

Article

Ethylammonium Lead Iodide Formation in MAPbI₃ Precursor Solutions by DMF Decomposition and Organic Cation Exchange Reaction

Ryan Taoran Wang, Elton Enchong Liu, Alex Fan Xu, Lory Wenjuan Yang, Jason Yuanzhe Chen and Gu Xu *

Department of Materials Science and Engineering, McMaster University, 1280 Main St W, Hamilton, ON L8S 4L8, Canada; wangt41@mcmaster.ca (R.T.W.); liue26@mcmaster.ca (E.E.L.); xuf21@mcmaster.ca (A.F.X.); yangw48@mcmaster.ca (L.W.Y.); skeaixing@gmail.com (J.Y.C.)

* Correspondence: xugu@mcmaster.ca

Received: 30 January 2020; Accepted: 28 February 2020; Published: 2 March 2020



Abstract: Extra peaks have constantly been observed in the X-ray diffraction measurement for the CH₃NH₃PbI₃ film. Such mysteries have now been uncovered in this paper, in which powder X-ray diffraction, in situ X-ray diffraction, and scanning electron microscopy measurements were conducted, and these peaks were attributed to the ethylammonium lead iodide (CH₃CH₂NH₃PbI₃/EAPbI₃). It was found that the formation of EAPbI₃ was triggered by the breakdown of N, N-dimethylformamide (DMF), which was adopted as the solvent in the preparation of the precursor solutions. EAPbI₃ was generated by the organic cation exchange reaction in the subsequent annealing process. A simple solution for this problem is proposed in this paper as well, which would hopefully help the community to eradicate this impurity.

Keywords: organic perovskite; organic cation exchange reaction; In-situ XRD

1. Introduction

The power conversion efficiency of CH₃NH₃PbI₃ (MAPbI₃) and HC(NH₂)₂PbI₃ (FAPbI₃) perovskite solar cells has soared from 3.8% to 25.2% in the past decade [1,2], which now rivals that of other technologies such as silicon or cadmium telluride (CdTe) solar cells [3,4]. While such record performance seems to be inspiring for renewable energy development, the device lifetime, especially under moisture environment, remains at a low level, which prevents its commercialization. The devices usually degrade within a day unless an extra encapsulation layer is adopted [5–7], and even with the encapsulation layer the longest lifetime reported is still less than 4000 hours, which is far from enough for commercialization [8–10].

Although various strategies have been proposed, such as doping at A, B, and X sites of the ABX₃ perovskite structure [11–13], grain boundary passivation [7,14,15], or replacing hydrophilic hole transport layer [16], none has resolved the stability issue successfully. Therefore, uncovering the scientific mechanism of the decomposition is imperative to address this issue. Despite many mechanisms having been reported before [17–22], they were often inconsistent and self-contradictory. Hopefully, some of the conflicts can be neutralized by our recently published work, where we revealed the importance of hydrogen bonding for the perovskite structural stability and discovered the true cause of the irreversible degradation [10]. However, there remains some other substance detected during the synthesis of the CH₃NH₃PbI₃ thin film, which has yet to be identified by the perovskite solar cell community, despite the fact that a similar phenomenon was also reported before elsewhere [23,24]. As the impurity could influence the device performance, and thus it calls for a systematic investigation.

It is, therefore, the purpose of the current article to systematically investigate this substance, discovered in the perovskite thin film during the synthesis process, using powder X-ray diffraction (PXRD), in situ X-ray diffraction, and scanning electron microscopy (SEM). We prepared various PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ precursor solutions to investigate the influence of heating temperature and time on the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film formation. It was discovered that N, N-dimethylformamide (DMF) could decompose at a higher temperature, which enabled the organic cation exchange reaction and led to the formation of $\text{CH}_3\text{CH}_2\text{NH}_3\text{I}$ (EAI). Subsequently, EAI could react with PbI_2 and form EAPbI_3 , which, as confirmed by the PXRD results, was identified to be the impurity presented in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film. This discovery is expected to help the community, to eliminate the EAPbI_3 impurities and to enhance the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film morphology, thereby leading to a better device performance.

2. Experimental

Methylammonium iodide (> 99.98%, anhydrous) and lead iodide (> 99.98%) were purchased from Xi'an Polymer Light Technology Corp. (Xi'an, China). N, N-dimethylformamide (> 99%) and methanol (anhydrous, 99.8%) were purchased from Sigma-Aldrich. PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ precursors were made by dissolving 1mmol PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ in 1ml N, N-dimethylformamide. Various dissolving temperatures and stirring times were adopted, including 90 °C/45min and 120 °C/120min. $\text{CH}_3\text{NH}_3\text{PbI}_3$ was synthesized by the spin-coating of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 solutions at 6000 rpm on FTO glass substrate (composition: SiO_2/F ; film thickness: 500 nm; purchased from Huanan-Xiangcheng Tech Ltd, Hunan, China), and next annealed at 90 °C for 30 min.

XRD, instead of chemical characterization methods such as FTIR or NMR, was adopted for material characterization, as XRD is more powerful for material structure and impurity analysis. In situ XRD measurement was conducted by a Bruker D8 ADVANCE diffractometer in an enclosed chamber. The thin film sample was placed in the sample stage of the chamber. Desiccant was also adopted, which has a composition of 98% CaSO_4 and 2% CoCl_2 (purchased from McMaster chemical store, Hamilton, ON, Canada). The measurement range was 24°–26.5° due to the long time required to scan the whole two theta range. This measurement lasted for 3 days. Powder XRD was conducted by Bruker D8 DISCOVER diffractometer (Bruker Corporation, Billerica, Massachusetts, USA) with a range of 10° to 76°. A diagram of the XRD chamber is shown in Figure 1. SEM was conducted by FEI Magellan 400 XHRSEM (FEI Company Magellan™ XHR, Midland, ON, Canada). All diagrams were drawn in Origin 9.0 (OriginLab, Northampton, MA, USA)

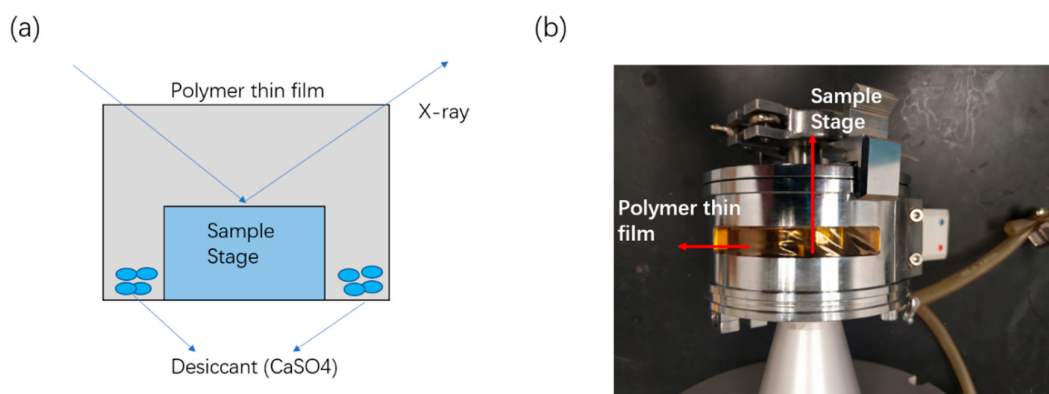


Figure 1. (a) Schematic illustration of the XRD chamber; (b) photo of the chamber.

3. Results & Discussion

To identify the influence of the dissolving temperature and the stirring time on the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite formation, both powder and in situ XRD measurements were adopted in a methanol and water environment. As circled in Figure 2a, $\text{CH}_3\text{CH}_2\text{NH}_3\text{PbI}_3$ (EAPbI_3) was detected when the

precursor solutions were heated at 120 °C for 2 h; while such structure disappeared when the heating temperature and time were reduced to 90 °C and 45 min. These extra peaks exactly matched the peak of EAPbI₃ from the database. The peaks for EAPbI₃ were also observed in the in situ measurement, where a more controlled observation was conducted. As shown in Figure 2b, the peaks at 24.8° and 25.8° were attributed to EAPbI₃. This proved that EAPbI₃ was generated gradually as time passing by, and we speculated that the solvent (DMF) could be the cause of the EAPbI₃ formation, as only DMF contains the structure of ethylammonium.

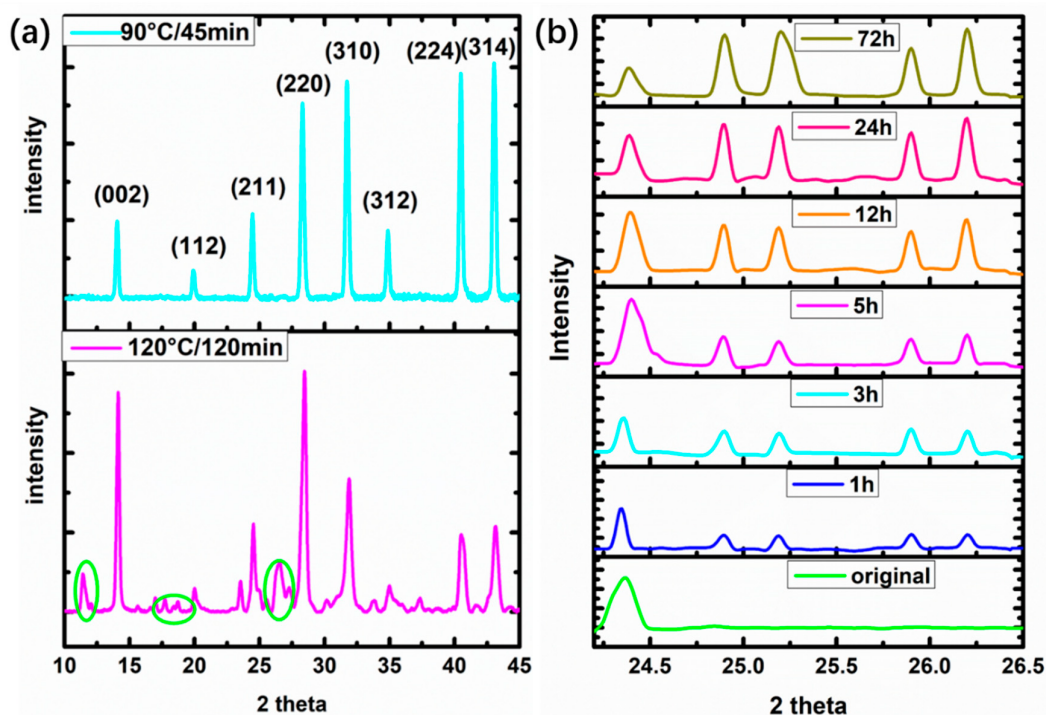


Figure 2. (a) The results of XRD measurements for CH₃NH₃PbI₃ synthesized from various precursor solutions, including 90 °C/45min and 120 °C/120min; (b) In situ XRD results of CH₃NH₃PbI₃ thin film under methanol environment.

In the subsequent analysis, we found the supporting evidence from the literature, where the DMF was proven to be unstable at a temperature higher than 100 °C [25,26]. Therefore, DMF could be decomposed at higher heating temperatures, starting from the breakdown of the bond between the nitrogen atom and the carboxyl group, generating ethylammonium ion intermediate, which reacted with CH₃NH₃I by an organic cation exchange reaction. Eventually, EAI was generated. In the following annealing process, EAI reacted with PbI₂ to form EAPbI₃. Only weak peaks were observed for the first few hours in the XRD diagram, indicating a slow decomposition rate of DMF under heating. A schematic illustration of this process is shown in Figure 3.

It is thus clear now, that the substance detected in the CH₃NH₃PbI₃ film is indeed EAPbI₃, which not only reduces the film purity, but also affects the film morphology, as can be confirmed in Figure 4a,b. When there was no EAPbI₃ present in the film, large CH₃NH₃PbI₃ grains could be observed with a size of several microns, as shown in Figure 4; while such morphology changed greatly when EAPbI₃ was generated. In Figure 4b, the large grain was damaged, and voids were also generated, which proved that EAPbI₃ is detrimental for the CH₃NH₃PbI₃ film growth and device performance.

To summarize the results, the formation of EAPbI₃ in the CH₃NH₃PbI₃ film is triggered by the degradation of DMF solvent, which is unstable at a higher temperature and decomposes into EA⁺ intermediate. This is followed by an organic cation exchange reaction, where EA⁺ switches position with MA⁺, resulting in the formation of EAI, which subsequently reacts with PbI₂ in the following

annealing process. Although other methods could be adopted to avoid the formation of impurities, including chemical vapor deposition or physical vapor deposition [27,28], a much easier method has been proposed here by reducing the heating time and temperature during the preparation of the precursor solution.

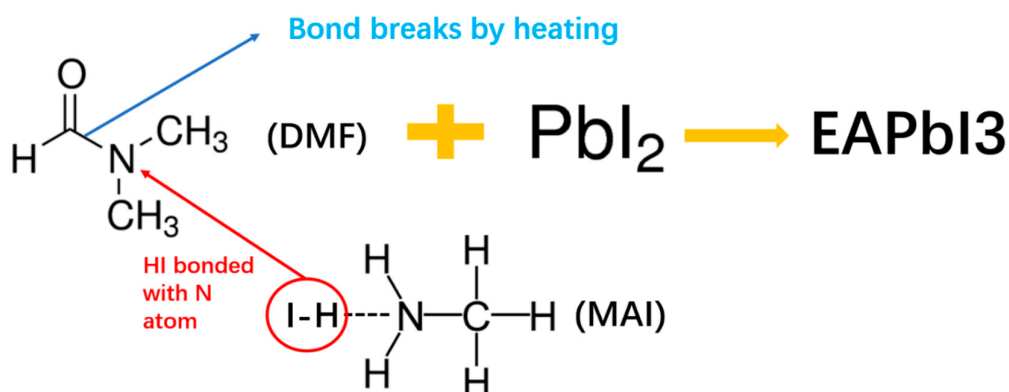


Figure 3. Schematic illustration of EAPbI₃ formation process.

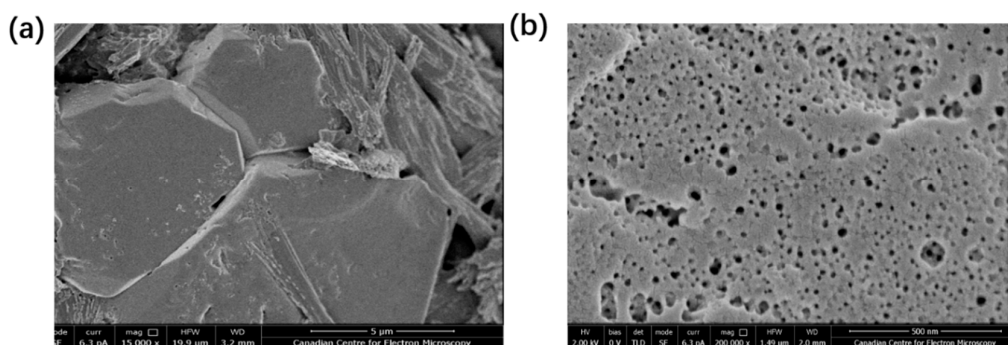


Figure 4. (a) Morphology of CH₃NH₃PbI₃ film with no EAPbI₃; (b) Morphology of CH₃NH₃PbI₃ film with some EAPbI₃ impurities.

4. Conclusions

To conclude the manuscript, the extra peaks detected by many others in the CH₃NH₃PbI₃ film have been successfully identified, and attributed to EAPbI₃, a perovskite that has a similar structure to CH₃NH₃PbI₃, which is why it was so difficult to identify. The formation of EAPbI₃ in the CH₃NH₃PbI₃ film was found to be detrimental to the grain growth, which could lower the power conversion efficiency. The EAPbI₃ could easily be eradicated by reducing the heating time and temperature when preparing the precursor solution. Hopefully, our discovery could be of immediate help to the community in the near future.

Author Contributions: R.T.W. conducted the experiments and wrote the manuscript. E.E.L. and L.W.Y. completed the diagram plot and proofreading. A.F.X. assisted with the SEM and XRD measurements. J.Y.C. assisted with the materials synthesis. G.X. provided the funding and overall supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Natural Sciences and Engineering Research Council of Canada, grant number 10546964.

Acknowledgments: The authors acknowledge Canadian Center of Electron Microscopy for their SEM support.

Conflicts of Interest: The authors declare no conflicts of interests.

References

1. Matsui, T.; Yamamoto, T.; Nishihara, T.; Morisawa, R.; Yokoyama, T.; Sekiguchi, T.; Negami, T. Compositional Engineering for Thermally Stable, Highly Efficient Perovskite Solar Cells Exceeding 20% Power Conversion Efficiency with 85 °C/85% 1000 h Stability. *Adv. Mater.* **2019**, *31*. [[CrossRef](#)] [[PubMed](#)]
2. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051. [[CrossRef](#)] [[PubMed](#)]
3. Wu, X. High-efficiency polycrystalline CdTe thin-film solar cells. *Sol. Energy* **2004**, *77*, 803–814. [[CrossRef](#)]
4. Jellison, G.E.; Joshi, P.C. Crystalline silicon solar cells. In *Springer Series in Optical Sciences*; Florida Atlantic University: Boca Raton, FL, USA, 2018; Volume 212, pp. 201–225.
5. Wang, R.T.; Xu, A.F.; Yang, W.; Chen, J.Y.; Kitai, A.; Xu, G. Magnetic-field-induced energy bandgap reduction of a perovskite by spin-orbit coupling via a low strength magnet. *J. Mater. Chem. C* **2020**.
6. Wang, R.T.; Tai, E.G.; Chen, J.Y.; Xu, G.; LaPierre, R.; Goktas, N.I.; Hu, N. A KMnF_3 perovskite structure with improved stability, low bandgap and high transport properties. *Ceram. Int.* **2019**, *45*, 64–68. [[CrossRef](#)]
7. Tai, E.G.; Wang, R.T.; Chen, J.Y.; Xu, G. A water-stable organic-inorganic hybrid perovskite for solar cells by inorganic passivation. *Crystals* **2019**, *9*, 83. [[CrossRef](#)]
8. Xu, A.F.; Wang, R.T.; Yang, L.W.; Jarvis, V.; Britten, J.F.; Xu, G. Pyrrolidinium lead iodide from crystallography: A new perovskite with low bandgap and good water resistance. *Chem. Commun.* **2019**, *55*, 3251–3253. [[CrossRef](#)]
9. Xu, A.F.; Wang, R.T.; Yang, L.W.; Liu, N.; Chen, Q.; Lapierre, R.; Isik Goktas, N.; Xu, G. Pyrrolidinium containing perovskites with thermal stability and water resistance for photovoltaics. *J. Mater. Chem. C* **2019**, *7*, 11104–11108. [[CrossRef](#)]
10. Wang, R.T.; Xu, A.F.; Chen, J.Y.; Yang, L.W.; Xu, G.; Jarvis, V.; Britten, J.F. Reversing Organic-Inorganic Hybrid Perovskite Degradation in Water via pH and Hydrogen Bonds. *J. Phys. Chem. Lett.* **2019**, *10*, 7245–7250. [[CrossRef](#)]
11. Ava, T.T.; Al Mamun, A.; Marsillac, S.; Namkoong, G. A review: Thermal stability of methylammonium lead halide based perovskite solar cells. *Appl. Sci.* **2019**, *9*, 188. [[CrossRef](#)]
12. Bai, X.; Zou, X.; Zhu, J.; Pei, Y.; Yang, Y.; Jin, W.; Chen, D. Effect of Rb doping on modulating grain shape and semiconductor properties of MAPbI_3 perovskite layer. *Mater. Lett.* **2018**, *211*, 328–330. [[CrossRef](#)]
13. Chang, J.; Chen, H.; Yuan, H.; Wang, B.; Chen, X. The mixing effect of organic cations on the structural, electronic and optical properties of FAXMA1-xPbI_3 perovskites. *Phys. Chem. Chem. Phys.* **2018**, *20*, 941–950. [[CrossRef](#)] [[PubMed](#)]
14. Huang, J.; Gu, Z.; Zuo, L.; Ye, T.; Chen, H. Morphology control of planar heterojunction perovskite solar cells with fluorinated PDI films as organic electron transport layer. *Sol. Energy* **2016**, *133*, 331–338. [[CrossRef](#)]
15. Gao, Y.; Wu, Y.; Lu, H.; Chen, C.; Liu, Y.; Bai, X.; Yang, L.; Yu, W.W.; Dai, Q.; Zhang, Y. Corrigendum to “ CsPbBr_3 perovskite nanoparticles as additive for environmentally stable perovskite solar cells with 20.46% efficiency” (Nano Energy (2019) 59 (517–526), (S2211285519301818), (10.1016/j.nanoen.2019.02.070)). *Nano Energy* **2019**, *63*, 517–526. [[CrossRef](#)]
16. Xiong, H.; Rui, Y.; Li, Y.; Zhang, Q.; Wang, H. Hydrophobic coating over a $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorbing layer towards air stable perovskite solar cells. *J. Mater. Chem. C* **2016**, *4*, 6848–6854. [[CrossRef](#)]
17. Yang, J.; Siempelkamp, B.D.; Liu, D.; Kelly, T.L. Investigation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ degradation rates and mechanisms in controlled humidity environments using in situ techniques. *ACS Nano* **2015**, *9*, 1955–1963. [[CrossRef](#)]
18. Leguy, A.M.A.; Hu, Y.; Campoy-Quiles, M.; Alonso, M.I.; Weber, O.J.; Azarhoosh, P.; Van Schilfgaarde, M.; Weller, M.T.; Bein, T.; Nelson, J.; et al. Reversible hydration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in films, single crystals, and solar cells. *Chem. Mater.* **2015**, *27*, 3397–3407. [[CrossRef](#)]
19. Zhu, Z.; Hadjiev, V.G.; Rong, Y.; Guo, R.; Cao, B.; Tang, Z.; Qin, F.; Li, Y.; Wang, Y.; Hao, F.; et al. Interaction of Organic Cation with Water Molecule in Perovskite MAPbI_3 : From Dynamic Orientational Disorder to Hydrogen Bonding. *Chem. Mater.* **2016**, *28*, 7385–7393. [[CrossRef](#)]
20. Ahn, N.; Kwak, K.; Jang, M.S.; Yoon, H.; Lee, B.Y.; Lee, J.K.; Pikhitsa, P.V.; Byun, J.; Choi, M. Trapped charge-driven degradation of perovskite solar cells. *Nat. Commun.* **2016**, *7*. [[CrossRef](#)]

21. Niu, G.; Li, W.; Meng, F.; Wang, L.; Dong, H.; Qiu, Y. Study on the stability of CH₃NH₃PbI₃ films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells. *J. Mater. Chem. A* **2014**, *2*, 705–710. [[CrossRef](#)]
22. Niu, G.; Guo, X.; Wang, L. Review of recent progress in chemical stability of perovskite solar cells. *J. Mater. Chem. A* **2015**, *3*, 8970–8980. [[CrossRef](#)]
23. Rajendra Kumar, G.; Dennyson Savariraj, A.; Karthick, S.N.; Selvam, S.; Balamuralitharan, B.; Kim, H.J.; Viswanathan, K.K.; Vijaykumar, M.; Prabakar, K. Phase transition kinetics and surface binding states of methylammonium lead iodide perovskite. *Phys. Chem. Chem. Phys.* **2016**, *18*, 7284–7292. [[CrossRef](#)] [[PubMed](#)]
24. Im, J.H.; Chung, J.; Kim, S.J.; Park, N.G. Synthesis, structure, and photovoltaic property of a nanocrystalline 2H perovskite-type novel sensitizer (CH₃CH₂NH₃)PbI₃. *Nanoscale Res. Lett.* **2012**, *7*. [[CrossRef](#)] [[PubMed](#)]
25. Taft, R.W.; Abraham, M.H.; Doherty, R.M.; Kamlet, M.J. The molecular properties governing solubilities of organic nonelectrolytes in water. *Nature* **1985**, *313*, 384–386. [[CrossRef](#)]
26. Chadwick, S.S. Ullmann's Encyclopedia of Industrial Chemistry. *Ref. Serv. Rev.* **1988**, *16*, 31–34. [[CrossRef](#)]
27. Li, Z.; Klein, T.R.; Kim, D.H.; Yang, M.; Berry, J.J.; Van Hest, M.F.A.M.; Zhu, K. Scalable fabrication of perovskite solar cells. *Nat. Rev. Mater.* **2018**, *3*. [[CrossRef](#)]
28. Leyden, M.R.; Ono, L.K.; Raga, S.R.; Kato, Y.; Wang, S.; Qi, Y. High performance perovskite solar cells by hybrid chemical vapor deposition. *J. Mater. Chem. A* **2014**, *2*, 18742–18745. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).