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

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ABSTRACT

Porous carbon nanotubes (PCNTs) containing sulfur were successfully fabricated through a simple approach, which is the simultaneous activation and carbonization of sulfonated polydivinylbenzene 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 sulfide and 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.

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 (O_2, CO_2 or steam) or chemical (KOH, H_3PO_3, $ZnCl_2$, 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

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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 polydivinylbenzene 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 CO_2 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 specific surface area up to 866 m^2 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 into 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 N_2 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 materials 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 N_2 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 ploy(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 cm^2), 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. SPNTs with abundant sulfonic acid groups were used as the carbon precursor. The sulfonic acid groups of SPNTs became to potassium sulfonates after the addition of KOH solutions. The subsequent carbonization and KOH activation produce carbon nanotubes with well-controlled morphologies.

The influence of the activation time on the carbonization structure of the prepared samples was characterized by XRD. The results are shown in Fig. S2. The wide diffraction peaks at 42° for all samples can be indexed to the turbostratic graphite structure [26]. There is a broad peak at about 18° in XRD curve of CNTs-1, which is attributed to that of SPNTs [23]. The result indicates that the carbonized product CNTs-1 is impure due to the incomplete decomposition of the polymer. However, PCNTs-*x* have a broad peak at about 30°, which implies that the existence of KOH can promote the carbonization degree of PCNTs, and the wide band suggests the largely disordered structure of all samples. With the extension of activation time, the peak at 18° of PCNTs-*x* gradually disappears, which indicates that the carbonization degree of PCNTs-*x* gets better.

Raman spectroscopy was adopted to study the graphitization degree of CNTs-1 and PCNTs-*x* (Fig. 1). The peaks at 1344, 1587 and 2793 cm^{-1} are assigned to the D, G and 2D bands, respectively. The intensity ratio ($R = I_D/I_G$) of the D band to the G band was 0.68, 0.95, 0.90, 0.96, 0.93 and 0.95 for CNTs-1, PCNTs-1, PCNTs-2, PCNTs-