## Integrated electrospun carbon nanofibers with vanadium and single-

## walled carbon nanotubes through covalent bond for high-performance

## supercapacitor

Kexin Tang abc, Yuping Li\*b, Hongbin Caoabc, Feng Duanb, Jason Zhanga, Yi Zhangabc, Yi Wang b

a National Engineering Research Center for Distillation Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

b Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

c Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, PR China

> \* Corresponding author. Tel.:+ 86-10-82544844-810; Fax: +86-10-82544844-816. E-mail address: ypli@ ipe.ac.cn (Yuping Li).

# **Electronic Supplementary Information**

#### 1. Transitional pre-oxidized process

From the results of TGA/DSC, it is noticed that the pre-oxidized temperature under air flow was located around 300 °C; however, by considering temperature drifting under fast heating rate by 10 °C min<sup>-1</sup> during measurement of TGA/DSC, the oxidized temperature would be deviated from the real oxidized temperature, so the oxidized temperature was finally set at 270 to 290 °C, namely longer keeping time during this period. The whole pre-oxidized process was departed for 9 stages. The purpose of Stage 1 was to heat materials in higher rate of 2 °C min<sup>-1</sup> but without deformation and crimp for materials. From stage 2 to 5, the as-synthesized materials began to cross link and pyrolysis. When coming into stage 6, the cross-linking reaction and pyrolysis reaction went more violently. We supposed these reactions became gentle when oxidized temperature reached 290 °C. For the purpose of sufficient oxidizing for materials, we finally keep materials at 300 °C for another 8 min.

Because the frameworks of carbon matrix were fundamentally formed during pre-oxidation process, the heating rate was increased to 5 °C min<sup>-1</sup> to reach to carbonized temperature faster. In this work, we only considered two carbonized temperature, but still could reveal some characteristics for materials.

Atmosphere	Stage	Initial Temp. (°C)	End Temp. (°C)	Heating Rate (°C min <sup>-1</sup> )	Heating up time (min)	Keeping Time (min)
	1	25	225	2	100	8
	2	225	245	1	20	8
	3	245	255	1	10	8
	4	255	265	1	10	8
Air	5	265	275	1	10	8
	6	275	280	1	5	8
	7	280	285	1	5	8
	8	285	290	1	5	8
	9	290	300	1	10	38
N	10-1	300	800	5	100	120
1N <sub>2</sub>	10-2	300	900	5	120	120

Table S1 PAN/PVP precursor nanofibers oxidizing and carbonizing procedure

#### 2. Morphology for samples under low magnification

From the low magnification of SEM images of as-synthesized materials, we can clearly notice the shrink of nanofibers from precursors, hybrid CNFs annealed at 800 °C (CNFs-800) to that at 900 °C (CNFs-900). Notably, all characterized samples possessed uniform diameter for precursors, CNFs-800 and CNFs-900, indicating stable pre-oxidation and carbonization process and uniform distribution of vanadium and SWCNTs in hybrid CNFs.



Fig. S1 FE-SEM images of nanofibers taken at relatively low magnification: (A1-A3) PNFs, PCNFs-800, PCNFs-900, (B1-B3) SNFs, SCNFs-800, SCNFs-900, (C1-C3) VNFs, VCNFs-800, VCNFs-900 and (D1-D3) 15VSNFs, 15VSCNFs-800, 15VSCNFs-900.

#### 3. Pore structure of CNFs-900

CNFs-900 samples demonstrate very different structure and properties relative to CNFs-800. As shown in Fig. S2, nitrogen isotherm curves (a) of samples annealed at 900 °C and their pore size distribution curves (b) are obtained. For PCNFs, only micropores are detected, resulting in larger specific surface area. However, differential pore structure is obtained if SWCNFs are added into PCNFs, like larger adsorption volume and specific surface area and hierarchical pore structure with both micropores and mesopores. When increasing carbonized temperature from 800 to 900 °C, the effects of vanadium on the elements and internal structure for CNFs are changed: To much content of vanadium or without the assistant from SWCNTs, micropores would fracture to mesopores, resulting in smaller adsorption volume and specific surface area, or in plugging ion channels.



Fig. S2 (A) N<sub>2</sub> adsorption isotherm curves of samples annealed at 900 °C and (B) their pore size distribution curves

#### 4. FT-IR measurements of samples

FT-IR measurements have been carried out to further understand the chemical bond and functional group on hybrid CNFs surface on a Spectra spectrometer (Nicolet iS50, Thermal Fisher Scientific, USA) (Fig. S3). For SCNFs and VSCNFs samples with SWCNTs, the absorbing vibration at 1378 and 1568 cm<sup>-1</sup> are corresponding to the symmetric and asymmetric vibration of the aliphatic nitro functional group, respectively [1]; such absorbing vibration is not obtained in SWNTs-free samples (PCNFs and VCNFs); this suggests that SWCNTs have been successfully acidized by 30% nitric acid. In addition, the absorption of hydrophilic functional groups, like R<sub>2</sub>-OH (deformation vibration at 1100 cm<sup>-1</sup> and stretching at 3630 cm<sup>-1</sup>), R-NH<sub>2</sub> (deformation at 1610 cm<sup>-1</sup>) and (R')RCH-OH (1695 cm<sup>-1</sup>), are detected [2]. These functional groups are greatly helpful when used in aqueous electrolyte, and they may be decomposed when carbonized temperature reaches 900 °C as seen from Fig. 3S.



Fig. S3 FT-IR spectra of PCNFs, SCNFs, VCNFs and VSCNFs (Solid line: 800 °C; Short dash line: 900 °C).

#### 5. Diameter distribution and average diameter of as-synthesized samples

The diameter distribution and average diameter were obtained from low magnified SEM images by nanomeasure-1.2 software based on 100 data. As shown in Fig. S4 and table S2, even if SWCNTs are attributed to thinner nanofiber compared to PNFs, the carbonized sample-800 possesses nearly the same diameter. However, VCNFs have much wider diameter. Based on the DSC curves of PNFs and VNFs, two kinds of reactions were observed: cross-linking and pyrolysis of polymers (500 to 800 °C), and disrupting reactions between VO(acc)<sub>2</sub> and polymers (450 to 650 °C). The nanofibers shrinkage was mainly caused by the former. With competed disrupting reactions, polymers shrinkage was slowed down, but tended to form bonds with vanadium and emission small molecular.

Table S2 Average diameter obtained from SEM images of samples before and after calcination.

Samples	PNFs	SNFs	VNFs	VSNFs
electrospun	930 nm	540 nm	900 nm	670 nm
800 °C	340 nm	350 nm	450 nm	350 nm
900 °C	310 nm	300 nm	440 nm	310 nm
shrinkage-800	63.4%	35.2%	50.0%	47.8%
shrinkage-900	66.7%	44.4%	51.1%	53.7%





Fig. S4 Diameter distribution of samples obtained by nanomeasure-1.2 software: samples from left to right are

electrospun precursor, CNFs-800 and CNFs-900, respectively, and from up to down, they are PNFs, SNFs, VNFs

and 15VSNFs, respectively.

#### 6. Capacitive performance based on cyclic voltammetry curves

The CV curves for CNFs/900 are more close to rectangle than those for CNFs-800, because the carbon content of hybrid CNFs is increased from 800 to 900 °C which directly leads to electric double-layer capacitor behavior. However, the relative smaller current response indicates that carbonizing at 900 °C ruins some electric double-layer structure.



**Fig. S5** Cyclic voltage curves of samples annealed at 900 °C scanning from 5 to 100 mV s<sup>-1</sup>: (A) PCNFs; (B) SCNFs; (C) VCNFs; (D) VSCNFs.

#### 7. Capacitive performance for 10VSCNFs and 20VSCNFs

For comprehensively studying the optimum content of vanadium compound in CNFs, the electrochemistry measurements for 10VSCNFs and 20VSCNFs are necessary. Fig. S6 demonstrates CV curves and GCD curves for these four samples, which are 10VSCNFs-800, 10VSCNFs-900, 20VSCNFs-800 and 20VSCNFs-900. The shape of CV curves of 10VSCNFs-800 are similar to that of 15VSCNFs-800 except the relative low current response, however, with 20% vanadium

compound in CNFs, the oxidation and reduction potential drift from -0.7 V and -0.9 V, respectively, in the meantime, the area of CV curves shrink as well in result of smaller  $C_{cv}$ . The rising of carbonized temperature reduce current response as well. In conclusion, the  $C_{cv}$  and  $C_{GCD}$  tendency changing with adding vanadium indicates that 15% VO(acc)<sub>2</sub> and 10% SWCNTs can make the best performance VSCNFs electrode.



Fig S6 Cyclic voltage curves of (A) 10VSCNFs-800, (B) 20VSCNFs-800, (C) 10VSCNFs-900 and (D) 20VSCNFs-900.

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	Rate		800 °C			900 °C	
	performance	2 A g <sup>-1</sup>	5 A g <sup>-1</sup>	10 A g <sup>-1</sup>	2 A g <sup>-1</sup>	5 A g <sup>-1</sup>	10 A g <sup>-1</sup>
	PCNFs	96.2%	91.8%	88.1%	91.5%	84.6%	77.9%
	SCNFs	96.6%	92.9%	87.8%	97.6%	92.9%	89.4%
	VCNFs	86.2%	76.1%	66.3%	83.6%	73.9%	68.3%
	<b>10VSCNFs</b>	91.1%	82.7%	76.7%	94.8%	87.2%	80.5%
	15VSCNFs	89.3%	83.5%	76.7%	88.5%	81.3%	76.0%
	20VSCNFs	96.4%	85.0%	76.0%	92.2%	65.1%	53.7%

**Table S3** Capacitance rate performance of samples as a function of charge-discharge current density relative to 1 A  $g^{-1}$ .

#### 8. Adsorption mechanism and internal structure of samples annealed at 900 °C

Nyquist plots could directly reveal the capacitive behavior and mass transfer and diffusion capability for electrodes. As shown in Fig S7, according to semi-circle at high frequency, the series resistance of 15VSCNFs changes little from 800 to 900 °C, however, the decreasing of slope at relative low frequency indicates mass transfer ability is also decreased, suggesting that 800°C is an appropriate carbonized temperature for 15VSNFs. For all samples inserted with SWCNTs, increasing vanadium content from 0 to 20% relative to PAN impairs the conductivity and mass transfer at the same time, which is different for CNFs-800. On the other hand, without SWCNTs, vanadium is still benefit for pure CNFs by improving its conductivity according to the nyquist plots for PCNFs-900 and VCNFs-900.



Fig. S7 Nyquist plots of samples carbonized at 900 °C, and the inserted graph in Nyquist plots is partially enlarged details at high frequency

9. Digital images of as-synthesized materials and working electrode.





Fig. S8 Digital images of (a) CNFs sheet, (b) working electrode, (c) thickness measurement.

### 10. TEM and HRTEM images for PCNFs and 15VSCNFs-800

Fig. S9 displays the TEM and HRTEM images of PCNFs and 15VSCNFs-800. TEM generates electron beam under electric field of 200 KV. However, the penetrability of electron beam is really weak (< 50 nm). With nearly the same diameter around 350 nm, PCNFs shows dense black shape, indicating electron beams are almost absorbed. However, on the edge of 15VSCNFs-800, some electron beams do penetrate the surface, indicating more loose structure compared to PCNFs. The more dense structure of PCNFs is also clearly observed from HRTEM images. By considering the analysis of nitrogen isothermal curves and pore distribution, one of the pore structure differences between PCNFs and 15VSCNFs-800 is that the latter possesses much larger mesopores. Therefore, we make the conclusion that it is the mesopores in 15VSCNFs-800 lead some electron beams penetrate the edge of CNFs. The reason why the core of nanofibers shows black shape is because those mesopores are arranged irregular and vermicular.







Fig. S9 TEM images for (a) PCNFs and (b) 15VSCNFs-800 and HRTEM images for (c) PCNFs and (d) 15VSCNFs-800.

## Reference

P.S. Vijayanand, Y. Wang, S. Satokawa, S. Kato and T. Kojima, J Macromol Sci A. 44(2007) 913-921.
F. Shao, X.F. Ni and Z.Q. Shen, Chinese Chem Lett. 23(2012) 347-350.