml/2020/ma/d0ma00577k, Mater. Adv., 2020, 1, 2395-2400). We included a brief description about this in the revised supporting information.

3. Page 10, "Whereas under illumination the conductivity values of 3D@2D devices are one order of magnitude lower compared to 3D only devices." Why?

Response: The 2D perovskite contain bulky organic cations which are electrically insulating in nature, this gives rise to lower electrical conductivities in pure 2D perovskites. When 3D perovskites are coated with such 2D materials the overall resistivity of the 3D@2D system increases giving rise to an observable drop in the conductivity values. The increase in the resistance of the system after coating with 2D perovskite is further supported by the EIS results.

4. It is strange that the device stability was measured under ambient atmosphere with RH at a wide range of 25-80%. As this work mainly focus on the improved moisture stability of 3D@2D PSCs, how about the device stability in high RH ~80%?

Response: The main idea behind this project was to improve the stability of the perovskite solar cells under ambient condition where the variation in humidity is within (25-80%). We do not have an appropriate instrumentation/facilities to maintain high humidity levels and check stability as a function of time. We appreciate the suggestion given by reviewer to test the solar cell stabilities at higher humidity levels, we will try to incorporate this in our future studies.

5. How about the thermal stability of the devices? Could 3D@2D perovskite improve the thermal stability? Could 3D@2D perovskite improve the stability of PSCs under continues light (1 Sun) soaking? The authors are suggested give some come comments or experiments results as the readers would be very interested in it.

Response: We tested the stability of the 3D@2D perovskite solar cells at higher temperatures (around 90 ^{o}C). We observed that coating 2D perovskite on the top of 3D perovskite does not improve the thermal stability of the 3D@2D device.

It should be noted that the thermal instability of the spiro HTM could limit the thermal stability of the solar cell in general.

We monitored the effect of light soaking in 3D only and 3D@2D perovskite solar cell for about an hour. We did not observe any significant changes in the performance of the 3D only and 3D@2D devices, please see Fig. 2g.

Reviewer #3 (Remarks to the Author):

In this work, the authors have used 2D cations based on highly moisture resistive alkylammonium cation. They show long term stability due to the encapsulation effects of the 2D and a maximum efficiency of 17%.

Despite a lot of attention has been recently focused on such systems, the manuscript does not include enough novelty: the idea of the 2D/3D encapsulation has been widely explored in literature and the results obtained (PCE=17%) below most recent literature on that demonstrating 20-21% efficiency or above - as the authors correctly mentioned. In addition, there is a lack of a solid evidence of the presence of such 2D layer. The XRD in Figure S1 and the absorption spectra reported in the SI denote a bizarre behaviour. What is the number of layer of this 2D? Why it is not seen in the PL in Fig. 1e? Moreover, the performances are lower than the controller, indicating that the use of these cations is not beneficial and should not be considered for future device optimisation. This can be expected given the possibly lower mobility in this compounds. The analysis on the transient PL is also poor, how can the author conclude that carrier lifetime is longer without analysing the data (normalisation of PL, Intensity dependance to check the density of carriers generated). For the above mentioned reasons I think this manuscript cannot be published.

Response: Yes, we have used a common approach of coating the 3D perovskite with 2D perovskite to prevent the light absorbing layer from the moisture, this does not imply that our work is routine work as no one tried such long alkylammonium cation based 2D perovskite in solar cells before. The moisture stability of these materials is absolutely unique. We are unaware of any examples that produce such comparatively long-term stability upon direct immersion in water.

Our group is mainly interested in exploring new hybrid perovskite materials and their possible use in optoelectronic devices. While other groups have produced high efficiency solar cells (>22% PCE) solar we know that we do not yet have the expertise to fabricate such devices. However, we do not see why this makes the results presented herein any less significant/impactful. The main aim of this study was to explore the effect of long alkylammonium cation based 2D perovskites on the photovoltaic efficiency and stability, even if we would have achieved efficiencies more than 22% in 3D only solar cells the effect of 2D perovskite on the solar cell efficiencies and stability could be the same.

We agree that despite our efforts evidence for the presence of the 2D perovskite on the top of the 3D perovskite is indirect and there are not any straightforward measurements available

which can tell us directly about the 2D perovskite. That is why we went for the concentration dependent experiments where we increased the quantity of the 2D perovskite in THF. As shown in the supporting information (Fig. S1) with increase in the concentration of the 2D perovskite we could see the diffraction peaks other than the 3D perovskite, this makes it clear that the surface of the 3D perovskite is coated with some crystalline material and not only with the organic cations. The fact that we used diluted precursor solution of 2D perovskites while fabricating the solar cells it is hard to get diffraction peaks from such a thin layered perovskite.

The changes observed in the XRD pattern (shown in Fig S1) are further justified with some other complimentary experiments where we deliberately doped FA cations into the 2D perovskite (see Figure S2 and S3) and observed that the XRD pattern of the FA doped 2D perovskite matches well with the XRD pattern of the new phase. So, the results presented here are not unusual, it is very well known that the hybrid perovskite are very easy to dope either at A and B sites and the new phases we observed here is as a result of doping of FA from 3D perovskite to 2D perovskite while making the 3D@2D films.

We are not quite sure about the number of layers (n) in this new phase.

As discussed before we do not observe PL signal arising from 2D perovskite because we used diluted precursor solution of 2D perovskite which after annealing forms a very thin layer. As well, the emission from the 2D perovskite has direct spectral overlaps with the absorption spectra for the 3D perovskite. It would be highly unusual for emission from the 2D perovskite to observed in this scenario. As well, the 2D and 3D perovskites are in direct electrical contact; such that excited states can be quenched by charge transfers between the layers.

We had expected that using such a bulky organic cation in perovskite solar cells would result in a drop in the device performance, but the drop in the efficiency after coating the 3D perovskite with 2D perovskite is at the expense of improved stability. Yes, we completely agree that if we use thicker layer of 2D perovskite on the top of 3D perovskite then the solar cell performance will drop drastically, and this has been already observed and discussed in this study. So, one needs to optimize the percentage of 2D perovskite in solar cell so that the solar cells efficiencies/ performance does not have to compromise. Furthermore, the excess use of 2D perovskite has to be avoided to achieve decent electrical properties out of devices.

Thank you for the suggestion, we now revised Fig. 3a, where we normalized the TRPL curves. The TRPL data is fitted with biexponential decay function to extract the decay components.

We carried out the TRPL measurements to know whether the coating of 2D perovskite improves the carrier lifetime or not, because we have figured out that 2D perovskite coating leads to the suppression in the PbI2 impurity phase which could help in formation of lower trap states. Moreover, the intensity dependent TRPL measurements will have the same impact on both 3D only and 3D@2D thin films, so this measurement would not give any new information or the impact of 2D perovskite coating on 3D perovskite.

19th Apr 21

Dear Dr Gardner,

Your manuscript titled "Moisture Tolerant Perovskite Solar Cells: Alloying Stable 2D and Efficient 3D Perovskite Materials" has now been seen again by the three referees, whose comments appear below (Reviewer 1 provided remarks to the editors in which they said their comments had been addressed). In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

You will see that Reviewer 3 continues to raise concerns regarding the lack of direct evidence for the 2D perovskite layer, and we have checked with the other two referees what their thoughts are on this matter. Before we can accept your paper we do ask that you acknowledge in the text, at the relevant point, that the paper does not show direct evidence for the 2D layer, and you may wish to mention the difficulties in doing this.

We also invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS
* Your manuscript should comply with our policies and format requirements, detailed in our style and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf).

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Solar cells reporting summary:
https://www.nature.com/documents/nr-photovoltaic-reporting.pdf

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** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

This is an interesting paper. The authors have addressed my concerns. I think it should be accepted

for publication.

Reviewer #3 (Remarks to the Author):

The authors have revised the paper with a good amount of additional data which enrich the work and make it more interesting. However they did not provide any experimental evidence and they could not reply to the evident lack of experiments clearly indicating the presence of the 2D perovskite. The authors mention "We are not quite sure about the number of layers (n) in this new phase.
As discussed before we do not observe PL signal arising from 2D perovskite because we used diluted precursor solution of 2D perovskite which after annealing forms a very thin layer. " This is the core of the work, so, without the knowledge of the phases of the 2D perovskite I think the conclusions might lead to some misunderstanding. For this reason I believe the paper cannot be accepted for publication.

Manuscript ID: COMMSMAT-21-0026A

Manuscript title: Moisture Tolerant Perovskite Solar Cells: Alloying Stable 2D and Efficient 3D Perovskite Materials

We thank both reviewers for insightful and useful comments on our manuscript. We are glad to note that the reviewers find our work acceptable in Communications Materials. We are happy to have this opportunity to further improve the manuscript with the help of the suggestions given by the reviewers and have revised the manuscript accordingly. The point-by-point response to the reviewers' comments can be found below with the comments appearing in normal black font, while our responses follow each comment in the italics and blue font.

Reviewer #2 (Remarks to the Author):

This is an interesting paper. The authors have addressed my concerns. I think it should be accepted for publication.

We are happy to note that the reviewer recommends publication of our manuscript in Communications Materials.

Reviewer #3 (Remarks to the Author):

The authors have revised the paper with a good amount of additional data which enrich the work and make it more interesting. However they did not provide any experimental evidence and they could not reply to the evident lack of experiments clearly indicating the presence of the 2D perovskite. The authors mention "We are not quite sure about the number of layers (n) in this new phase.

Response: We would like to thank the reviewer for finding revised version of our manuscript more interesting. The data clearly illustrates that diluted concentrations of 2D perovskite solution used in spin coating form trace amounts of 2D perovskite material on the top of 3D perovskite, which can not be easily detected by X-ray diffraction measurements. Furthermore, to exclude the possibility of covering the 3D perovskite surface with only organic cations (alkylammonium ligands), complementary experiments indicated that the surface of the 3D perovskite is covered with crystalline materials. While the formation of a new phase in our study was unexpected, careful investigation of the thin films with additional experiments suggests that FA cations from the 3D perovskite are incorporated within the 2D perovskite layer resulting in the new crystallographic phase. A thorough investigation of this new crystallographic phase is beyond the scope of the present study, which is why the number of layers (n) in this new phase is undetermined. Follow up investigations of the crystallographic and physical properties of this new phase are presently underway.

As discussed before we do not observe PL signal arising from 2D perovskite because we used diluted precursor solution of 2D perovskite which after annealing forms a very thin layer. " This is the core of the work, so, without the knowledge of the phases of the 2D perovskite I think the conclusions might lead to some misunderstanding. For this reason I believe the paper cannot be accepted for publication.

Response: We understand the frustration of the reviewer and wish that the material yielded itself to simpler studies. However, there is no misunderstanding about this study, the data clearly illustrate the formation of a new 2D perovskite phase and provide enough experimental evidence such that anyone can reproduce the work.