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Preparation and Characterization of PAN Derived Activated Carbon Nanofibers with High Specific Surface Area via Electrospinning Technique

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Abstract: Carbon nanofibers (CNFs) were synthesized by pyrolysis of polyarylonitrile (PAN) nanofibers that were prepared by dissolving of PAN in N,N-dimethylformamide (DMF) solution followed by electrospinning and drying. The obtained CNFs were further treated via a CO_2 activation process. The morphology and porous structures of the obtained nanofibers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N_2 sorption measurements. Effects of polymer solution concentration and static voltage during the electrospinning process on the morphology and diameter of nanofibers were studied. Their unique microstructural features enable the CNFs to present outstanding high specific capacitance in aqueous, non-aqueous and novel ionic liquid electrolytes. Moreover, the CO_2 activated carbon nanofibers (ACNFs) exhibit a high specific area (2866 m^2 g^{-1}) and pore volume which is almost three times higher than that of the raw carbon nanofibers. Overall, combinations of the high surface areas and outstanding electrical conductivity make the activated carbon nanofibers have a further application in supercapacitor electrode materials.

Key words: electrospinning; carbon nanofiber; activation; specific surface area

Carbon nanofibers (CNFs), like other one-dimensional nanostructures such as nanotubes and nanowires, have drawn great attention owing to their outstanding mechanical properties, remarkable electrical and thermal conductivities, strong fatigue and corrosion resistance[1-3]. And thus, they are required for various technologies ranging from catalysts and nanoelectronics to bearing composites and supercapacitors[4-7]. Commonly, carbon fibers are prepared from organic precursors and the fibers typically have diameters ranging from 5 μm to 10 μm. To produce carbon fibers with diameters in the nanometer range, the method of chemical vapor deposition (CVD) has been investigated[8]. However, the CVD method is complicated with safety risks and high cost, and is only capable of producing relatively short fibers which are difficult to apply to mass production. To overcome these disadvantages, in recent years, the technique of electrospinning has attracted considerable attentions as a straightforward and cost-effective approach for further application of carbon nanofibers[9-11].

Electrospinning is simple and versatile technique for producing nanofibers, and in the past few years, various polymer solutions or melts, composites and sol-gel ceramics have been successfully electrospun into nanoscale, or ultrafine fibers[12-14]. Presently polyacrylonitrile (PAN) precursor has been widely used as an organic precursor in the manufacture of the majority of carbon nanofibers because of relatively high carbon yield and a thermally stable, extremely oriented molecular structure. And the PAN nanofibers can be transformed into CNFs or ACNFs by the process of stabilization and carbonization-activation. The produced CNFs/ACNFs have a good electrical conductivity and a high specific surface area from shallow pores size, which can be in favor of enhancing the specific capacitance and energy density when they are used as anode material of supercapacitors and rechargeable batteries. Since 2000, several papers on preparation PAN-based carbon nanofibers have been published. C. Kim et al[7] used PAN solution as precursor to prepare nanofibers by electrospinning, and the nanofibers were oxidatively stabilized and activated by steam resulting in ACNFs. The ACNF activated at 700 ℃ had the highest specific surface area and exhibited maximum specific capacitance at 10 mA g^{-1}[7]. Y. Wang et al[15] fabricated PAN-based CNFs by electrospinning and subsequent pyrolysis, and found that the graphitization of CNFs led to a sharp increase in electrical conductivity to around 490 S m^{-1}. H. Hou *et al* reported an approach to use the carbonized electrospun PAN

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nanofibers as substrates for the formation of multi-wall carbon nanotubes[16]. These reports mainly focused on the electrochemical properties or compound modification of PAN-based carbon nanofibers. However, the optimization of preparation parameters to obtain uniform morphology and diameter of carbon nanofibers has not been studied yet.

In this study, CNFs were synthesized by pyrolysis of polyarylonitrile (PAN) nanofibers that were prepared by dissolving of PAN in N,N-dimethylformamide (DMF) solution followed by electrospinning and thermal treatments. The obtained carbon nanofibers were further treated *via* a CO_2 activation process. The morphology and microstructures of CNFs obtained by different polymer solution concentration and static voltage and CNFs before and after CO_2 activation were studied. Compared to PAN nanofibers, the CNFs prepared by carbonizing PAN nanofibers exhibit much higher specific surface areas from micropores, which are further enhanced by CO_2 activation. Their unique microstructural features will enable the activated carbon nanofibers (ACNFs) present outstanding high specific capacitance in electrolytes and show application potentials in low-cost supercapacitor and battery electrode materials.

1 Experiment

All chemicals were used without further purification. polyacrylonitrile (PAN) (catalog number 18131-5) with average molecular weight of 150 000 was purchased from Sigma-Aldrich. The N,N-dimethylformamide (DMF) and acetone were purchased from Shanghai Chemical Reagent Company (Shanghai, China).

The predetermined amount of PAN powders was dissolved in DMF to produce a homogeneous PAN solution for electrospinning. The concentration of PAN in the polymer solution was systematically varied from 8 wt% to 14 wt%. Typically, 1.5 g of PAN (Mw=150 000) powder was dissolved in 14.28 mL of DMF solution. After stirring at 60 ℃ water bath for 6 h, the above precursor solution was loaded into a plastic syringe with a stainless steel needle having an inner diameter of 0.35 mm. The flow rate of the polymer solution was controlled at 0.5 mL h^{-1}. The needle was electrically connected to a positive high voltage power that is capable of generating direct current (DC) voltages up to 20 kV. A ground metal roller covered by an aluminum foil was placed at 15 cm (from the tip of the needle to the surface of the roller) below the syringe as the collector, and the roller was electrically connected to a negative high voltage power supply. During electrospinning, the applied voltage was adjusted from 10 to 20 kV and the rotational speed of the roller was set at 1500 r/min. The electrospun PAN nanofiber mesh was carefully peeled off from the aluminum foil and then stabilized in air for 2 h at 260 ℃. The stabilized PAN nanofibers were pyrolyzed at 1000 ℃ under N_2 atmosphere for 1 h with the heating rate set of 5 ℃ min^{-1}. The derived carbon nanofibers were designated. The CO_2 activation was carried out under flowing CO_2 (40 mL min^{-1}) and N_2 (80 mL min^{-1}) at 1000 ℃ for 2 h.

The morphology of the sample was characterized by a scanning electron microscope (XL 30FEG, Netherland) and a transmission electron microscope (JEOL-1230). Raman spectra (Jobin-Yvon HR800) were recorded from 1000 to 2000 cm^{-1} using a 514 nm argon ion laser (source power 17 mW). Organic groups were investigated by a Fourier transform infrared spectroscope (TEN-SOR27, Germany). The porous attributes of CNFs and ACNFs were measured by a N_2 adsorption analyzer (TriStar 3000, USA) using the BET nitrogen adsorption/desorption technique.

2 Result and Discussion

2.1 Morphologies of electron-spun PAN nanofibers

In the electrospinning process, when the electric force on induced charges on the polymer liquid overcomes surface tension, a thin polymer jet is ejected. Due to bending instability, the traveling path of the electrospinning jet is complicated and chaotic, and the concentration of precursor solution and applied voltage are the key factors affecting the morphology and diameters of the resulting nanofibers. Fig.1 shows some SEM images of as-spun PAN nanofibers with varying the concentration of PAN/DMF solutions. The diameters of as-electrospun PAN nanofibers at different concentrations are listed in Table 1. The diameters gradually increase from several hundred nanometers to a few microns with the solution concentration increasing (8 wt%~14 wt%). Particularly, when precursor concentration is low (8 wt% and 10 wt%), the PAN nanofibers in Fig.1 are uniform without microscopically identifiable beads or beaded nanofibers; and the fiber diameters are 510 and 660 nm, respectively. This is attributed to the increase in volume percent of solid in the precursor solution resulting in increasing the viscosity of precursor solution which may prevent the thin-charged polymer jet from stretching and cause the initial increase in the fiber size. The SEM images in Fig.2 show the representative morphologies of the as-electrospun PAN nanofibers with different applied voltages and the diameter values of the corresponding PAN nanofibers are listed in Table 2. The same result was found by S. Y. Gu et al[17,18], when they studied the variation of nanofiber diameter of PAN as process parameters were changed. It is demonstrated that the fiber's diameter decreases as the applied voltage of electrospinning increases. This is the reason that the increase of applied voltages will result in an increase in the pulling and electrostatic force acting on the charged jet, creating smaller diameter fibers. These results indicate that decreasing polymer solution concentration and increasing voltage appropriately in a certain range can fabricate PAN nanofibers with smooth and uniform fiber diameter around 600 nm which may prepare highly porous carbon nanofibers by the subsequent process of carbonization and activation.

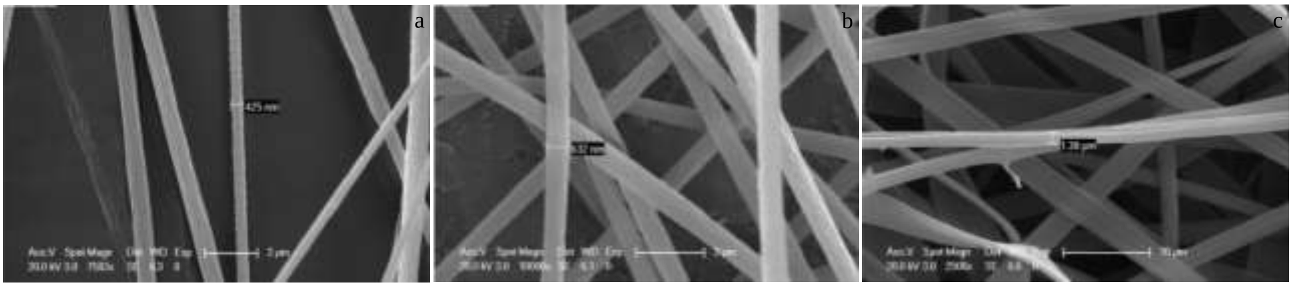

Fig.1 SEM images of PAN nanofibers with different concentrations of solutions: (a) 8 wt%, (b) 10 wt%, and (c) 14 wt% (electrospinning conditions: applied voltage, 15 kV; flow rate, 0.5 mL·h^{-1}; tip-to-collector, 15 cm)

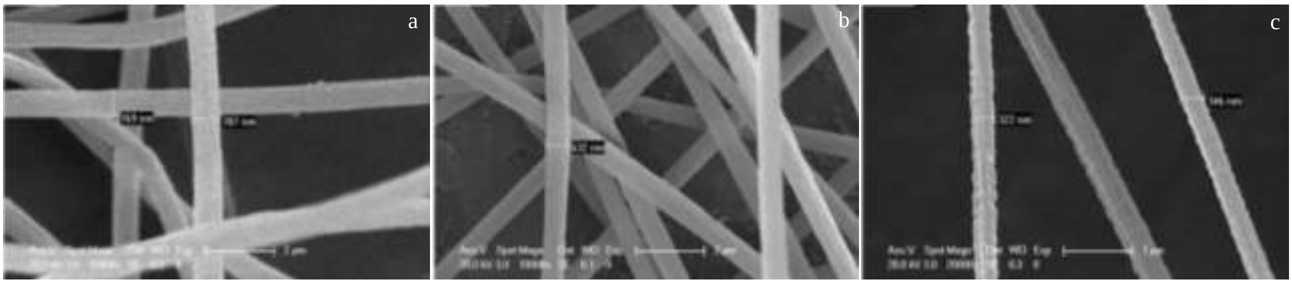

Fig.2 SEM images of PAN nanofibers with different applied voltages: (a) 10 kV, (b) 15 kV, (c) 20 kV (electrospinning conditions: precursor solution concentration, 10 wt%; flow rate: 0.5 mL·h^{-1}; tip-to-collector: 15 cm)

Table 1 Diameters of as-electrospun PAN nanofibers at various polymer solution concentrations

Polymer solution concentration/wt%	8	10	14
Diameter/nm	510	660	1940

Electrospinning conditions: applied voltage is 15 kV; flow rate is 0.5 mL·h^{-1}; tip-to-collector is 15 cm

Table 2 Diameters of as-electrospun PAN nanofibers at various applied voltages

Applied voltage/kV	10	15	20
Diameter/nm	764	631	334

Electrospinning conditions: precursor solution concentration is 10 wt%; flow rate is 0.5 mL·h^{-1}; tip-to-collector is 15 cm

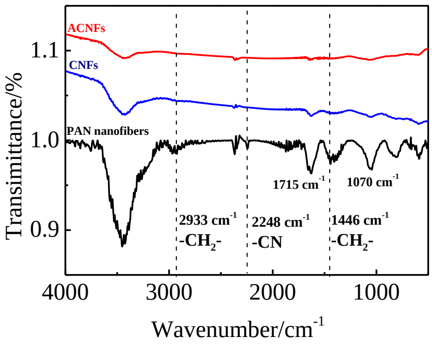

Fig.3 FTIR spectra of PAN nanofibers, CNFs and ACNFs

2.2 Characterization of PAN, CNFs and ACNFs nanofibers

FTIR spectra of PAN nanofibers, CNFs and ACNFs are illustrated in Fig.3 and show the prominent structural changes after thermal treatments. For the electrospun PAN nanofibers, the bands centered at 1446 and 2933 cm^{-1} are associated with the stretching and bending vibration of methylene (-CH$_2$) group, respectively. The peak centered at 1070 cm^{-1} is due to the stretching vibration of carbon bonds (C-CN). The peak at 2248 cm^{-1} is attributed to the nitrile (-CN) stretching mode. PAN deposited from DMF solution often has a peak at about 1715 cm^{-1}, which may be attributed to the vibration of the carbonyl (C=O) bonds formed in the hydrolyzed PAN nanofibers and the stretching vibration of the carbonyl bonds in residual DMF solvent[19]. After carbonizing PAN nanofibers at high temperature, the bands at 1070, 1446 and 2933 cm^{-1} of CNFs and ACNFs are declined dramatically and almost disappear which may be due to decomposition reactions including breaking C-CN bands and C-H bands, according to band strength data. And the nitrile band totally disappears, indicating the total cyclization of the structure. Finally, after the thermal treatments, all of the functional groups almost disappear, which result in equivalent composition that is pure carbon. Raman spectra of electrospun PAN nanofibers, CNFs and ACNFs are shown in Fig.4. After the thermal treatments, the samples exhibit two strongest bands at around 1358 and 1576 cm^{-1}

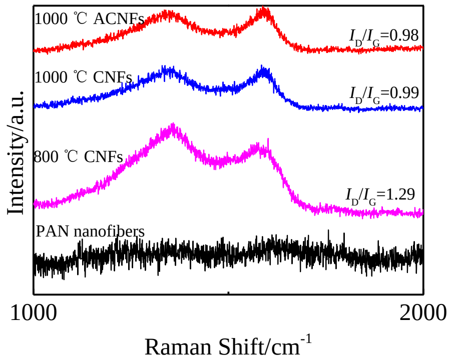

Fig.4 Raman spectra of PAN nanofibers, ACNFs and CNFs obtained at different carbonized temperatures

that correspond to D band and G band, respectively. The G band arises from the zone center E_{2g}, corresponding to order sp^2-bonded carbon, while the D band is attributed to disordered carbon and other defects[20]. As calculated from the spectra, the ratio of the intensities between D and G bands (the I_D and I_G ratio) decreases with the increase of carbonization temperature, as shown in Fig.4. These indicate that the thermal treatments decrease some disorder and defects of carbon nanofibers and disordered carbonaceous components are converted into more ordered graphite crystallites with increase of the final carbonization temperature.

2.3 Morphologies and textural properties of CNFs and ACNFs

The SEM images of “a”, “b” and “c” in Fig.5 show the representative morphologies of the as-electrospun, low temperature (800 ℃) carbonized, and high-temperature (1000 ℃) carbonized PAN nanofibers, respectively. After the carbonization process, the nanofibers retain their shape with uniform morphologies and the average diameter decreases with carbonization temperature. As shown in Table 3, the diameters of the 800 and 1000 ℃ carbonized PAN nanofibers are reduced to 480 nm and 340 nm, respectively, and the corresponding radical carbonized shrinkage are 24.1% and 46.2%. During carbonization, a variety of gases (e.g., H_2O, N_2, HCN and others) are evolved and carbon content increases to 90 wt% or higher. Hence, the process of carbonization leads to the reduction of fiber diameter and the formation of hierarchical porous carbonaceous structures. CO_2 activation is one of the most common techniques used to increase the microporosity of carbon materials. Oxidation by the activating gas significantly increases the specific surface area of the final product[21]. Fig.5b shows the SEM image of typical sample of ACNFs. It could be seen that ACNFs obtained by activating with CO_2 at 1000 ℃ exhibit the same uniform morphologies with CNFs carbonizing at 1000 ℃; and the diameter of ACNFs is about 300 nm. In addition, the TEM images of ACNFs shown in Fig.6 with different magnifications, are in good agreement with the results discussed above.

The pore structure and specific surface areas of PAN nanofibers, CNFs and ACNFs were investigated by a N_2 adsorption analyzer using the BET N_2 adsorption-desorption technique. N_2 adsorption-desorption isotherms (Fig.7a) provide information about the microstructure of PAN nanofibers before and after thermal treatments. According to the IUPAC classification[22], the adsorption-desorption isotherms exhibit typical type I characteristics to both CNFs and ACNFs, which imply that two samples are micropore-based material. From Fig.7a, it could be observed that the isotherms of CNFs and

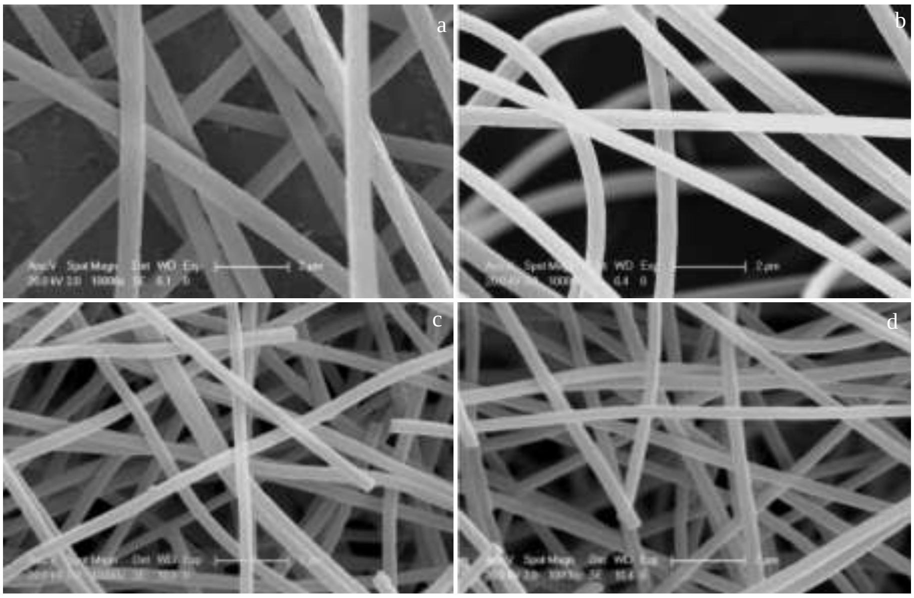

Fig.5 SEM images of as-electrospun PAN nanofibers (a), CNFs (800 ℃) (b), CNFs (1000 ℃) (c), and ACNFs (d)

Table 3 Diameters and radical carbonized shrinkage of samples

Sample	Diameter/nm	Carbonized shrinkage/%
PAN nanofibers	632	-
800 ℃-CNFs	480	24.1
1000 ℃-CNFs	340	46.2
ACNFs	308	51.2

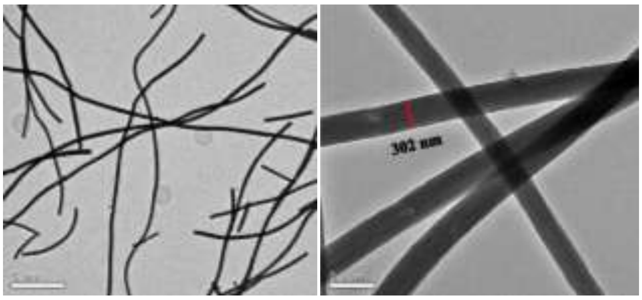

Fig.6 TEM images of ACNFs

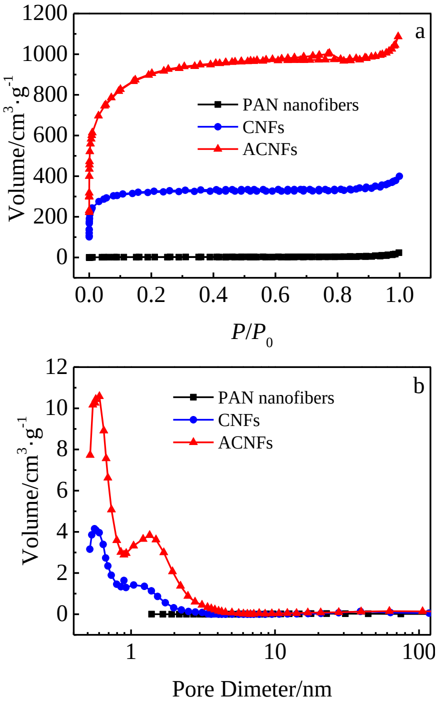

Fig.7 N_2 adsorption-desorption isotherms of samples (a); the pore size distribution of the corresponding samples (b)

Table 4 Pore structural parameters of samples

Sample	S_{BET}/ $m^2\ g^{-1}$	S_{mic}/ $m^2\ g^{-1}$	V_{tot}/ $cm^3\ g^{-1}$	V_{mic}/ $cm^3\ g^{-1}$	D/ nm	V_{mic}/V_{tot}/ %
PAN	7.55	-	0.03	-	-	-
CNFs	987.9	939.8	0.62	0.54	2.0	87
ACNFs	2866	2548	1.68	1.42	1.9	85

S_{BET}: apparent surface area calculated by BET method; S_{mic}, V_{mic}: micropore surface area and micropore volume calculated by t-plot method, respectively; V_{tot}: total pore volume at p/p_0=0.99; D: average pore diameter

ACNFs show increased adsorption at low relative pressures, indicating the formation of new porosity within nanofibers after thermal treatments. Moreover, ACNFs exhibit much larger adsorption volume than CNFs at low relative pressure, indicating that CO_2 activation would greatly increase the amount of micropores[23,24]. The corresponding pore-size distributions are given in Fig.7b, which are in good agreement with the trend discussed above. ACNFs contain a large number of micropores, and both CNFs and ACNFs almost have no adsorption capacity in the range of mesopores and macropores. These more micropores are derived from the CO_2 activation, thus becoming the major contributor to the dramatic increase of specific surface areas. According to the texture parameters of samples listed in Table 4, after carbonization, the specific surface areas of PAN nanofibers increase to 987.9 $m^2\ g^{-1}$, which may be due to the increase of the amount micropores within fibers. The S_{mic} and V_{mic} of CNFs are 939.8 $m^2\ g^{-1}$ and 0.54 $cm^3\ g^{-1}$, respectively, which contribute 87% of the V_{tot}. It should be noted that the activated CNFs (ACNFs) exhibit 2866 $m^2\ g^{-1}$, which are much higher than those of CNFs without activation. Similarly, the higher specific surface areas are probably attributed to the great increase of the amount of micropores after CO_2 activation. ACNFs with very high specific surface areas (2866 $m^2\ g^{-1}$) and highly microporous structure have a more dispersed pore size distribution over the range from 0.5 nm to 2 nm with a bimodal feature at ~ 0.6 and ~ 1.4 nm. This kind of structure is very suitable for electrolyte ions to transfer and enhance the energy density as electrode materials in supercapacitor and battery[25].

3 Conclusions

1) Nanofibers with diameter ranging from 322 nm to 1.3 μm are obtained by electrospinning of PAN/DMF solution with varying electrospinning conditions, such as precursor solution concentration and applied voltage. The diameters of as-electrospun fibers decrease as the applied voltage increases, and increase as the concentration of the precursor solution increases.

2) The electrospun PAN nanofibers are used as the raw materials to prepare carbon nanofibers through carbonization at different temperatures and high-specific-surface-area ACNFs are synthesized by the subsequent CO_2 activation. Compared to the PAN nanofibers, the CNFs exhibit much higher specific surface areas (987.9 $m^2\ g^{-1}$) and pore volumes (0.62 $cm^3\ g^{-1}$), which are further enhanced to 2866 $m^2\ g^{-1}$ and 1.68 $cm^3\ g^{-1}$, respectively. After CO_2 activation their unique microstructural features enable the ACNFs to show great application potentials in electrode materials of supercapacitor and battery.

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电纺法制备 **PAN** 基高比表面积活性纳米碳纤维

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摘 要：将聚丙烯腈（PAN）粉末配制为 PAN/DMF 溶液，通过静电纺丝工艺制备了 PAN 纳米纤维，然后依次进行预氧化、碳化处理得到纳米碳纤维；采用 CO_2 作为活化剂制备了超大比表面积活性碳纤维。使用扫描电镜、场发射透射电镜、拉曼光谱、傅里叶红外光谱和 N_2 吸附等手段对样品的形貌、成分和结构进行了全面表征，研究了聚合物溶液浓度和静电压对 PAN 纳米纤维形貌和直径的影响。结果表明，活性碳纤维独特的孔结构使其作为电极材料在多种电解液中保持了较高的比容量。活化后的碳纤维的比表面积、总孔容和微孔孔容都明显增加。本研究所制备的活性碳纤维具有极高的比面积和良好的电导率，使其在超级电容器电极材料领域有着进一步的应用。

关键词：静电纺丝；碳纤维；活化；比表面积

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