



Room Temperature Synthesis of Formamidinium Lead Iodide (FAPbI₃) Perovskite for Low-Cost Absorber in Solar Cells

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Abstract

We report room temperature synthesis technique for the formamidinium lead iodide (FAPbI₃) perovskite. The low-cost sequential room temperature chemical synthesis technique resulted in formation of α -phase FAPbI₃, suitable for solar cell absorber application. The chemical precursors formamidine acetate (CH₄N₂·xC₂H₄O₂) and lead iodide (PbI₂) were used in the process. The drop casted and spin coated films of FAPbI₃ on soda-lime glass and were then annealed at temperature of 80 °C. The FAPbI₃ materials films were characterized by X-ray diffraction, UV-Visible spectroscopy, photoluminescence (PL) measurements, and transmission electron microscopic (TEM) measurement. The X-ray diffraction pattern confirms α -phase of FAPbI₃ perovskite. The crystallite size as calculated from x-ray diffraction was found to be 40 nm corresponding to (001) peak. UV-Visible analysis shown broad absorption with bandgap value of 1.55 eV. The PL analysis show emission peak at 727 nm with estimated bandgap to be a 1.57 eV, in agreement with the UV-Visible spectroscopy. TEM analysis confirms the crystalline phase of FAPbI₃ material and the inter-planar spacing was deduced to be 0.62 nm. We conclude successful synthesis of FAPbI₃ perovskite with desirable properties in α -phase composition of FAPbI₃ that are suitable for solar cell application.

Keywords: FAPbI₃ Perovskite; Photoluminescence of perovskites: Cubic FAPbI₃.

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1. Introduction

Thin film solar cell technology is actively researched due to many advantages for use in special applications like flexible portable machines, building integrated photovoltaic (BIPV) and indoor applications due to ease of production and versatility at end use. The present-day market leader, the CdTe thin film solar cell technology have been surpassed for champion cell efficiency of 23.4% by Perovskite family of thin film solar cells.^[1] There are several advantages of perovskite materials to use as light capturing active layer in thin-film solar cells like cheaper in production cost, less complex manufacturing process and highest efficiency in the thin film family of photovoltaic cells.^[2-5] The hybrid organ lead trihalide perovskite material have ABX₃ structure, where A is an alkali metal cation, B is a divalent cations (Pb²⁺, Sn²⁺) and X

is halide anions (Br⁻, Cl⁻, I⁻), have attracted much more attention from the researchers all over the world. Because of the fact that the materials exhibit the desirable optical and electrical properties, with facile synthesis approaches and low cost production, this ABX₃ family of perovskites have been actively researched for photovoltaic applications^[1,6] and light-emitting devices.^[7,8] The research efforts are mainly directed to utilize some or many of the advantages of high absorption coefficient, long charge carrier lifetimes, high charge carrier mobility and long carrier diffusion distance of metal halide perovskites.

In comparison to other perovskite, the larger Formamidinium cations in a FAPbI₃ Perovskite occupies the A site of the ABX₃ structure, forming the symmetric crystal structure and reducing the electronic bandgap.^[9-11] Formamidinium lead Iodide (FAPbI₃) perovskite shows the wider absorption spectrum and better thermal stability.^[12,13] These research findings lead to wide acceptance that FAPbI₃ perovskite materials are a suitable candidate for absorber material in solar cell application as well as photodetectors and light-emitting application.^[14,15]

Recently Han *et al.* reported 5 mm sized single crystal

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growth of FAPbI₃ perovskite using a modified inverse temperature crystallization method.^[16] They also fabricated single crystal photodetectors and investigated photoconductivity and photoresponse. The FA and MA based perovskites have shown efficiency of 20.1% by cation-Intermixing technique as reported by Mateen *et al.*^[6] Time resolved PL measurements for stability of MA based perovskite was reported by Guo *et al.*^[17] Niu *et al.* have shown that RP/3D heterostructure combined with molecule passivation within α -phase FAPbI₃ films leads to better charge collection efficiency and better solar cells device performance and also the device becomes ambient-air stable.^[18] Despite of many studies on FA-based perovskite structures, the intrinsic electrical, optical, and structural properties of FAPbI₃ still require further study. Besides this, a main problem in synthesizing FAPbI₃ based perovskites is α -phase purity. FAPbI₃ material have two phases, the desirable and important semiconducting perovskite phase (α -phase) and the another as less suitable perovskite (δ – phase) which is mostly formed in at room temperature.^[19,20]

In this article, we focus on very simple and low-cost synthesis technique for the formation of α -FAPbI₃ structure required for achieving the high performance in optoelectronic devices. The synthesis was achieved at room temperature and post synthesis annealing at temperature of 80 °C. We introduce the synthesis of desirable and important semiconducting perovskite α -FAPbI₃ structure using sequential room temperature synthesis method. Polycrystalline α -FAPbI₃ thin film was prepared by spin coating method followed by annealing treatment. The structural and optical properties of FAPbI₃ thin film were

studied using X-Ray diffraction, transmission electron microscopy, UV-Visible and photoluminescence spectroscopy.

2. Synthesis Method

For the synthesis of FAPbI₃, Formamidinium acetate (FA) (CH₄N₂·xC₂H₄O₂), lead iodide (PbI₂) and N, N-dimethylformamide (DMF) were procured from Sigma-Aldrich and used without further processing. The entire range of chemicals used in the synthesis process were of analytical grade and were used without further purification. The FAPbI₃ perovskite were synthesized using one step method with Formamidinium acetate (CH₄N₂·xC₂H₄O₂) as a FA precursor and lead iodide (PbI₂) as a Pb and I source and N, N-dimethylformamide (DMF) is used as capping agent or reactant. In experiment, 0.12 gm FA and 0.32 gm PbI₂ were dissolved into 2 ml N, N-dimethylformamide (DMF) under magnetic stirring for 8 hours to clear the solution. Strong green emission was observed after adding both precursor into the DMF. After completion of reaction, the FAPbI₃ solution was used for preparation of films of the material.

Soda lime glass was used as substrate for the FAPbI₃ film preparation. The substrates were cleaned sequentially with DI-water, acetone and ethanol and DI water for 5 min each. After dry nitrogen flush, the substrate were deposited with FAPbI₃ film by spin coating. Then the FAPbI₃ coated film were dried under vacuum at 80 °C for 30 min. These dried films were used for further characterization. The Fig. 1 represent the schematic of the steps in the synthesis of FAPbI₃ reported in this article.

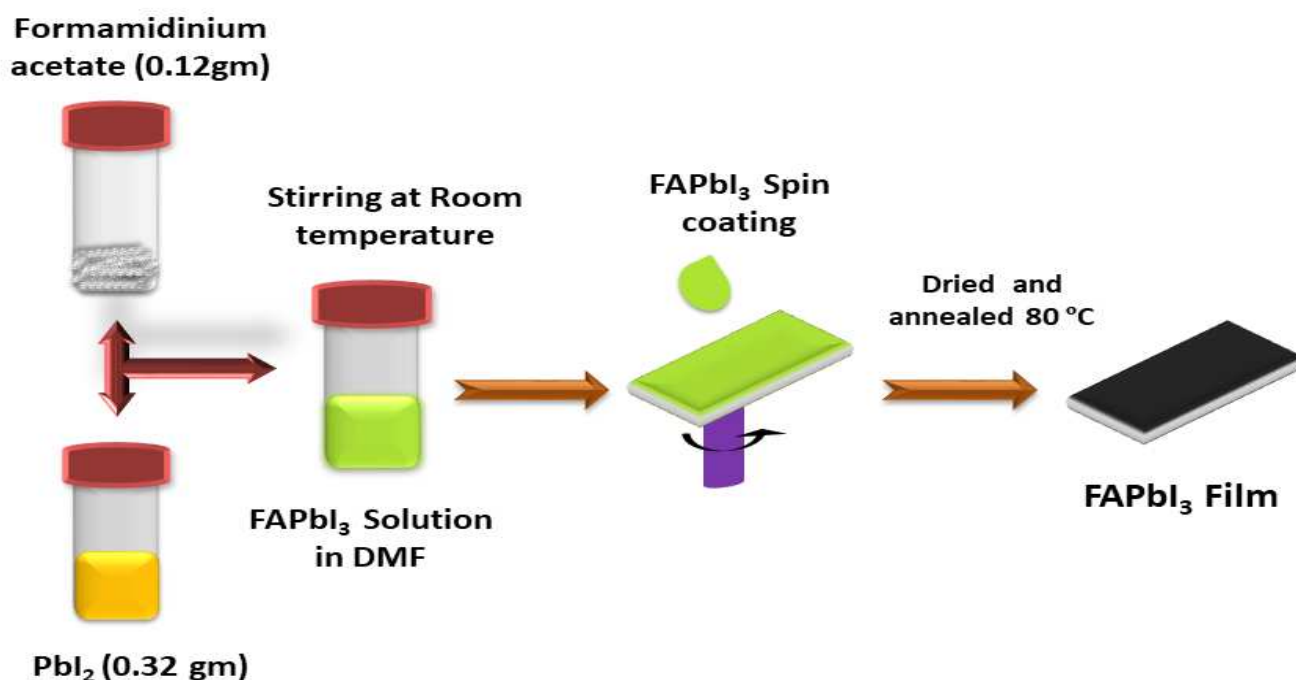


Fig. 1 Steps in synthesis process of FAPbI₃ perovskite using sequential room temperature technique.

3. Characterization techniques

The synthesized FAPbI₃ perovskite were systematically investigated by range of characterization techniques including x-ray diffraction, UV-Visible spectroscopy and photoluminescence (PL) spectroscopy and transmission electron microscopy (TEM). The average crystalline size, lattice parameter and phase identification of FAPbI₃ perovskite were studied in depth using x-ray diffraction (Bruker D8 Advance, Germany make) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at grazing angle 1° . The optical bandgap of the FAPbI₃ perovskite was estimated from absorbance spectra measured using a JASCO, V-670 UV-visible spectrophotometer in the range of 200–1500 nm. The photoluminescence spectra were recorded using spectrophotometer (Horiba FluoroLog Spectrophotometer) at an excitation wavelength of 430 nm. The microstructural information of the FAPbI₃ Perovskite was obtained using transmission electron microscopy (TEM) by JEOL, JEM-2200FS at an acceleration voltage of 200 kV.

4. Results and Discussion

4.1 X-ray diffraction analysis

The x-ray diffraction pattern of spin coated thin film FAPbI₃ perovskite synthesized using the one-step solution method are shown in Fig. 2.

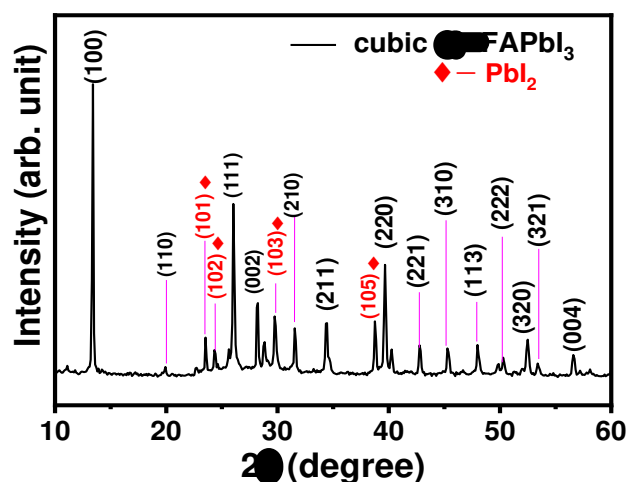


Fig. 2 X-Ray diffraction pattern of FAPbI₃ material.

The most intense peaks located at $2\theta = 13.7^\circ, 19.8^\circ, 26^\circ, 28.3^\circ, 31.5^\circ, 34.1^\circ, 39.7^\circ, 42.9^\circ, 45.1^\circ, 47.9^\circ, 50.4^\circ, 52.4^\circ$, and 56.7° which are attributed to the diffraction of (100), (110), (111), (002), (210), (220), (221), (310), (113), (222), (320), (321) and (004) planes of the cubic phase of α -FAPbI₃ perovskite thin film respectively. As observed, the peak position of FAPbI₃ perovskite thin film was confirmed and good agreement with other reported data^[21,14] Also peaks located at $23.4^\circ, 24.5^\circ, 38.5^\circ$ and 47.9° which are attributed to unconverted PbI₂ in FAPbI₃ material.^[21] No any δ -FAPbI₃ phases were detected in the sample thus, confirms the synthesis of high-quality α -FAPbI₃ perovskite thin film. The sharp diffraction peak of α -FAPbI₃ indicate the high crystallinity of as synthesized compound. The crystalline size ($d_{x\text{-ray}}$) of the synthesized α -FAPbI₃ perovskite thin film calculated by measuring full-width half maxima (FWHM) corresponding to (100) peak using the Debye-Scherrer equation.

$$d_{x\text{-ray}} = \frac{0.9\lambda}{\beta \cos(\theta)} \quad (1)$$

where, $d_{x\text{-ray}}$ is the crystalline size, λ is the wavelength of diffracted radiation which is equal to 1.54 \AA , θ is the Bragg angle, β is the full width at half maximum (FWHM) line width of the diffraction peak. The calculated crystalline size α -FAPbI₃ perovskite thin film for corresponding to (001) peak is found to be 40 nm. An inter-planar distance of α -FAPbI₃ perovskite thin film for the first-order diffraction is 6.38 \AA . The estimated lattice constant for α -FAPbI₃ perovskite cubic structure is $a=b=c = 6.376 \text{ \AA}$,^[22] the estimated values are a good agreement with the values reported in the literature.^[23]

4.2 UV-Visible-NIR spectroscopic analysis

The basic requirement for high performance of solar cell is optical properties such as band gap (E_{opt}) and absorbance. The UV-Visible-NIR spectroscopic measurements of the α -FAPbI₃ perovskite synthesized using the one-step solution method are shown in Fig. 3. To record the UV-Visible-NIR spectroscopic measurements, the thin film of FAPbI₃ were spin coated on soda lime glass. The FAPbI nanoparticles were dispersed uniformly in the DMF with adequate viscosity and spin coated on a thoroughly cleaned soda lime glass. The absorption spectra of FAPbI₃ perovskite were then recorded in the wavelength range 300–1500 nm.

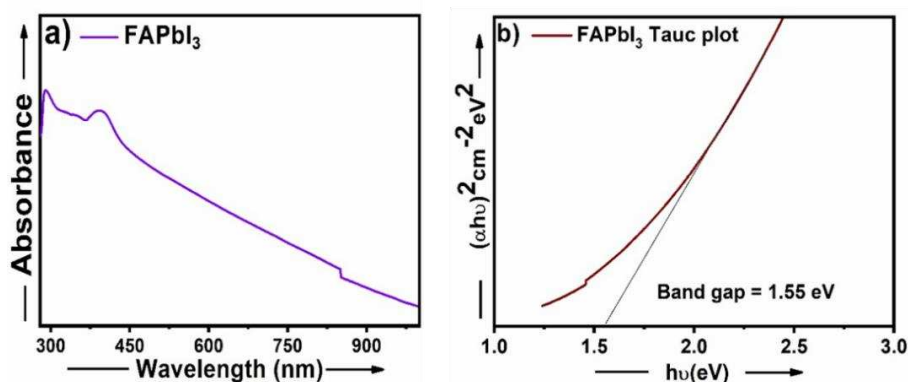


Fig. 3 a) Absorbance Spectra b) Tauc's plot of FAPbI₃ perovskite.

As shown in Fig. 3a, the synthesized α -FAPbI₃ perovskite shows absorption upto 900 nm. For direct allowed transition of α -FAPbI₃ perovskite, absorption coefficient (α) and band gap can be expressed as equation (2) below:

$$(\alpha h\nu) = B(h\nu - E_g)^n \quad (2)$$

where, B is Tauc's constant, α is the absorption coefficient, h is the Planck's constant, ν is photon frequency, and E_g is the optical band gap energy of the material. To determine the band gap, $(\alpha h\nu)^{1/2}$ is plotted against energy $E(h\nu)$ as shown in Fig. 3b. A straight line is fitted through the data points. The band gap of α -FAPbI₃ perovskite was estimated to be 1.55 eV which is good agreement with reported values in literature.^[24] The synthesized FAPbI₃ perovskite in the present study have good crystallinity and thus better candidate for used in semiconducting device like absorber layer in solar cell, batteries, sensors, etc.

4.3 Photoluminescence spectroscopic analysis

The photoluminescence (PL) measurement of α -FAPbI₃ perovskite thin film prepared using one step deposition method were recorded at excitation wavelength of 430 nm. Fig. 4 shows PL spectra of FAPbI₃ perovskite which is obtained by diluting the sample in two ml N, N-dimethylformamide (DMF). This result is confirmed by the evolution of the wavelength for FAPbI₃ perovskite from 710 nm - 740 nm, thus it involves the passage to most stable α phase, which is confirmed by the results of X-ray diffraction. The result support further the claim that the α -FAPbI₃ perovskite are promising materials for the application in light – emitting diode and photovoltaic solar devices. The deviation in the bandgap value of the material by UV-VIS-NIR and PL measurement are due to slightly different size distribution of nanocrystallite during the two measurements.

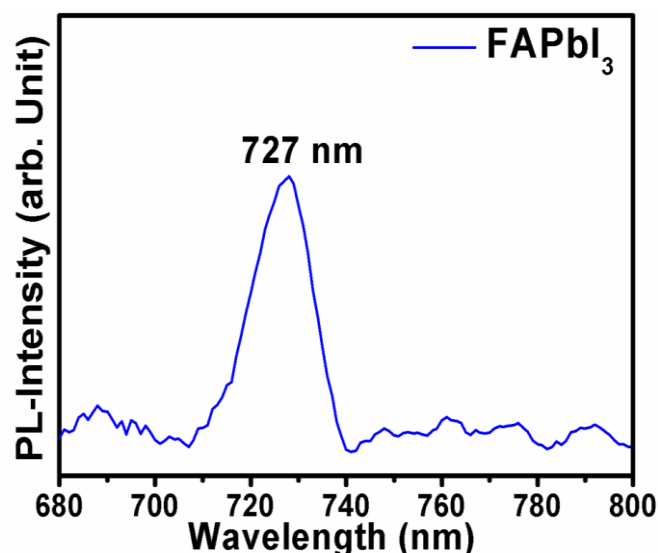


Fig. 4 Photoluminescence (PL) spectra of FAPbI₃ perovskite material.

4.4 Transmission electron microscopic analysis

The transmission electron microscopy (TEM) was employed to deduce microscopic, crystallographic and compositional information of the FAPbI₃ material. The microstructural information of the FAPbI₃ perovskite as obtained from transmission electron microscopy (TEM) at an acceleration voltage of 200 kV is shown in Fig. 5a. Morphology with agglomerate of FAPbI₃ perovskite nanocrystals shows presence of particles with differently oriented crystallites. The Fig. 5b shows a sample estimation of the inter-planar distance to be 0.657 nm, which is very close to the inter-planar distance measured from XRD measurements.

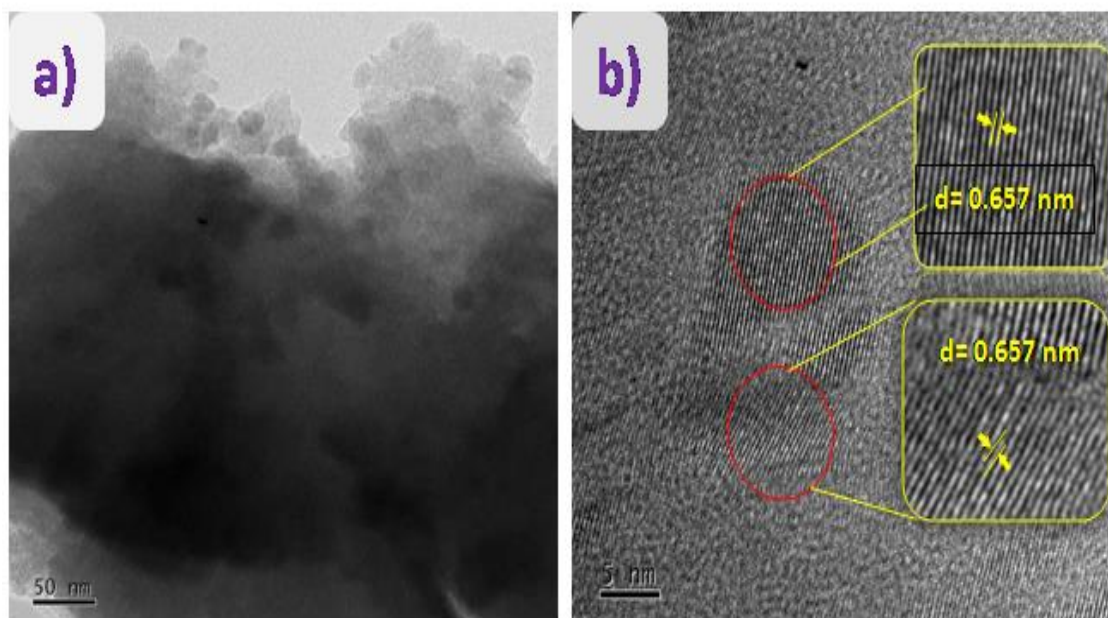


Fig. 5 a) Low magnification Transmission electron microscopic image and b) high resolution Transmission electron microscopic image with fringe analysis for interplanar spacing measurement of FAPbI₃ perovskite sample.

5. Conclusion

In summary, we report a successfully synthesized of FAPbI₃ perovskite, using a simple room temperature one step chemical method. The synthesized FAPbI₃ materials was thoroughly investigated for structural, and optical properties using XRD, photoluminescence, UV-Visible absorption and transmission electron microscopy. The confirmation of cubic α -FAPbI₃ structure was confirmed using XRD and crystallite size of nanoparticle was found to be 40 nm. The UV –Visible spectra were used to deduce the bandgap value of direct transition to be 1.55 eV of FAPbI₃. The transmission electron microscopic analysis shows the conglomerate of crystallites and the inter-planar spacing of 0.625 nm. This leads to conclusion that the FAPbI₃ perovskite synthesized by a simple low temperature chemical technique is a better candidate for applications in optoelectronic and photovoltaic device application.

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Supporting information

Not Applicable.

Conflict of interest

There are no conflicts to declare.

References

- [1] J. J. Yoo, S. Wieghold, M. C. Sponseller, M. R. Chua, S. N. Bertram, N. T. P. Hartono, J. S. Tresback, E.C. Hansen, J. P. Correa-Baena, V. Bulović, T. Buonassisi, S. S. Shin, M.G. Bawendi, *Energ. Environ. Sci.*, 2019, **12**, 2192-2199, doi: 10.1039/c9ee00751b.
- [2] H. J. Snaith, *Nat. Mater.*, 2018, **17**, 372-376, doi: 10.1038/s41563-018-0071-z.
- [3] J.-P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, A. Hagfeldt, *Science*, 2017, **358**, 739, doi: 10.1126/science.aam6323.
- [4] Y. Fan, H. Meng, L. Wang, S. Pang, *Sol. RRL*, 2019, **3**, 1900215, doi: 10.1002/solr.201900215.
- [5] T. Zhang, Q. Xu, F. Xu, Y. Fu, Y. Wang, Y. Yan, L. Zhang, Y. Zhao, *Sci. Bull.*, 2019, **64**, 1608-1616, doi: 10.1016/j.scib.2019.08.029.
- [6] M. Mateen, Z. Arain, C. Liu, Y. Yang, X. Liu, Y. Ding, P. Shi, Y. Ren, Y. Wu, S. Dai, T. Hayat, A. Alsaedi, *ACS Sustain. Chem. Eng.*, 2019, **7**, 11760-11768, doi: 10.1021/acssuschemeng.9b02031.
- [7] Z. K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, R. H. Friend, *Nat. Nanotechnol.*, 2014, **9**, 687-692, doi: 10.1038/nnano.2014.149.
- [8] Z. Yuan, C. Zhou, Y. Tian, Y. Shu, J. Messier, J. C. Wang, L.J. van de Burgt, K. Kountouriotis, Y. Xin, E. Holt, K. Schanze, R. Clark, T. Siegrist, B. Ma, *Nat. Commun.*, 2017, **8**(1), 14051, doi: 10.1038/ncomms14051.
- [9] S. Luo, W. A. Daoud, *J. Mater. Chem. A*, 2015, **3**, 8992-9010, doi: 10.1039/c4ta04953e.
- [10] N. J. Jeo, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok, *Nature*, 2015, **517**, 476-480, doi: 10.1038/nature14133.
- [11] M. Hu, L. Liu, A. Mei, Y. Yang, T. Liu, H. Han, *J. Mater. Chem. A*, 2014, **2**, 17115-17121, doi: 10.1039/c4ta03741c.
- [12] S. Wozny, M. Yang, A. M. Nardes, C. C. Mercado, S. Ferrere, M. O. Reese, W. Zhou, K. Zhu, *Chem. Mater.*, 2015, **27**, 4814-4820, doi: 10.1021/acs.chemmater.5b01691.
- [13] Y. Zhang, J. Wang, J. Xu, W. Chen, D. Zhu, W. Zheng, X. Bao, *RSC Adv.*, 2016, **6**, 79952-79957, doi: 10.1039/c6ra15210d.
- [14] M. Zhang, F. Zhang, Y. Wang, L. Zhu, Y. Hu, Z. Lou, Y. Hou, F. Teng, *Sci Rep-Uk*, 2018, **8**, 11157, doi: 10.1038/s41598-018-29147-6.
- [15] R. Begum, X. Y. Chin, M. Li, B. Damodaran, T.C. Sum, S. Mhaisalkar, N. Mathews, *Nat. Commun.*, 2019, **55**, 5451-5455, doi: 10.1039/c9cc01526d.
- [16] Q. Han, S. H. Bae, P. Sun, Y. T. Hsieh, Y. M. Yang, Y. S. Rim, H. Zhao, Q. Chen, W. Shi, G. Li, Y. Yang, *Adv. Mater.*, 2016, **28**, 2253-2258, doi: 10.1002/adma.201505002.
- [17] X. Guo, C. McCleese, W. Gao, M. Wang, L. Sang, C. Burda, *Mater. Renew. Sustain. Energy*, 2016, **5**, 17, doi: 10.1007/s40243-016-0081-1.
- [18] T. Niu, J. Lu, M. Tang, D. Barrit, D. M. Smilgies, Z. Yang, J. Li, Y. Fan, T. Luo, I. McCulloch, A. Amassian, S. Liu, K. Zhao, *Energ. Environ. Sci.*, 2018, **11**, 3358-3366, doi: 10.1039/c8ee02542h.
- [19] Y. Zhou, J. Kwun, H. F. Garces, S. Pang, N. P. Padture, *Chem. Commun.*, 2016, **52**, 7273-7275, doi: 10.1039/c6cc02086k.
- [20] Z. Wang, Y. Zhou, S. Pang, Z. Xiao, J. Zhang, W. Chai, H. Xu, Z. Liu, N. P. Padture, G. Cui, *Chem. Mater.*, 2015, **27**, 7149-7155, doi: 10.1021/acs.chemmater.5b03169.
- [21] B. Slimi, M. Mollar, I. Ben Assaker, A. Kriaa, R. Chtourou, B. Mari, *Monatsh. Chem.*, 2017, **148**, 835-844, doi: 10.1007/s00706-017-1958-0.
- [22] F. C. Hanusch, E. Wiesenmayer, E. Mankel, A. Binck, P. Angloher, C. Fraunhofer, N. Giesbrecht, J. M. Feckl, W. Jaegermann, D. Johrendt, T. Bein, P. Docampo, *J. Phys. Chem. Lett.*, 2014, **5**, 2791-2795, doi: 10.1021/jz501237m.
- [23] Y. Zhou, M. Yang, J. Kwun, O. S. Zame, Y. Zhao, S. Pang, N. P. Padture, K. Zhu, *Nanoscale*, 2016, **8**, 6265-6270, doi: 10.1039/c5nr06189j.
- [24] M. I. Saidaminov, A. L. Abdelhady, G. Maculan, O. M. Bakr, *Chem. Commun.*, 2015, **51**, 17658-17661, doi: 10.1039/c5cc06916e.

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