## Supporting Information

# Sustainable solvent system for processing CsPbBr3 films for solar cells via an anomalous sequential deposition route

Xiaobing Cao[1]*, Guoshuai Zhang[1], Yifan Cai[1], Long Jiang[1], Weijia Yang[1], Weidong Song[1], Xin He[1], Qingguang Zeng[1], Yi Jia[2]*, Jinquan Wei[3]*

1. School of Applied Physics and Materials,Wuyi University, Jiangmen, Guangdong 529020, P.R. China
2. Qian Xuesen Laboratory of Space Technology, China Academy of Space Technology, Beijing 100094, PR China
3. State Key Lab of New Ceramic and Fine Processing, Tsinghua University, Beijing 100084, P.R. China

*Corresponding Author. E-mail: caoxb14@tsinghua.org.cn; jiayi@qxslab.cn; jqwei@tsinghua.edu.cn. Phone: +86-10-62781065.

**Figure S1.** Photograph of the $PbBr_2$/TEP solution with highest concentration of ~ 60 mg $mL^{-1}$.

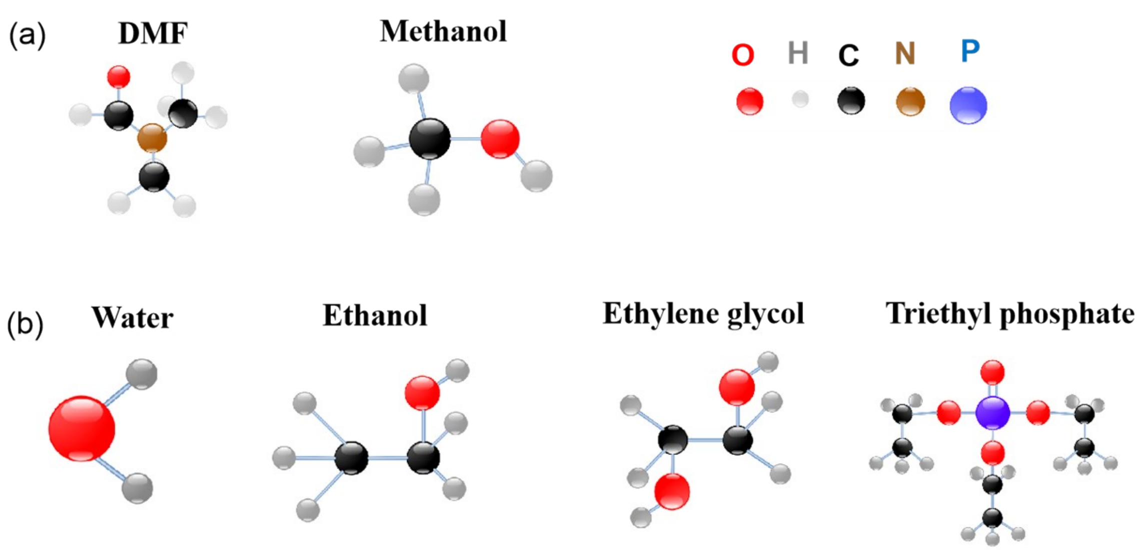


**Figure S2.** (a) Molecular structure of the toxic solvent used in traditional sequential deposition route. (b) Molecular structure of the green solvents used in the anomalous sequential deposition route.

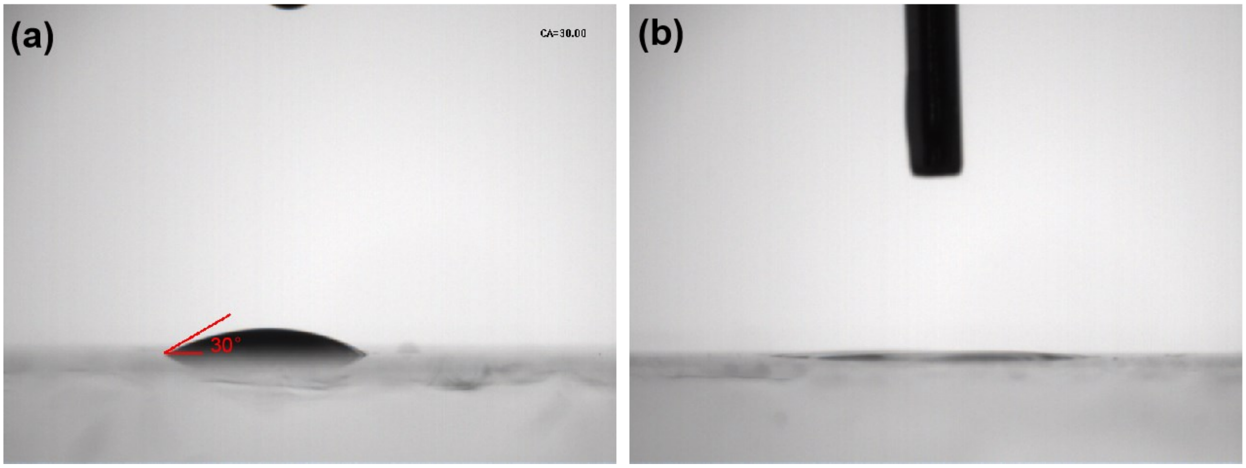


**Figure S3.** (a) Contact angle of water on the $TiO_2$/FTO substrate; (b) Contact angle the mixture of water and ethanol (v:v=1:1) on the $TiO_2$/FTO substrate.

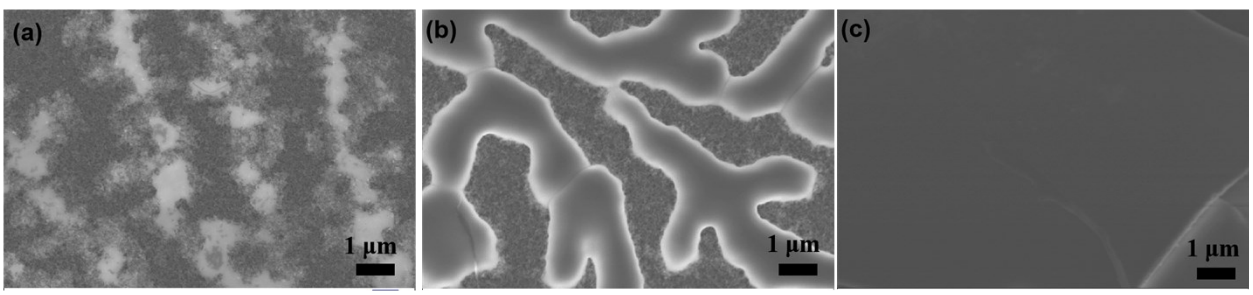


**Figure S4.** The low magnification SEM images of CsBr films fabricated from different solvent system. (a) water; (b) $H_2O$+Ethanol; (c) $H_2O$+Ethanol+EG.

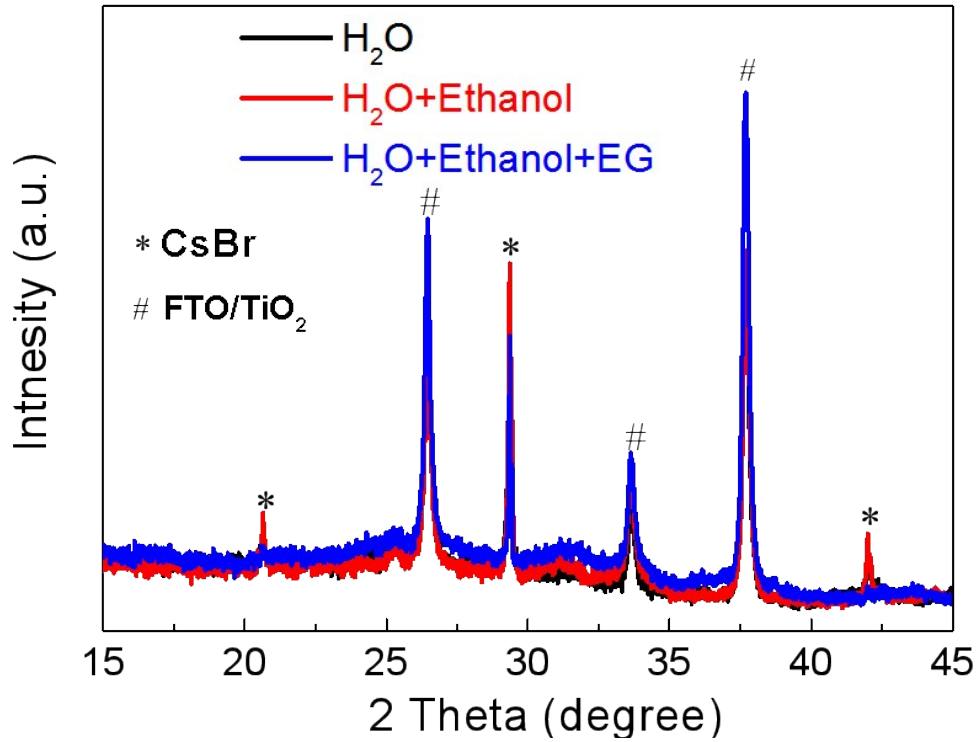


**Figure S5**. Full XRD curves of the CsBr films fabricated from different solvent system.

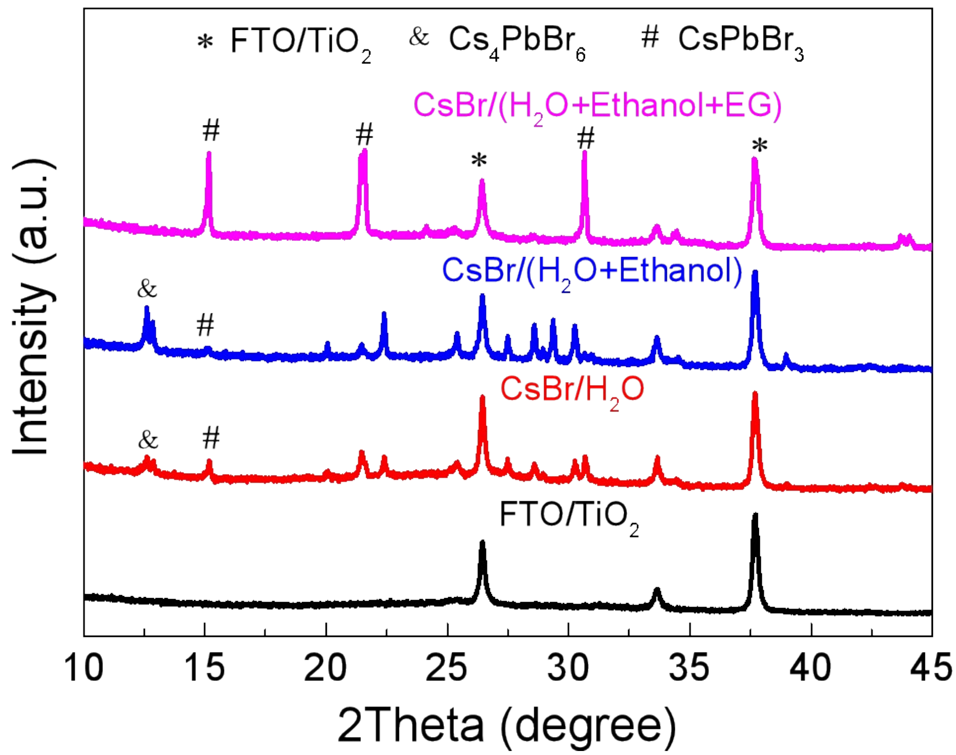


**Figure S6**. XRD curves of the Cs-Pb-Br films fabricated from different solvent system.

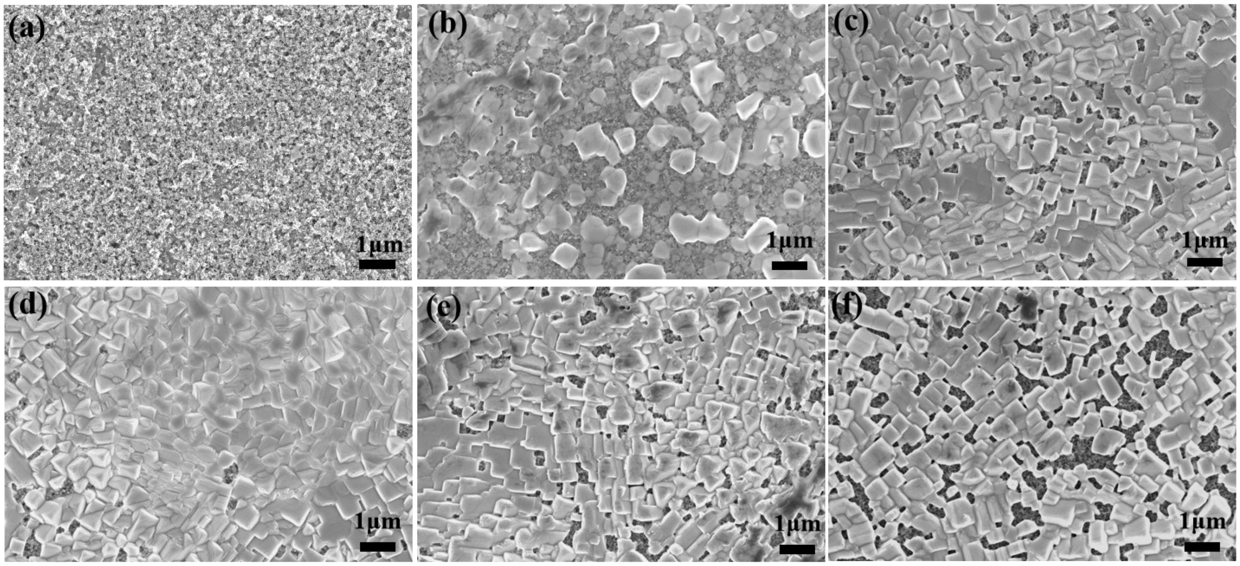


**Figure S7**. SEM images showing the evolution of the $CsPbBr_3$ films prepared by dipping $PbBr_2$ films into the CsBr/methanol solution at 50 ºC for different time. (a) 0 min, (b) 3 min, (c) 6 min, (d) 9 min, (e) 12 min, (f) 15 min. It exhibits best morphology of Cs-Pb-Br films by dipping the $PbBr_2$ films into CsBr/methanol for 9 min.

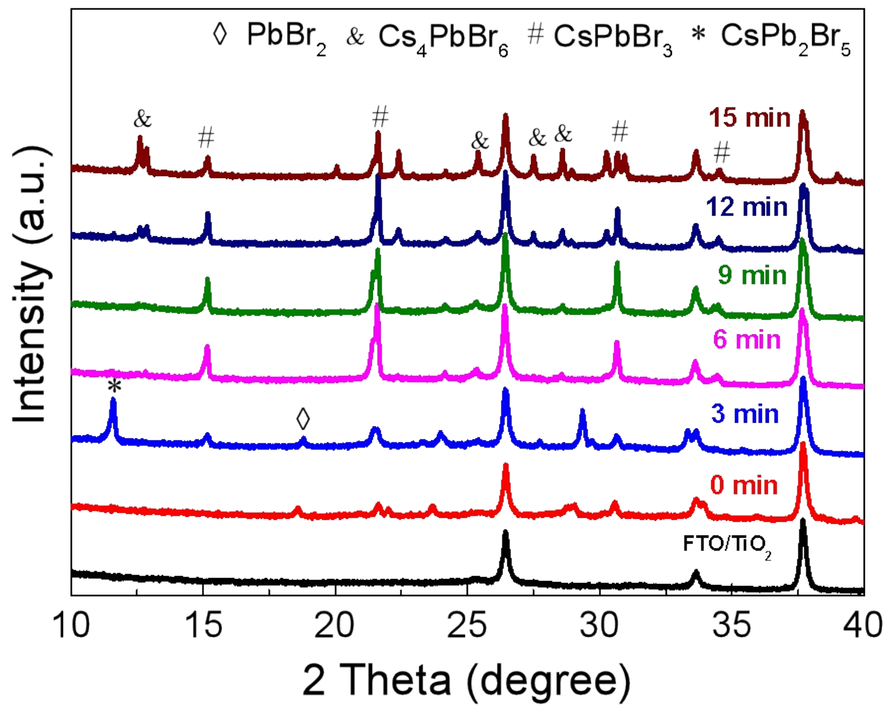


**Figure S8.** XRD patterns showing the evolution of $CsPbBr_3$ prepared by dipping $PbBr_2$ films in CsBr/methanol solution at 50 ºC for different time. It exhibits desired pure phase of $CsPbBr_3$ for solar cells by dipping $PbBr_2$ films into CsBr/methanol for 9 min.

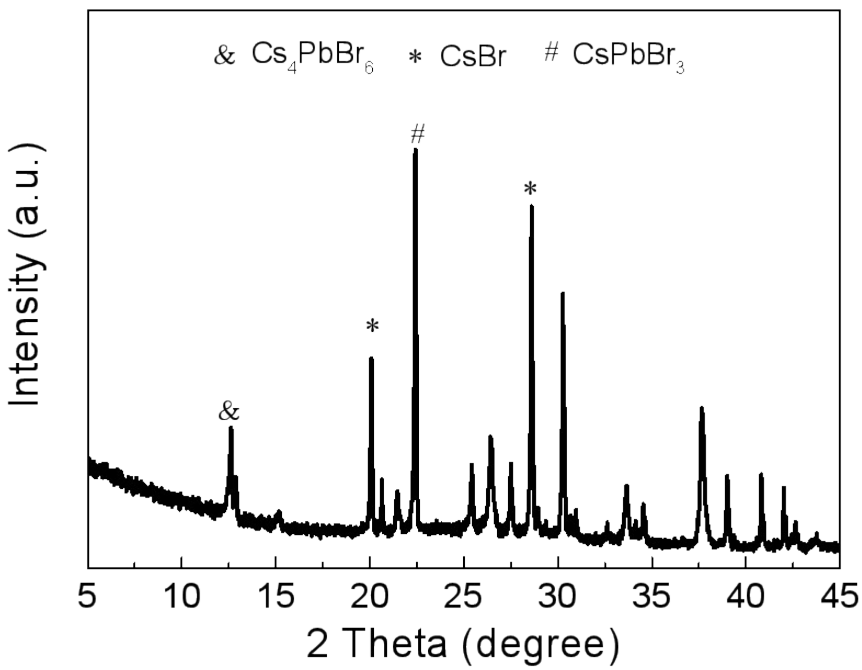


**Figure S9** The XRD curve of Cs-Pb-Br films prepared by using CsBr/(($H_2O$+EG+ethanol) solution with a concentration of 1.5 M in the first step.

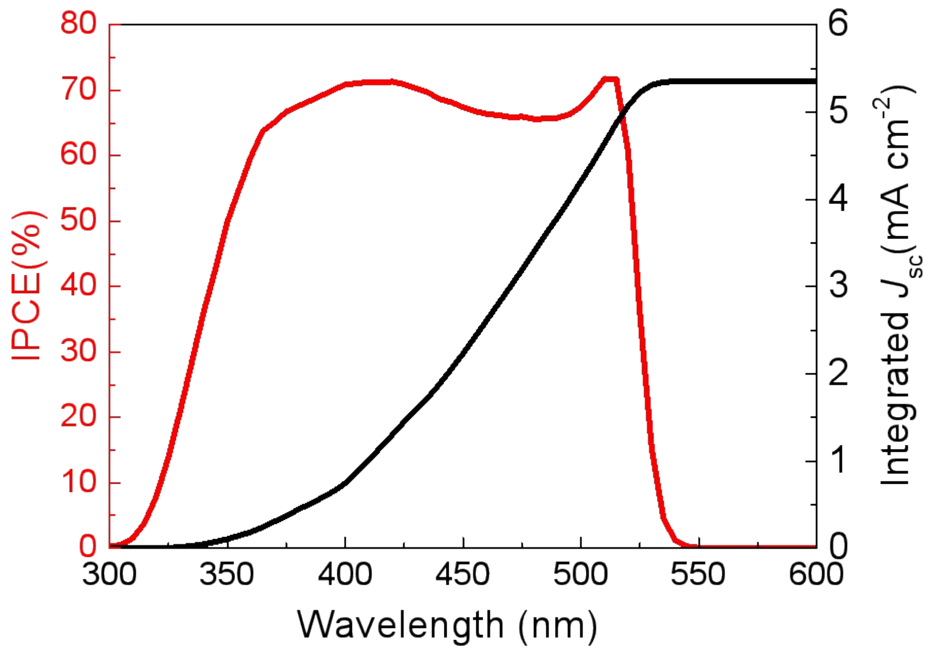


**Figure S10.** IPCE spectrum of the best PSC fabricated from the abnormal sequential deposition route using green solvents.

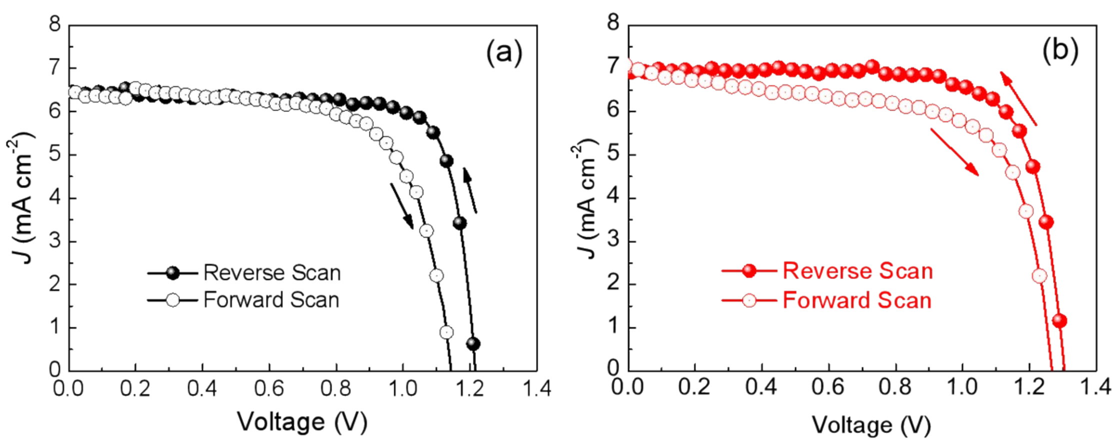


**Figure S11.** Hysteresis behavior the PSCs prepared by (a) traditional route using toxic solvents and (b) anomalous route using green solvents.

**Table S1.** The comparison of the parameters of solar cells basing on unmodified configuration of FTO/$TiO_2$/$CsPbBr_3$/Carbon and the solvent used for fabrication of $CsPbBr_3$ films in solar cells.

| $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF | PCE (%) | Solvents | Ref. |
|---|---|---|---|---|---|
| 5.30 | 1.20 | 0.640 | 3.90 | (DMF+DMSO)/Methanol | 1 |
| 6.46 | 1.34 | 0.680 | 5.86 | DMF/Methanol | 2 |
| 4.50 | 1.23 | 0.690 | 3.80 | DMF/Methanol | 3 |
| 7.75 | 1.44 | 0.735 | 8.19 | DMF/Methanol | 4 |
| 6.10 | 1.38 | 0.711 | 6.10 | DMF/Methanol | 5 |
| 6.89 | 1.37 | 0.768 | 7.25 | DMF/Methanol | 6 |
| 7.46 | 1.31 | 0.773 | 7.54 | DMF/Methanol | 7 |
| 6.13 | 1.34 | 0.732 | 6.01 | DMF/Methanol | 8 |
| 5.73 | 1.29 | 0.771 | 5.68 | DMF/Methanol | 9 |
| 6.86 | 1.44 | 0.786 | 7.76 | DMF/Methanol | 10 |
| 6.90 | 1.25 | 0.637 | 5.49 | DMF/Methanol | 11 |
| 6.72 | 1.41 | 0.771 | 7.28 | DMF/Methanol | 12 |
| 6.44 | 1.23 | 0.764 | 6.06 | DMF/Methanol | 13 |
| 6.11 | 1.21 | 0.740 | 5.47 | DMF/Methanol | 14 |
| 7.40 | 1.24 | 0.730 | 6.70 | DMF/Methanol | 15 |
| 7.14 | 0.98 | 0.719 | 5.04 | DMF/Methanol | 16 |
| 6.94 | 1.35 | 0.745 | 6.99 | DMF/Methanol | 17 |
| 6.75 | 1.41 | 0.776 | 7.39 | DMF/Methanol | 18 |
| 6.04 | 1.43 | 0.737 | 6.37 | DMF/Methanol | 19 |
| 5.87 | 1.40 | 0.738 | 6.07 | DMF/Methanol | 20 |
| 6.76 | 1.30 | 0.771 | 6.79 | DMF/Methanol | 21 |
| 5.88 | 1.47 | 0.715 | 6.17 | DMF/Methanol | 22 |
| 5.98 | 1.43 | 0.776 | 6.62 | DMF/Methanol | 23 |
| 7.07 | 1.29 | 0.590 | 5.38 | (DMF+DMSO)/Methanol | 24 |
| 6.75 | 1.44 | 0.687 | 6.68 | DMF/Methanol | 25 |
| 7.03 | 1.43 | 0.736 | 7.38 | DMF/Methanol | 26 |
| 7.27 | 1.29 | 0.730 | 6.85 | DMF/Methanol | 27 |
| 6.97 | 1.32 | 0.700 | 6.47 | DMF/Methanol | 28 |
| 7.12 | 1.49 | 0.688 | 7.29 | DMF/(2-methoxyethanol+IPA) | 29 |
| 5.81 | 1.31 | 0.743 | 5.66 | DMF/Methanol | 30 |
| 7.48 | 1.19 | 0.688 | 6.12 | DMF/$H_2O$ | 31 |
| 7.04 | 1.30 | 0.750 | 6.86 | ($H_2O$+Ethanol+EG)/TEP | This work |

**Table S2** The fitted parameters of the TRPL spectra of $CsPbBr_3$ films.

| Samples | $\tau_1$ (ns) | $A_1$ (%) | $\tau_2$ (ns) | $A_2$ (%) | $\tau_{ave}$ (ns) |
|---|---|---|---|---|---|
| Traditional/Toxic solvents | 0.87 | 33.14 | 2.27 | 66.86 | 2.04 |
| Anomalous/Green solvents | 1.71 | 33.38 | 3.74 | 66.62 | 3.36 |

# References


[1] Chang, X.; Li, W.;Zhu ,L.; Liu, H.; Geng, H.;Xiang, S.; Liu, J.;Chen, H. Carbon-based $CsPbBr_3$ perovskite solar cells: all-ambient processes and high thermal stability. *ACS Appl. Mater. Interfaces,* **2016,** 8, 33649− 33655.

[2] Teng, P.;Han, X.;Li, J.; Xu, Y.; Kang, L.; Wang, Y.;Yang, Y.;Yu, T. Elegant face-down liquid-space-restricted deposition of $CsPbBr_3$ films for efficient carbon-based all-inorganic planar perovskite solar cells. *ACS Appl. Mater. Interfaces,* **2018,** 10,9541−9546.

[3] Liu, Z.;Sun, B.;Liu, X.; Han, J.;Ye, H.; Shi, T.;Tang, Z.;Liao, G. Efficient carbon-Based $CsPbBr_3$ inorganic perovskite solar cells by using Cu-Phthalocyanine as hole transport material. *Nano-Micro Lett.,* **2018,** 10, 34.

[4] Poli, I.; Baker, J.;McGettrick, J.;Rossi, F. D.; Eslava, S. V.; Eslava,T.; Cameron, P. J. Screen printed carbon $CsPbBr_3$ solar cells with high open-circuit photovoltage. *J. Mater. Chem. A,* **2018,** 6, 18677-18686

[5] Ding, J.; Zhao, Y.; Duan, J.; He, B.;Tang, Q. Alloy-controlled work function for enhanced charge extraction in all-Inorganic $CsPbBr_3$ perovskite solar cells. *ChemSusChem ,***2018,** 11, 1432–1437.

[6] Zhao, Y.;Wang, Y.; Duan, J.; Yang, X.; Tang, Q. Divalent hard Lewis acids doped $CsPbBr_3$ films for 9.63%-efficiency and ultra-stable all-inorganic perovskite solar cells. *J. Mater. Chem. A,* **2019,** 7, 6877-6882.

[7] Duan, J.;Zhao, Y.;He, B.;Tang, Q. High-purity inorganic perovskite films for solar cells with 9.72% efficiency. *Angew. Chem. Int. Ed.,* **2018,** 130,3849–3853.

[8] Ding, J.; Duan, J.; Guo, C.; Tang, Q.; Toward charge extraction in all-inorganic perovskite solar cells by interfacial engineering. *J. Mater. Chem. A,* **2018,** 6, 21999-22004.

[9] Duan, J.; Dou, D.; Zhao, Y.; Wang, Y.; Yang, X.; Yuan, H.; He, B.; Tang, Q. Spray-assisted deposition of $CsPbBr_3$ films in ambient air for large-area inorganic perovskite solar cells. *Materials Today Energy,* **2018,** 10,146-152.

[10] Duan, J.; Hu, T.; Zhao, Y.; He, B.;Tang, Q. Carbon electrode tailored all-inorganic perovskite solar cells to harvest solar and water-stream energies. *Angew. Chem. Int. Ed.,* **2018,** 57, 5746-5749.

[11] Xu, H.; Duan, J.; Zhao, Y.; Jiao, Z.; He, B.; Tang, Q. 9.13%-efficiency and stable inorganic $CsPbBr_3$ solar cells lead-free $CsSnBr_{3-x}I_x$ quantum dots promote charge extraction. *J. Power Sources,* **2018,** 399, 76–82.

[12] Li, Y.; Duan, J.; Yuan, H.; Zhao,Y.;He, B.;Tang, Q. Lattice modulation of alkali metal cations doped $Cs_{1-x}R_xPbBr_3$ halides for inorganic perovskite solar cells. *Sol. RRL,* **2018,** 1800164.

[13] Yuan, H.; Zhao, Y.; Duan, J.; He, B.; Jiao, Z.; Tang ,Q. Enhanced charge extraction by setting intermediate energy levels in all-inorganic $CsPbBr_3$ perovskite solar cells. *Electrochim. Acta,* **2018,** 279, 84-90

[14] Kulbak, M.; Cahen, D.; Hodes, G.; How Important is the Organic part of lead halide perovskite photovoltaic cells? Efficient $CsPbBr_3$ Cells. *J. Phys. Chem. Lett.,* **2015,** 6, 2452−2456.

[15] Liang, J.; Wang, C.; Wang, Y.; Xu, Z.; Lu, Z.; Ma, Y.; Zhu, H.; Hu, Y.; Xiao, C.; Yi, X.; Zhu, G.; Lv, H.; Ma, L.; Chen, T.; Tie, Z.; Jin, Z.; Liu, J. All-inorganic perovskite solar cells. *J. Am. Chem. Soc.,* **2016,** 138, 4915829-15832.

[16] Li, B.; Zhang, Y.; Zhang, L.; Yin, L. $PbCl_2$-tuned inorganic cubic $CsPbBr_3$(Cl) perovskite solar cells with enhanced electron lifetime, diffusion length and photovoltaic performance. *J. Power Sources,* **2017,** 360, 11-20.

[17] Duan, J.; Zhao, Y.;Yang, X.; Wang, Y.; He, B.;Tang, Q. Lanthanide ions doped $CsPbBr_3$ halides for HTM-free 10.14%-efficiency inorganic perovskite solar cell with an ultrahigh open-circuit voltage of 1.594 V. *Adv. Energy Mater.,* **2018,** 1802346.

[18] Duan, J.;Zhao, Y.;Wang, Y.; Yang, X.; Tang Q. Hole-Boosted Cu(Cr,M)$O_2$ nanocrystals for all-inorganic $CsPbBr_3$ perovskite solar cells. *Angew. Chem. Int. Ed.,* **2019,** 58, 1-6.

[19] Tang, M.; He, B.; Dou, D.; Liu, Y.; Duan, J.;Zhao, Y.; Chen, H.;Tang, Q.; Toward effi cient and air-stable carbon-based all-inorganic perovskite solar cells through substituting $CsPbBr_3$ films with transition metal ions. *Chem. Eng. J.,* **2019,** 375, 121930.

[20] Zhu, J., He, B.; Gong, Z.; Ding, Y.; Zhang, W.; Li, X. Zong, Z.; Chen, H.; Tang, Q. Grain enlargement and defect passivation with melamine additive for high efficiency and stable $CsPbBr_3$ perovskite solar cells. *ChemSusChem*, **2020,** 13,1834-1843.

[21] Wang, D.; Li, W.; Du, Z.; Li, G.; Sun,W.; Wu, J.; Lan Z. $CoBr_2$-doping-induced efficiency improvement of $CsPbBr_3$ planar perovskite solar cells. *J. Mater. Chem. C,* **2020,** 8, 1649-1655.

[22] Bu, F.; He, B.; Ding, Y.; Li, X.; Sun, X.; Duan, J.; Zhao, Y.; Chen, H.; Tang, Q. Enhanced energy level alignment and hole extraction of carbon electrode for air-stable hole-transporting material-free $CsPbBr_3$ perovskite solar cells. *Sol. Energy Mater. Sol. Cells,* **2020,** 205, 110267.

[23] Ding,Y.; He, B.; Zhu, J.; Zhang,W.; Su, G.; Duan, J.; Zhao,Y.; Chen, H.; Tang, Q.; Advanced modification of perovskite surfaces for defect passivation and efficient charge extraction in air-stable $CsPbBr_3$ perovskite solar cells. *ACS Sustainable Chem. Eng.* **2019,** 7, 23, 19286–19294.

[24] Liu, J.; Zhu, L.; Xiang, S.; Wei, Y.; Xie, M.; Liu, H.; Li, W.; Chen H. Growing high-quality $CsPbBr_3$ by using porous$CsPb_2Br_5$ as an intermediate: a promising light absorber in carbon-based perovskite solar cells. *Sustainable Energy Fuels,* **2019,** 3,184-194.

[25] Zong, Z.; He, B.; Zhu, J.; Ding, Y.; Zhang, W.; Duan, J.; Zhao, Y.; Chen, H.; Tang, Q. Boosted hole extraction in all-inorganic $CsPbBr_3$ perovskite solar cells by interface engineering using $MoO_2$/N-doped carbon nanospheres composite. *Sol. Energy Mater. Sol. Cells,* **2020,** 209, 110460

[26] Duan,, J.; Wang, Y.; Yang, X.; Tang, Q. Alkyl Chain regulated charge transfer in fluorescent inorganic $CsPbBr_3$ perovskite solar cells. *Angew. Chem. Int. Ed.,* **2020,** 59, 4391-4395.

[27] Guo, H.; Pei, Y.; Zhang, J.; Cai, C.; Zhou, K.; Zhu, Y. Doping with $SnBr_2$ in $CsPbBr_3$ to enhance the efficiency of all-inorganic perovskite solar cells. *J. Mater. Chem. C,* **2019,** 7, 11234-11243.

[28] Pei, Y.; Guo, H.; Hu, Z.; Zhang, J.; Zhu, Y. $BiBr_3$ as an additive in $CsPbBr_3$ for carbon-based all-inorganic perovskite solar cell. *J. Alloys. Compd*. **2020,** 835, 155283.

[29] Meng, Q.; Feng, J.; Huang, H.; Han, X., Zhu, Z.; Yu, T.; Li, Z.; Zou, Z. Simultaneous optimization of phase and morphology of $CsPbBr_3$ films via controllable Ostwald ripening by ethylene glycol monomethylether/isopropanol bi-solvent engineering. *Adv. Eng. Mater.,* **2020,** 22, 2000162.

[30] Karunakaran, S. K.; Arumugam, G. M.; Yang, W.; Ge, S.; Khan, S. N.; Mai, Y.; Lin, X.; Yang, G. Europium (II)-doped all-Inorganic $CsPbBr_3$ perovskite solar cells with carbon electrodes. *Sol. RRL,* **2020,** DOI:10.1002/solr.202000390.

[31] Cao, X.; Zhang, G.; Jiang, L.; Cai, Y.; Gao, Y.; Yang, W.; He, X.; Zeng, Q.; Xing, G.; Jia, Y.; Wei, J. Water, a green solvent for fabrication of high-quality $CsPbBr_3$ films for efficient solar cells. *ACS Appl. Mater. Interfaces,* **2020,** 12, 5925−5931.