Supplementary Information

Flexible Solvent-free Supercapacitors with High Energy Density Enabled by Electrical-ionic Hybrid Polymer Nanocomposites

Cheng Chi [a], Yang Li [a], Dezhao Li [b], He Huang [a], Qi Wang [a], Yuewang Yang [a], and Baoling Huang [a*]

[a]Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

[b]Collaborative Innovation Center for Bio-Med Physics Information Technology, College of Science, Zhejiang University of Technology, Hangzhou 310023, China.

[*]Corresponding author: *B. L. Huang*, Tel.: 00852 2358-7181, email: mebhuang@ust.hk

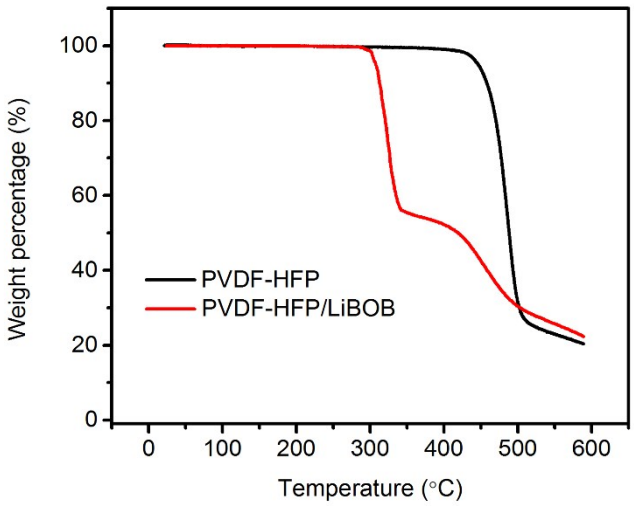

Figure S1. TGA curves of PVDF-HFP and PVDF-HFP/LiBOB (1: 1, wt/wt) PSE.

The control experiments to study the effect of the weight ratios of GO/CNT on the performance of the device. We tested GO: CNT weight ratios of 1:4, 1:1, and 4:1 composite electrodes and found that the GO: CNT weight ratio of 1:4 led to the highest performance of 170 F g^{-1}, as shown in **Figure S2.** Thus, the GO: CNT weight ratio of 1:4 was chosen for the study to further enhance the performance.

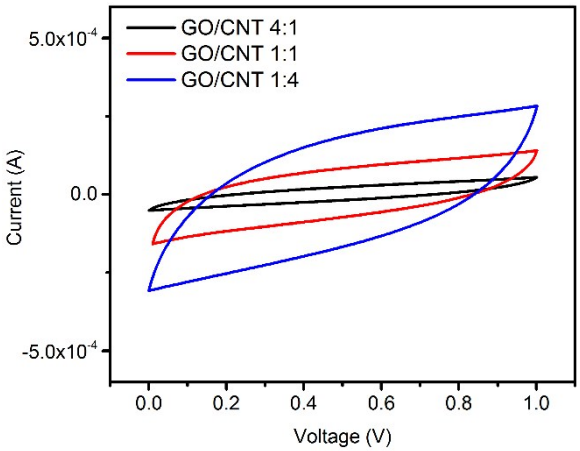

Figure S2. CV curves of GO/CNT supercapacitors with different GO/CNT weight ratios in PSE electrolyte at a scan rate of 20 mV s^{-1}.

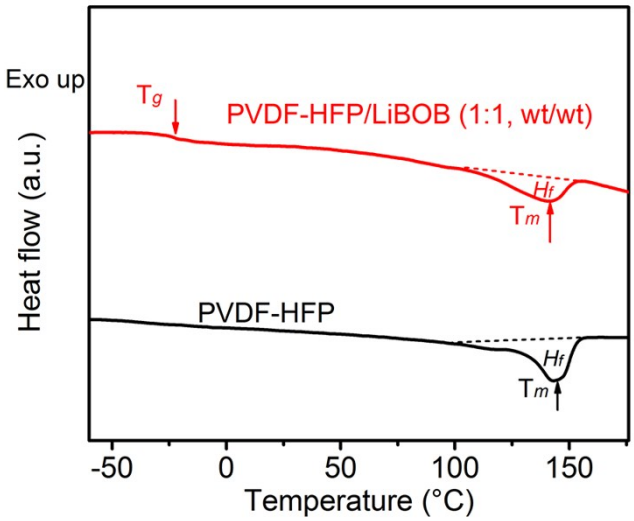

Figure S3. DSC curves of LiBOB powder, PVDF-HFP and PVDF-HFP/LiBOB (1: 1, wt/wt) PSE.

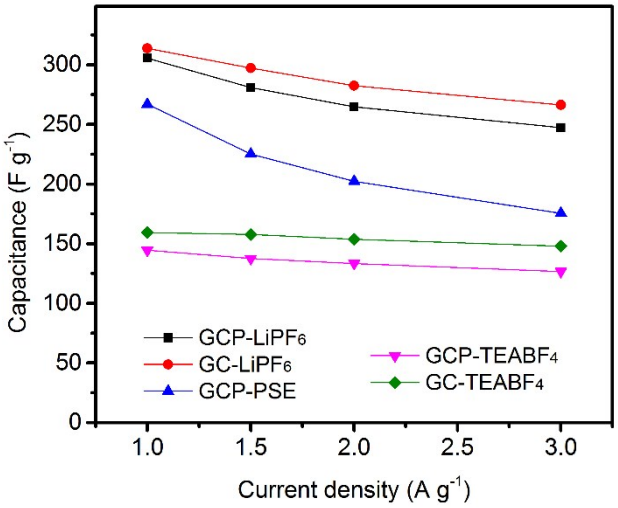

Figure S4. Specific capacitances of GCP-PSE, GCP-$TEABF_4$, GCP-$LiPF_6$, GC-$TEABF_4$, GC-$LiPF_6$ supercapacitors versus current densities

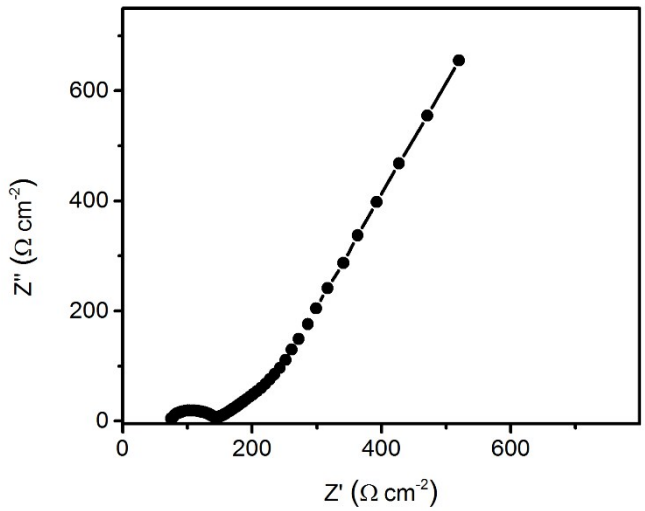

Figure S5. Nyquist impedance plots of all-solid-state SPs with GO/CNT/PSE without lamination process.

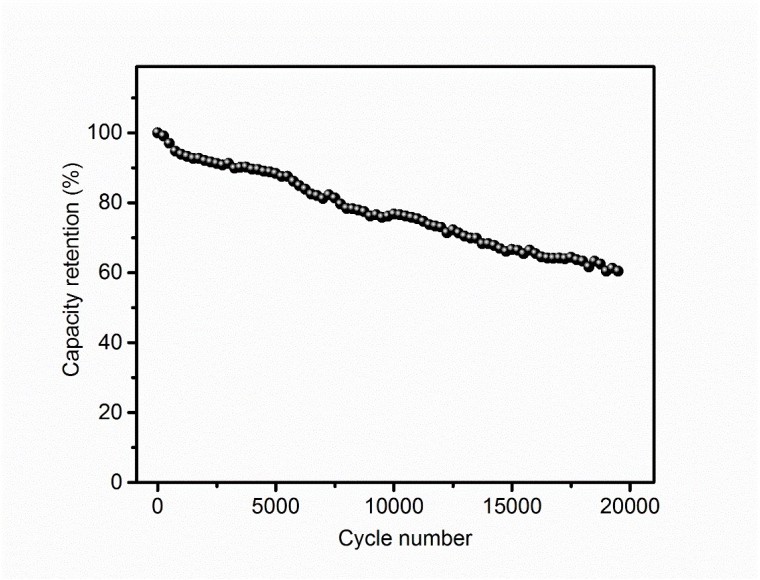

Figure S6. Long-term cycling performance (20000 cycles) of GO/CNT-SPs at 2 A g^{-1}.

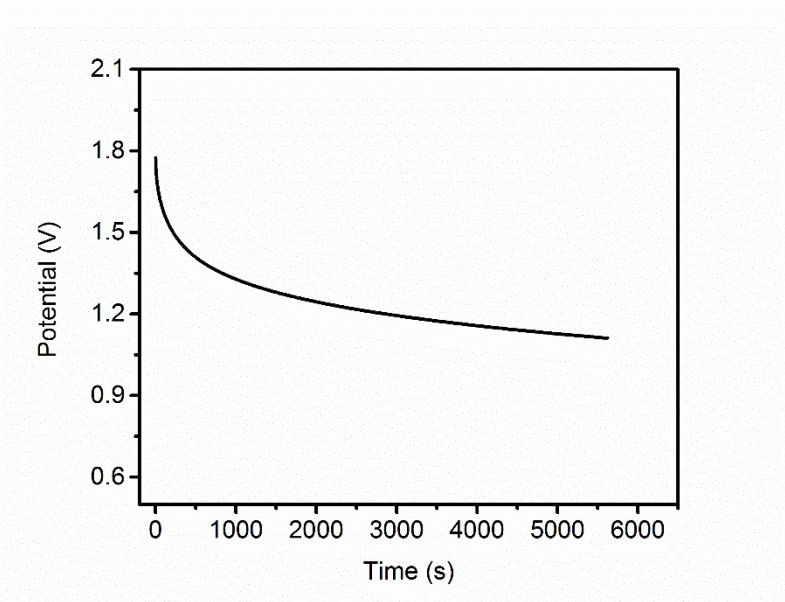

Figure S7. Self-discharge curve of the GO/CNT/PSE-SPs after charging at 1.8 V.

Table S1. Electrochemical performance comparison of solvent-free GO/CNT/PSE SP with reported solid or gel SPs and pseudocapacitors.

Electrode	Type	Electrolyte	Voltage window (v)	C_s (F g^{-1})	E_{device} (Wh kg^{-1})	P_{device} (W kg^{-1})	Cycling number (%)	*Ref.*
SWCNTs	EDLC	PVA-H_3PO_4	1.0	120 @ 1 A g^{-1}	6	70000	/	1
3D-graphene	EDLC	PVA-H_2SO_4	1.0	260 @ 5 mV s^{-1}	8.8	178.5	10,000	2
AC	EDLC	PMMA/$LiClO_4$-PC	2.5	111 @ 0.25 A g^{-1}	6.51	3225	9000 (81%)	3
AC	EDLC	PAEK-g-PEG-$LiClO_4$	1.5	118.6 @ 1.0 A g^{-1}	7.87	98.97	5000 /	4
AC	EDLC	PAEK-PEG/$LiClO_4$	1.5	92.8 @ 0.1 A g^{-1}	5.72	~9.0	2000 (~100%)	5
GO/CNT	EDLC	1M H_2SO_4	0.7	251 @ 5mV^{-1}	/	/	/	6
AC	EDLC	KOH-saturated mCel-membrane	1.0	110 @ 1.0 A g^{-1}	4.37	249	10000 (84.7%)	7
PEDOT:PSS / MWCNT	EDLC &pseudo-	PVA/KOH gel	1.0	380 @ 0.25 A g^{-1}	13.2	126	2000 (95%)	8
rGO/CNT//CFP/PPy	pseudo-	PAAK/KCl	1.6	82.4 @ 0.5 A g^{-1}	28.6	395	2000 (93%)	9
AC /MCNTs	EDLC	PAN-b-PEG-b-PAN-DMF-$LiClO_4$	2.1	101 @ 0.125 A g^{-1}	11.5	10000	30000	10
GO/CNT/PSE (30 µm)	EDLC	**PVDF-HFP/LiBOB**	**1.8**	**267 @ 1 A g^{-1}**	**30**	**430**	**20,000 (88%) @ 2A g^{-1}**	**This work**

AC: Activated carbon; rGO: reduced graphene oxide; PEDOT: poly(3,4-ethylenedioxythiophene); PSS: poly(styrene sulfonate); CFP: carbon fiber paper, PPy: polypyrrole.

Table S2. Electrochemical performance comparison of solvent-free GO/CNT/PSE SP with reported solid or gel SPs and pseudocapacitors.

Electrode	**Type**	**Electrolyte**	**Test condition**	C_{aeral} **(mF cm^{-2})**	C_{vol} **(F cm^{-3})**	$E_{v,device}$ **(mWh cm^{-3})**	$P_{v,device}$ **(W cm^{-3})**	***Ref.***
MoS_2/rGO/MWCNT	EDLC& pseudo-	PVA-H_2SO_4	0.8V @ 0.5 A cm^{-3}	/	4.8 (single electrode)	/	/	11
MnO_2/rGO/SWCNT	EDLC& pseudo-	PVA-H_2SO_4	0.8V @50 mV s^{-1}	4.28	11.4 (single electrode)	0.21	1.32	12
ZnO/MnO_2	pseudo-	PVA/LiCl	0.8V@ 0.5 mA cm^{-2}	26	0.325 (two electrodes)	0.04	0.002	13
Graphene	EDLC	PVA-H_2SO_4	1.0V@ 10 mV s^{-1}	0.087	17.9 (two electrodes)	2.5	0.495	14
PEDOT-cellulose	pseudo-	PVA-H_2SO_4	1.2V@ 0.5A cm^{-3}	/	145 (single electrode)	28 (single electrode)	/	15
RGO/CNT	EDLC	PVA-H_3PO_4	0.8V@ 0.1A cm^{-2}	177	158 (single electrode)	3.5	0.018	16
TiN-Fe_2N	pseudo-	PVA-LiCl	0.8V@ 2 A g^{-1}	60 F g^{-1}	/	0.61	0.05	17
EGMX 1:3	quasi-EDLC	PVA-H_3PO_4	0.8V @ 0.1 A cm^{-3}	/	216 (single electrode)	4.8	0.04	18
Graphite/polyaniline	EDLC& pseudo-	PVA-H_2SO_4	0.8V @ 0.5 mA cm^{-2}	355.6	3.55 (single electrode)	0.32	0.054	19
Carbon/MnO_2	EDLC	PVA-H_3PO_4	0.8V @ 0.02 A cm^{-3}	/	2.5 (single electrode)	0.22	0.08	20
MnO_2−FP/AC−FP	EDLC& pseudo-	PVA/Na_2SO_4	2.5V @ 10mVs^{-1}	/	1.76 (single electrode)	0.78	0.05	21
G-hydrogel/MnO_2-G	pseudo-	PAAK/KCl	1.6V @ 0.2 mA cm^{-2}	50.8	2.54 (single electrode)	0.9	/	22
NPCNFs	pseudo-	PVA-H_2SO_4	1.0 V @ 0.5 A g^{-1}	0.35	4.3 (single electrode)	0.61	0.017	23
GO/CNT/PSE (100 µm)	EDLC	**PVDF-HFP/LiBOB**	**1.8 V @ 1 mA cm^{-2}**	**590**	**59** (single electrode)	**6.64**	**0.05**	**This work**

G: graphene; EGMX: (exfoliated graphene, MXene); AC: active carbon; rGO: reduced graphene oxide; FP: Filter paper; NPCNFs: nitrogen-doped porous carbon nanofibers;

References:

1. M. Kaempgen, C. K. Chan, J. Ma, Y. Cui and G. Gruner, *Nano Lett.*, 2009, **9**, 1872-1876.
2. A. Ramadoss, K. Y. Yoon, M. J. Kwak, S. I. Kim, S. T. Ryu and J. H. Jang, *J. Power Sources*, 2017, **337**, 159-165.
3. V. Vijayakumar, B. Anothumakkool, A. T. A. Torris, S. B. Nair, M. V. Badiger and S. Kurungot, *J. Mater. Chem. A*, 2017, **5**, 8461-8476.
4. R. Q. Na, G. Z. Huo, S. L. Zhang, P. F. Huo, Y. L. Du, J. S. Luan, K. Zhu and G. B. Wang, *J. Mater. Chem. A*, 2016, **4**, 18116-18127.
5. R. Q. Na, P. F. Huo, X. R. Zhang, S. L. Zhang, Y. L. Du, K. Zhu, Y. N. Lu, M. H. Zhang, J. S. Luan and G. B. Wang, *Rsc Adv.*, 2016, **6**, 65186-65195.
6. S. H. Aboutalebi, A. T. Chidembo, M. Salari, K. Konstantinov, D. Wexler, H. K. Liu and S. X. Dou, *Energ. Environ. Sci.*, 2011, **4**, 1855-1865.
7. D. W. Zhao, C. J. Chen, Q. Zhang, W. S. Chen, S. X. Liu, Q. W. Wang, Y. X. Liu, J. Li and H. P. Yu, *Adv. Energy Mater.*, 2017, **7**, 1700739.
8. D. W. Zhao, Q. Zhang, W. S. Chen, X. Yi, S. X. Liu, Q. W. Wang, Y. X. Liu, J. Li, X. F. Li and H. P. Yu, *Acs Appl. Mater. Inter.*, 2017, **9**, 13213-13222.
9. C. Y. Yang, J. L. Shen, C. Y. Wang, H. J. Fei, H. Bao and G. C. Wang, *J. Mater. Chem. A*, 2014, **2**, 1458-1464.
10. C. W. Huang, C. A. Wu, S. S. Hou, P. L. Kuo, C. T. Hsieh and H. S. Teng, *Adv. Funct. Mater.*, 2012, **22**, 4677-4685.
11. G. Z. Sun, X. Zhang, R. Z. Lin, J. Yang, H. Zhang and P. Chen, *Angew. Chem. Int. Edit.*, 2015, **54**, 4651-4656.
12. P. Xu, T. L. Gu, Z. Y. Cao, B. Q. Wei, J. Y. Yu, F. X. Li, J. H. Byun, W. N. Lu, Q. W. Li and T. W. Chou, *Adv. Energy Mater.*, 2014, **4**, 1300759
13. P. H. Yang, X. Xiao, Y. Z. Li, Y. Ding, P. F. Qiang, X. H. Tan, W. J. Mai, Z. Y. Lin, W. Z. Wu, T. Q. Li, H. Y. Jin, P. Y. Liu, J. Zhou, C. P. Wong and Z. L. Wang, *Acs Nano*, 2013, **7**, 2617-2626.
14. Z. S. Wu, K. Parvez, X. L. Feng and K. Mullen, *Nat. Commun.*, 2013, **4**, 2487
15. B. Anothumakkool, R. Soni, S. N. Bhange and S. Kurungot, *Energ. Environ. Sci.*, 2015, **8**, 1339-1347.
16. L. Kou, T. Q. Huang, B. N. Zheng, Y. Han, X. L. Zhao, K. Gopalsamy, H. Y. Sun and C. Gao, *Nat. Commun.*, 2014, **5**, 3754.
17. C. R. Zhu, P. H. Yang, D. L. Chao, X. L. Wang, X. Zhang, S. Chen, B. K. Tay, H. Huang, H. Zhang, W. J. Mai and H. J. Fan, *Adv. Mater.*, 2015, **27**, 4566-4571.
18. H. Y. Li, Y. Hou, F. X. Wang, M. R. Lohe, X. D. Zhuang, L. Niu and X. L. Feng, *Adv. Energy Mater.*, 2017, **7**, 1601847.
19. B. Yao, L. Y. Yuan, X. Xiao, J. Zhang, Y. Y. Qi, J. Zhou, J. Zhou, B. Hu and W. Chen, *Nano Energy*, 2013, **2**, 1071-1078.
20. X. Xiao, T. Q. Li, P. H. Yang, Y. Gao, H. Y. Jin, W. J. Ni, W. H. Zhan, X. H. Zhang, Y. Z. Cao, J. W. Zhong, L. Gong, W. C. Yen, W. J. Mai, J. Chen, K. F. Huo, Y. L. Chueh, Z. L. Wang and J. Zhou, *Acs Nano*, 2012, **6**, 9200-9206.
21. L. C. Zhang, P. Zhu, F. R. Zhou, W. J. Zeng, H. B. Su, G. Li, J. Gao, R. Sun and C. P. Wong, *Acs Nano*, 2016, **10**, 1273-1282.
22. Z. Y. Zhang, F. Xiao and S. Wang, *J. Mater. Chem. A*, 2015, **3**, 11215-11223.
23. F. J. Miao, C. L. Shao, X. H. Li, K. X. Wang and Y. C. Liu, *J. Mater. Chem. A*, 2016, **4**, 4180-4187.