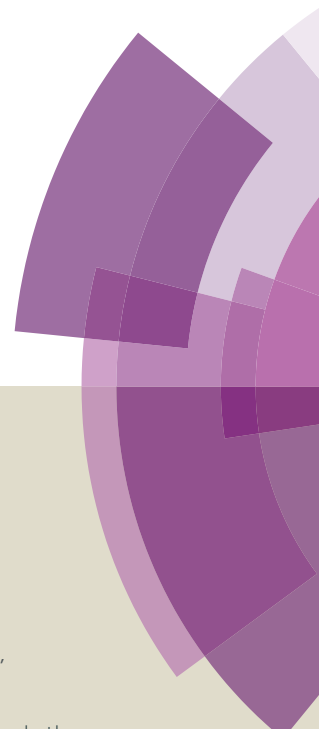


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ARTICLE TYPE

Pressure-assisted $\text{CH}_3\text{NH}_3\text{PbI}_3$ morphology reconstruction to improve the high performance of perovskite solar cells

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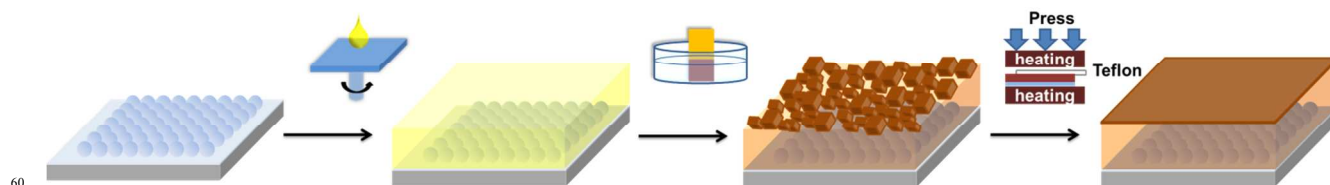
The pressure is introduced as a parameter in the post-treat process for perovskite solar cells. Via a hot-pressing method, the rough surface of perovskite film become smooth, and the pin-holes can be cured. This modified perovskite morphology can help to improve charge transporting and eliminate recombination in the perovskite solar cells. And significantly enhanced photovoltaic performances with high PCEs of 10.84% and 16.07% are thus achieved in HTM-free type and spiro-OMeTAD based cells, respectively.

Recent years, inorganic-organic hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ and its analogues are seen as star materials in photovoltaic field.¹ With a series of miraculous properties, such as strong absorption coefficients, low non-radiative carrier recombination rates and ease of fabrication, these perovskite materials were successfully employed in different types of solar cells (mesoporous structure vs. planer structure, hole-transporting material contained type vs. hole-transporting material free type etc.).²⁻⁵ The highest certified power conversion efficiencies (PCE) of these so-called perovskite solar cells can reach 20.1%. Moreover, the simple fabrication process of perovskite materials also helps to reduce the cost of perovskite solar cells, promising potential commercial applications. Currently, these perovskite materials can be deposited on the cell substrate by mixing the corresponding metal halide and amine halide directly via in situ solution processes as one-step method or sequential deposition method.^{6,7} However, the fast crystallization of perovskite material

with solvent evaporation may result in uncontrollable film morphology and thus affecting the cell performance.^{8,9} To solve this issue, the post-treatment of thermal annealing is commonly adopted to modify the morphology and improve the crystallinity, and its effect has been widely recognized.^{10,11} Based on this, even a new solvent annealing method was developed to further improve the cell performance.^{12,13}

Herein, we introduce the pressure as a parameter for the first time and post-treat the perovskite with a hot-pressing process. After hot-pressed, the top surface of perovskite layer will become more smooth and compact, meanwhile, the pin-holes can be cured. Moreover, the charge transporting and recombination properties in the devices are improved. According to these changes, the cell performances are distinctly enhanced for both hole-transporting material free (HTM-free) type and spiro-OMeTAD based perovskite solar cells, yielding high PCEs of 10.84% and 16.07% respectively.

The preparation procedure of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ is exhibited in Scheme 1. In this work, the perovskite is deposited on FTO/mesoporous TiO_2 substrate via sequential deposition method.¹⁴ That is first spin-coating PbI_2 in N,N -dimethylformamide (DMF) solution on the substrate to form PbI_2 filled and covered structure, and then dipping into $\text{CH}_3\text{NH}_3\text{I}$ isopropanol solution to achieve the chemical conversion from PbI_2 to $\text{CH}_3\text{NH}_3\text{PbI}_3$. Subsequently, place this FTO/mesoporous TiO_2 /perovskite film on a hot-press machine and perform the hot-pressing operation under certain temperature and pressure.



Scheme 1 Preparation procedure of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ on FTO/mesoporous TiO_2 .

Fig. 1a is the SEM image of a partially hot-pressed perovskite film. A piece of Teflon film is attached on the surface of perovskite film to avoid contaminated by hot plate. So the area with Teflon on it will be post-treated by hot-pressing, such as the left part in Fig. 1a, while the other area will be just thermal annealed, as shown in the right part. Apparently, the right part and left part are quite different in appearance. The thermal

annealed perovskite film has a rough surface, and in contrast, the hot-pressed part is quite smooth and flat. Fig. 1b and c are the corresponding high-resolution SEM images of thermal annealed and hot-pressed areas. As can be seen, the surface layer of perovskite prepared by sequential deposition is mainly composed of about 200nm-sized grains and even some larger particles, which are stacked together and show a porous structure, as

reported by other researchers.¹⁵ Post-treated via hot-pressing, the surface becomes quite smooth and compact. The large perovskite particles disappear, and the grains are deformed to fill a plane, even the pin-holes in the former porous structure are almost cured. This surface morphology is quite similar to the ones obtained by some modified perovskite deposition methods, such as additives or solvent engineering.^{9,16-19} Although inorganic-organic hybrid perovskite is soft due to its relatively weak chemical bonds in the compound,²⁰ without heating, the pressure can hardly afford this modification, as shown in Fig. S1.

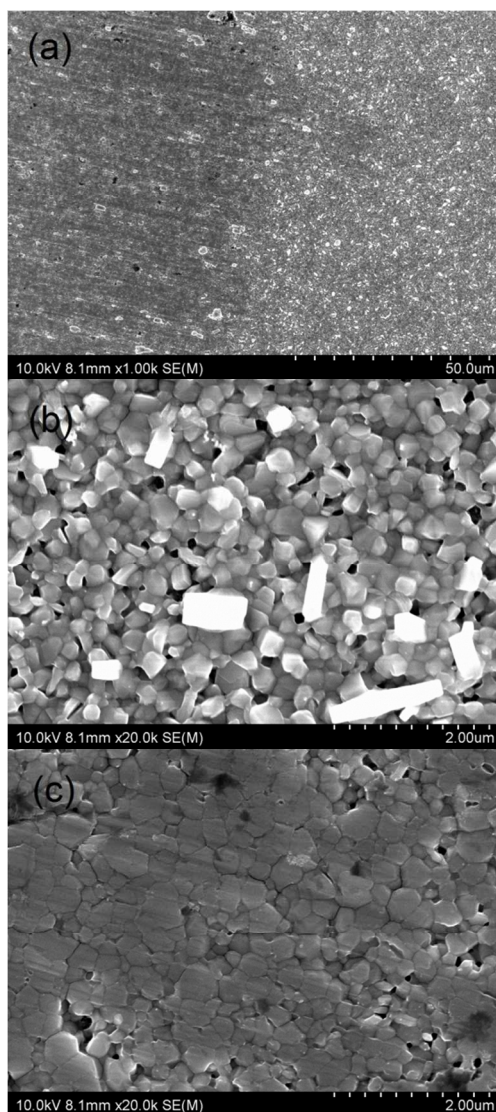


Fig. 1 (a) SEM image of partially hot-pressed perovskite film, (b) magnified SEM image of thermal annealed area and (c) magnified SEM image of hot-pressed area.

The effect of hot-pressing process on the crystal structure was investigated by X-ray diffraction (XRD). An FTO/mesoporous TiO_2 /perovskite films were first thermal annealed for a while, and then hot-pressed for different time. The characteristic peaks of $\text{CH}_3\text{NH}_3\text{PbI}_3$'s (100) and (200) lattice planes can be seen in Fig. 2. A trace amount of residual PbI_2 is also shown in the XRD patterns, which is difficult to avoid in sequential deposition.²¹ The peak intensity ratio of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PbI_2 has no change

under different operation time. And the absolute intensity of (100) and (200) peaks increased and half peak width decreased slightly while extending the hot-pressing time, indicating the improved crystallinity and grown grains. It is revealed that the hot-pressing process has no significant effect on the composition of perovskite film, and it only changes the morphology, as a physical process.

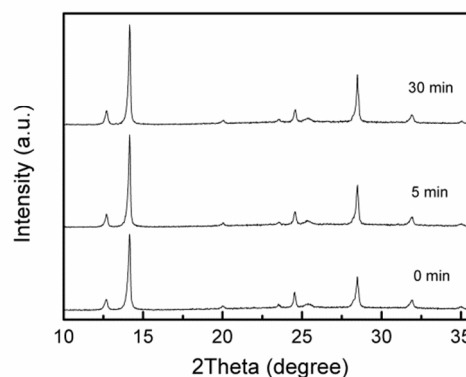


Fig. 2 X-ray diffraction patterns of FTO/mesoporous TiO_2 /perovskite under different hot-pressing time.

Perovskite was also deposited on slide glass/mesoporous Al_2O_3 substrate for photoluminescence (PL) measurement. Due to the insulating substrate, the time-resolved PL decay spectra can reflect the quality of individual perovskite films, as shown in Fig. 3a. The hot-pressed sample has nearly the same PL lifetime ($\tau = 14.9$ vs. 14.0 ns) and even overlapped decay curve with the no hot-pressing sample, once again confirming the composition stability of perovskite under hot-pressing condition. However, in the case of FTO/mesoporous TiO_2 based samples, the research object is quite different. The TiO_2 will extract the photo-generated electron from perovskite and quench PL, therefore, the corresponding decay spectra can represent the charge transfer characteristics of the TiO_2 /perovskite composite system.^{22,23} After hot-pressing, the PL lifetime amazingly decreased from 12.0 ns to 7.6 ns with a rapid PL intensity decay. This phenomenon can be attributed to the shorter carrier-transporting distance between perovskite grains or from perovskite to TiO_2 in the compact perovskite film than that in porous structure, as shown in Fig. 3c. It should be the smooth carrier-transporting capacity that accelerates the PL decay.

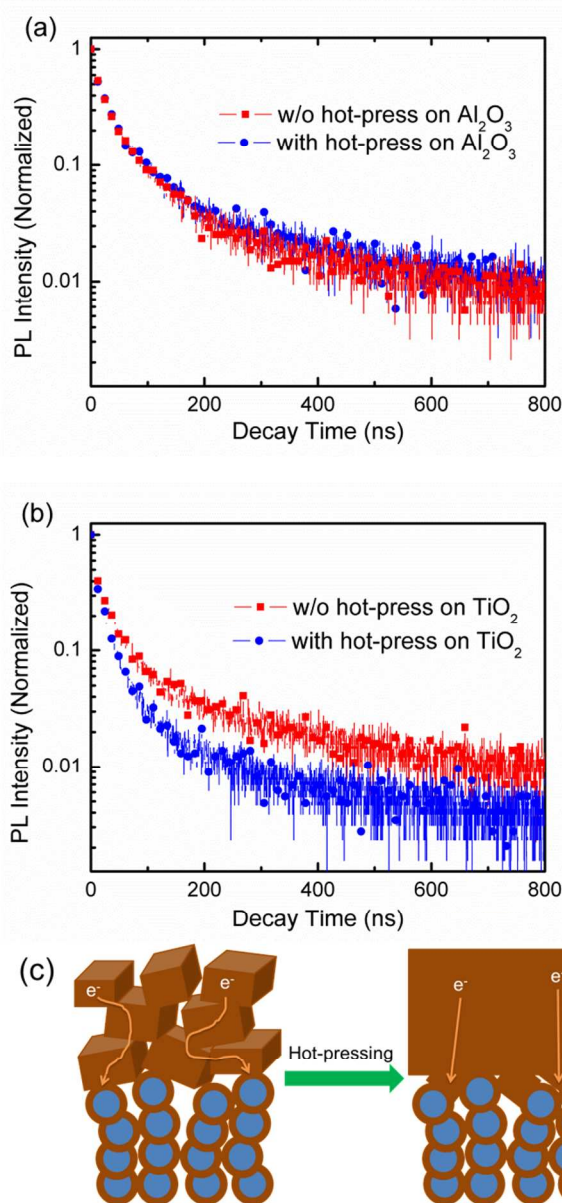
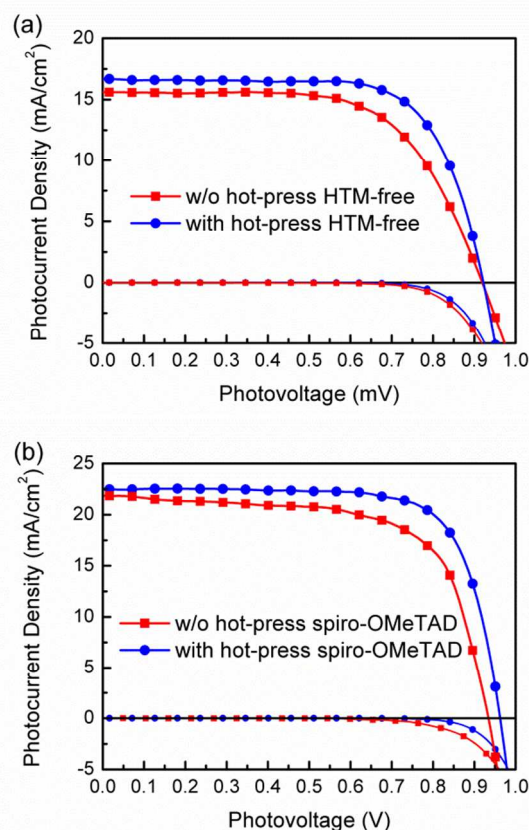


Fig. 3 Normalized time-resolution photoluminescence spectra of (a) FTO/ Al_2O_3 /perovskite and (b) FTO/ TiO_2 /perovskite samples with and without hot-pressing; (c) scheme of charge transporting in mesoporous TiO_2 /perovskite films without and with hot-pressing.

Evaporating Au electrode to fabricate HTM-free structured perovskite solar cells, the J - V characteristics were tested under both standard AM 1.5 illumination and dark condition. The J - V curves of best cells with either condition are shown as Fig. 4a, and the parameters are exhibited in Table 1. High PCEs of 9.16% and 10.84% were achieved in thermal annealed and hot-pressed devices, which are among the best results with perovskite/Au contact.^{14,24} In comparison, the cell with hot-pressing exhibits better performance. Specifically, the open-circuit voltage (V_{oc}) values are almost the same (0.919 vs. 0.922 V) in the cells with and without hot-pressing, consistent with the substantially coincident dark current curves. But the short-circuit current density (J_{sc}) is enhanced from 15.62 to 16.70 mA/cm^2 . The statistical data of ten devices fabricated with either condition are also provided in Fig. S2, showing the same result. Further

measuring the incident-photon-to-current conversion efficiency (IPCE) spectra, the IPCE values of hot-pressed device are significantly enhanced in the long wavelength region, as shown in Fig. 4c. Considering the optical property of perovskite film maintains no change during the hot-pressing, this difference may be attributed to the higher electron separation and collection efficiency, especially at the back contact region,¹⁴ thus increasing J_{sc} value. And the fill factor (FF) is significantly improved from 0.638 to 0.704. Observing the shape of J - V curves, it can be seen the one representing thermal annealed cell exhibits smaller slope around the V_{oc} , indicating larger series resistance value than the hot-pressed one. These improvements on carrier separation/collection efficiency and conductance of whole device should due to the enhanced charge-transporting capacity confirmed by PL decay.



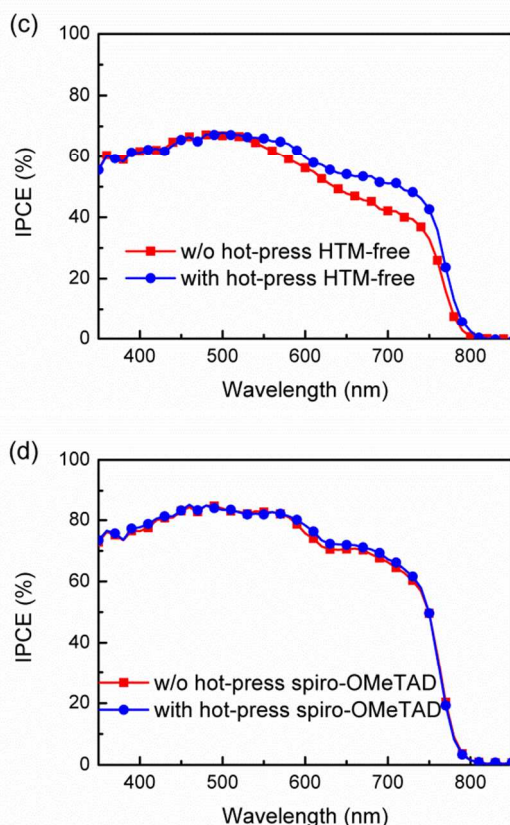


Fig. 4 *J*-*V* curves of (a) HTM-free type perovskite solar cells and (b) spiro-OMeTAD based perovskite solar cells under standard AM 1.5 illumination and dark condition; corresponding IPCE spectra (c) and (d).

Table 1 Photovoltaic parameters of different perovskite solar cells.

Type	J_{sc} mA/cm ²	V_{oc} V	FF	PCE %
w/o hot-press HTM-free	15.62	0.919	0.638	9.16
with hot-press HTM-free	16.70	0.922	0.704	10.84
w/o hot-press spiro-OMeTAD	21.85	0.934	0.664	13.55
with hot-press spiro-OMeTAD	22.51	0.962	0.742	16.07

As reported so far, the perovskite solar cells with spiro-OMeTAD as HTM exhibit superior performances to the HTM-free cells.¹² We also fabricated spiro-OMeTAD based cells to investigate the influence of hot-pressing. When spin-coating a spiro-OMeTAD layer on the perovskite and then evaporating Au electrode, the obtained cells can yield higher PCEs of 13.55% and 16.07%, as in Fig. 4b. The extra HTM can really favor the separation and transporting of carriers, thus significantly increasing the J_{sc} value. Consequently, the IPCE values of spiro-OMeTAD based cells are enhanced within a wide range of wavelength from 350 to 750 nm, as shown in Fig. 4d. Similarly, the hot-pressed cells exhibit better performance, but the main different parameters are V_{oc} and FF in this case. The V_{oc} increased from 0.934 to 0.962 V, and the FF from 0.664 to 0.742 after hot-pressing operation. Through the shape of photocurrent density and dark current density curves, it can be inferred that the improvement on V_{oc} and FF may due to the lower charge recombination rate.

This inference can be further examined with transient photovoltage spectroscopy method, which is always used to

evaluate the charge recombination rate.¹³ As shown in Fig. 5a, in the case of HTM-free structure, the photovoltage decay curves of cells with and without hot-pressing are essentially coincident. Whereas, in the spiro-OMeTAD based cells, hot-pressing process evidently slow up this decay (Fig. 5b). It is revealed that the improvement on V_{oc} value is indeed related to the depressed recombination.

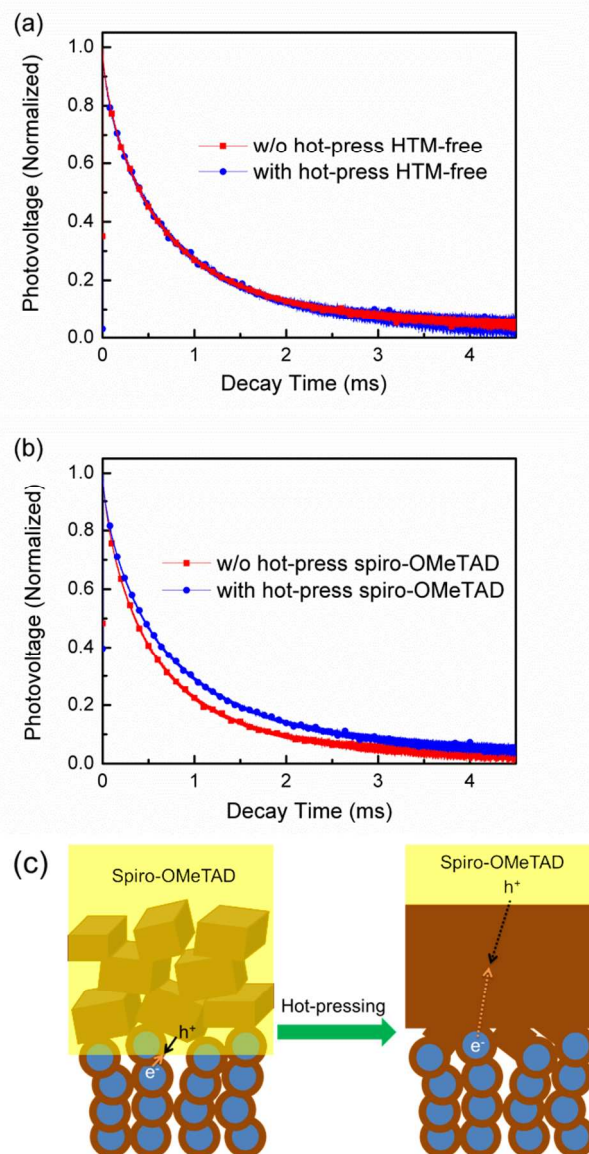


Fig. 5 Normalized transient photovoltage spectra of (a) HTM-free type perovskite solar cells and (b) spiro-OMeTAD based perovskite solar cells; (c) scheme of charge recombination between TiO₂ and spiro-OMeTAD in mesoporous TiO₂/perovskite/spiro-OMeTAD films without and with hot-pressing.

Considering the recombination rates have no change for the HTM-free devices, it should be the introducing of HTM that render the difference. In this work, the perovskite CH₃NH₃PbI₃ is deposited on mesoporous TiO₂, forming a bilayer structure. However, the upper layer of individual perovskite exhibits porous structure, and the TiO₂ nanocrystalline in lower layer may be incompletely coated. Therefore, strong charge recombination will

occur when the spiro-OMeTAD infiltrates into the pin-hole and directly contacts the bare TiO₂. While after hot-pressed, the perovskite upper layer becomes compact with rare pin-holes. This change in morphology can effectively prevent the direct contact between TiO₂ and HTM, eliminating this recombination, as shown in Fig. 5c. Similar phenomenon was reported in planar perovskite solar cells.²⁵

Conclusions

In conclusion, we introduce the pressure as a parameter in the post-treat process for perovskite solar cells. Via a hot-pressing method, a compact perovskite layer with smooth surface and rare pin-holes can be prepared on the mesoporous TiO₂. PL and photovoltage decay spectra suggest improved charge transporting and reduced recombination with this modified morphology. Thus, significantly enhanced photovoltaic performance can be achieved in both HTM-free and spiro-OMeTAD based cells with high PCEs of 10.84% and 16.07% respectively. Future work on applying this post-treat method to perovskite solar cells with other device structures and deposition method would be expected to further improve the photovoltaic performance.

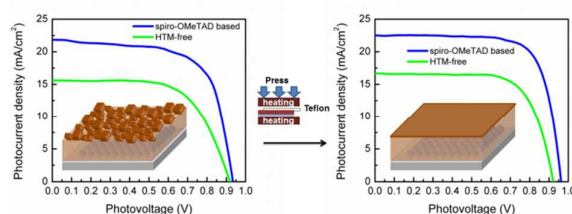
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Notes and references

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- † Electronic Supplementary Information (ESI) available: [details of experimental section, Fig. S1 and Fig. S2]. See DOI: 10.1039/b000000x/
- M.A. Green, A. Ho-Baillie and H.J. Snaith, *Nat. Photonics*, 2014, **8**, 506.
 - H.S. Kim, C.R. Lee, J.H. Im, K.B. Lee, T. Moehl, A. Marchioro, S.J. Moon, R. Humphry-Baker, J.H. Yum, J.E. Moser, M. Grätzel and N.G. Park, *Sci. Rep.*, 2012, **2**, 591.
 - M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami and H.J. Snaith, *Science*, 2012, **338**, 643.
 - M.Z. Liu, M.B. Johnston and H.J. Snaith, *Nature*, 2013, **501**, 395.
 - L. Etgar, P. Gao, Z. Xue, Q. Peng, A.K. Chandiran, B. Liu, M.K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2012, **134**, 17396.
 - A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050.
 - J. Burschka, N. Pellet, S.J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316.
 - Y.Z. Wu, A. Islam, X.D. Yang, C.J. Qin, J. Liu, K. Zhang, W.Q. Peng and L.Y. Han, *Energy Environ. Sci.*, 2014, **7**, 2934.
 - M. Xiao, F. Huang, W. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y.B. Cheng and L. Spiccia, *Angew. Chem. Int. Ed.*, 2014, **126**, 10056.
 - G.E. Eperon, V.M. Burlakov, P. Docampo, A. Goriely and H.J. Snaith, *Adv. Funct. Mater.*, 2014, **24**, 151.

- A. Dualeh, N. Tétreault, T. Moehl, P. Gao, M.K. Nazeeruddin and M. Grätzel, *Adv. Funct. Mater.*, 2014, **24**, 3250.
- H.P. Zhou, Q. Chen, G. Li, S. Luo, T.B. Song, H.S. Duan, Z.R. Hong, J.B. You, Y.S. Liu and Y. Yang, *Science*, 2014, **345**, 542.
- Z. Xiao, Q. Dong, C. Bi, Y. Shao, Y. Yuan and J. Huang, *Adv. Mater.*, 2014, **26**, 6503.
- J.J. Shi, Y.H. Luo, H.Y. Wei, J.H. Luo, J. Dong, S.T. Lv, J.Y. Xiao, Y.Z. Xu, L.F. Zhu, X. Xu, H.J. Wu, D.M. Li and Q.B. Meng, *ACS Appl. Mater. Interfaces*, 2014, **6**, 9711.
- B. Cohen, S. Gamliel and L. Etgar, *APL Mater.*, 2014, **2**, 081502.
- P. Liang, C. Liao, C. Chueh, F. Zuo, S.T. Williams, X.K. Xin, J. Lin and A.K. Jen, *Adv. Mater.*, 2014, **26**, 3748.
- C.T. Zuo and L.M. Ding, *Nanoscale*, 2014, **6**, 9935.
- N.J. Jeon, J.H. Noh, Y.C. Kim, W.S. Yang, S. Ryu and S.I. Seok, *Nat. Mater.*, 2014, **13**, 897.
- F. Huang, Y. Dkhissi, W. Huang, M. Xiao, I. Benesperi, S. Rubanov, Y. Zhu, X. Lin, L. Jiang, Y. Zhou, A. Gray-Weale, J. Etheridge, C.R. McNeill, R.A. Caruso, U. Bach, L. Spiccia and Y.B. Cheng, *Nano Energy*, 2014, **10**, 10.
- J. Feng, *APL Materials*, 2014, **2**, 081801.
- N. Li, H.P. Dong, H. Dong, J.L. Li, W.Z. Li, G.D. Niu, X.D. Guo, Z.X. Wu and L.D. Wang, *J. Mater. Chem. A*, 2014, **2**, 14973.
- G. Xing, N. Mathews, S. Sun, S.S. Lim, Y.M. Lam, M. Grätzel, S. Mhaisalkar and T.C. Sum, *Science*, 2013, **342**, 344.
- S.D. Stranks, G.E. Eperon, G. Grancini, C. Menelaou, M.J. Alcocer, T. Leijtens, L.M. Herz, A. Petrozza and H.J. Snaith, *Science*, 2013, **342**, 341.
- S. Aharon, S. Gamliel, B.E. Cohen and L. Etgar, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10512.
- Y.L. Guo, C. Liu, K. Inoue, K. Harano, H. Tanaka and E. Nakamura, *J. Mater. Chem. A*, 2014, **2**, 13827.



Pressure is introduced as a parameter in the fabrication process of perovskite solar cells for the first time. After hot-pressing The morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film becomes smooth and compact. The performance of both HTM-free and HTM-contained solar cells are thus improved.