

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

Ultra-stable 2D Layered Methylammonium Cadmium Trihalide Perovskite Photoelectrodes

Hsien-Yi Hsu, Li Ji, Chengxi Zhang, Chun Hong Mak, Rugeng Liu, Tie Wang, Xingli Zou, Shao-Yuan Leu and Edward T. Yu

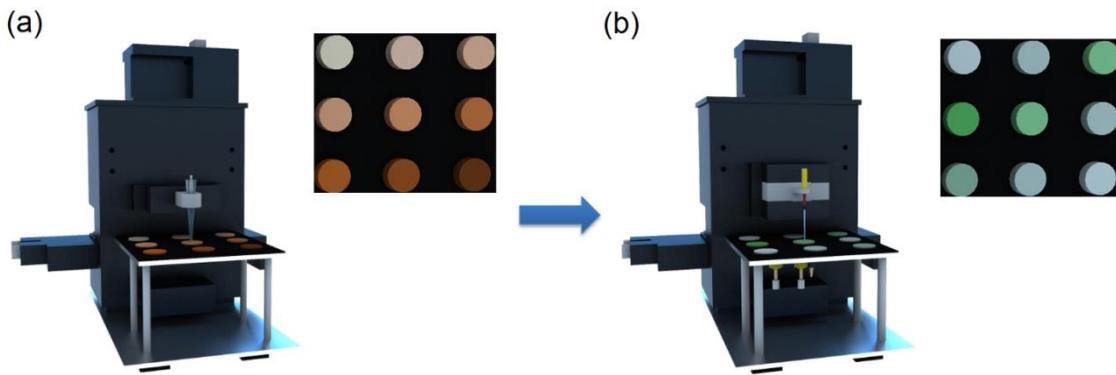


Figure S1. Scanning electrochemical microscopy (SECM) system. (a) Fabrication of perovskite spot array with different compositions using a piezoelectric dispenser (b) Screening analysis on perovskite photoelectrode arrays by SECM.

Table S1. Crystal data and structure refinement for MACdI_3 .

Empirical Formula	$\text{CH}_6\text{CdI}_3\text{N}$
Molecular Formula	MACdI_3
FW	525.17
T(K)	293
Lattice	Monoclinic
Space group	$P21/n$
$a(\text{\AA})$	9.05
$b(\text{\AA})$	7.048
$c(\text{\AA})$	14.74
$\alpha(^{\circ})$	90
$\beta(^{\circ})$	90.23
$\gamma(^{\circ})$	90
$V(\text{\AA}^3)$	940
Z	4
$d_{\text{calc}} (\text{g/cm}^3)$	1.855

$\mu(\text{mm}^{-1})$	6.042
-----------------------	-------

Table S2. Crystal data and structure refinement for $(\text{MA})_2\text{CdI}_4$.

Empirical Formula	$\text{CH}_6\text{CdCl}_3\text{N}$
Molecular Formula	$(\text{MA})_2\text{CdI}_4$
FW	250.82
T(K)	293
Lattice	Orthorhombic
Space group	<i>Cmca</i>
<i>a</i> (\AA)	7.391
<i>b</i> (\AA)	19.636
<i>c</i> (\AA)	7.5139
$\alpha(^{\circ})$	90
$\beta(^{\circ})$	90
$\gamma(^{\circ})$	90
<i>V</i> (\AA^3)	1090.5
<i>Z</i>	1
d_{calc} (g/cm ³)	4.583
$\mu(\text{mm}^{-1})$	7.977

Table S3. Crystal data and structure refinement for $\text{MACd}_3\text{Cl}_7 \cdot 3\text{H}_2\text{O}$.

Empirical Formula	$\text{CH}_6\text{Cd}_3\text{Cl}_9\text{NO}$
Molecular Formula	$\text{MACd}_3\text{Cl}_7 \cdot 3\text{H}_2\text{O}$
FW	704.32
T(K)	296
Lattice	Monoclinic
Space group	<i>P21/m</i>
<i>a</i> (\AA)	6.7315
<i>b</i> (\AA)	15.9916
<i>c</i> (\AA)	6.9266
$\alpha(^{\circ})$	90
$\beta(^{\circ})$	90.922
$\gamma(^{\circ})$	90
<i>V</i> (\AA^3)	745.534
<i>Z</i>	2
d_{calc} (g/cm ³)	3.137
$\mu(\text{mm}^{-1})$	5.824

Table S4. Photoluminescence decay times (τ_s and τ_{PL}) and corresponding parameters of Cd-based hybrid materials, CD-1, CD-2, CD-3 and CD-4.

Materials	$\tau_1/\text{ns} (\alpha_1)$	$\tau_2/\text{ns} (\alpha_2)$	$\tau_{PL}^{\text{a})}/\text{ns}$	R^2
CD-1	0.12 (95%)	1.68 (5%)	0.20 ± 0.02	0.99
CD-2	0.21 (87%)	1.70 (13%)	0.40 ± 0.03	0.98
CD-3	0.37 (72%)	1.75 (28%)	0.76 ± 0.01	1.00
CD-4	0.63 (69%)	3.45 (31%)	1.50 ± 0.02	0.99
CD-4, Day 60	0.32 (15%)	0.92 (85%)	0.83 ± 0.01	1.00

a) $\tau_{PL} = \langle \tau \rangle = \sum_i \alpha_i \tau_i$.

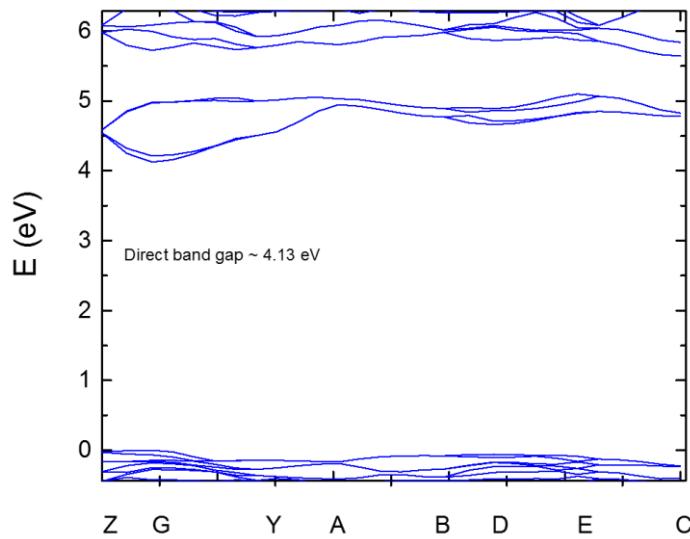


Figure S2. Band structures of MACdI_3 calculated by density functional theory.

Table S5. Long-term stability test for hybrid perovskite materials.

Materials	Time (h)	Testing condition				Remaining Photocurrent	Ref.
		Light/Dark	Temp. (°C)	Atmosphere (RH %)	Sealing		
$(\text{MA})_2\text{CdCl}_4$	1440	Light	RT	Air(50)	No	>80%	This work
MAPbI ₃	230	Light	RT	Air(50)	No	>80 %	This work
$(\text{FAI})_{0.81}(\text{PbI}_2)_{0.85}(\text{MABr})_{0.15}(\text{PbBr}_2)_{0.15}$	1080	Dark	RT	Air(40)	No	~80%	1
MAPbI ₂ Br	50	Dark	RT	Air	No	~80%	2
MAPbI _{3-x} Cl _x (PVK)	55	Light	RT	Air(40~50)	No	~80%	3
MAPbI ₃	960	Dark	RT	N ₂	No	~80%	4
MAPbI _{3-x} Cl _x	1000	Light	40	N ₂	Yes	~80 %	5
MAPbI ₃	216	Dark	RT	Air(50)	No	~80%	6
MAPbI ₃	70	Light	RT	Air(45~50)	No	~70%	7
MAPbI ₃	130	Dark	RT	Air	No	~80%	8
CsPbI ₂ Br	30	Dark	RT	Air(20)	No	~80%	9
$\text{Cs}_{0.925}\text{K}_{0.075}\text{PbI}_2\text{Br}$	125	Dark	RT	Air(20)	No	~80%	9
CsSnI ₃	336	Dark	RT	Air	No	~80%	10
FAPbI ₃	360	Dark	RT	Desiccator(15)	No	~70%	11
CsPbI ₂ Br	990	Dark	RT	Glovebox	No	~80%	12
$(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}(\text{LiTFSI})$	710	Dark	RT	Air(30)	No	~80%	13

Reference

1. Zhang, F. et al. Isomer - Pure Bis - PCBM - Assisted Crystal Engineering of Perovskite Solar Cells Showing Excellent Efficiency and Stability. *Advanced Materials* **29** (2017).
2. Zhang, M. et al. Stable and Low - Cost Mesoscopic CH₃NH₃PbI₂Br Perovskite Solar Cells by using a Thin Poly (3 - hexylthiophene) Layer as a Hole Transporter. *Chemistry-A European Journal* **21**, 434-439 (2015).
3. Huang, L. et al. Efficient and stable planar perovskite solar cells with a non-hygroscopic small molecule oxidant doped hole transport layer. *Electrochimica Acta* **196**, 328-336 (2016).
4. Gujar, T.P. & Thelakkat, M. Highly Reproducible and Efficient Perovskite Solar Cells with Extraordinary Stability from Robust CH₃NH₃PbI₃: Towards Large - Area Devices. *Energy Technology* **4**, 449-457 (2016).
5. Leijtens, T. et al. Overcoming ultraviolet light instability of sensitized TiO₂ with meso-superstructured organometal tri-halide perovskite solar cells. *Nature communications* **4**, 2885 (2013).
6. Christians, J.A., Miranda Herrera, P.A. & Kamat, P.V. Transformation of the excited state and photovoltaic efficiency of CH₃NH₃PbI₃ perovskite upon controlled exposure to humidified air. *Journal of the American Chemical Society* **137**, 1530-1538 (2015).
7. Li, Y. et al. Multifunctional fullerene derivative for interface engineering in perovskite solar cells. *Journal of the American Chemical Society* **137**, 15540-15547 (2015).
8. Kim, J.H. et al. High - Performance and Environmentally Stable Planar Heterojunction Perovskite Solar Cells Based on a Solution - Processed Copper - Doped Nickel Oxide Hole - Transporting Layer. *Advanced Materials* **27**, 695-701 (2015).
9. Nam, J.K. et al. Potassium incorporation for enhanced performance and stability of fully inorganic cesium lead halide perovskite solar cells. *Nano letters* **17**, 2028-2033 (2017).
10. Yi, C. et al. Entropic stabilization of mixed A-cation ABX₃ metal halide perovskites for high performance perovskite solar cells. *Energy & Environmental Science* **9**, 656-662 (2016).
11. Li, Z. et al. Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys. *Chemistry of Materials* **28**, 284-292 (2015).
12. Zeng, Q. et al. Polymer - Passivated Inorganic Cesium Lead Mixed - Halide Perovskites for Stable and Efficient Solar Cells with High Open - Circuit Voltage over 1.3 V. *Advanced Materials* (2018).
13. Qu, J. et al. Improved performance and air stability of perovskite solar cells based on low-cost organic hole-transporting material X60 by incorporating its dicationic salt. *Science China Chemistry* **61**, 172-179 (2018).