Supporting Information

Highly Porous Mn₃O₄ Nanosheets with *in-situ* Coated Carbon Enabling Fully Screen-Printed Planar Supercapacitors with Remarkable Volumetric Performance

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Experimental Section

Materials: MnSO₄·H₂O (> 98%), NaOH (> 98%) and glucose (> 99.5%) were purchased from Sigma Aldrich. CO(NH₂)₂ (> 98%) was purchased from Alfa Aesar. Na₂SO₄ (> 99%), carboxymethyl cellulose sodium (CMC), polydimethylsiloxane (PDMS), conductive carbon and silver (Ag) conductive paste, N-methyl-pyrrolidone (NMP) and polyvinylidene fluoride (PVDF) were purchased from Energy Chemical. LA132 (a water-based adhesive, polyacrylonitrile latex) was purchased from Indigo Technology Co., Ltd. Commercial solar cell was purchased from Dongguan Xinliangguang New Energy Technology Co., Ltd.

Fabrication of p-Mn₃O₄@C hexagonal nanosheets: All of the chemical reagents were of analytical grade and used as received without any further purification throughout the experiments. In a typical procedure, 40 mL of 0.1 M MnSO₄ aqueous solution was slowly dropped into 40 mL of 0.2 M NaOH solution to generate Mn(OH)₂ flakes with vigorously magnetic stirring for 60 min, followed by the addition of 4 mmol urea $(CO(NH_2)_2)$ and 16 mmol glucose. After stirring for 30 min, the above solution was transferred into a Teflon-lined autoclave with heat treatment at 160 °C for 24 h and then cooled to room temperature. The MnCO₃ hexagonal nanosheets with carbon precursors obtained by centrifugation, which was also purified with ethanol and deionized water and dried at 80 °C overnight. Subsequently, the products were calcined in Ar atmosphere at 400 °C with a heating rate of 2 °C min⁻¹ for 5 h. For comparison, the pure Mn₃O₄ was prepared with the same process except for glucose.

Formulation of the p-Mn₃O₄@C ink: The composition of p-Mn₃O₄@C ink included the p-Mn₃O₄@C powder, conductive carbon and LA132 resin with the weight ratio of 75: 15: 10 were mixed and uniformly dispersed through intermittent high-speed agitator and ultrasonic treatment. After uniform dispersion, the thick black liquid could be directly used as the ink for screen printing.

Construction of PSCs: Flexible printable PSCs were constructed via a screen-printing

method. First, the PET substrate was treated with an O_2 plasma. The Ag interdigital electrode was printed on the as-treated substrate and sintered at 120 °C as conductive current collector. Then, the p-Mn₃O₄@C ink was printed in overlay on the Ag current collector and dried at 80 °C for the preparation of p-Mn₃O₄@C electrode. PSCs with a range of film thicknesses were produced by changing various printed cycles. Next, The Cu conductive tape was pasted over the lead as the current collectors. To complete the fabrication of PSC, the gel electrolyte was uniformly coated on the patterned electrodes. The aqueous gel electrolyte was prepared by adding 5 g of Na₂SO₄ and 3 g of carboxymethyl cellulose sodium (CMC) into 50 mL of deionized water under quick stirring at 90 °C for 3 h until the gel became transparent. Finally, the PDMS (silicone elastomer base: curing agent = 10:1 in weight) was used as a passivation layer to encapsulate the PSCs for enhanced stability.

Materials characterizations

The field emission scanning electron microscopy (FE-SEM, FEI, QuanTA-200F), transmission electron microscopy (TEM, JEOL, JEM-2100F), and high-resolution transmission electron microscopy (HRTEM) were used to characterize the surface morphologies and microstructures of the as-fabricated samples. X-ray diffraction (XRD, PERSEE, XD-3 with Cu K α radiation), energy-dispersive X-ray spectrometry (EDS, Tecnai G2 F30 S-TWIN), and X-ray photoelectron spectroscopy (XPS, Thermo-VG, ESCALAB 250) were used to examine the structure and phase purity of the samples. Raman spectra were measured by a HORIBA Scientific LabRAM HR Raman spectrometer system. The nitrogen adsorption-desorption isotherms were measured at 77 K with a Quantachrome Autosorb-iQ. The rheological properties of inks were recorded on the Anton Paar MCR 302 rheometer.

Electrochemical measurements

All electrochemical measurements were evaluated with a CHI 660E electrochemical workstation (Chenhua, Shanghai). To test the electrode of $p-Mn_3O_4@C$, $p-Mn_3O_4@C$ was mixed with PVDF, carbon black in the weight ratio of 8:1:1 with N-methyl-2-

pyrrolidone. The mixture was grinded for 15 min to obtain slurry. The obtained-slurry was later coated onto carbon cloth which served as a current collector, and the dried at 90 °C overnight. In the half-cell (three electrode), 1 M Na₂SO₄ was used as the electrolyte, and the as-prepared samples as the working electrode. A platinum plate counter electrode was used as the counter electrode and Ag/AgCl was used as the reference electrode. For the full cell (two electrode), CMC-Na₂SO₄ was used as a gel electrolyte.

Electrochemical calculations:

The specific capacitance C (F g⁻¹) of p-Mn₃O₄@C electrode was calculated from the GCD curves by using the following formula:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where I(A) is the discharge current, m(g) is the mass of the active material, Δt is the discharge time (s), ΔV is the potential window (V).

The specific areal capacitance C_A (mF cm⁻²) and volumetric capacitance C_V (mF cm⁻³) of the PSC devices were also calculated from the GCD curves based on equation (2):

$$C_A = \frac{I\Delta t}{S\Delta V} \text{ or } C_V = \frac{I\Delta t}{A\Delta V}$$
(2)

where I (mA) is the discharge current, Δt (s) is the discharge time, ΔV (V) is the potential window, S (cm⁻²) is the area of the device including the electrodes and the gap between the electrodes, and A (cm⁻³) is the volumetric of the PSC devices.

The areal energy density E_A (mWh cm⁻²), volumetric energy density E_V (mWh cm⁻³), areal power density P_A (mW cm⁻²) and volumetric power density P_v (mW cm⁻³) were defined according to equations (3) and (4), respectively:

$$E_{A} = \frac{C_{A} \Delta V^{2}}{7200} \text{ or } E_{V} = \frac{C_{V} \Delta V^{2}}{7200}$$
(3)

$$P_A = \frac{E_A \times 3600}{\Delta t} \text{ or } P_V = \frac{E_V \times 3600}{\Delta t}$$
(4)

where Δt (s) is the discharge time, ΔV (V) is the potential window.

The contribution from diffusion-controlled process and surface reaction can be evaluated by using CV curves.^{1,2} The relationship between current (*I*) and scan rate (v) can be written as:

$$I = av^b \tag{5}$$

Where *a* and *b* are constant can be obtained from log *v* versus log *I* plots. Importantly, b-value gives valuable insight on charge storage kinetics. When b = 0.5 indicates an ideal diffusion-dominated process and when b = 1.0 indicates surface-determined capacitive-controlled behavior. Furthermore, the capacitive contribution to the total current can be differentiated quantitively by using the following equations:

$$I(V) = k_1 v + k_2 v^{\frac{1}{2}}$$

$$\frac{I(V)}{\frac{1}{v^2}} = k_1 v^{\frac{1}{2}} + k_2$$
(6)
(7)

Where *I* is the current density at a voltage (V), *v* is the scan rate (mV s⁻¹), k_1 and k_2 can be obtained from the slope and intercept, respectively. Where k_1v can be attributed to the current from surface capacitance contribution, while $k_2v^{1/2}$ is indexed to the diffusion process.



Fig. S1. SEM image of $Mn(OH)_2$ nanosheets.



Fig. S2. (a) SEM and (b) TEM images of MnCO₃@C precursors.



Fig. S3. XRD pattern of MnCO₃@C precursors.



Fig. S4. SEM images of p-Mn₃O₄@C nanosheets.



Fig. S5. (a, b) TEM images of p-Mn₃O₄@C nanosheets with single nanosheet thickness of ~ 9.6 nm. (c) The lateral size distribution of p-Mn₃O₄@C nanosheets by nano measurer software. The lateral size of p-Mn₃O₄@C nanosheets range in 85 ~ 134 nm with an average value of 107 nm.



Fig. S6. EDS spectrum of $p-Mn_3O_4@C$ nanosheets.



Fig. S7. (a) SEM and (b) TEM images of pure Mn_3O_4 nanosheets.



Fig. S8. Raman spectra of p-Mn₃O₄@C and pure Mn₃O₄ nanosheets.



Fig. S9. XPS spectra of $p-Mn_3O_4@C$. (a) survey, (b) Mn 2p, (c) Mn 3s, (d) C 1s and

(e) O 1s.

The full survey scan spectrum reveals the co-existence of Mn, C and O elements in the as-prepared sample (Figure S9a). As for Mn 2p spectrum (Figure S9b), distinct peaks at the binding energies of 641.8 and 643.3 eV for Mn $2p_{3/2}$ can be observed, which agree well with literature reports for the coexistence of Mn²⁺ and Mn³⁺ in Mn₃O₄.³ The Mn 3s spectrum also shows two distinct peaks located at 83.4 and 88.7 eV, agreeing well with that of Mn₃O₄ (Figure S9c).⁴ The C 1s spectrum is resolved into three peaks observed at 284.2, 284.6, and 288.1 eV, which can be indexed to the C-C, C-O, and C=O bonds, respectively (Figure S9d). Similarly, The O 1s spectrum can be divided into three components centering at 529.3, 529.8, and 531.2 eV, corresponding to different oxygen species in Mn₃O₄, hydroxyl groups, and absorbed water, respectively (Figure S9e).³



Fig. S10. N2 adsorption/desorption isotherms of MnCO₃@C precursors.



Fig. S11. (a) CV curves of p-Mn₃O₄@C electrode in different potential windows at 50

mV/s.



Fig. S12. (a) The b-values at variation potentials. (b) CV curve of p-Mn₃O₄@C electrode from 0 to 1.3 V with shadowed area representing the surface capacitive contribution.



Fig. S13. CV curves of p-Mn₃O₄@C electrode in different potential windows of (a) 0-1.2 V, (c) 0-1.1 V and (e) 0-1.0 V at different scan rates. GCD curves of p-Mn₃O₄@C electrode in different potential windows of (b) 0-1.2 V, (d) 0-1.1 V and (f) 0-1.0 V at different current densities.



Fig. S14. The specific capacitances of p-Mn₃O₄@C electrode in different potential windows.



Fig. S15. (a) CV curves of the pure Mn₃O₄ electrode at different scan rates. (b) GCD curves of the pure Mn₃O₄ electrode at different current densities. (c) Specific capacitances of the pure Mn₃O₄ electrode calculated at different current densities.



Fig. S16. SEM images of (a) p-Mn₃O₄@C and (b) pure Mn₃O₄ electrodes after 10000 cycling stability test.



Fig. S17. EIS spectra of pure Mn_3O_4 and $p-Mn_3O_4@C$ electrodes.



Fig. S18. The optimized crystal structures of (a) Mn_3O_4 and (b) p- $Mn_3O_4@C$.

The density functional theory (DFT) calculations were performed in the Vienna ab initio simulation package (VASP).⁵ A spin-polarized GGA PBE functional with pseudopotentials was used with an energy cutoff of 400 eV, and a projector augmented wave (PAW) method were adopted.^{6,7} A ($3 \times 3 \times 1$) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled.⁸ The conjugate gradient algorithm was used in the optimization. The convergence threshold was set 1×10^{-4} eV in total energy and 0.05 eV/Å in force on each atom.



Fig. S19. Optical images of fine-printed Ag conductive patterns on different substrates of (a) PET and (b) PI. (c, d) SEM images of the printing Ag conductive paste. Ag flakes compactly stacked on the various substrates, and formed a continuous, electrically conductive network.



Fig. S20. SEM images of printed p- $Mn_3O_4@C$ patterns. The printed electrode clearly shows a fine edges and smooth appearance.



Fig. S21. Screen printing of $p-Mn_3O_4@C$ on different substrates to show the print versatility.



Fig. S22. CV curves of p-Mn₃O₄@C PSCs at different scan rates from 1 V/s to 5 V/s.



Fig. S23. (a) The b-values at variation potentials. (b) CV curve of the printed PSCs from 0 to 1.3 V with shadowed area representing the surface capacitive contribution.
(c) Separations of diffusion-controlled and capacitive charge at different scan rates for p-Mn₃O₄@C PSCs.



Fig. S24. (a) The specific areal and volumetric capacitances of p-Mn₃O₄@C PSCs at different current densities. (f) Ragone plot comparison of this work with other previously reported symmetric PSCs.



Fig. S25. The Nyquist plots of as-prepared PSCs before and after 10 000 chargedischarge cycling and after 500 bending cycles measurement.



Fig. S26. The optical photograph of the screen-printed PSCs, showing the great prospect of scale-up production of high-performance PSCs.



Fig. S27. (a) GCD curves of four serially-connected p-Mn₃O₄@C PSCs. (b) Output voltage and capacitance as functions of serial cell number. (c) GCD curves of four parallelly-connected p-Mn₃O₄@C PSCs.



Fig. S28. XRD patterns of $p-Mn_3O_4@C$ electrode before and after self-discharge measurement.



Fig. S29. Core level (a) Mn 2p, (b) Mn 2s, (c) C 1s and (d) O 1s XPS spectra collected for p-Mn₃O₄@C electrode before and after self-discharge measurement.

Mn-based electrodes	Electrolyte	Voltage range (V vs. Ag/AgCl or SCE)	Specific capacitance (F/g)	Rate capability (F/g)	Ref.
rGO@Mn ₃ O ₄	1 M Na ₂ SO ₄	-0.1 to 1.2 V	288 at 0.7 A/g	174 at 24 A/g	4
α -MnO ₂ / δ -MnO ₂	1 M LiCl	0 to 1.0 V	233 at 1 mV/s	116 at 20 mV/s $$	9
m-MnO ₂ nanosheets	5 M LiTFSI	0 to 1.0 V	243 at 1 mV/s		10
D-MnO ₂	1 M Na ₂ SO ₄	0 to 0.8 V	202 at 1 A/g	137 at 20 A/g	11
GrMnO ₂	1 M Na ₂ SO ₄	-0.1 to 0.9 V	350 at 0.2 A/g	162 at 10 A/g	12
HCC@MnO ₂	1 M LiCl	0 to 0.8 V	243 at 1 A/g	139 at 10 A/g	13
3D MnO ₂ /Graphene	0.5 M Na ₂ SO ₄	0 to 0.8 V	422.5 at 1 A/g	228.8 at 10 A/g	14
MnO _x @C@MnO _x	6 M KOH	-0.1 to 0.55 V	350 at 1 A/g	122 at 20 A/g	15
α -MnO ₂	1 M Na ₂ SO ₄	0 to 0.9 V	304 at 3 mA/m ²		16
MnO ₂ /EG	0.5 M K ₂ SO ₄	-0.1 to 1.2 V	308 at 2 mA/cm ²	250 at 20 mA/cm ²	17
CC/Na _{0.5} MnO ₂ NWAs	1 M Na ₂ SO ₄	0 to 1.3 V	366 at 1 A/g	231 at 16 A/g	18
rGO/MnO _x	0.5 M Na ₂ SO ₄	0 to 0.8 V	202 at 1 mV/s		19
MnO2@PPy NWs	1 M Na ₂ SO ₄	0 to 0.9 V	325 at 1 A/g	200 at 20 A/g	20
β-MnO ₂	1 M Na ₂ SO ₄	-0.1 to 0.9 V	306 at 0.25 A/g	177 at 32 A/g	21
MnO ₂ hollow structure	1 M Na ₂ SO ₄	-0.2 to 0.8 V	306 at 5 mV/s		22
α -MnO ₂ nanowire	0.5 M Na ₂ SO ₄	-0.1 to 0.9 V	345 at 1 A/g	60 at 50 A/g	23
p-Mn ₃ O ₄ @C	1 M Na ₂ SO ₄	0 to 1.3 V	386 at 1 A/g	260 at 30 A/g	This work

Table S1. Electrochemical properties for $p-Mn_3O_4@C$ in comparison with those Mn-based electrode materials in earlier reports.

Table S2. Comparison study on the electrochemical performance of symmetric PSCs in this work with previously reported results. *V*: voltage window (V); C_a : areal capacitance (mF cm⁻²); E_a : maximum areal energy density (μ Wh cm⁻²); P_a : maximum areal power density (mW cm⁻²); E_{ν} : maximum volumetric energy density (mWh cm⁻³); P_{ν} : maximum volumetric power density (W cm⁻³).

Electrode materials	Electrolyte	V	C_a	E_a	Pa	E_{v}	P_{v}	Ref.
Ti ₃ C ₂ T _x -rGO	PVA/KOH	0.6	34.6	2.18	0.18			24
$2D-Ti_3C_2T_x$	PVA/H ₂ SO ₄	0.6	1035	8.4	3.7	56	24.9	25
RGO/CNT	3 M KCl	1.0	6.1	0.39	51.9	0.68	77	26
EG/V ₂ O ₅	PVA/LiCl	1.0	3.92			18.2	235	27
MWNT/Mn ₃ O ₄	PMMA-PC-LiClO ₄	1.2				1.8	4.4	28
$I-Ti_3C_2T_x$	PVA/H ₂ SO ₄	0.6	61	0.76	0.33			29
Graphene-CNT	PVA/H ₃ PO ₄	1.0	9.81	1.36	0.25			30
PEDOT:PSS-CNT	PVA/H ₃ PO ₄	0.9		0.015	1.05	3	210	31
B-doped graphene	PVA/H ₂ SO ₄	1.0	16.5	1.4	3.2	0.56	8	32
Mn/Mo@MWCNT	ADN/SN/LiTFSI/P	2.0	7.5	4.2	1.0			33
	MMA							
G-/CNT/PH1000	PVA/H ₃ PO ₄	0.8	107.5	1.27	1.22			34
Polypyrrole nanowires	PVA/H ₂ SO ₄	0.5		0.427	0.50	15.25	17.7	35
Graphene/EC	PVA/H ₃ PO ₄	1.0		0.0052	1.112	1.29	278	36
MXene	PVA/H ₂ SO ₄	0.6	27	2.34	1.95	18	15	37
rGO/Fe ₂ O ₃	PVA/KOH	1.0	0.347			1.61	9.82	38
rGO	PVA/H ₂ SO ₄	1.0	0.081			2.5	495	39
N-doped graphene	PVA/H ₃ PO ₄	0.8	3.4			0.3	0.2	40
ECG/CNT	H ₃ PO ₄ /PVA	1.0	7.7			10.7	3.17	41
Polypyrrole/graphene	PVA/H ₂ SO ₄	0.8	38			2.5	0.397	42
g-C ₃₄ N ₆ -COF	LiCl/PVA	0.8	15.2			7.3	10.4	43
Graphene/CNTcarpets	1 M Na ₂ SO ₄	1.0	2.16			2.42	115	44
Exfoliated graphene	PVA/H ₂ SO ₄	0.8	9.8	0.29	0.76	2.9	2.34	45
p-Mn ₃ O ₄ @C	CMC/Na ₂ SO ₄	1.3	30.1	7.07	1.30	14.14	2.60	This work

References

- M. Salanne, B. Rotenberg, K. Naoi, K. Kaneko, P. L. Taberna, C. P. Grey, B. Dunn and P. Simon, *Nat. Energy*, 2016, 1, 1.
- Z. Peng, J. Huang, Y. Wang, K. Yuan, L. Tan and Y. Chen, J. Mater. Chem. A, 2019, 7, 27313-27322.
- Y. Jiang, J. L. Yue, Q. Guo, Q. Xia, C. Zhou, T. Feng, J. Xu and H. Xia, *Small*, 2018, 14, 1704296.
- R. Sahoo, D. T. Pham, T. H. Lee, T. H. T. Luu, J. Seok and Y. H. Lee, *ACS Nano*, 2018, 12, 8494-8505.
- 5. G. Kresse and J. Furthmüller, Phys. Rev. B, 1996, 54, 11169-11186.
- 6. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
- 7. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
- 8. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.
- C. Zhu, L. Yang, J. K. Seo, X. Zhang, S. Wang, J. Shin, D. Chao, H. Zhang, Y. S. Meng and H. J. Fan, *Mater. Horiz.*, 2017, 4, 415-422.
- J. Qin, S. Wang, F. Zhou, P. Das, S. Zheng, C. Sun, X. Bao and Z.-S. Wu, *Energy Storage Mater.*, 2019, 18, 397-404.
- Y.-P. Zhu, C. Xia, Y. Lei, N. Singh, U. Schwingenschlögl and H. N. Alshareef, Nano Energy, 2019, 56, 357-364.
- J. Chang, M. Jin, F. Yao, T. H. Kim, V. T. Le, H. Yue, F. Gunes, B. Li, A. Ghosh,
 S. Xie and Y. H. Lee, *Adv. Funct. Mater.*, 2013, 23, 5074-5083.
- Z. Chen, L. Zheng, T. Zhu, Z. Ma, Y. Yang, C. Wei, L. Liu and X. Gong, *Adv. Electron. Mater.*, 2019, 5, 1800721.
- Z. Zhang, F. Xiao, L. Qian, J. Xiao, S. Wang and Y. Liu, *Adv. Energy Mater.*, 2014, 4, 1400064.
- Z. Ma, F. Jing, Y. Fan, L. Hou, L. Su, L. Fan and G. Shao, *Small*, 2019, 15, 1900862.
- Z. H. Huang, Y. Song, D. Y. Feng, Z. Sun, X. Sun and X. X. Liu, ACS Nano, 2018, 12, 3557-3567.
- 17. Y. Song, P. Deng, Z. Qin, D. Feng, D. Guo, X. Sun and X.-X. Liu, *Nano Energy*, S-37

2019, 65, 104010.

- N. Jabeen, A. Hussain, Q. Xia, S. Sun, J. Zhu and H. Xia, *Adv. Mater.*, 2017, 29, 1700804.
- Y. Wang, W. Lai, N. Wang, Z. Jiang, X. Wang, P. Zou, Z. Lin, H. J. Fan, F. Kang, C.-P. Wong and C. Yang, *Energy Environ. Sci.*, 2017, **10**, 941-949.
- W. He, C. Wang, F. Zhuge, X. Deng, X. Xu and T. Zhai, *Nano Energy*, 2017, 35, 242-250.
- S. Zhu, L. Li, J. Liu, H. Wang, T. Wang, Y. Zhang, L. Zhang, R. S. Ruoff and F. Dong, *ACS Nano*, 2018, **12**, 1033-1042.
- Y. Gu, J. Cai, M. He, L. Kang, Z. Lei and Z.-H. Liu, *J. Power Sources*, 2013, 239, 347-355.
- W. Li, Q. Liu, Y. Sun, J. Sun, R. Zou, G. Li, X. Hu, G. Song, G. Ma, J. Yang, Z. Chen and J. Hu, *J. Mater. Chem.*, 2012, 22, 14864.
- Y. Yue, N. Liu, Y. Ma, S. Wang, W. Liu, C. Luo, H. Zhang, F. Cheng, J. Rao, X. Hu, J. Su and Y. Gao, *ACS Nano*, 2018, **12**, 4224-4232.
- J. Orangi, F. Hamade, V. A. Davis and M. Beidaghi, ACS Nano, 2020, 14, 640-650.
- 26. M. Beidaghi and C. Wang, Adv. Funct. Mater., 2012, 22, 4501-4510.
- P. Zhang, F. Zhu, F. Wang, J. Wang, R. Dong, X. Zhuang, O. G. Schmidt and X. Feng, *Adv. Mater.*, 2017, 29, 1604491.
- G. Lee, D. Kim, D. Kim, S. Oh, J. Yun, J. Kim, S.-S. Lee and J. S. Ha, *Energy Environ. Sci.*, 2015, 8, 1764-1774.
- C. J. Zhang, M. P. Kremer, A. Seral-Ascaso, S.-H. Park, N. McEvoy, B. Anasori, Y. Gogotsi and V. Nicolosi, *Adv. Funct. Mater.*, 2018, 28, 1705506.
- Y. Wang, Y. Zhang, G. Wang, X. Shi, Y. Qiao, J. Liu, H. Liu, A. Ganesh and L. Li, *Adv. Funct. Mater.*, 2020, **30**, 1907284.
- W. Liu, C. Lu, H. Li, R. Y. Tay, L. Sun, X. Wang, W. L. Chow, X. Wang, B. K. Tay, Z. Chen, J. Yan, K. Feng, G. Lui, R. Tjandra, L. Rasenthiram, G. Chiu and A. Yu, *J. Mater. Chem. A*, 2016, 4, 3754-3764.
- 32. Zhiwei Peng, Ruquan Ye, Jason A. Mann, Dante Zakhidov, Yilun Li, Preston R. S-38

Smalley, J. Lin and J. M. Tour, ACS Nano, 2015, 9, 5868-5875.

- 33. G. Lee, J. W. Kim, H. Park, J. Y. Lee, H. Lee, C. Song, S. W. Jin, K. Keum, C. H. Lee and J. S. Ha, ACS Nano, 2019, 13, 855-866.
- H. Xiao, Z.-S. Wu, F. Zhou, S. Zheng, D. Sui, Y. Chen and X. Bao, *Energy Storage Mater.*, 2018, 13, 233-240.
- M. Zhu, Y. Huang, Y. Huang, H. Li, Z. Wang, Z. Pei, Q. Xue, H. Geng and C. Zhi, *Adv. Mater.*, 2017, 29, 1605137.
- L. Li, E. B. Secor, K.-S. Chen, J. Zhu, X. Liu, T. Z. Gao, J.-W. T. Seo, Y. Zhao and M. C. Hersam, *Adv. Energy Mater.*, 2016, 6, 1600909.
- Y.-Y. Peng, B. Akuzum, N. Kurra, M.-Q. Zhao, M. Alhabeb, B. Anasori, E. C. Kumbur, H. N. Alshareef, M.-D. Ger and Y. Gogotsi, *Energy Environ. Sci.*, 2016, 9, 2847-2854.
- 38. S. Gu, Z. Lou, L. Li, Z. Chen, X. Ma and G. Shen, *Nano Res.*, 2015, 9, 424-434.
- 39. Z.-S. Wu, K. Parvez, X. Feng and K. Müllen, Nat. Commun., 2013, 4, 2487.
- S. Liu, J. Xie, H. Li, Y. Wang, H. Y. Yang, T. Zhu, S. Zhang, G. Cao and X. Zhao, J. Mater. Chem. A, 2014, 2, 18125-18131.
- 41. J.-K. Chih, A. Jamaluddin, F. Chen, J.-K. Chang and C.-Y. Su, *J. Mater. Chem. A*, 2019, **7**, 12779-12789.
- J. Qin, J. Gao, X. Shi, J. Chang, Y. Dong, S. Zheng, X. Wang, L. Feng and Z. S. Wu, *Adv. Funct. Mater.*, 2020, **30**, 1909756.
- 43. J. Xu, Y. He, S. Bi, M. Wang, P. Yang, D. Wu, J. Wang and F. Zhang, *Angew. Chem. Int. Ed.*, 2019, **58**, 12065-12069.
- 44. J. Lin, C. Zhang, Z. Yan, Y. Zhu, Z. Peng, R. H. Hauge, D. Natelson and J. M. Tour, *Nano Lett.*, 2013, 13, 72-78.
- S. Zheng, X. Tang, Z.-S. Wu, Y. Z. Tan, S. Wang, C. Sun, H. M. Cheng and X. Bao, *ACS Nano*, 2017, **11**, 2171-2179.