

1 **Supporting Information**

2 **Recyclable Amphiphilic Porous Thin Films as Electrodes for High-Performance**

3 **Potassium-Ion Transport and Storage**

4 *Chuanting You^{a,†}, Weiwei Wei^{b, c,†}, Jianyong Yu^a, Shichang Sun^a, Wei Xiao^a, Liwei*
5 *Wang^b, Zhanhui Yuan^{a*}, Fan Zhang^{c*}*

6

7 ^aCollege of Materials Science and Engineering, Fujian Agriculture and Forestry
8 University, Shangxiadian Road 15, 350002 Fuzhou, P. R. China

9 E-mail: zhanhuiyuan@fafu.edu.cn (Z. Y.)

10

11 ^bOcean College, Minjiang University, Fuzhou 350108, P. R. China

12

13 ^cSchool of Chemistry and Chemical Engineering, Shanghai Jiao Tong University,
14 Dongchan Road 800, 200240 Shanghai, P. R. China

15 E-mail: fan-zhang@sjtu.edu.cn (F. Z.)

16

17 ^cOcean College, Minjiang University, Fuzhou 350108, P. R. China

18

19 [†]These authors contributed equally to this work.

20

21

22

23

24

25

26

27

28

29

30

31

32

33

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29

Table of Contents

1. Experimental section.....	3
2. Supplementary Figures.....	6
3. Supplementary Tables	13

1 **1 Experimental section:**

2 **1.1 Fabrication of the rGO/NFC thin film**

3 The synthetic method of rGO/NFC thin film is exhibited in Figure 1a. As the shown
4 in the figure, 210 mg NFC solution (1wt%) and 12 mg rGO powder (prepare via
5 Hummers method) is added into 10 mL deionized water and fully stir for 10 min. The
6 NFC solution (1 wt%) is an aqueous solution containing nanofibrillated cellulose
7 (NFC) in a mass fraction of 1%. The NFC solution was prepared by slowly adding 1 g
8 of NFC into 99 g of deionized water, and then fully stirred to form a uniform
9 suspension. Then the NFC/rGO slurry was subject to continuous ultrasonic treatment
10 for 3 h in 30 °C-60 °C and had a rest for 1 h, this process was repeated over 5 times.
11 Until a uniformly dispersed inky solution was formed, the NFC/rGO gelatinous thin
12 film was prepared after filtration by using polytetrafluoroethylene (PTFE) membrane
13 (0.22 μm pore diameter). The gelatinous film was dried at room temperature for over
14 24 h to form a flexible thin film called **85-rGO/NFC**. In the same way, using the above
15 method and only changing the content of NFC in the composite to prepare different
16 rGO/NFC films (is defined as *n*-rGO/NFC, *n*=65, 75, 85, and 90, *n* is represented the
17 percentage of rGO in the composite).

18 **1.2 Preparation of Lithium-ion, Sodium-ion, and Potassium-ion Supercapacitor**

19 All these three kinds of symmetric supercapacitors were assembled with two flexible
20 rGO/NFC films with same size as electrodes separated by one acetyl cellulose paper
21 used as a separator to avoid short circuit. The difference is that they respectively used
22 1_M LiPF₆ in DMC, 1_M NaPF₆ in EC: DMC (1:1), and 1_M KPF₆ in EC: DMC: DEC
23 (1:1:1) as electrolyte. To investigate the wettability of solvent in electrode, the contact
24 angle of DMC, EC: DMC (1:1) and EC: DMC: DEC (1:1:1) on the surface of the **85-**
25 **rGO/NFC** sample were monitored, respectively. These mixed solvents showed the
26 similar wettability with the contact angles of about zero degree ([Figure S10](#)).
27 Supercapacitors need to be assembled without water and oxygen in the glovebox.

28 **1.3 Electrochemical Measurements**

29 The electrochemical tests were carried out using an electrochemical station

1 (CHI660D, Shanghai) with symmetric supercapacitors at room temperature.
 2 Galvanostatic charge/discharge investigation was carried out in voltage range of 0-3 V
 3 with difference current density from 0.1 to 0.8 A cm⁻³. Cyclic voltammetry was
 4 measured in the voltage range of 0-3 V at difference scan rates (5 mV s⁻¹, 10 mV s⁻¹,
 5 20mV s⁻¹, 50 mV s⁻¹, and 100 mV s⁻¹). The electrochemical impedance spectroscopy
 6 (EIS) was performed at open circuit potential within a frequency range from 10⁵ Hz to
 7 10⁻² at 0.5V.

8 Gravimetric specific capacitance (C_g) was calculated using the following equation
 9 (1) and (2)

$$10 C_g(\text{F g}^{-1}) = A/(2msV) \quad (1)$$

$$11 C_g(\text{F g}^{-1}) = I \Delta t / mV \quad (2)$$

12 where A is the area of CV curve, s is the scan rate of CV curve (V s⁻¹), V is the potential
 13 window (V), m is the mass of the electrodes (g), I is the current density (A g⁻¹), and Δt
 14 is the discharge time (s). The volumetric specific capacitance (C_v) was calculated by
 15 equation (3)

$$16 C_v(\text{F cm}^{-3}) = \rho C_g \quad (3)$$

17 where ρ is the volumetric density of the films (g cm⁻³), which was measured through
 18 equation (4)

$$19 \rho (\text{g cm}^{-3}) = m / Sd \quad (4)$$

20 where m (g) is the dried electrode quality, S (cm²) and d (cm) are the area and thickness
 21 of electrode. The volumetric energy density (E_v) and the power density (P_v) of electrode
 22 were calculated according to equation (5) and equation (6)

$$23 E_v(\text{Wh L}^{-1}) = C_v V^2 / (2 \times 3.6) \quad (5)$$

$$24 P_v(\text{W L}^{-1}) = 3600 \times E_v / \Delta t \quad (6)$$

25 where V is the potential window (V), and Δt is the discharge time (s)

26 **1.4 Galvanostatic intermittent titration technique (GITT) measurements**

27 The kinetics of lithium ion, sodium ion and potassium ion extraction/insertion in the
 28 **85-rGO/NFC** electrodes were measured by using the galvanostatic intermittent
 29 titration technique (GITT). The technique was be used to confirm the diffusion
 30 coefficient of Li⁺ in Li₃Sb by Weppner and Huggins. By the ionic diffusion follows

1 Fick's second law, the diffusion can be calculated by the following equation.

$$D = \frac{4}{\pi\tau} \left(\frac{m V_M}{M S} \right)^2 \left(\frac{\Delta E_S}{\tau \left(\frac{\Delta E_\tau}{d\sqrt{\tau}} \right)} \right)^2 \quad (\tau \ll L^2/D)$$

2

(7)

3 Where D is the diffusion coefficient of the ion; τ is the relaxation time; m is the mass
4 of active matter; V_M is the molar volume; L is the electrodes' average thickness. Other
5 parameters in the equation 6 can be defined in Figure S4.

6 Because a linear relationship exists between the voltage and $\tau^{1/2}$ in Figure S4, the
7 equation 6 can be simplified as

$$D = \frac{4}{\pi\tau} \left(\frac{m V_M}{M S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2$$

8

(8)

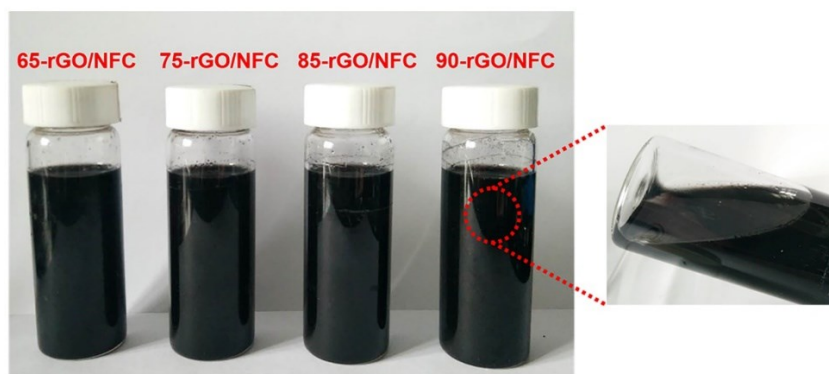
9 For the GITT measurement (use Land system), the constant current density was set as
10 30 mA g⁻¹ for a given time period (30 min), followed by an open-circuit stand for a
11 specified time interval (60 min). The sequence was repeated until the target voltage was
12 reached.

13 1.5 Material Characterization

14 The samples for tensile test were tailored into strip with the width of 5 mm and length
15 of 15 mm by a bistoury. The testing was carried out via dynamic thermomechanical
16 analysis (Q850, China) at room temperature. The morphology of rGO/NFC films was
17 observed using Raman Imaging combined with Emission Scanning Electron
18 Microscope (TESCAN-MAIA3, Czech). And the chemical element distribution of
19 rGO/NFC electrodes after electrochemistry was detected using a FE-TEM (FEI Talos
20 F200X) using an accelerating voltage of 200 kV. The rGO/NFC electrodes before
21 electrochemistry and after electrochemistry were investigated by X-ray diffraction
22 (XRD) using a Bruker D8 Advance diffractometer with Cu K α radiation ($\approx 1.54^\circ \text{A}$) at
23 40 kV and 30 mA. [Raman spectra were recorded on a RM2000 microscopic confocal](#)
24 [Raman spectrometer employing a h14 nm laser beam.](#) The X-ray photoelectron
25 spectroscopy (XPS) analyses were performed an AXIS Ultra DLD (Kratos, Japan)
26 photoelectron spectroscopy at 0.48 eV electronic resolution. [Nitrogen](#)
27 [adsorption/desorption isothermal was performed with a Micromeritics ASAP 2020 HD](#)

1 Analyzer at 77 K. Pore size distribution was estimated based on BJH model.

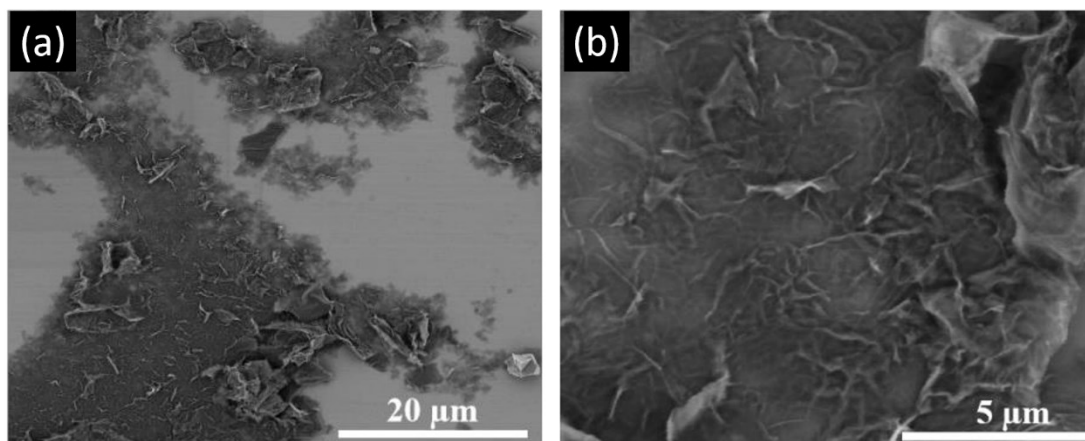
2 2 Supplementary Figures



3

4 **Figure S1.** Digital images of rGO/NFC dispersion with different content of rGO and 90-rGO/NFC
5 after 48 hours.

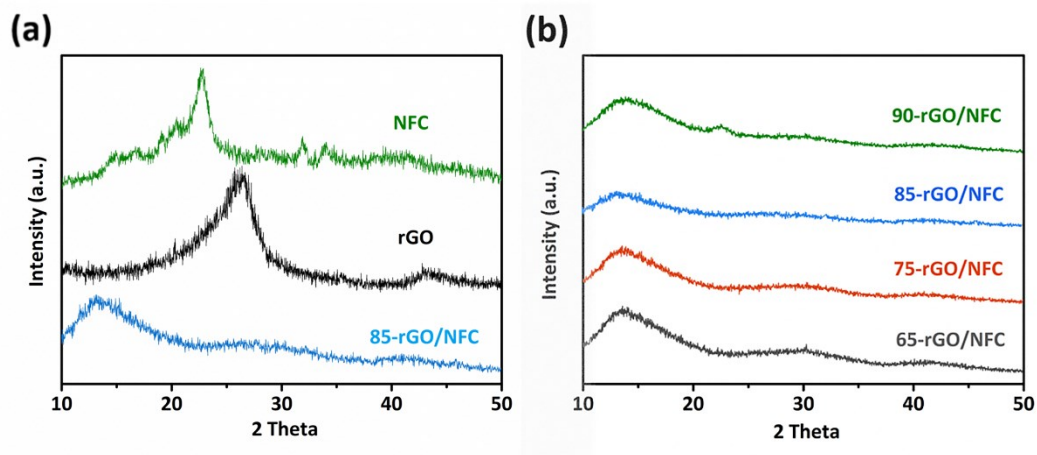
6



7

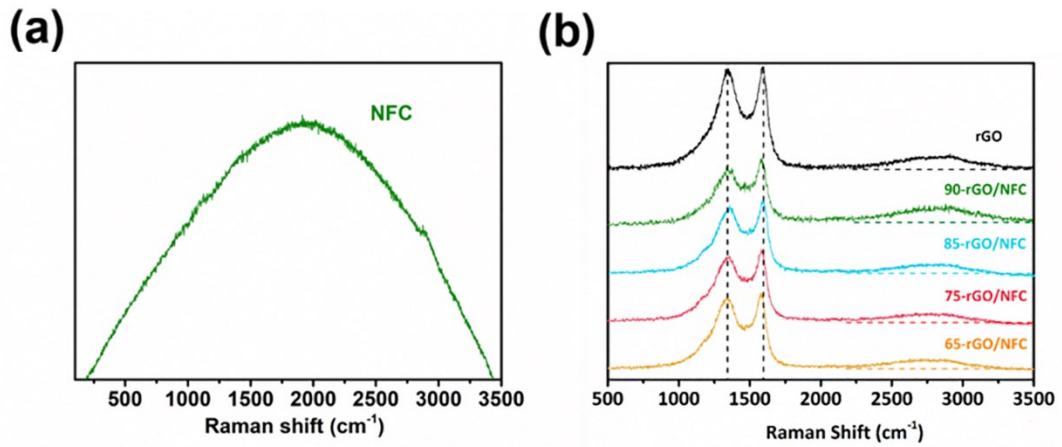
8 **Figure S2.** Scanning electron microscopy (SEM) images of NFC/rGO assembly dispersion solution.

9

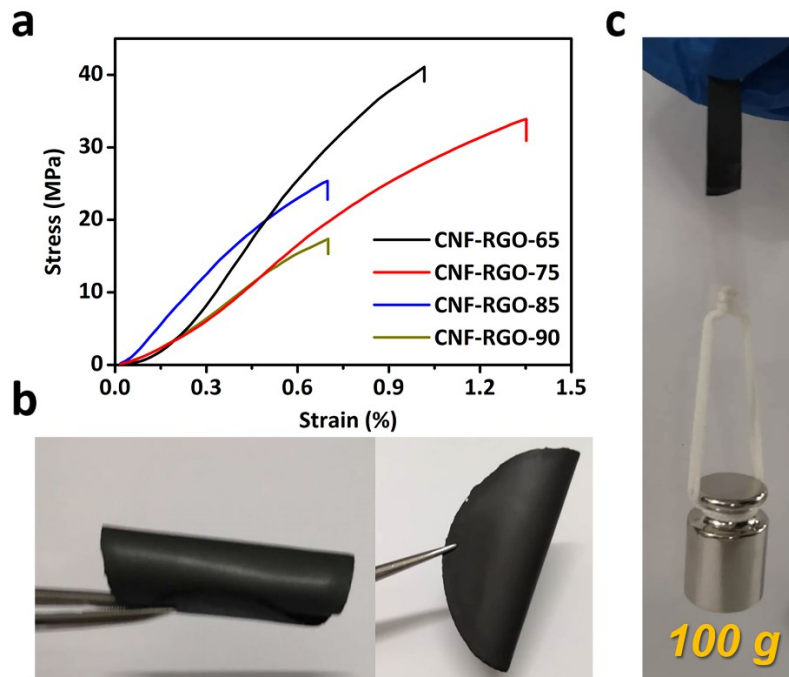


10

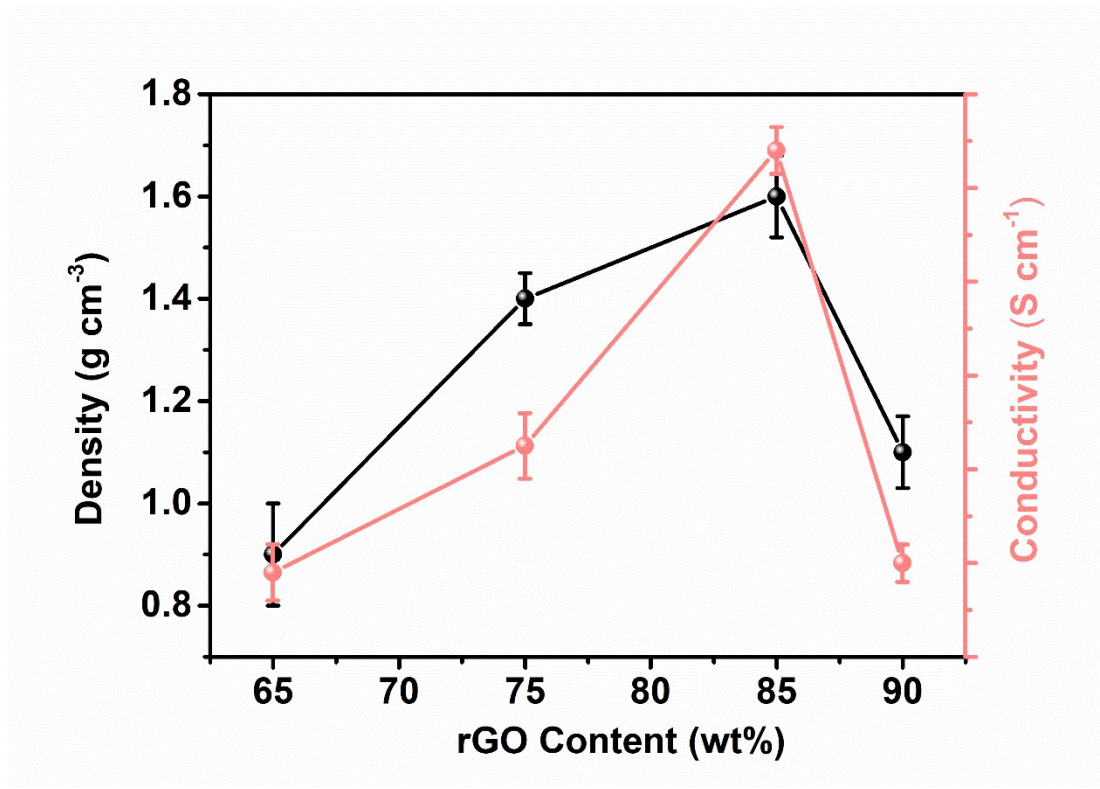
11 **Figure S3.** (a) XRD pattern of NFC, rGO and 85-rGO/NFC. (b) XRD of the different films.



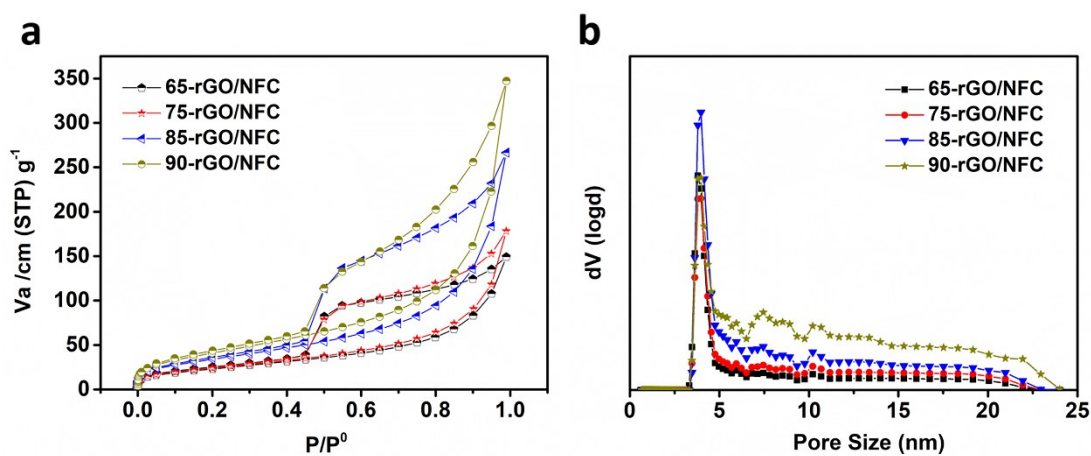
1
 2 **Figure S4.** The Raman spectra of (a) NFC, (b) the neat rGO and the as-prepared *n*-rGO/NFC films.
 3



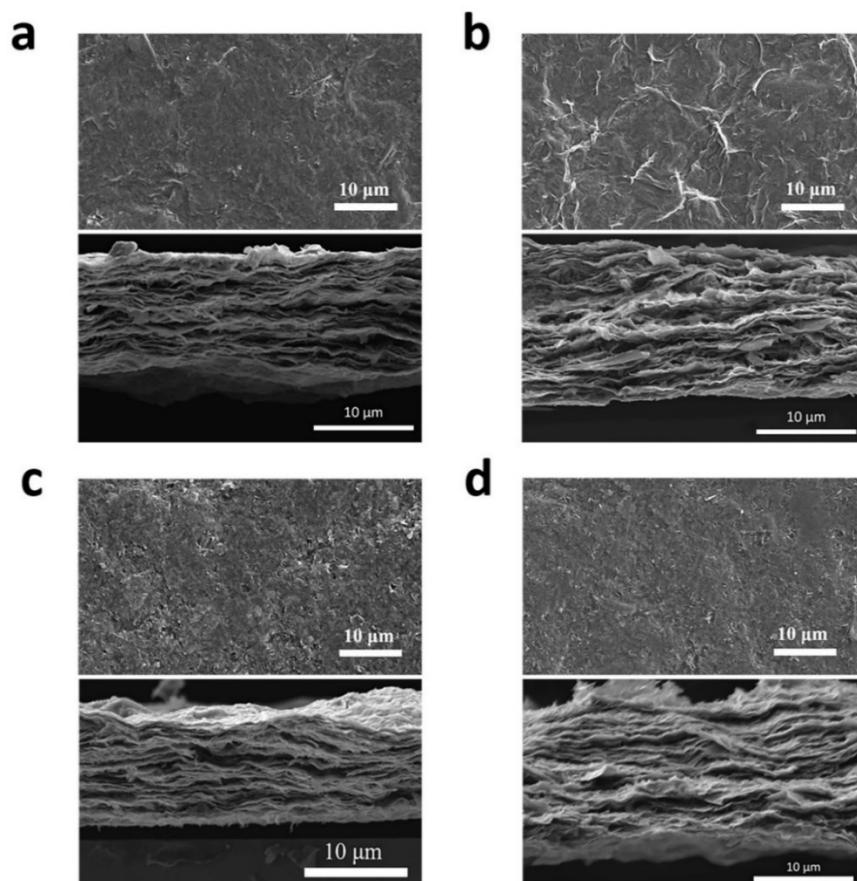
4
 5 **Figure S5.** (a) Mechanical characters of *n*-rGO/NFC; (b-c) Real images of reassembling film after
 6 being rolled, folded and bended.



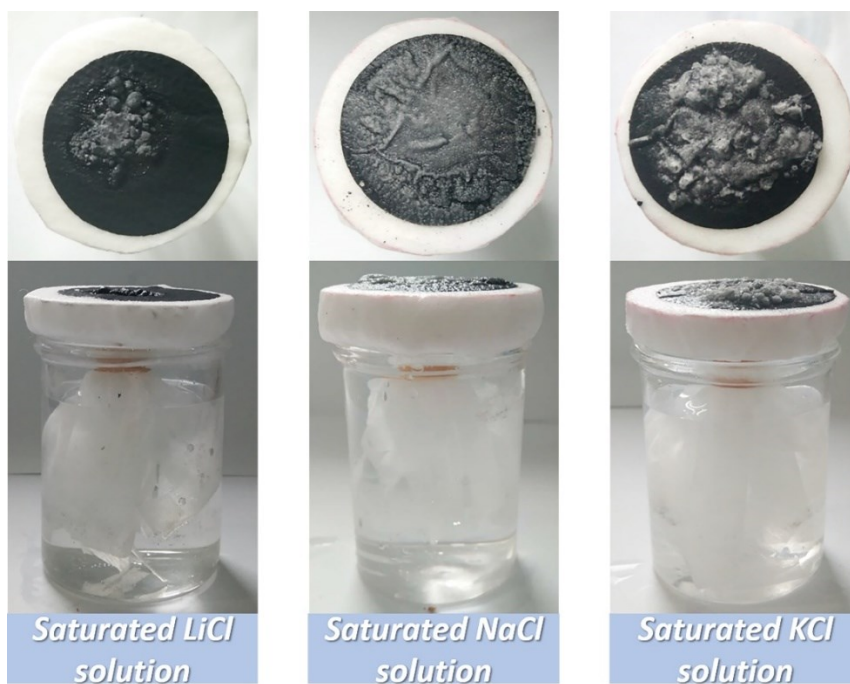
1
 2 **Figure S6.** The variation trends of density and conductivity of *n*-rGO/NFC films.
 3



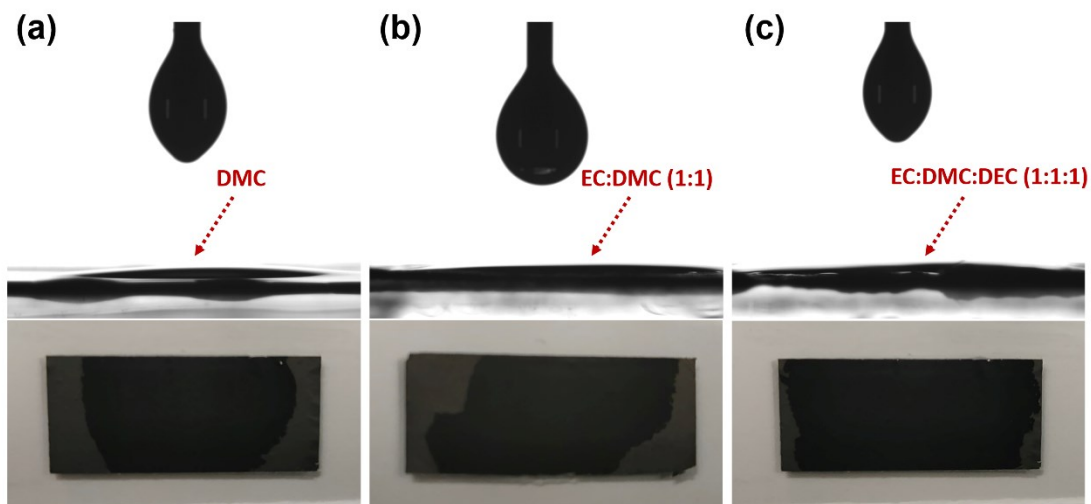
4
 5 **Figure S7.** (a) N₂ adsorption-desorption isotherms and (b) The pore size distributions of *n*-
 6 rGO/NFC



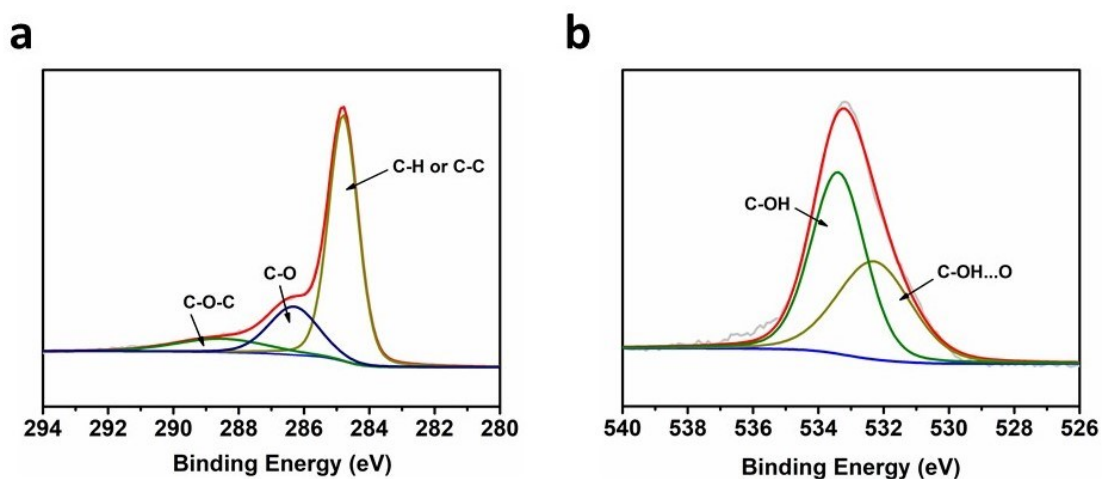
1
 2 **Figure S8.** Top and side view of SEM images of different rGO/NFC weight ratio (a) 65-rGO/NFC,
 3 (b) 75-rGO/NFC, (c) 85-rGO/NFC and (d) 90-rGO/NFC, respectively.
 4



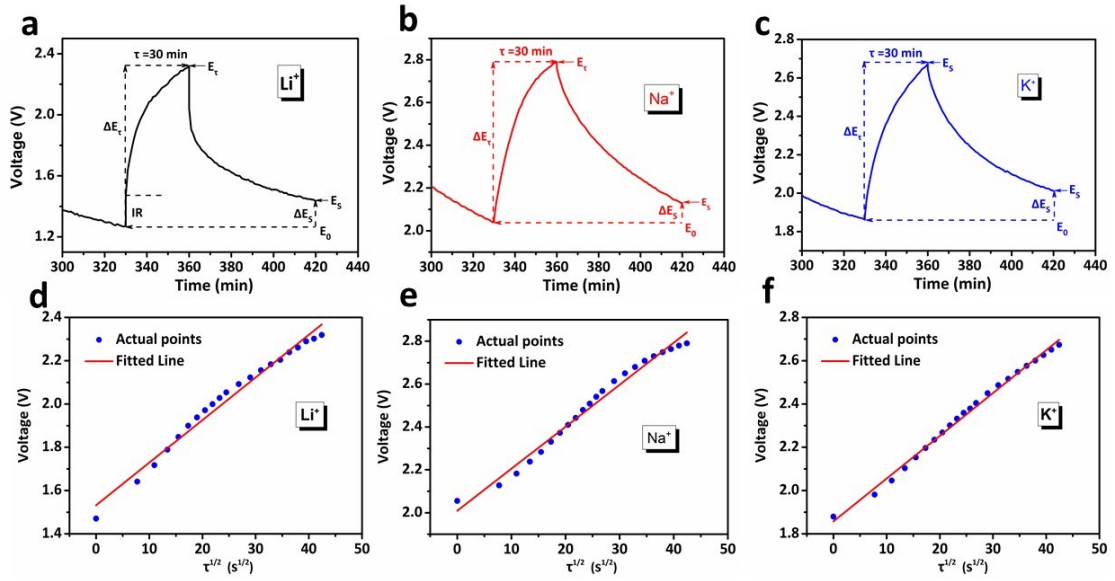
5
 6 **Figure S9.** Digital photographs for appearing the crystalline salts of 85-rGO/NFC with a substrate
 7 of airlaid paper, which were floated on crystalline salts appeared.



1
 2 **Figure S10.** The wettability of the surface of **85-rGO/NFC** of difference solvent: (a) DMC (b) EC:
 3 DMC (1:1) and (c)EC: DMC: DEC (1:1:1).
 4

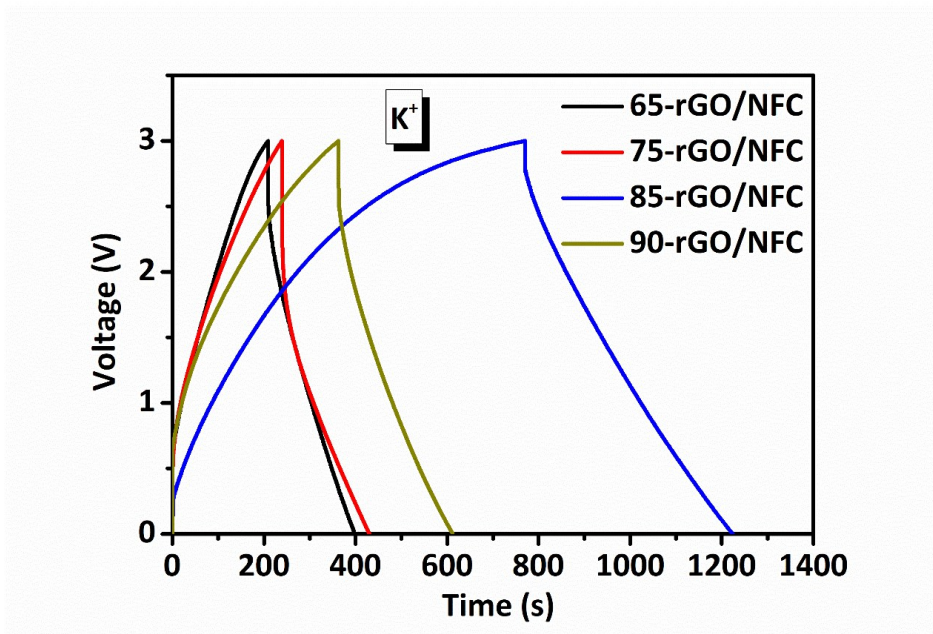


5
 6 **Figure S11.** XPS spectra of **85-rGO/NFC** electrodes: (a) C 1s region (b) O 1s region
 7



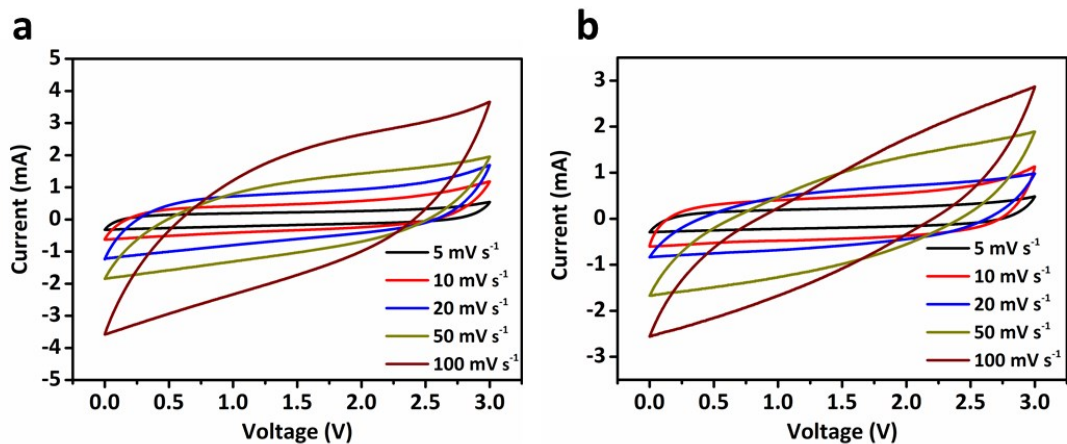
1

- 2 **Figure S12.** A single step of GITT of **85-rGO/NFC** electrode in the (a) LiPF_6 , (b) NaPF_6 and (c)
 3 KPF_6 electrolyte. Linear behavior of voltage vs. $\tau^{1/2}$ relationship in GITT of the electrode in the (d)
 4 LiPF_6 , (e) NaPF_6 and (f) KPF_6 electrolyte.

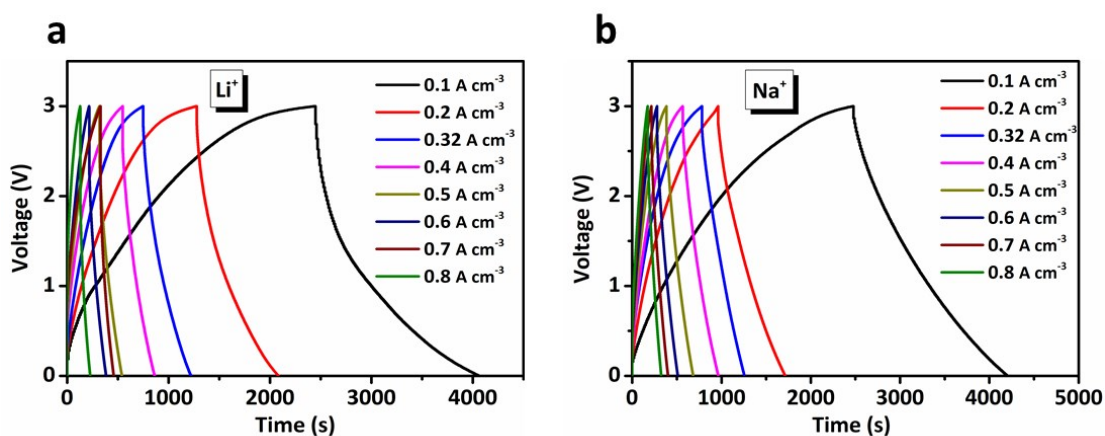


5

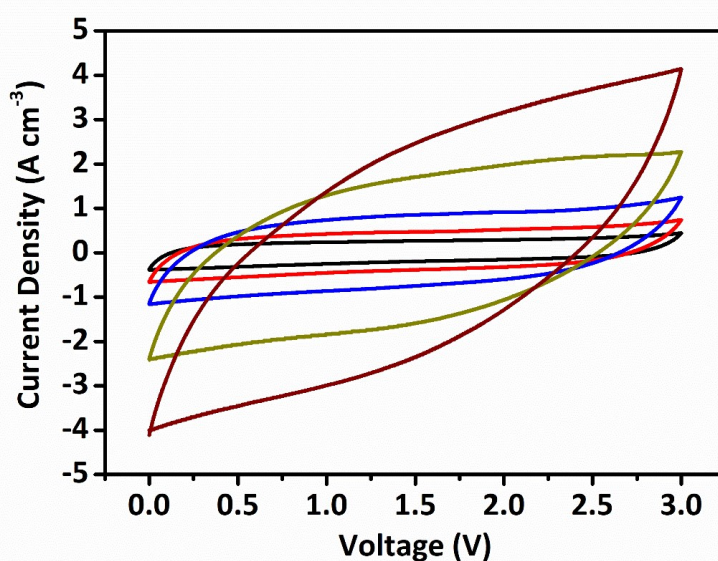
- 6 **Figure S13.** The GCD curves of n -rGO/NFC film electrodes ($n=65, 75, 85, 90$) at current density
 7 of 0.32 A cm^{-3} in the potassium ion-based capacitor.



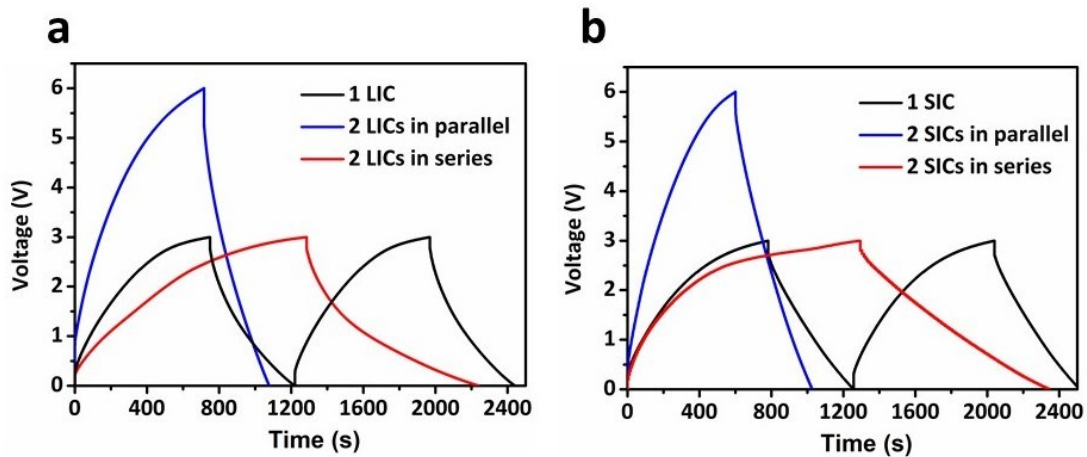
1
 2 **Figure S14.** The CV curve of **85-rGO/NFC** at different scan rates in the (a) LiPF_6 and (b) NaPF_6
 3 electrolyte.



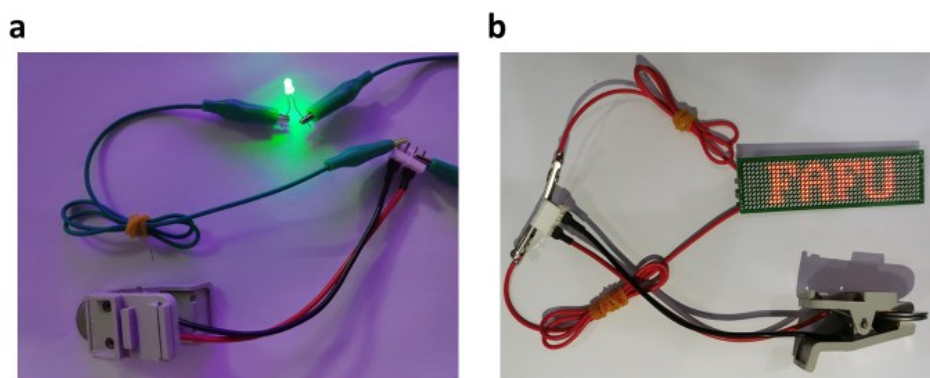
4
 5 **Figure S15.** The GCD curve of **85-rGO/NFC** at different volumetric current densities in the (a)
 6 LiPF_6 and (b) NaPF_6 electrolyte.



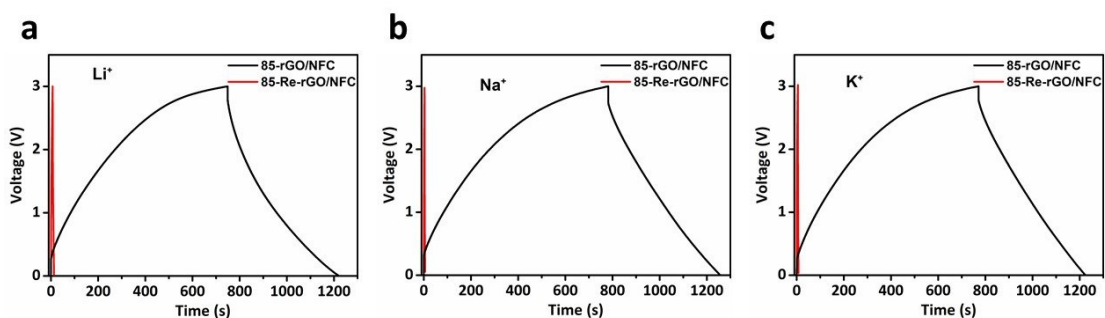
7
 8 **Figure S16.** The CV curve of reassembling electrode at different scan rates in the KPF_6 electrolyte.



1
 2 **Figure S17.** GCD profiles of single device and two devices in parallel and in series at a current
 3 density of 0.32 A cm^{-3} , respectively (a) lithium ion-based capacitor and (b) sodium ion-based
 4 capacitor



5
 6 **Figure S18.** The digital photos of (a) a green LED scroller that is powered by device and (b) two
 7 MICs in series to power a LED scroller.



8
 9 **Figure S19.** The GCD curve of **85-rGO/NFC** and **85-Re-rGO/NFC** at 0.32 A cm^{-3} in the (a) LiPF_6 ,
 10 (b) NaPF_6 and (c) KPF_6 electrolyte.
 11

1 **Table S1.** Comparison of electrochemical performance between the ion supercapacitor used **85-**
 2 **rGO/NFC** electrodes and other supercapacitors used different electrodes.

Electrodes	Electrolyte	Voltage window (V)	Volumetric energy density (Wh L ⁻¹)	Volumetric power density (W L ⁻¹)	reference
85-rGO/NFC	LiPF ₆	0-3	70	514	This work
	NaPF ₆		74	560	
	KPF ₆		67	552	
HPNC@NSs	EMIMBF ₄	0-3.5	42.3	411	<i>ACS Nano</i> , 2015 ¹
GH@NC@Co ₉ S ₈	Alkaline	0-1.6	28.7	971.9	<i>J. Mater. Chem. A</i> , 2019 ²
Mxene@graphene	1M KCl	-0.7-0.3	32.6	74400	<i>Adv. Funct. Mater.</i> , 2017 ³
CNF@GO@MoO ₃	PVDF-P407-[BMPY][NTf ₂]	0-3.6	18.8	72.5	<i>J. Mater. Chem. A</i> , 2017 ⁴
PANI/RGO	PVA/H ₂ SO ₄	0-1	8.8	30.77	<i>Adv. Mater.</i> , 2018 ⁵
NGMn	5 M LiCl	0-1.8	3.5	19	<i>ACS Appl. Mater. Interfaces</i> , 2016 ⁶
Nb ₂ O ₅ @AC	LiPF ₆	1-3.5	6.7	374.6	<i>Adv. Funct. Mater.</i> , 2018 ⁷
2D-HPC	EMIMBF ₄	0-4	8.4	24.9	<i>Adv. Mater.</i> , 2018 ⁸
Ni-MOF@AC	3M KOH	0-1.2	4.18	231.2	<i>J. Mater. Chem. A</i> , 2016 ⁹
Ni _{0.25} Mn _{0.75} O@C	PVA-LiCl	0-1.4	4.72	776	<i>Adv. Mater.</i> , 2017 ¹⁰
Carbon cloth	PVA/H ₂ SO ₄	-0.5-1	4.27	1320	<i>ACS Appl. Mater. Interfaces</i> , 2019 ¹¹
Nb ₂ O ₅ @CNF	NaPF ₆	0-4	11.2	5400	<i>Small</i> , 2019 ¹²
BP@CNT	PVA/H ₃ PO ₄	0-1	5.71	11000	<i>ACS Appl. Mater. Interfaces</i> , 2017 ¹³

3

4

1 Reference

- 2 1. C. C. Jianhua Hou, Faryal Idrees, and Xilan Ma, *ACS Nano*, 2015, **9-3**, 2556.
- 3 2. H. Niu, Y. Zhang, Y. Liu, B. Luo, N. Xin and W. Shi, *J. Mater. Chem. A*, 2019, **7**, 8503.
- 4 3. J. Yan, C. E. Ren, K. Maleski, C. B. Hatter, B. Anasori, P. Urbankowski, A. Sarycheva and Y.
5 Gogotsi, *Adv. Funct. Mater.*, 2017, **27**, 1701264.
- 6 4. Q. Zheng, A. Kvit, Z. Cai, Z. Ma and S. Gong, *J. Mater. Chem. A*, 2017, **5**, 12528.
- 7 5. P. Li, Z. Jin, L. Peng, F. Zhao, D. Xiao, Y. Jin and G. Yu, *Adv. Mater.*, 2018, **30**, e1800124.
- 8 6. Y. Liu, X. Miao, J. Fang, X. Zhang, S. Chen, W. Li, W. Feng, Y. Chen, W. Wang and Y. Zhang,
9 *ACS Appl. Mater. Interfaces*, 2016, **8**, 5251.
- 10 7. B. Deng, T. Lei, W. Zhu, L. Xiao and J. Liu, *Adv. Funct. Mater.*, 2018, **28**, 1704330.
- 11 8. L. Yao, Q. Wu, P. Zhang, J. Zhang, D. Wang, Y. Li, X. Ren, H. Mi, L. Deng and Z. Zheng, *Adv.*
12 *Mater.*, 2018, **30**, 1706054.
- 13 9. Y. Yan, P. Gu, S. Zheng, M. Zheng, H. Pang and H. Xue, *J. Mater. Chem. A*, 2016, **4**, 19078.
- 14 10. W. Zuo, C. Xie, P. Xu, Y. Li and J. Liu, *Adv. Mater.*, 2017, **29**, 1703463.
- 15 11. Z. Miao, Y. Huang, J. Xin, X. Su, Y. Sang, H. Liu and J. J. Wang, *ACS Appl. Mater. Interfaces*,
16 2019, **11**, 18044.
- 17 12. Y. Li, H. Wang, L. Wang, Z. Mao, R. Wang, B. He, Y. Gong and X. Hu, *Small*, 2019, **15**,
18 1804539.
- 19 13. B. Yang, C. Hao, F. Wen, B. Wang, C. Mu, J. Xiang, L. Li, B. Xu, Z. Zhao, Z. Liu and Y. Tian,
20 *ACS Appl. Mater. Interfaces*, 2017, **9**, 44478.
- 21