Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Improving the Stability and Efficiency of Polymer-based Selenium Solar Cells through the Usage of Tin (IV) oxide as Electron Transport Layers and the Analysis of Aging Dynamics

Wenbo Liu,[a,b] Fei Yu, [a] Weijun Fan [b,*] and Qichun Zhang [a,c*]

[a]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798. Email: qczhang@ntu.edu.sg.
[b]School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798. Email: ewjfan@ntu.edu.sg
[c]Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong SAR, China. Email: qiczhang@cityu.edu.hk

Experimental section

ITO covered glasses were purchased from Shenzhen Huyu Union technology. SnO_2 aqueous colloid were purchased from Alfa Aesar. PTAA was purchased from Xian Bolaite. Selenium, P3HT, 1,2-Dichlorobenzene (DCB, 99%, anhydrous), and Ag were purchased from Sigma Aldrich.

The ITO-coated glass substrates were cleaned successively with Decon 90(detergent) diluted solution, deionized water, acetone, isopropanol and ethanol in an ultrasonic bath for 20 min, respectively, and dried with nitrogen gas purge. An electron transport layer of SnO_2 was spin coated onto cleaned ITO transparent glass substrates at 6000 rpm for 60 s in ambient condition and annealed at 150 °C for 30 min. After that, 0.5nm Te layer and Se layer with different thickness were deposited on the PEDOT:PSS substrate and annealed at glove box with a slow crystallization process (10 °C/min). PTAA or P3HT in DCB solution with different concentration was spun at 2000 rpm for 60 s and immediately heat-treated at 80 °C for 10 min. Finally, about 100nm silver was deposited onto the surface of HTL by high temperature vacuum evaporation.

Table S1. Summary of SSCs with different organic HTLs

Publication date ref.	Structure of SSCs	PCE(%)	Stability Performance
2014[1]	FTO/compact-TiO_2/mp-TiO_2/Se(thermal evaporation)/ P3HT/PEDOT:PSS/Ag	2.63	N/A
2014[1]	FTO/compact-TiO_2/mp-TiO_2/Se(thermal evaporation)/ Spiro-OMeTAD/PEDOT:PSS/Ag	1.83	N/A
2016[2]	FTO/bl-TiO_2, mp-TiO_2/Se(spin-coating)/PTAA/Au	3.55	Maintaining 90% of efficiency after 720 hours
2018[3]	FTO/TiO_2/Se(spin-coating)//Spiro-OMeTAD/Au	1.23	Maintaining 90% of efficiency after 720 hours
2018[3]	FTO/TiO_2/Se(spin-coating)/P3HT/Au	1.08	Maintaining 90% of efficiency after 1440 hours
2018[3]	FTO/TiO_2/Se(spin-coating)/PTAA/Au	0.62	Maintaining 50% of efficiency after 720 hours
This work	ITO/SnO_2/Se(thermal evaporation)/P3HT/Ag	3.7	Maintaining 92% of efficiency after 1512 hours

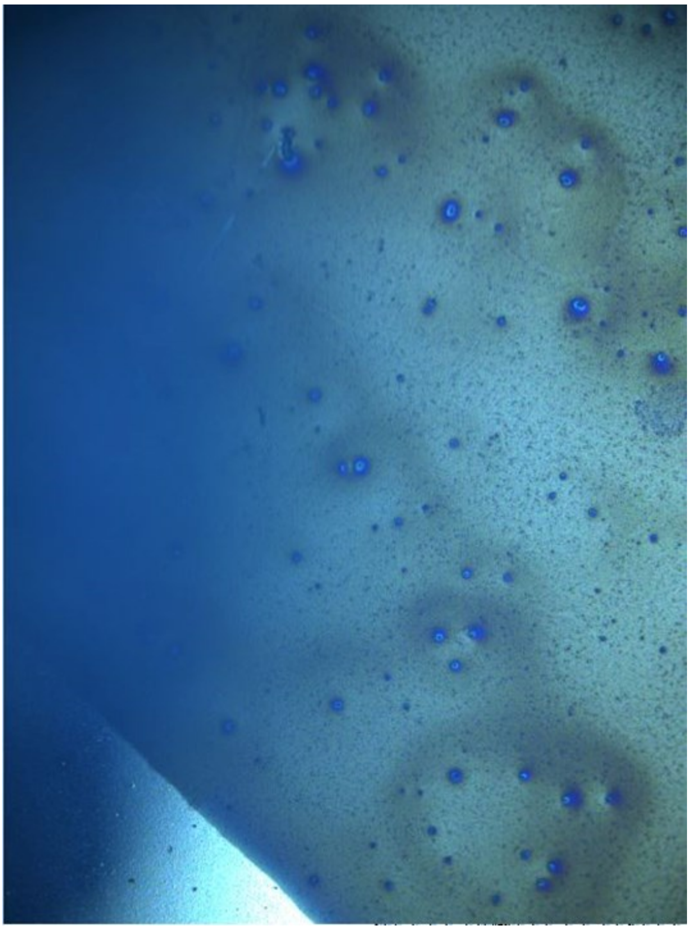

Figure S1. The rough surface of PTAA layer on the Glass/ITO/SnO_2/Te/Se substrate.

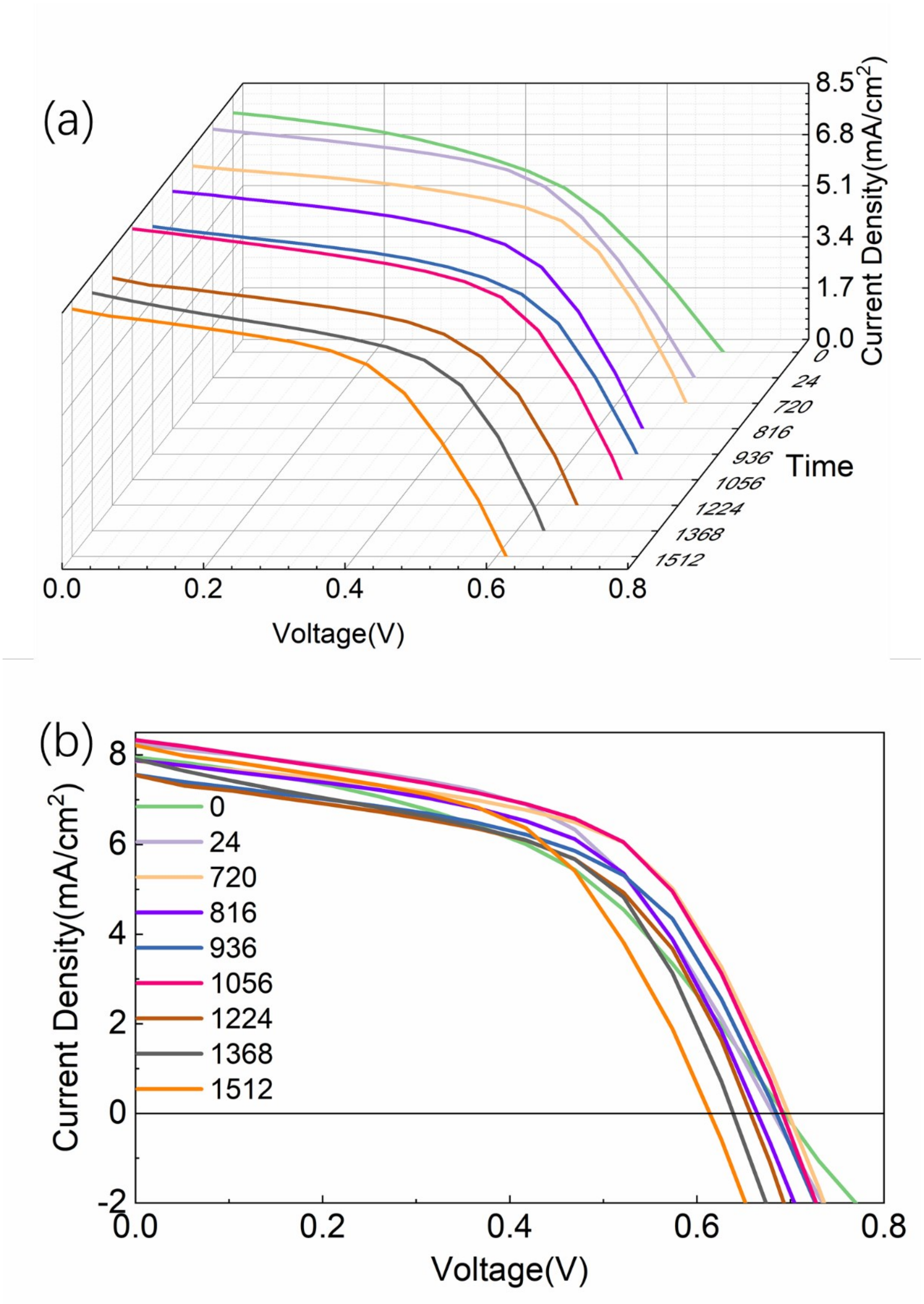

Figure S2 C-V curve of SSCs changing with time in 3D(a) and 2D(b).

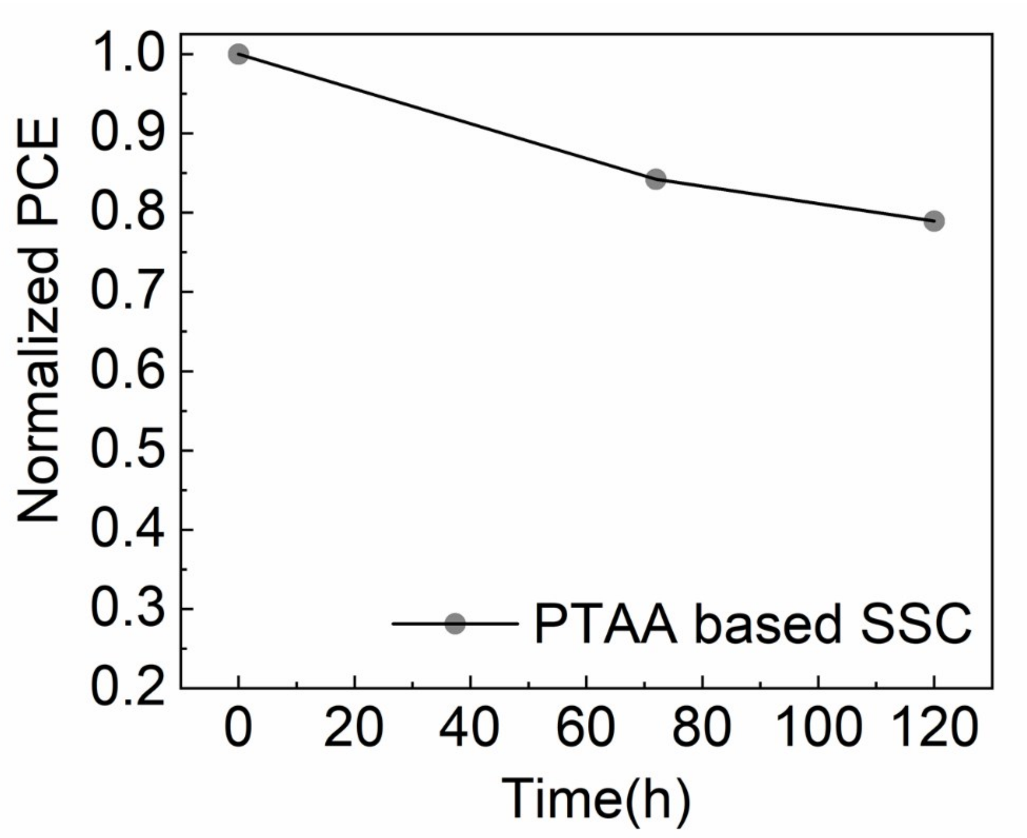

Figure S3. Stability performance of PTAA based SSCs.

Table S2. EIS fitted data

	R1(Ω)	**R2(Ω)**	**CPE1-t(ohm^{-1}s^{n})**	**CPE1-p**
P3HT	28.64	2693	3.532 × E-9	0.969
P3HT (days)	31.70	1219	1.147 × E-8	0.889
PTAA	41.77	126	6.607 × E-10	1.099

Table S3 Comparison of lattice constant of ETLs used in other works and crystal stress releasing time. Form this table, we could find out that, the larger the difference between lattice constant a and b of Se and ZnMgO, the longer it needs to release the stress. Here, we only compared the SSCs with thermal evaporated Se active layer. The reason for SSC with SnO_2 as ETLs showing more ambiguous releasing time is that there are other degrading factors such as diffusion of metal anode existing in the SSCs.

ETL/Se used in the SSCs	Lattice constant (Å)	Days of stress releasing (days)
ZnMgO	a=b=3.25-3.26 c=5.16-5.20[4]	~150[5]
CdSe	a=b=4.30 c=7.01[6]	~40[7]
SnO_2	a=b=4.72 c=3.17[8]	~39-44 (this work)
Se	a=b=9.05, c=11.60[9]	

Reference

[1] K. Wang, Y. Shi, H. Zhang, Y. Xing, Q. Dong and T. Ma, *Phys. Chem. Chem. Phys*., 2014, **16**, 23316–23319.

[2] M. Zhu, F.Hao, L.Ma, T.-B. Song, C. E. Miller, M. R. Wasielewski, X. Li and M. G. Kanatzidis, *ACS Energy Lett*., 2016, **1**, 469–473.

[3] M. Zhu, Y. Deng, W. Liu, and X. Li, *Chin. Phys. B*, 2018, **27**, 015202.

[4] T. A. Wassner, B. Laumer, S. Maier, A. Laufer, B. K. Meyer, M. Stutzmann, and M. Eickhoff, *J. Appl. Phys.* 2009, **105**, 023505.

[5] T. K. Todorov, S. Singh, D. M. Bishop, O. Gunawan, Y. S. Lee, T. S. Gershon, K. W. Brew, P. D. Antunez and R. Haight, *Nat. Commun.*, 2017, **8**, 682–690.

[6] K. Sarmah, R. Sarma, H. L. Das, *Chalcogenide Lett.*, 2008, **5**, 153 – 163.

[7] H. Ito, M. Oka, T. Ogino, A. Takeda and Y. Mizushima, *Jpn. J. Appl. Phys.*, 1984, **21**, 77–81.

[8] A. Rahal, A. Benhaoua, M. Jlassi, B. Benhaoua, *Superlattices and Microstructures*, 2015, *86,* 403–411.