Dear Nam Nguyen,

We would like to **thank the reviewers for valuable comments as well as their favorable evaluation of our manuscript “Influence of hybrid perovskite fabrication methods on film formation, electronic structure and solar cell performance”. We have now revised the paper, taking into account the editors and reviewers’ comments. A summary of changes and a brief response are included. We hope you find the revised manuscript suitable for publication in Journal of Visualized Experiments.**

**Best regards,**

**Selina Olthof**

*All the corrected parts are highlighted in turquoise in the manuscript.*

**Editorial comments:**  
  
1. What is the concentration of the HCl-FeCl3 solution?

"(1 mol/L)" was added. (Line 99)

2. Please abbreviate all journal titles.  
Done

3. Formatting:  
-Please define all abbreviations at first occurrence (ie DMF, JV).

“in N,N-Dimethylformamide,” added. (Line 146)

"current density versus voltage (JV)" was added. (Line 244)

-All figure legends should have a title and a brief description (see Figure 5).

Fig. 5 has a figure caption (description) similar to the other Figures. Please specify what the necessary changes are.

-References – Please abbreviate journal titles.  
Done

4. Grammar:  
-4.1.1.1 – “PbI2 dissolved DMF”

“in” added. (Line 146)

-4.2.1.4 – “a quartz crystal monitors”

This section has been corrected for better understanding (see 4.2.1.4 below)

-Line 261 – “subfigures 1 a1 - a5)” – this is not clear

"subfigures a1) - a5) of figure 1" was added. (Line 266)

5. Additional detail is required:  
-3.3, 4.1.2.7 – Is this done on a hotplate or in an oven?

"on a hotplate" was added. (Line 130 and 174)

-4.1.1.4 – What is meant by spinning off the substrate? Where is it spun?

"substrate on spin coater and drop" was added (additional detail for spin coating process which is used through the whole paper)

-4.1.2.6 – How many layers are spun?

One layer of perovskite material is spin coated per substrate.

-4.1.3.1 – Is this an alternative to the other solution from 4.1.2.1? If part of the process, after how many layers of the previous solution? How many layers are spun from this solution?

Yes, using a molecular additive is an alternative from 4.1.2.1. Here also only one layer of perovskite is spin coated.

-4.2.1.4 – How is calibration performed?

"Calibrate the evaporation rates for the two materials using one quartz crystal monitor (QCM) positioned close to the source while the other one is at the sample position. The calibration is done by heating the material to an evaporation temperature and simultaneously writing down the respective thicknesses shown on both QCMs. The tooling factor is calculated by the ratio of the two values." was added to understand calibration process. (Line 191)

-4.2.2.1 – How is this done?

"Adjust the rates of PbI2 to MAI to approximately 1:2 by increasing or decreasing the temperature of the sources to achieve a stoichiometrically correct perovskite film" was added to understand the evaporation process. (Line 199)

-5.6 – What contacts are referred to here?

We refer to the silver contacts that we evaporate on top of the perovskite layer.

-5.7 – What ITO anode? Please clarify.

The layers we mentioned before were all deposited on to a ITO substrate. The ITO is used as an anode in our solar cell setup.

-5.10 – What is the solar simulator used for? How is reverse bias measured?

Reverse bias is measured the same way the forward bias is measured - with a source measurement unit. To ensure understanding the following sentence is added: “). To ensure that no hysteresis is appearing in the JV characteristics, measure the reverse scan direction as well, by sweeping the bias from 1.5 to -0.5V as well.” (Line 245)

6. Branding: 1.4 – mucasol

"mucasol" deleted. (Line 102)

7. Discussion: Please discuss the limitations of the protocol.

In our last revision (June) we added the following section from line 382 on that represents the limitations of our protocol:

“This is the reason why a lot of research groups publish different results regarding solar cell performance and ionization potential for the same perovskite materials. In order to ensure reproducibility, it is crucial for all the processing steps and characterization methods to be performed under inert atmosphere (or vacuum) to avoid degradation by humidity. Also the purity and vendor of the educts play an important role (not investigated herein). It is clear that vacuum deposited perovskite layers feature highly crystalline films; however in comparison, solution processed films can be fabricated with a higher throughput.”

Please specify, if necessary, what specifically should be further added to the text.

**Reviewers' comments:**

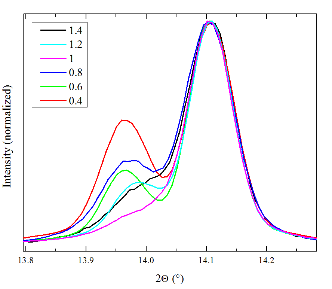
**Reviewer #1:**  
  
1. Line 118: a aqueous to "an aqueous"

“an” added. (Line 119)

2. No scale bar in Figure 1.  
Figure 1 features a white bar that indicates a length of 1µm as described in the figure caption.

**Reviewer #3:**  
  
*Minor Concerns:*  
Nevertheless, the manuscript raises few questions that need to be addressed prior to publication:  
1) Lines 393-395: "…PbI2 is incorporated not as a separate phase but as dilute interstitials…" This sentence is too speculative and requires further explanation. It PbI2 nanocrystalline? Amorphous? What do the authors think about the option that the excess of PbI2 stays in the solution, perhaps facilitating the crystal growth? Also the powder data merit some comments as to why the two peaks are clearly resolved for the PbI2-rich films, whereas the PbI2-rich do not? Is this related with the crystallite size?

Due to the XRD measurements in Fig. 2 we are very certain about the dilute nature of the PbI2 interstitials. If they would be present in a (nano)crystalline form, they would produce a peak at 2θ=12.6° as discussed in the article. As we do not observe that diffraction peak, the additional material cannot be crystalline. Regarding the excess PbI2 remaining in the solution: From the XPS measurements, we can see how much Pb is present in the film (at least on the surface), as discussed from line 934 (original manuscript) on. As the measured value agrees perfectly with the amount that is dissolved in the solution we can be certain that the stoichiometry of the solution is reproduced in the perovskite film, so the excess does not remain in the solution. Finally, regarding the double peak around 14° in the XRD spectra (which are thin film spectra, not powder ones) indicate changes in crystal orientation with composition. While at the correct stoichiometry only the (110) diffraction is visible, there are (002) contributions at the other mixing ratios, indicating a somewhat higher degree of disorder. The FWHM of the main peak does not change significantly (as shown for the reviewer in the plot below), so we do not assume that the size of the crystallites play a major role in the observed features.



To clarify this last point we added the sentence: ”…which can be seen by the appearance of weak (002) and (004) reflections, however no significant broadening of the XRD diffraction peak is observed. Intriguingly, no sign of separate phases of PbI2 at 12.63° are found, even for larger excess amounts of incorporated PbI2.” (Line 398)

2) Line 410: "We find an IE of 6.05 ± 0.10 eV for the optimal molar ratio of Rexp = 1, which is considerably larger than the often published IE of 5.4 eV." This is a strange result. If it is indeed that high, then notably the devices should not work because the electrons cannot be injected in PCBM at -3.9eV. This needs to be rationalized in some way even if this is a hypothetical one.

The higher ionization energy comes from the fact, that we use the linear slope of the UPS spectrum to evaluate the data, which for other organic or inorganic semiconductors is the common way to do it and which in our opinion is the only reproducible way of data evaluation, even though it might overestimate the ionization energy. Other groups that evaluate the data in the same way get similar IEs (e.g. Lo et al., Adv. Funct. Mater. 25, 1213 (2015) or Li et al., ACS Appl. Mater. Interfaces 8, 11526 (2016)) and we discussed the detailed reasons for this in a recent Review paper: S. Olthof, APL Mater. 4, 091502 (2016). To clarify this point we now refer to the review paper and added the following sentence to the manuscript: This discrepancy is not likely to be due to processing conditions, as we find this value for a variety of differently prepared perovskite films. It is rather due to differences in data evaluation where the linear density of states slope used here results in higher readout values. An extensive discussion of this issue can be found in Ref[17]. (Line 417)

3) Figure 4, Bottom left panel: There is an obvious extra peak at ~622 eV. It need to be assigned. Is this related to the excess PbI2?

The peak around 622 eV does not represent another bonding state of the iodide, it is rather a shake-up peak. The shake-up process is a two electron process in which a part of the kinetic energy of the photoelectron is used to lift up an additional electron into an excited state (e.g. above the bandgap), therefore leaving behind an excited ion. Due to the loss in kinetic energy, the apparent binging energy of the emitted photoelectron is hereby increased by the energy necessary for the excitation (typically a few eV). To clarify this point we added: “All signals can be fitted by a single mixed Gaussian/Lorentzian peak, only in the case of iodine a small feature at higher binding energies is typically observed which is however a shake-up peak and therefore not related to an actual additional bonding state.” (Line 301)

4) Some typos:  
a) Line 289: Change "4-iodphenyl)-amin" to "4-iodphenyl)-amine"

“e” added. (Line 294)

b) There are two captions for figure 5. Delete one of them.

In our version there is no second caption for figure 5.

c) Line 402: The reference is in error.

In our version there is no error here. We hope they by reformatting the bibliography this problem is removed.  
  
Should these comments get addressed I would be happy to recommend acceptance of the manuscript for publication.

We thank the reviewer for his/her thorough reading of the manuscript and his valuable comments and hope that the changes made to the article lead to a recommendation for publication.