A simple approach of constructing sulfur-containing porous carbon nanotubes for high-performance supercapacitors

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Porous carbon nanotubes (PCNTs) containing sulfur were successfully fabricated through a simple approach, which is the simultaneous activation and carbonization of sulfonated polyaniline/hexamethylenimine nanotubes with KOH. The PCNTs take on hierarchical porous structure composed of well interconnected mesopores and numerous micropores. Chemical analysis shows that the PCNTs contain sulfone groups. When assessed as electrodes by a three-electrode system in 6 M KOH aqueous solution, the PCNTs displayed the excellent electrochemical performance. An optimal sample of PCNTs activated at 650 °C for 3 h not only exhibits a high specific capacitance of 331 F g−1 at 1 A g−1, but also shows considerable rate capability with the retention of 80.4% at 20 A g−1. Additionally, it has the good cycling performance with 84% capacitance retention, while a high capability of about 243 F g−1 still reaches over 5000 cycles at 5 A g−1. We presented a promising route to scale-up synthesize porous carbon nanotube electrode materials for high-performance supercapacitors.

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1. Introduction

Supercapacitors have attracted tremendous attention as a class of efficient energy storage devices, owing to the good electrochemical stability, fast charge process, high power output and safe operation mode [1–3]. They have been widely applied in hybrid electrical vehicles, mobile devices, portable electronic devices, and pulsed laser systems [4–6]. Transition metal oxides, conducting polymers and carbon materials are the fundamental candidates for electrode materials of supercapacitors [7]. To date, carbon based materials, especially activated carbons, have been dominant in the commercially available supercapacitors, due to the low cost, excellent electrical conductivity, stable electrochemical response and environmental benignity [8].

Activated carbons (ACs) are prepared by the physical (O2, CO2 or steam) or chemical (KOH, H3PO4, ZnCl2, etc.) activation of carbon precursors/carbon materials [9–11], which are in the bulk form, lacking of flexibility in dimensionalities or morphologies. And the electrical charge in the assembled supercapacitors is stored by the function of electrical double-layer capacitors (EDLCs), where the energy storage is formed through reversible electrostatic attraction of electrolyte ions onto porous carbon electrodes and virtually no charge transfer take place through redox reactions [8,12]. However, the dimensionality, morphology, surface area, porosity and surface functional groups of electrode materials greatly influenced the electrochemical performance of carbon based supercapacitors. Therefore, activated carbon materials with the desirable morphology, high surface area and surface functional groups are preferable for high-performance supercapacitors.

As electrode materials for supercapacitors, carbon nanotubes (CNTs) have attracted extensive attention, owing to one-dimensional tubular structure, the high ratio of surface to volume, good chemical stability, excellent electrical conductivity, and ready commercial availability [13–15]. However, the small specific surface of CNTs and the sluggish ionic diffusion rate result in the lower specific capacitance of CNTs-based electrode materials in comparison of ACs [16]. A variety of methods have been developed to improve the capacitance of CNTs-based electrodes. For example, functional groups can be introduced to the surface of CNTs through surface modification (such as wet oxidation, plasma, and electrochemical treatments), which can modify the intrinsic chemical and physical properties of CNTs to improve the electrochemical
performance [17–19]. In addition, hierarchical porous structure could be constructed by the physical/chemical activation, which would offer adequate ion transport paths to improve the capacitive performance of CNTs [20,21]. Therefore, intelligent design of electrode materials is an effective way to improve the performance of supercapacitors.

Recently, bamboo-like highly crosslinked polydicyclobenzene nanotubes (PNTs) have been quickly synthesized at room temperature [22]. Bamboo-like carbon nanotubes (BCNTs) could be obtained by the simple pyrolysis of sulfonated PNTs, which is a potential high-performance anode material for lithium-ion batteries [23]. Additionally, bamboo-like carbon nanotubes containing sulfur (BCNT-S) were also successfully prepared by the carbonization and physical activation of sulfonated polymer nanotubes in CO₂ atmosphere, which exhibits excellent performance for supercapacitors [24]. These results indicate that bamboo-like polymer nanotubes is a promising precursor for electrode materials.

In this study, porous carbon nanotubes (PCNTs) with the well-controlled morphology and the surface function were prepared by the facile carbonization and chemical activation of bamboo-like polymer nanotubes with KOH. By tuning the activation time, the hierarchical micro/mesoporous structure of the obtained PCNTs could be controlled. The electrochemical performances of the as-prepared PCNTs in supercapacitors were assessed. PCNTs-3 synthesized under the optimal condition, displays a remarkable electrochemical performance with a substantially high specific capacitance up to 331 F g⁻¹ in a three-electrode cell at 1 A g⁻¹, extraordinary rate capability with a capacitance retention of 80.4% at 20 A g⁻¹, and good cycling stability with 84% capacitance retention over 5000 cycles at 5 A g⁻¹. This could be attributed to its unique tubular structure with a high surface area up to 866 m² g⁻¹, hierarchical porous structure and appropriate ratio of micropore volume to total volume of 42.0%, good wettability of sulfur-containing groups and pseudo-capacitance contribution of sulfone.

2. Experimental section

2.1. Synthesis

The PNTs with an average exterior diameter of 100–150 nm were synthesized according to the literature [22]. Then, PNTs were sulfonated for 12 h in concentrated sulfuric acid at 50 °C, resulting in the formation of sulfonated polymer nanotubes (SPNTs) [23–25].

Preparation of PCNTs: For a typical example, 0.2 g of the obtained SPNTs were dispersed in 20 mL deionized water, 2 mL KOH (1 M) solution were added to the above system and kept for 30 min under ultrasound. After stirring for 2 h at ambient temperature, the mixture was dried in an oven at 80 °C. Then, the dried mixture was calcined in N₂ atmosphere for 1–5 h at 650 °C. The calcined products were washed with 1 M HCl solution and deionized water to remove the potassium oxides or salts. Finally, the samples were dried at 80 °C to obtain the final products. The as-synthesized materials were denoted as PCNTs-x, where x is the time of activation (x = 1, 2, 3, 4 and 5, referring to the activated time of 1, 2, 3, 4 and 5 h). For comparison, SPNTs were dealt with above procedure without being added KOH solution, and carbonized at 650 °C for 1 h under N₂ atmosphere, which was designated as CNTs-1.

2.2. Characterizations

Morphologies and structure features of the materials were characterized by scanning electron microscopy (FESEM Hitachi S-4800) and a transmission electron microscope (TEM Hitachi H-600). X-ray diffraction (XRD) measurements were carried out with a Bruker D8 using filtered Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were recorded by a Bruker VERTEX 70 spectrometer. Nitrogen adsorption-desorption isotherms were obtained by an Autosorb-iQ (Quantachrome Instruments U. S.) apparatus at 77K. Specific surface areas of the samples were calculated by the Brunauer Emmett Teller (BET) method, while pore size distribution was calculated by the Density Functional Theory (DFT) method. X-ray photoelectron spectroscopy (XPS) measurements were performed by a Thermo ESCALAB 250 instrument.

2.3. Electrochemical measurements

The samples were tested using a conventional three-electrode system in a 6 M KOH aqueous solution on a CHI 660D (Chenhua, China) electrochemical workstation at room temperature. In a three-electrode system, a platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Working electrodes were prepared by mixing the active material, carbon black and poly(tetrafluoroethylene) (PTFE) binder with a weight ratio of 90:5:5. After coating the above mentioned slurry on a nickel foam current collector (1 × 1 cm²), the electrode was dried at 60 °C before pressing under 10 MPa. Each working electrode contained about 2.5–3.0 mg of electroactive material. Cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) measurements were carried out in the three-electrode systems. EIS measurement was tested at the frequency range of 100 kHz to 10 mHz with an AC amplitude of 5 mV under an open circuit potential. The cyclic stability of the electrode was also evaluated by a Land Battery Test System (CT2001A, China).

3. Results and discussion

3.1. Structure analysis

Generally, the fabrication of PCNTs is easily realized by the physical or chemical activation of the carbon nanotubes. However, the fabrication mechanism of PCNTs by a facile simultaneous chemical activation and carbonization process might be different from the normal preparation of the porous carbon nanotubes. The preparation process of PCNTs in this work is illustrated in Fig. S1. The samples were tested using a conventional three-electrode system in a 6 M KOH aqueous solution on a CHI 660D (Chenhua, China) electrochemical workstation at room temperature. In a three-electrode system, a platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Working electrodes were prepared by mixing the active material, carbon black and poly(tetrafluoroethylene) (PTFE) binder with a weight ratio of 90:5:5. After coating the above mentioned slurry on a nickel foam current collector (1 × 1 cm²), the electrode was dried at 60 °C before pressing under 10 MPa. Each working electrode contained about 2.5–3.0 mg of electroactive material. Cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) measurements were carried out in the three-electrode systems. EIS measurement was tested at the frequency range of 100 kHz to 10 mHz with an AC amplitude of 5 mV under an open circuit potential. The cyclic stability of the electrode was also evaluated by a Land Battery Test System (CT2001A, China).

3. Results and discussion

4. Conclusions

In summary, a novel strategy for the fabrication of PCNTs was presented and systematically investigated. The results showed that PCNTs with abundant functional groups were synthesized by a facile simultaneous chemical and physical activation of the mixture of PNTs and KOH in CO₂ atmosphere. The as-synthesized PCNTs showed a high specific capacitance and extraordinary rate capability, which could be attributed to their unique tubular structure, hierarchical porous structure and appropriate ratio of micropore volume to total volume. These results suggest that the current method for the fabrication of PCNTs is a potential route to the production of high-performance supercapacitors.
When the activated time was extended, the obtained PCNTs-2 displays the uniform tubular shape, and the cross-linking degree of SPNTs and favors to keep the tubular structure of SPNTs. The presence of potassium sulfonate slows down the heat shrinkage rate of SPNTs. As the extension of activation time, it can be clearly observed that the moderate activation would produce more imperfect carbon atoms to react with sulfur atoms, and increase the sulfur content in PCNTs, but the excessive activation would lead to the leaching of carbon and further the release of sulfur.

In order to estimate the amount of elements on the surface of carbonization materials, CNTs-1 and PCNTs-x were selected for XPS characterization. The composition data from XPS for each sample are listed in Table 1. Obviously, there are C, O and S elements in the surface region of the PCNTs-x samples, but the S element has not been detected in the surface region of CNTs-1.

Fig. 4a shows the XPS survey spectrum of PCNTs-3. The fitting of XPS peaks was performed to reveal the chemical state of the sulfur element in detail by the XPS peak software. As displayed in Fig. 4b and Fig. 5, the S 2p spectra ranging from 158 to 175 eV can be approximately divided into four peaks at 163.9, 165.1, 167.9 and 169.5 eV, which are assigned to sulfide (-C-S-C-) and sulfone (-C=SO2-C-). These sulfur species might be derived from the reaction between sulfur atoms in incomplete decomposition of sulfonate and imperfectly located carbon atoms resulting from the activation of SPNTs with KOH [12,29,30]. The retained sulfur leads to the high carbonization degree of PCNTs. Fig. 5 illustrates the formation mechanism of sulfur-containing PCNTs. It is worthy to note that the sulfur content in PCNTs increases from PCNTs-1 to PCNTs-3, but it gradually decreases for PCNTs-4 and PCNTs-5 samples. This might be attributed to that the moderate activation would produce more imperfect carbon atoms to react with sulfur atoms, and increase the sulfur content in PCNTs, but the excessive activation would lead to the leaching of carbon and further the release of sulfur.

N₂ adsorption-desorption measurements are conducted to investigate the specific surface area and the porous structure of materials. As shown in Fig. 6a, the CNTs-1 sample exhibits a type-I isotherm of microporous structure material. These micropores should originate from the elimination of surface −S−, O− and H− groups during the carbonization [26,31,32]. When KOH is added, the isotherms of the corresponding PCNTs-x show typical type-I curves with H4 type hysteresis loop in the relative pressure region between 0.5 and 1.0, suggesting the existence of a silt-shaped pore structure. While a highly adsorption capacity exists in the low pressure area (P/Po < 0.1), which indicates that PCNTs-x mainly consists of micropores. The adsorption capacity of PCNTs-x is greatly enhanced, which should be ascribed to the sharp increase of the specific area stemming from the KOH activation. Fig. 6b displays the pore size distribution of CNTs-1 and PCNTs-x. The porous structure of materials gradually change from simplex micropores to hierarchical pores (namely, micropore and mesopore) along with the addition of KOH, and the mesopore proportion and size gradually increase with the activation time. The BET specific surface areas and porous structure of the prepared samples are summarized in Table 2. It can be easily concluded that the activated time greatly influence the structure of materials. CNTs-1 exhibits a low surface area (337 m² g⁻¹), a small micropore volume and a small micropore size of 0.53 nm. When KOH is added, the surface area and pore volume of the PCNTs-1 sample are apparently enhanced. PCNTs-1 possesses high surface area up to 984 m² g⁻¹ and some mesopores at 3.5−4 nm, which should be produced by the carbon consumption during the activation process. When the activation time was extended, both surface areas and pore size of PCNTs-x continue to increase. Numerous micropores coalesced to form a mesopore along with the extension of activation time, thus enhancing the ratio of mesopore volume to total volume. Therefore, controlling the activation time is an effective method to adjust the ratio of mesopores/micropores. The high surface area, well-

![Image](51x560 to 265x727)

Fig. 1. Raman spectra of CNTs-1 and PCNTs-x. (A colour version of this figure can be viewed online.)
developed porosity and extensive pore distribution provide the possibility of efficient transport of ions and electrons, which favors the improvement of electrochemical properties.

3.2. Electrochemical performance

Electrochemical behaviors of CNTs-1 and PCNTs-x were evaluated by a three-electrode system in 6 M KOH. The gravimetric specific capacitances of the electrodes at various current densities were calculated based on the galvanostatic charge-discharge curves according to the following equation:

$$C = \frac{I \Delta t}{m \Delta V}$$

Where $C$ (F g$^{-1}$) is the gravimetric specific capacitance, $I$ (A) is the current loaded, $m$ (g) is the mass of active material, $\Delta t$ (s) is the discharge time and $\Delta V$ (V) is the range of potential.

Fig. 7a compares the cyclic voltammograms of CNTs-1 and PCNTs-x at a scan rate of 50 mV s$^{-1}$. The nearly rectangular shape between $-1.1$ V and $-0.1$ V suggested the EDLCs behavior of electrode materials. The CV curve of PCNTs-3 encircles a larger curve area than those of other electrode materials, suggesting a higher specific capacitance. It is obvious that the CV curves of PCNTs-x reveal a broad peak around $-0.7$ V, which may be attributed to the pseudo-capacitive contribution from the redox reactions of sulfone on the surface of the electrode materials [12,33]. The improved capacitive properties of electrode materials resulting from the effects of surface functional groups and active agent KOH can be directly verified by their specific capacitance values. The specific capacitance of PCNTs-1 is much larger than that of CNTs-1, which indicates that both the surface functionality and superior porosity can greatly improve the capacitive performance. The areas surrounded by CV curves increase from PCNTs-2 to PCNTs-3, whereas they slightly decrease for PCNTs-4 and PCNTs-5, indicating that the capacitance does not strictly increase with specific surface area of electrode material. Taking advantage of the surface functional groups, large accessible surface area, more available mesoporous channels and appropriate proportion of micropore volume to total volume, PCNTs-3 exhibits the highest specific capacitance among all the electrode materials. Fig. 7b shows the CV curves of PCNTs-3 at different scan rates ranging from 5 to 200 mV s$^{-1}$. PCNTs-3 always retains its almost rectangular shape from $-1.1$ to $-0.1$ V over a wide range of scan rates, suggesting the EDLCs nature in the charge-discharge process, and resulting from the fast diffusion process of electrolyte ions into/out of the electrode material. What’s more, the CV curve of PCNTs-3 still could retain a stable rectangular shape even at a high scan rate of up to 200 mV s$^{-1}$, displaying a good rate capability of electrode materials. Fig. 7c shows the galvanostatic charge-discharge curves of the PCNTs-3 at various current densities ranging from 1 to 20 A g$^{-1}$. All the charge and discharge curves present approximately symmetrical triangular shapes, showing that PCNTs-3 electrode material possesses
excellent electrochemical reversibility. There is a slight distortion of the curves, which is caused by the pseudocapacitance of sulfone groups. The specific capacitance of PCNTs-3 was calculated from the discharge curve to be about 331, 314, 290, 273 and 266 F g\(^{-1}\), obtained at a current density of 1, 2, 5, 10 and 20 A g\(^{-1}\), respectively, which is a remarkable in carbon based supercapacitors at the same current density \([34,35]\). The electrochemical performance of the electrode with the mass loading of 10 mg has been tested. The specific capacitance of PCNTs-3 was calculated from the discharge curve to be about 262, 245, 229, 210 and 202 F g\(^{-1}\) at a current density of 1, 2, 5, 10 and 20 A g\(^{-1}\), respectively (Fig. S6).

![Fig. 3. TEM images of CNTs-1 (a), PCNTs-1 (b), PCNTs-2 (c), PCNTs-3 (d), PCNTs-4 (e) and PCNTs-5 (f).](image)

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Element (At%)</th>
<th>C</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs-1</td>
<td></td>
<td>90.08</td>
<td>9.92</td>
<td>-</td>
</tr>
<tr>
<td>PCNTs-1</td>
<td></td>
<td>85.18</td>
<td>13.83</td>
<td>0.99</td>
</tr>
<tr>
<td>PCNTs-2</td>
<td></td>
<td>79.61</td>
<td>19.21</td>
<td>1.18</td>
</tr>
<tr>
<td>PCNTs-3</td>
<td></td>
<td>85.43</td>
<td>11.59</td>
<td>2.97</td>
</tr>
<tr>
<td>PCNTs-4</td>
<td></td>
<td>89.85</td>
<td>8.41</td>
<td>1.74</td>
</tr>
<tr>
<td>PCNTs-5</td>
<td></td>
<td>88.18</td>
<td>11.09</td>
<td>0.72</td>
</tr>
</tbody>
</table>

![Table 1](image)

Fig. 3. TEM images of CNTs-1 (a), PCNTs-1 (b), PCNTs-2 (c), PCNTs-3 (d), PCNTs-4 (e) and PCNTs-5 (f).

excellent electrochemical reversibility. There is a slight distortion of the curves, which is caused by the pseudocapacitance of sulfone groups. The specific capacitance of PCNTs-3 was calculated from the discharge curve to be about 331, 314, 290, 273 and 266 F g\(^{-1}\), obtained at a current density of 1, 2, 5, 10 and 20 A g\(^{-1}\), respectively, which is a remarkable in carbon based supercapacitors at the same current density \([34,35]\). The electrochemical performance of the electrode with the mass loading of 10 mg has been tested. The specific capacitance of PCNTs-3 was calculated from the discharge curve to be about 262, 245, 229, 210 and 202 F g\(^{-1}\) at a current density of 1, 2, 5, 10 and 20 A g\(^{-1}\), respectively (Fig. S6).

![Fig. 8](image)

Fig. 8 shows the effect of current density on the specific capacitance of different electrodes. The PCNTs-1 electrode prepared using KOH active agent exhibits a specific capacitance of 287 F g\(^{-1}\) at 1 A g\(^{-1}\), which is much higher than 25 F g\(^{-1}\) at 1 A g\(^{-1}\) for CNTs-1. The result should be ascribed to the higher surface area, more developed pores, pseudo capacitance and good wettability of PCNTs-1 material. When the current density is lower than 5 A g\(^{-1}\), the specific capacitance of PCNTs-2 is higher than that of PCNTs-1. But the result is reversed when the current density increases above 5 A g\(^{-1}\), implying the instability of sulfone under high current density. The specific capacitance of PCNTs-3 is 266 F g\(^{-1}\) at 20 A g\(^{-1}\), which is about 80.4% of the capacitance of 331 F g\(^{-1}\) at 1 A g\(^{-1}\). However, when the current density increases from 1 A g\(^{-1}\) to 20 A g\(^{-1}\), PCNTs-1 has only the 69.9% capacitance retention. PCNTs-3 exhibits considerably better rate performance than PCNTs-1 sample. This result is due to PCNTs-3 has well-interconnected porous structure. As described above, PCNTs-3 has high specific surface area and appropriate ratio of micropore volume to total volume of 42.0%, which is advantageous for fast transportation of electrons and ions, resulting in higher capacitance than PCNTs-4 and PCNTs-5 samples. The excellent capacitive performance of PCNTs-3 should be attributed to the following reasons: (i) the high surface area provides more electroactive sites for ion accumulation and energy storage; (ii) sulfone on the surface of PCNTs provides pseudo capacitance through redox reactions; (iii) the hierarchical porous structure composed of well interconnected mesopores and numerous micropores provide adequate ion transport paths; (iv) the sulfur-containing groups on surface greatly enhance the wettability of PCNTs; (v) the porous nanotubular structure
facilitates the efficient access of electrolytes and shortens the ion transport length.

Fig. 9 shows the Nyquist plots of CNTs-1, PCNTs-1 and PCNTs-3 samples (the fitting plots are presented in Fig. S7). In all the plots, a semicircle can be clearly found in the high frequency region (inset, in Fig. 9), and the intercept on real axis is solution resistance ($R_s$), which is 0.400, 0.455 and 0.465 $\Omega$ for CNTs-1, PCNTs-1 and PCNTs-3, respectively. The contribution to $R_s$ includes resistance of the electrolyte solution, the intrinsic resistance of active material and the contact resistance of the electrode interface/current collector ($R_s$) [36]. The impedance arc diameter is a characteristic of charge transfer resistance ($R_{ct}$), which are 0.093, 0.142 and 22.890 $\Omega$ for PCNTs-3, PCNTs-1 and CNTs-1 electrodes, respectively. The

Table 2
BET specific surface areas and porous structure of the CNTs-1 and PCNTs-x.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ ($m^2 g^{-1}$)</th>
<th>$S_{micro}$ ($m^2 g^{-1}$)</th>
<th>$S_{meso}$ ($m^2 g^{-1}$)</th>
<th>$V_{total}$ ($cm^3 g^{-1}$)</th>
<th>$V_{micro}$ ($cm^3 g^{-1}$)</th>
<th>$D_p$ (nm)</th>
<th>$V_{micro}/V_{total}$ (%)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs-1</td>
<td>337</td>
<td>277</td>
<td>60</td>
<td>0.29</td>
<td>0.15</td>
<td>0.53</td>
<td>51.7</td>
<td>1.32</td>
</tr>
<tr>
<td>PCNTs-1</td>
<td>984</td>
<td>737</td>
<td>247</td>
<td>0.86</td>
<td>0.40</td>
<td>0.50/0.82/1.18/3.97</td>
<td>46.5</td>
<td>2.77</td>
</tr>
<tr>
<td>PCNTs-2</td>
<td>834</td>
<td>623</td>
<td>211</td>
<td>0.77</td>
<td>0.34</td>
<td>0.50/1.41</td>
<td>44.2</td>
<td>2.92</td>
</tr>
<tr>
<td>PCNTs-3</td>
<td>866</td>
<td>683</td>
<td>183</td>
<td>0.88</td>
<td>0.37</td>
<td>0.57/3.39</td>
<td>42.0</td>
<td>1.57</td>
</tr>
<tr>
<td>PCNTs-4</td>
<td>1216</td>
<td>907</td>
<td>309</td>
<td>1.50</td>
<td>0.54</td>
<td>0.57/1.10/3.39</td>
<td>36.0</td>
<td>3.97</td>
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<tr>
<td>PCNTs-5</td>
<td>1700</td>
<td>1176</td>
<td>524</td>
<td>1.69</td>
<td>0.57</td>
<td>0.52/1.19/3.39</td>
<td>33.7</td>
<td>3.98</td>
</tr>
</tbody>
</table>

a BET surface area.

b Micropore surface area calculated using the V-t plot method.

c Mesopore surface area calculated using the V-t plot method.

d The total pore volume calculated by single point adsorption at P/P0 = 0.99.

e The micropore volume calculated using the V-t plot method.

f Pore diameter of peak value in Fig. 6b.

g Ratio of micropore volume to total volume.
The lowest Rct value of PCNTs-3 could be attributed to the most sulfur-containing groups on its surface, which is advantageous for the wettability of electrolyte and active material \[37\]. A short slope of about 45° in the intermediate frequency can be seen in Nyquist plots of all the samples, which is the typical feature of Warburg resistance (W). The 45° segment in the Nyquist plot is related to the diffusion of the electroactive ions into the interface of electrode particles inside the small pores \[38\]. The PCNTs-3 material significantly decreases in the length of the 45° segment, suggesting a smaller W value, which indicates that a reduced resistance encountered by the ions during their migration inside the electrode particle. The results could be ascribed to the developed mesoporosity in the PCNTs-3 sample. Additionally, a more vertical straight lines of PCNTs-3 than those of PCNTs-1 and CNTs-1, at low frequencies, indicates the faster diffusion of electroactive ions through the PCNTs-3 materials \[39\]. In a word, predominantly hierarchical porous nanotubular structure of PCNTs-3 facilitates charge transfer and ion diffusion.

To validate the practical efficiency of the electrode materials for supercapacitor applications, the long-term cyclic stability of the PCNTs-3 electrode was investigated by galvanostatic charge-discharge cycling at a current density of 5 A g\(^{-1}\) for 5000 cycles (Fig. 10). The inset image in Fig. 10 shows the first and 5000th galvanostatic charge-discharge profiles at a current density of 5 A g\(^{-1}\). It can be seen that the PCNTs-3 electrode has a high degree of electrochemical reversibility. The obvious variation in the specific capacitance of the PCNTs-3 electrode during the first 1000 cycles is attributed to the decomposition of sulfone and the collapse of some pores in carbon nanotubes. In spite of the specific capacitance decreases fast at the beginning, it keeps steady from 2000 to 5000 cycles. The long-term cyclic performance is maintained at ca. 84.0% of the initial specific capacitance, about 243 F g\(^{-1}\) of capacitance value over 5000 cycles, which demonstrates that the PCNTs-
3 electrode possesses an optimal capacitance performance for supercapacitors. In addition, the two-electrode cell was measured by assembling a symmetrical capacitor with 6 M KOH. Fig. S8a shows the CV curves of the PCNTs-3 at scanning rates from 10 to 200 mV s⁻¹, and its galvanostatic charge-discharge curves in the potential range from 0 V to 1 V at different current densities from 1 A g⁻¹ to 15 A g⁻¹ (Fig. S8b). We found that the PCNTs-3 exhibit a specific capacitance of 67 F g⁻¹ at 1 A g⁻¹. The specific capacitance of the PCNTs-3 decreases with the increase in current density. The capacitance retention percentage at 15 A g⁻¹ compared to that at 1 A g⁻¹ is 78.4%. To manifest the practical operating performance for our two-electrode cell, some small electronics have been powered by our two-electrode cell. Notably, two-electrode cell in series (around 2.5–3 mg active materials for each) can light one LED for 60 min (Fig. S8c).

4. Conclusions

In summary, we have developed a simple, low-cost and scalable route to synthesize sulfur-containing porous carbon nanotubes by simultaneous activation and carbonization of sulfonated polymer nanotubes with KOH. The prepared PCNTs exhibit a high specific surface area, which provides more electroactive sites for ion accumulation. The porous structure and specific surface area of PCNTs can be controlled by adjusting the activation time. The PCNTs-3 sample prepared in optimal condition reaches as high as 331 F g⁻¹ in a three-electrode cell at a current density of 1 A g⁻¹. Moreover, high rate performance and remarkable cycling stability can be obtained. This work provides a promising route to fabricate porous carbon nanotubes as highly efficient electrodes materials for supercapacitors.

Acknowledgments

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Appendix A. Supplementary data

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