Date: 12 November 2016

Journal of Visualized Experiments (JoVE),

Dear Dr Nguyen,

We are herewith submitting our revised manuscript entitled, *“***Monovalent Cation Doping of CH3NH3PbI3 for Efficient Perovskite Solar Cells***”* to be considered for publication in ***Journal of Visualized Experiments.*** We consider the work to be of immense interest to the readers of ***Journal of Visualized Experiments*** for the following reasons.

We are providing below a detailed, point-by-point response to the questions raised by the Reviewers. We are grateful for the comments made by the Reviewers, which resulted in important additions to our work. We hope that our revised manuscript that addresses all the reviews concerns would be considered for publication in ***Journal of Visualized Experiments*** to which we look forward.

Thank you very much for your consideration.

Yours sincerely,

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**Editorial comments:**

The manuscript has been modified by the Science Editor to comply with the JoVE formatting standard. Please maintain the current formatting throughout the manuscript. The updated manuscript (55307\_R1\_083116.docx) is located in your Editorial Manager account. In the revised PDF submission, there is a hyperlink for downloading the .docx file. Please download the .docx file and use this updated version for any future revisions.  
  
1. Please abbreviate journal titles.

It is corrected now.

2. There are a few grammar issues to be corrected:  
-2.1.1.1. “Cover the active area of the FTO glass with scotch type” assuming you meant scotch tape, but this is also branding, so you should change this to simply tape, clear tape, or sticky tape.

It is corrected now.

-2.1.1.5. “Wash the FTO with water and remove the tapes.” Tape.

It is corrected now.

3. Additional detail is required in step 2.1.3: “Dissolve 2 M of hydrochloric acid (HCl) in distilled water” how much water, for what final volume?

M means moles.Liter-1. M is now replaced by moles.Liter-1 which shows the concentration of HCl in distilled water.

4. Unnecessary branding should be removed: Scotch tape.

Scotch tape is now eliminated from the manuscript.

**Reviewers' comments:**  
**Reviewer #1:**

*Manuscript Summary:*

The manuscript reports doping of various cations to improve the performance of MAPI based devices, with new insights on how the dopants improves various optoelectronic properties of the MAPI. Significant part of the manuscript have been reproduced from reference number 18 (Advanced energy material). The work can be published after a major revision, which are as following:

1) Why the dopants are improving the properties are not fully understood? Which site they are replacing? This should be shown with other experimental tools.

As we stated in the manuscript, monovalent cation halide with similar ionic radii to Pb2+, including Cu+, Na+ and Ag+, were added to explore possibility of doping in the CH3NH3PbI3 (Pb site). The enhancement in the properties (e.g. photovoltaic performance) is explained due to the various reasons created in the presence of these monovalent cations such as formation of uniform and continuous perovskite film, better conversion of PbI2 into CH3NH3PbI3, improved loading of perovskite into mesoporous scaffold as well as the enhancement in the bulk charge transport along with a minimization of electronic disorder, pointing towards possible surface passivation.

2) During doping with CuBr is there a possibility for the formation of MAPbBr(x)I(3-x)?

We agree with the reviewer that the Br might present in the final structure. However, since the concentration of the dopants is about 0.02 mol.L-1, which is very small for Br to effect on the properties as we observed the same band-edge for CuBr based perovskite (Figure 5a).

3) Why the CPD signals are noisy?

Since the surface of perovskite layer is normally rough, the CPD signals around the perovskite region are a bit noisy as the CPD signal for AgI based perovskite which is the smoothest sample shows the least noise. In addition, in the KPFM measurement, we are interested to find out the change of CPD at the interface between the perovskite film and the gold contact which is a representative of the change in the work function of the materials. Therefore, the signals in the perovskite region is not the main point of the data.

4) Device statistics needs to be presented to understand the improvement in various device parameters.

The JV parameters for the best performing devices are consistent with the statistics following the same trend. The statistics can be provided while for JOVE which is a method based journal, we think it is not necessary to include that in the main article. However, we add the below sentence in the manuscript to confirm this.

*“It is notable that the statistics of the photovoltaic parameters follow the same trend as the best performing devices”*

5) IPCE of 'MAPI' does not reflect an improvement compared to 'doped MAPI'.

We did calculate the integrated current from the IPCE curves and the resulted photocurrent density is in agreement with the Jsc improvement in presence of dopants extracted from the JV measurement.

6) Line number 289: "...filling the transport traps"- How the transport traps are filled? Should be discussed.

It is plausible that the presence of stable +1 oxidation states of the cations (e.g. Na+, Cu+, Ag+) results in passivation of hole traps in the system. This is indicated from the PDS spectra as well as the KPFM measurements which indicate a modification of the HOMO levels with cationic doping.

7) What could be the role of the dopants for improvement in crystallization and surface coverage (SEM)?

As it is shown in the Figure 3, the PbI2 peak is vanished for NaI and CuBr sample which confirms the complete conversion of PbI2 into CH3NH3PbI3 while a residue of PbI2 can be seen for the pristine sample. In addition, the SEM images (Figure 2) shows a different morphology of perovskite and PbI2 for the NaI sample and a full pin hole free film is formed for the AgI based perovskite. Therefore, these cations can indeed effect on the crystallization and conversion of PbI2 into CH3NH3PbI3 as well as the formation of perovskite capping layer.

*Major Concerns:*  
N/A  
  
*Minor Concerns:*  
N/A  
  
*Additional Comments to Authors:*  
N/A

**Reviewer #2:**

*Manuscript Summary:*

In this manuscript, authors doped monovalent cation halide salts (NaI, CuBr, CuI, and AgI) into the PbI2 precursor solution in the sequential deposition method. They studied the morphology and optoelectronic properties of the resultant perovskite films with the presence of these monovalent cations.  
  
*Major Concerns:*  
Although authors tried to investigate the effect of the monovalent cation additives on the perovskite layer from different aspects, some issues are not clear. For example:  
1. Authors studied the effect of CuBr additive on the perovsite film. Basically, the bromine additive could affect the properties of perovskite film. The reviewer thinks that the authors had better decouple the influences of Cu+ and Br-.

We agree with the reviewer that the Br might effect in the final structure. However, since the concentration of the dopants is about 0.02 mol.L-1, which is very small for Br to effect on the properties as we observed the same band-edge for CuBr based perovskite (Figure 5a) while the absorption tail in the PDS spectra for CuBr sample which is originated from the intrinsic absorption of Cu based halide (Figure 5b) confirms the influence of Cu+.

2. Authors claimed that, the density of charges, the charge mobility, and the conductivity of the perovskite layer were improved by monovalent cation doping. The reviewer thinks that the mobility and conductivity improvements are reasonable, but the reviewer is intrigued to know how the additives could increase the density of charges in the perovskite layer.

We believe, the presence of stable +1 oxidation states of the cations would result in passivation of hole traps in the system which can lead to a higher charge density. A clear signature of the increase in charge density is also shown from the modification of the sub-band gap levels in the PDS spectra and the shift in the HOMO level (valence band) of the perovskite upon addition of the cationic dopant.

Thus, the reviewer thinks that this manuscript may need some revision before publication.  
  
*Minor Concerns:*  
N/A  
  
*Additional Comments to Authors:*  
N/A