Supplementary Material (ESI) for RSC Advances
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Carbon nanofibers grown on the surface of graphite felt by chemical vapour deposition for vanadium redox flow batteries

Zhangxing He,[a] Lei Liu,[b] Zhen He,[a] Chao Gao,[a] Zhi Zhou,[a] Xinxing Liang,[a] Ying Lei[a], Zhen He*[a], and Suqin Liu*[a]

Details about cyclic voltammetry measurement

Cyclic voltammetry (CV) was performed using a three-electrode cell with the GF or CNGF as the working electrode, a Pt electrode as the counter electrode, and a saturated calomel electrode as the reference electrode. The working area of GF was kept at 1 cm^2, and the other part of GF was sealed with paraffine. The measured electrolyte is 0.1 M $VOSO_4$ + 3 M H_2SO_4 solution. The working electrode was soaked in the electrolyte for 4 hours before measurements. Cyclic voltammetry measurements were carried out on a CHI 660 C workstation (Shanghai Chenhua Instrument Co. Ltd., China) at a scan rate of 0.001 V s^{-1} in the potential range of 0.3 V to 1.4 V.

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Details about the cell configuration, cell assembly and operating conditions.

Cell performance with GF and CNGF electrodes was measured using an in-house designed single static cell system, which was mainly consisted of two pieces of polyacrylonitrile(PAN)-based graphite felt as the electrodes (Shenhe Carbon Fiber Materials Co., Ltd.), two current collectors and a perfluorinated ion-exchange membrane (Best Industrial & Trade Co., Ltd., China). The area of the electrode was kept at 2×2 cm^2. The positive electrode compartment was separated from the negative electrode compartment with a perfluorinated ion-exchange membrane. The electrode was encircled and fixed with polyurethane with a thickness of 4 cm, and the polyurethane and current collector were sealed with the silicon rubber. 1.2 M V(IV) + 3.0 M H_2SO_4 and 1.2 M V(III) + 3.0 M H_2SO_4 were employed as the original positive and negative electrolytes in the tests, respectively. Before the cell was assembled, the electrode was soaked in the original electrolyte for 24 h at an ambient temperature. Constant-current charge-discharge tests were carried out between 0.7 V and 1.7 V at a current density of 30 mA cm^{-2} with a battery test system CT2001A-10V/2A (Wuhan Land Co., China). Prior to the tests, the charge-discharge tests were performed for one cycle at a current density of 10 mA cm^{-2} to activate the electrode. The cell configuration and materials except for the electrode were kept the same for all the tests. The performance of the GF and CNGF as the electrodes in VRFB was discussed.

TEM Characterization

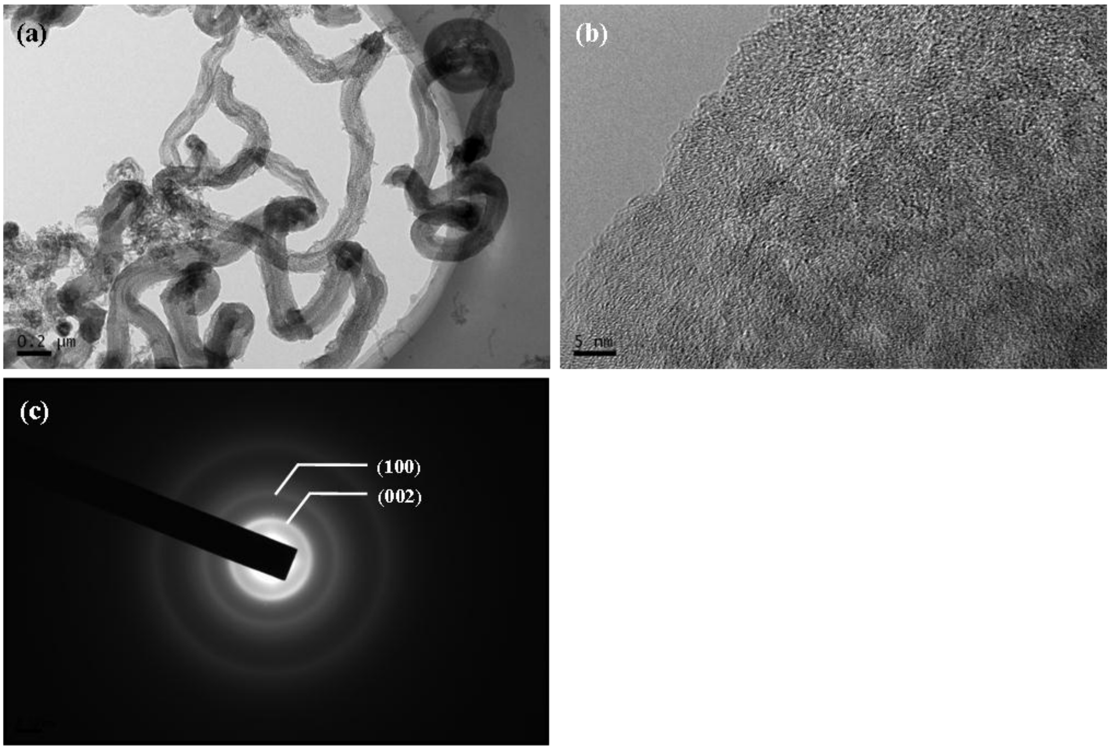

Fig. S1 (a) TEM image, (b) HRTEM (high resolution TEM) image and (c) selected area electron diffraction (SAED) pattern of flaking off carbon nanofibers from the graphite felt.

The morphology of the CVD-grown carbon nanofibers on the graphite felt were characterized using a transmission electron microscope (TEM, JEM-2100F). The carbon nanofibers were separated from the graphite felt by ultrasonication before the TEM characterization.

Fig. S1a shows that the carbon nanofibers have a width of 100-200 nm with a rough surface and a curled shape. There is no obvious fringe of the carbon nanofibers observed in the high-resolution TEM (HRTEM) image (Fig. S1b), which indicates the poor-crystalline nature of the carbon nanofibers.

In addition, selected area electron diffraction (SAED) pattern (Fig. S1c) was also performed to investigate the crystalline characteristics of the carbon nanofibers based on the selected area shown in Fig. S1a. The two most-distinct concentric diffraction rings from the center could be assigned to the (002) and (100) planes of graphite (PDF#65-6212), and the dim diffraction points of carbon fibers also show the poor-crystalline nature, which agrees well with the results obtained from the HRTEM (Fig. S1b).

BET and pore size measurements

The BET and pore size measurements were performed on a QUADRASORB *SI* automated surface area & pore size analyzer (Quantachrome Co., America).

As can be known from Fig. S2, S3 and S4, there are some pores in different radius appeared on the surface of CNGF. The BET area of graphite felt increases from 0.33 m^2 g^{-1} to 32.4 m^2 g^{-1} after the growth of carbon nanofibers on the surface of graphite felt. The average pore radius is 99.0 nm. The main pore radius appears at 18 nm and 180 nm. It is believed that the appeared pores are advantageous for the mass transfer of the active species.

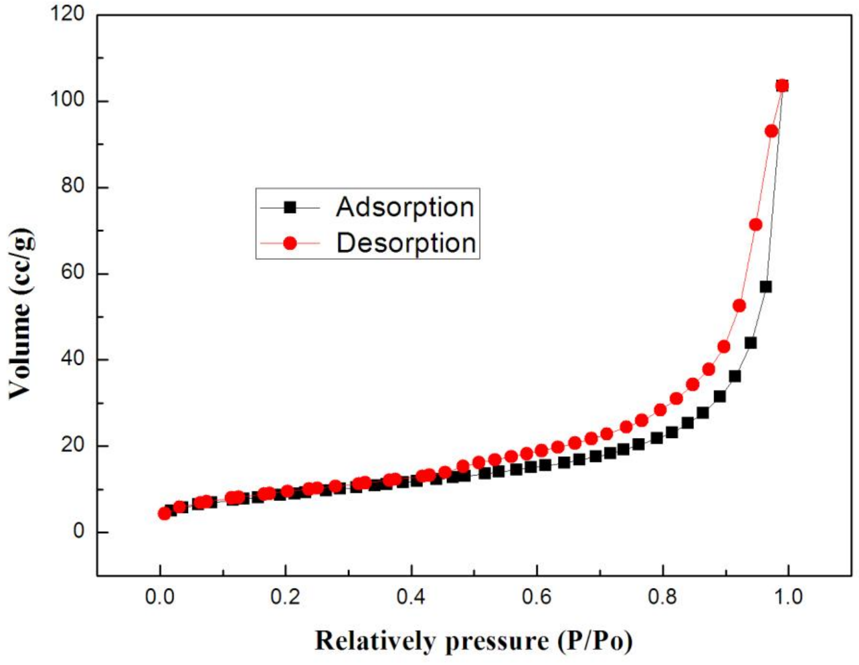

Fig. S2 Adsorption and desorption isotherm of CNGF

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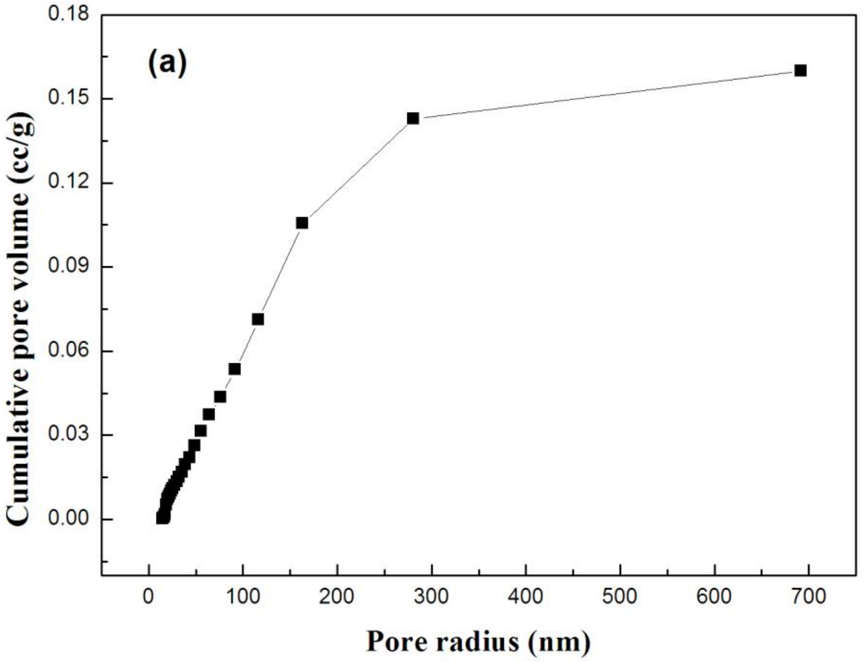

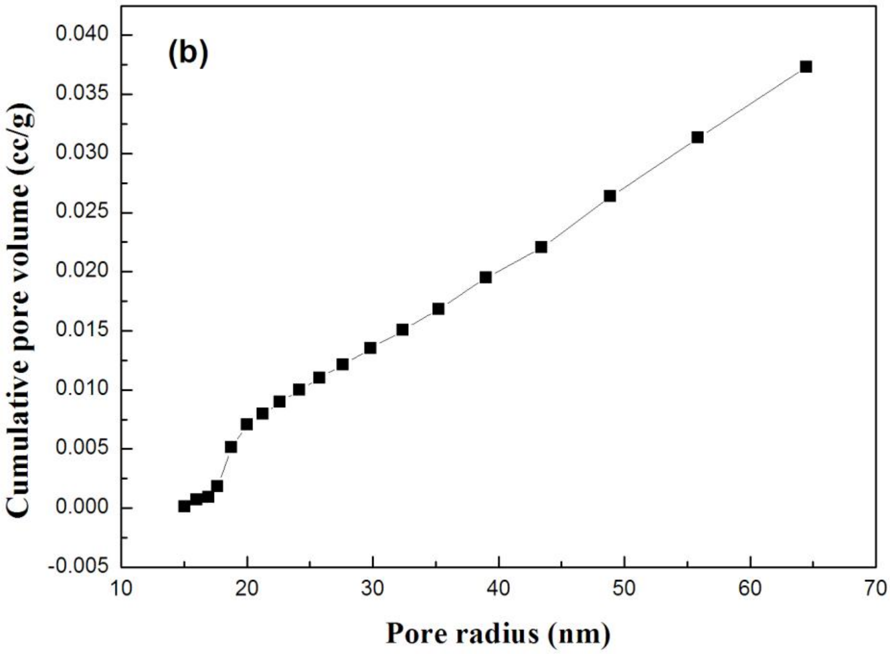

Fig. S3 Cumulative pore volume of CNGF as a function of pore radius by the desorption of N_2. (a) overall range, (b) small radius range.

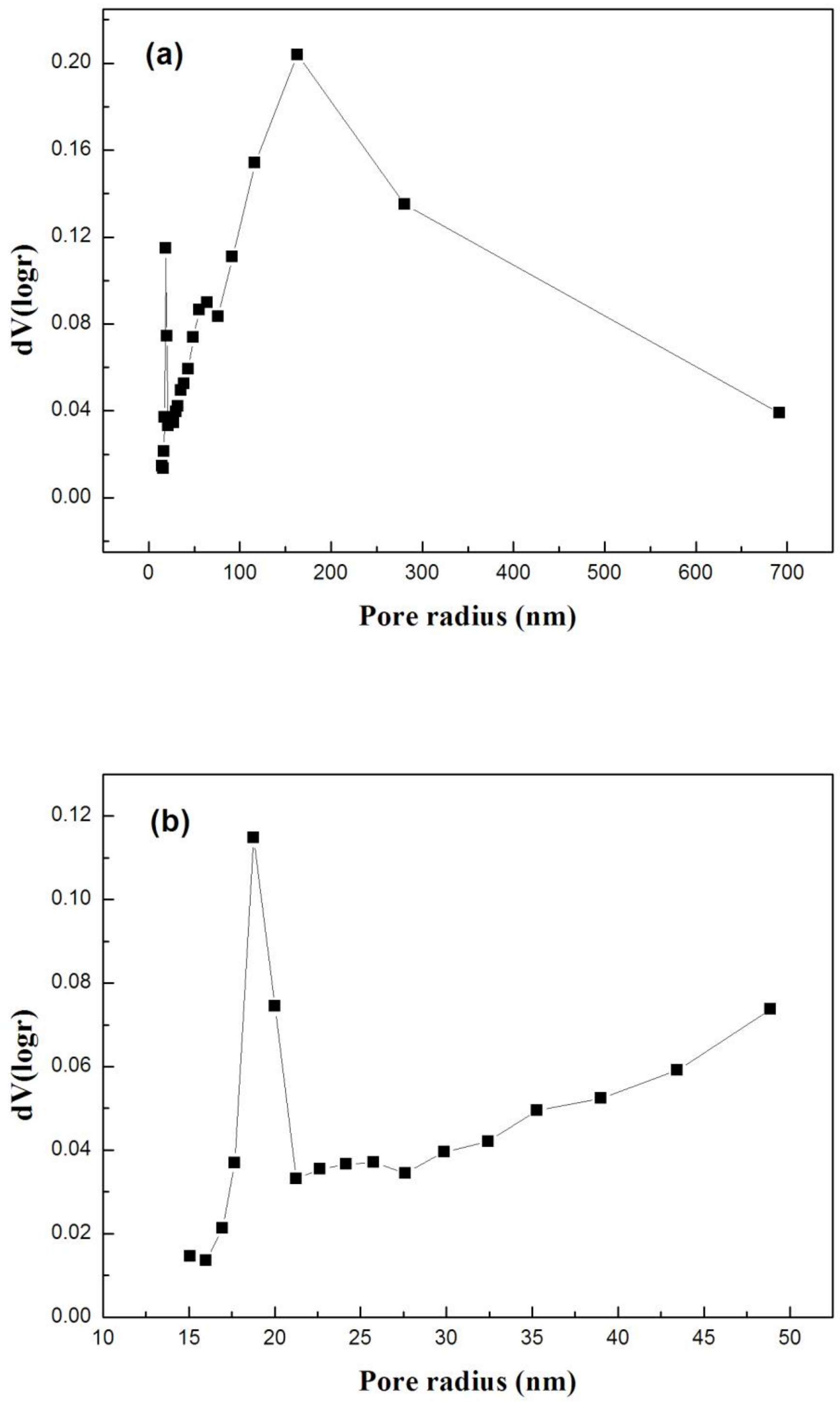

Fig. S4 Pore size distribution of CNGF by the desorption of N_2.
(a) overall range, (b) small radius range.