

## Supporting information

### **Sulfur-functionalized three-dimensional graphene monoliths as the high-performance anode for ultrafast sodium-ion storage**

Dequn Zheng<sup>a,‡</sup>, Jun Zhang<sup>b,‡</sup>, Wei Lv<sup>a,\*</sup>, Tengfei Cao<sup>b</sup>, Siwei Zhang<sup>b</sup>, Dong Qiu<sup>a</sup>,  
Ying Tao<sup>c</sup>, Yanbing He<sup>a</sup>, Feiyu Kang<sup>a, b</sup>, and Quan-Hong Yang<sup>a, c\*</sup>

<sup>a</sup>Engineering Laboratory for Functionalized Carbon Materials and Shenzhen Key Laboratory for Graphene-based Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China.

E-mail: lv.wei@sz.tsinghua.edu.cn

<sup>b</sup>Tsinghua-Berkeley Shenzhen Institute (TBSI), Tsinghua University, Shenzhen 518055, China.

<sup>c</sup>School of Chemical Engineering and Technology, Tianjin University, Tianjin 300372, China.

E-mail: qhyangcn@tju.edu.cn (Q.-H. Yang).

‡These authors are equal main contributors.

## **Material preparation**

Fig. S1† shows the preparation process of SPGM and the referenced sulfur-free porous graphene monolith (PGM). Graphene oxide was prepared using a modified Hummer's method and then sonicated in deionized water to form the GO hydrosol. First, TDDT was dissolved into 80 mL of 2 mg/mL GO hydrosol with different mass ratios of 2:1, 1:1 and 1:2 between TDDT and GO. The mixture was ultra-sonicated and stirred to get a homogeneous colloidal suspension. Then, the obtained colloidal suspension (80 mL) was sealed in a Teflon-lined autoclave (100 mL), and heated at 180 °C for 6 h, generating a black cylindrical hydrogel (Fig. S2†). The obtained hydrogel was washed and freeze-dried to prepare the SPGM. For reference, porous graphene macroform (PGM) was produced following the same process without the addition of TDDT.

## **Material characterization**

Scanning electron microscopy (SEM) observation was performed using FE-SEM (ZEISS SUPRA 55). Transmission electron microscopy (TEM) observation was performed on FE-TEM (JEM-3200FS) at 300 kV. X-ray diffraction (XRD) measurements were conducted at room temperature in a Rigaku D/MAX 2500/PC diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). Element analysis was performed using Elementa EL Cube. Raman spectra were collected on HORIBA Jobin Yvon LabRAM HR800 with a 532 nm laser source in the range of 200-3500 $\text{cm}^{-1}$ . The nitrogen gas adsorption isotherms of the samples were measured by using a BEL mini instrument, and the specific surface area was calculated by Brunauer–Emmett–Teller (BET) analyses of the adsorption isotherms. Fourier Transform infrared spectroscopy (FTIR) was performed on a Nicolet iS50 instrument. X-ray photoelectron spectroscopy (XPS) was conducted by an ESCALAB 250Xi (Thermo Fisher) using a monochromated Al K $\alpha$  source. Contact angle measurement was performed by using a DSA30 (Kruss) instrument.

### **Electrochemical measurement**

The ground samples were mixed with conductive carbon black and PVDF with a mass ratio of 7:2:1 in 1-Methyl-2-pyrrolidinone (NMP) to form homogeneous slurry. The slurry was then coated onto a carbon-coated Al foil with a constant thickness of 120  $\mu\text{m}$  and dried in vacuum oven at 110  $^{\circ}\text{C}$  for 12 h. After that, the foil was cut into circular pieces with a diameter of 12 mm and directly used as the electrode for electrochemical test. The electrolyte was 1 M sodium perchlorate ( $\text{NaClO}_4$ ) dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (volume ratio: 1:1). Pure sodium foil was used as the counter electrode and Whatman GF/A glass fibre was used as the separator. A 2032-type coin cell was assembled in an argon-filled glovebox where the contents of oxygen and moisture were all below 0.5 ppm. After the assembly of batteries in the argon-filled glovebox, the coin cell was rested for at least 12 h to ensure the infiltration of electrolyte. Galvanostatic charge–discharge tests were carried out on LAND CT2001 battery program controlling system with a cut-off voltage range of 0.005-3 V at different current densities (from 100 mA/g to 5000 mA/g). Cyclic voltammetry measurements were performed using an electrochemical workstation (VMP3, Bio Logic) between 0.005-3 V at a sweep rate of 0.2 mV/s. Electrochemical impedance spectra (EIS) measurements after ten cycles were performed in the frequency range from 0.01 Hz to 100000 Hz by applying a 5 mV ac oscillation on the VMP3 electrochemical workstation.

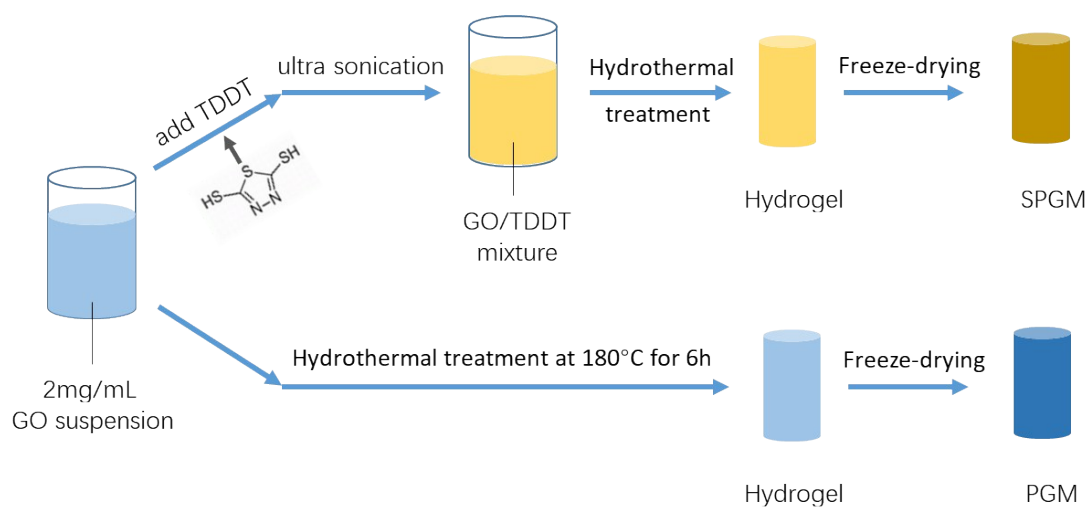


Fig. S1 Schematic illustration for preparation of SPGM/PGM

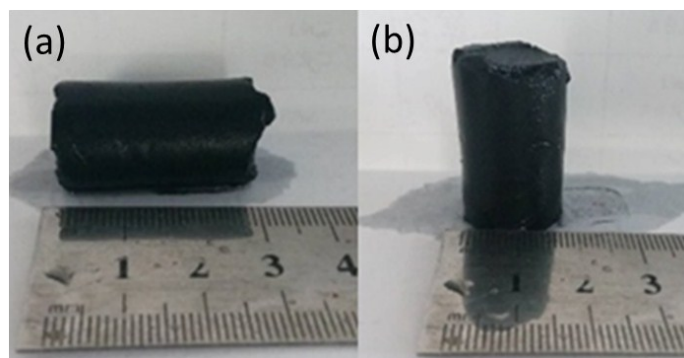


Fig. S2 Photographs of cylindrical graphene hydrogel

Table S1 The contents of C, N, S and O obtained by XPS and EA

		C (wt %)	N (wt %)	S (wt %)	O (wt %)
EA	PGM	76.8	--	--	20.8
	SPGM	66.7	3.2	16.8	11.5
XPS	PGM	80.9	--	--	19.1
	SPGM	73.6	2.5	14.2	9.7

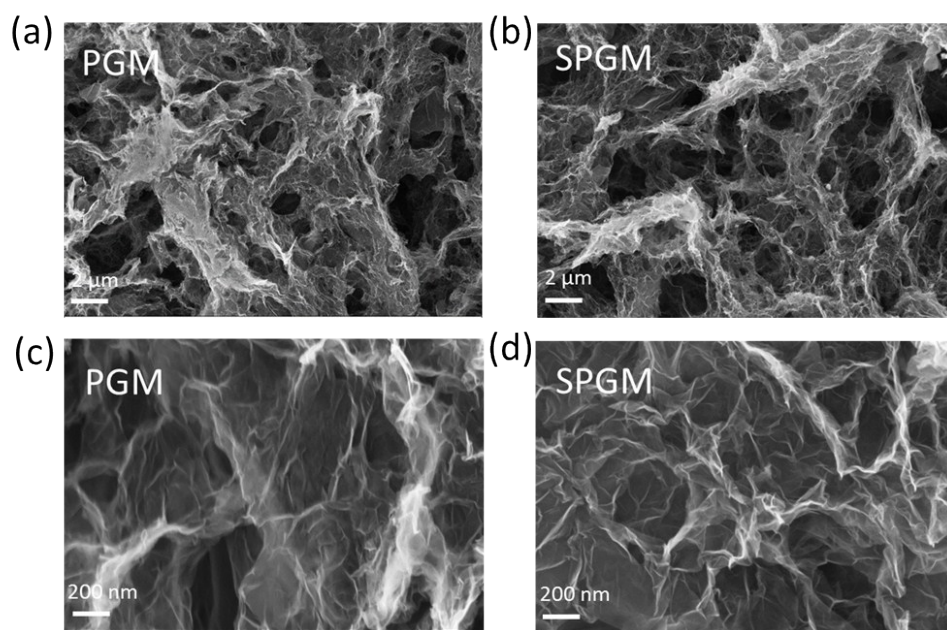


Fig. S3 SEM images of PGM (a, c) and SPGM (b, d)

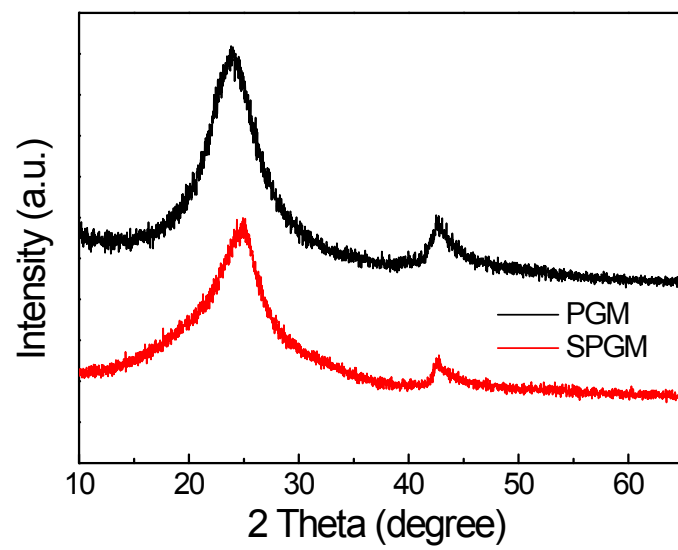


Fig. S4 XRD patterns of PGM and SPGM

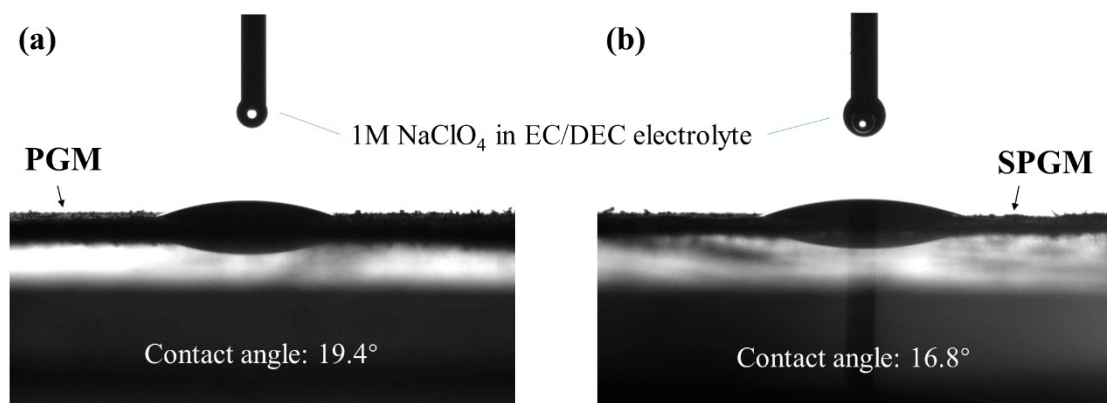


Fig. S5 The wetting ability of PGM (a) and SPGM (b) by the electrolyte



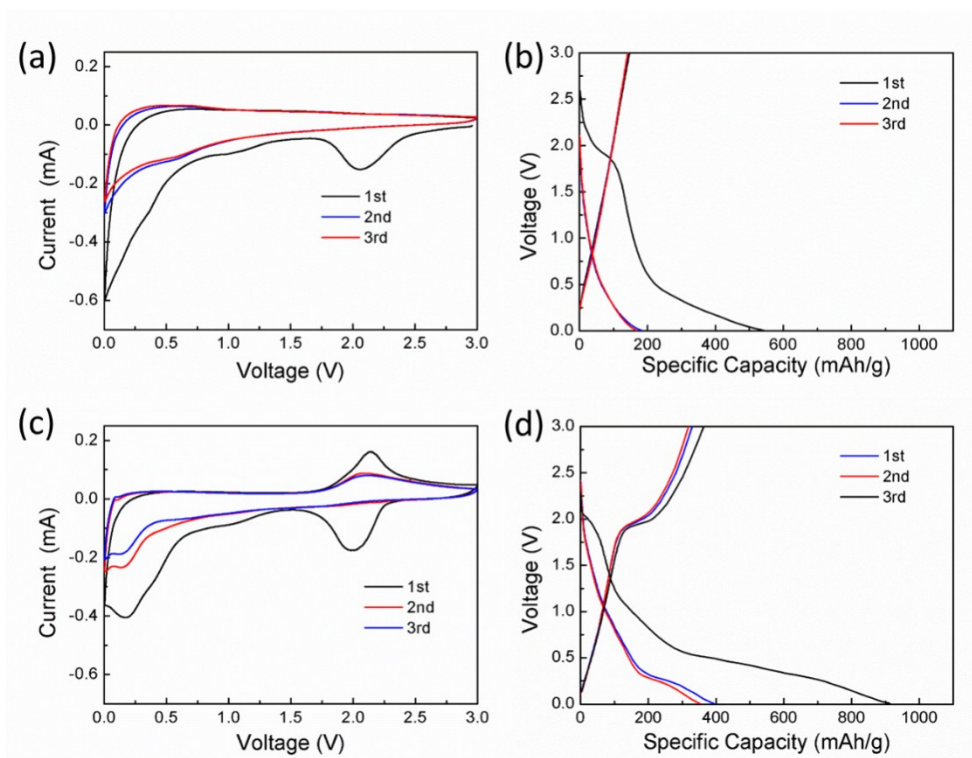


Fig. S6 The CV profiles of (a) PGM and (c) SPGM in a voltage range of 0.005-3.0 V at a scan rate of 0.2 mV/s. The charge–discharge profiles of (b) PGM and (d) SPGM at a current density of 0.5 A/g

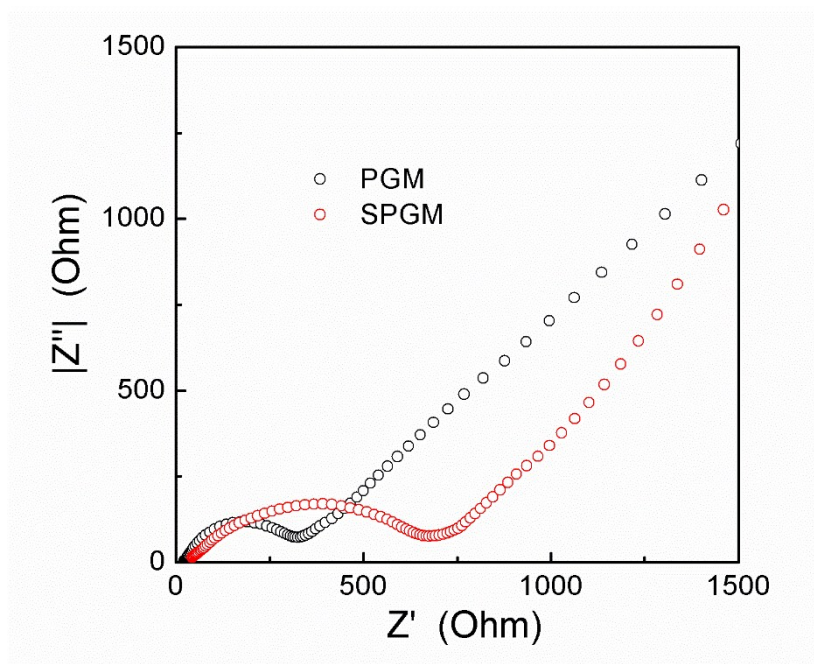


Fig. S7 Electrochemical impedance spectra (EIS) of PGM and SPGM after ten cycles at the current density of 0.5 A/g

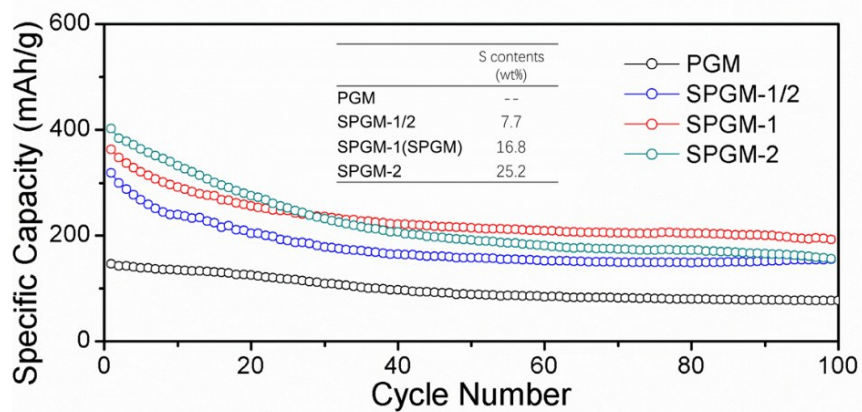


Fig. S8 The cycling performance of PGM and SPGMs with different S contents at a current density of 0.5 A/g

Table S2 Comparison of sodium storage performance of various graphene-based materials for SIBs

Materials	Preparation Method	Specific Capacity	Ref
Reduced Graphene Oxide	Heat-treatment at 450°C, then 750°C in N <sub>2</sub> atmosphere	174 m Ah/g at 40 mA/g 96 m Ah/g at 1 A/g	[1]
Crumpled graphene paper	Thionyl chloride assisted reduction and following heat-treatment at 600°C in Ar atmosphere	183 m Ah/g at 40 mA/g 61 m Ah/g at 8 A/g	[2]
Graphene nanosheets	Heat-treatment at 300 °C in Ar atmosphere	220 m Ah/g at 30 mA/g 105 m Ah/g at 5 A/g	[3]
Few-layered metal-reduced graphene oxide	Sn-induced GO reduction at room temperature	272 m Ah/g at 50 mA/g 59 m Ah/g at 1 A/g	[4]
Parallel oriented graphene	Hydrazine used as the reducing agent	225 m Ah/g at 50 mA/g 51 m Ah/g at 1 A/g	[5]
Sulfur covalently bonded graphene	Phenyl disulfide used as the sulfur precursor and heat-treatment at 1000°C in Ar atmosphere	127 m Ah/g at 2 A/g 83 m Ah/g at 5 A/g	[6]
Self-standing sulfur-doped flexible graphene films	Thiourea used as the sulfur precursor and two-step gelation process	377 m Ah/g at 100 mA/g 89 m Ah/g at 1 A/g	[7]
Sulfur-functionalized three-dimensional graphene monoliths	TDDT used as the sulfur precursor and one-step hydrothermal process	~400 m Ah/g at 100 mA/g 123 m Ah/g at 5 A/g	This work

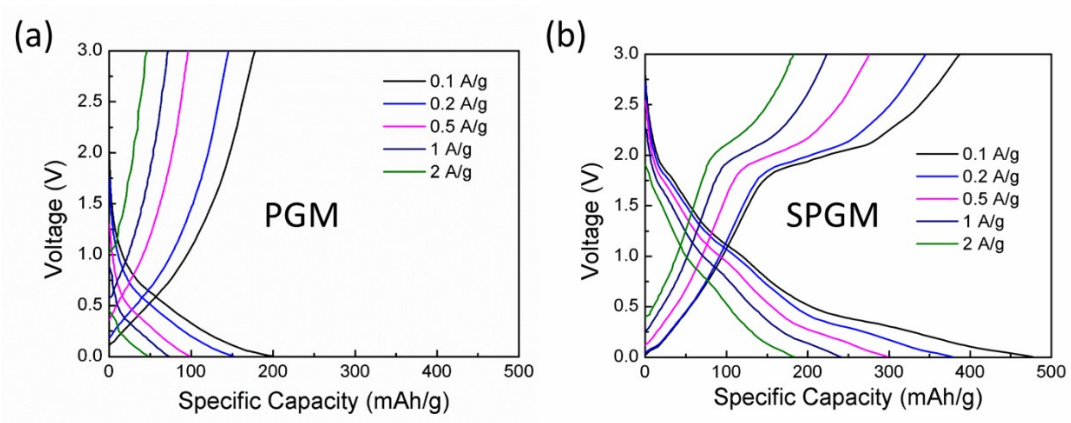


Fig. S9 The charge/discharge profiles of (a) PGM and (b) SPGM at different current densities of 0.1, 0.2, 0.5, 1 and 2 A/g

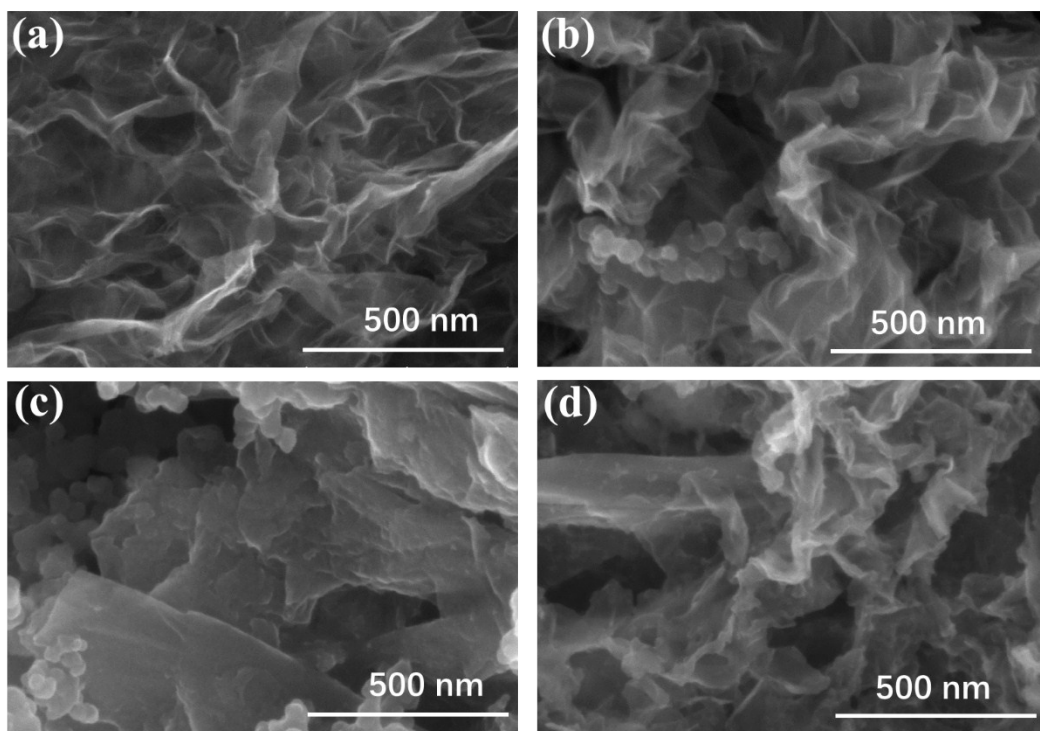


Fig. S10 SEM images of pristine PGM electrode (a) and SPGM electrode (b) and cycled PGM electrode (c) and SPGM electrode (d)

## Reference

- [1] Y.-X. Wang, S.-L. Chou, H.-K. Liu and S.-X. Dou, *Carbon*, 2013, 57, 202-208.
- [2] Y. S. Yun, Y.-U. Park, S.-J. Chang, B. H. Kim, J. Choi, J. Wang, D. Zhang, P. V. Braun, H.-J. Jin and K. Kang, *Carbon*, 2016, 99, 658-664.
- [3] X.-F. Luo, C.-H. Yang, Y.-Y. Peng, N.-W. Pu, M.-D. Ger, C.-T. Hsieh and J.-K. Chang, *J Mater. Chem. A*, 2015, 3, 10320-10326.
- [4] N. A. Kumar, R. R. Gaddam, S. R. Varanasi, D. Yang, S. K. Bhatia and X. S. Zhao, *Electrochim. Acta*, 2016, 214, 319-325.
- [5] Y. Sun, J. Tang, K. Zhang, J. Yuan, J. Li, D. M. Zhu, K. Ozawa and L. C. Qin, *Nanoscale*, 2017, 9, 2585-2595.
- [6] X. Wang, G. Li, F. M. Hassan, J. Li, X. Fan, R. Batmaz, X. Xiao and Z. Chen, *Nano Energy*, 2015, 15, 746-754.
- [7] X. Deng, K. Xie, L. Li, W. Zhou, J. Sunarso and Z. Shao, *Carbon*, 2016, 107, 67-73.