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Preparation and characterization of coaxial multiwalled carbon nanotubes/polyaniline tubular nanocomposites for electrochemical energy storage in the presence of sodium alginate

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ABSTRACT

Novel nanocomposites with coaxial tubular morphology based on sodium alginate-multiwalled carbon nanotubes/polyaniline (SA-MWCNTs/PANI) have been synthesized via the in situ chemical oxidative polymerization of aniline with SA-modified MWCNTs, and optimized preparation conditions were employed in order to achieve higher specific capacitance. The resulting SA-MWCNTs/PANI nanocomposites were fully characterized by means of FTIR, UV–vis, TEM, SEM, XRD and TGA methods, and the nanocomposites will hold well-defined core/shell structure in terms of their morphology, structure and thermal stability. Meanwhile, the electrochemical and conductivity of the resulting SA-MWCNTs/PANI nanocomposites were investigated by measurement of cyclic voltammetry, galvanostatic charge–discharge and conductivity. The results show that SA-modified MWCNTs as a support material could provide more electroactive sites for nucleation of PANI as well as excellent electron diffusion path, and SA-modified MWCNTs were homogeneously coated on both surfaces with PANI nanoparticles. In addition, the SA-MWCNTs/PANI nanocomposites achieved the maximum specific capacitance as high as 442 F/g at a current density of 0.5 A/g, long cycle life, and fast reflect of oxidation/reduction on high current changes, the highest value reported so far for biopolymer-doped PANI nanocomposites under the lowest doping amount of MWCNTs (0.6 wt%).

1. Introduction

With the rapid developments of modern digital life mean, the sustainable and renewable energy sources are becoming one of the most important fields of research. Green energy sources such as solar and wind energies are both intermittent, because energy harvesting may be interrupted during night or in places where wind does not blow [1,2]. Other energy harvesting devices such as nanogenerators could easily and efficiently convert vibration energy in living environment to electrical energy [3,4], but they cannot continuously drive small electronics because of their limited output power [5]. Therefore, energy storage devices are essential for providing stable and durable output which can be regulated. Nowadays, it has been accepted that electrochemical capacitors (ECs, also known as supercapacitors or ultracapacitors) are the best candidates for new energy storage devices, such as hybrid peak-power sources in electric vehicles, back-up systems for emergency use, and uninterrupted power supplies [6]. The mechanism by which ECs store energy has been discussed in detail [1,7]. In principle, supercapacitors can be classified into two types: electrochemical double-layer capacitors (EDLCs), and pseudo-capacitors or redox supercapacitors [8]. The high capacitive performance of materials is one of the most critical requirements for a myriad of applications of the energy storage devices, so the electrode materials become the most important controlling factors to determine the properties of the ECs [9].

So far, the materials studied for supercapacitor applications include three main categories. The first category is carbon material with a high surface area, including activated carbon [10], carbon nanotubes [11] and graphene [12]. The use of carbon material is based on the mechanism of EDLCs. It stores the charges electrostatically by reversible adsorption of ions in the electrolyte into active materials that are electrochemically stable and have high accessible surface area [13]. Although carbon materials have high specific surface area and good cycling stability, the low

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capacitance of carbon materials is limiting its application in high power density supercapacitors [14]. The second category is redox-based electrochemical capacitors using transition metal oxides such as MnO_2 [15] and RuO_2 [16], which have fast, reversible redox reactions at the surface of the active materials. However, transition metal oxides usually suffer from drawbacks of high cost, poor cycling stability, low electrical conductivity, large electrical resistance and this usually leads to a low power density. The third category is conducting polymers (CPs) with PANI [17] or polypyrrole (PPy) [18] being pseudo-capacitive active materials. The CPs have been extensively studied and widely applied in various energy storage devices because of their high flexibility and relatively high specific capacitance [19,20]. PANI is the most investigated and versatile CP due to its facile synthesis, environmental stability, biocompatibility, excellent specific capacitance, good electrical conductivity and uncommon conducting/insulating fast transition by doping/dedoping process [21]. However, the relative poor cycling life of PANI restricts its practical applications due to the swelling and the shrinkage of the polymer backbone during the charge–discharge processes, which severely influence their capacitive performance [22]. In order to obtain optimum electrode materials with high capacitance performance and good cycle stability, composites of PANI and carbon nanotubes (CNTs) have been investigated, because they combine the unique properties of individual material and show their special synergistic effects and the ability to store energy via two charge storage mechanisms [23,24]. Furthermore, it is reported that multiwalled carbon nanotubes (MWCNTs) can store approximately twice the energy density per mass unit than singlewalled carbon nanotubes (SWCNTs). For instance, Frackowiak et al. prepared the chemical polymerization of PANI/MWCNTs composites with the specific capacitance ranging from 100 to 300 F/g in different asymmertric configurations [17]. Deng et al. also prepared PANI/MWCNTs electrode material by chemical polymerization with a specific capacitance of 183 F/g being achieved [25]. All these results indicated that the combination of PANI and MWCNTs to form composites is a facile, cheap and effective method to increase the specific capacitance of electrodes, because the storage of energy in supercapacitors combines the pure electrostatic attraction of ions in the electrical double-layer with the pseudo-capacitance faradaic reactions.

In addition, small nanoscaled and nanostructured PANI can reduce the diffusion length, enhance the electroactive regions, and further increase the capacitive performance of nanocomposites [26]. Therefore, combining nanostructured PANI with biopolymer also has been extensively studied. Li et al. fabricated a porous and mat-like polyaniline/sodium alginate (PANI/SA) composite with uniform diameters from 50 to 100 nm, which exhibited an excellent specific capacitance [27]. SA consists of a linear block co-polymer of 1,4-linked β-D mannuronic (M) and α-L-guluronicacid (G), bearing abundant carboxyl and hydroxyl groups. However, to our knowledge, there were few reports related to the SA-MWCNTs/PANI nanocomposites for supercapacitor electrodes.

Here, we reported a facile method to synthesis the SA-MWCNTs/PANI nanocomposites with well-defined coaxial tubular morphology by the in situ chemical oxidative polymerization method based on SA-modified MWCNTs, which exhibited very good performance as supercapacitor electrode. The maximum specific capacitance of 442 F/g for the SA-MWCNTs/PANI nanocomposites can be obtained at 0.5 A/g current density, the highest value reported so far for biopolymer-doped PANI nanocomposites containing the lowest doping amount of MWCNTs (0.6 wt%). The effect of the MWCNTs and SA feeding ratio on the specific capacitance of the supercapacitors with the SA-MWCNTs/PANI nanocomposites as the electrode materials were investigated, and the electrical conductivity the nanocomposites were also discussed.

2. Experimental

2.1. Materials

MWCNTs (diameter, ~20 nm) were purchased from Chengdu Organic Chemical Co. Ltd., Chinese Academy of Sciences (China). Aniline (analytical grade reagent, Tianjin Chemical Reagent Co., Tianjin, China) was freshly distilled under pressure before use. Sodium alginate (SA, chemically pure) was purchased from Shanghai Chemical Co., used without further purification. Ammonium persulfate (APS, analytical grade reagent, Tianjin Chemical Reagent Co., Tianjin, China) was used as an oxidant without further purification. All other chemicals were analytical grade and used without further purification. Doubly deionized water (DI water) was used throughout.

2.2. Modification of multiwalled carbon nanotubes

The MWCNTs were modified with SA. Typically, The SA solution 1.0 mg/mL was prepared by dissolving 50 mg SA in 50 mL of aqueous solution. Equal masses of MWCNTs and SA solutions were mixed in a flask by ultrasonic treatment (150 W) for 30 min to obtain a mixture. Then the flask was put into a water bath at 60 °C, and allowed to react for at least 12 h. The resulting modified MWCNTs were filtered and then washed with DI water. Finally, the product was dried in vacuum at 60 °C for 24 h to obtain modified SA-MWCNTs.

2.3. Synthesis of SA-MWCNTs/PANI coaxial tubular nanocomposites

The SA-MWCNTs/PANI coaxial tubular nanocomposites were prepared by an in situ chemical oxidative polymerization method. The process for the preparation of SA-MWCNTs/PANI composites is shown in Scheme 1. The SA-MWCNTs were mixed with 30 mL of DI water. The mixture was then ultrasonically dispersed, and then aniline (1.0 mL) was added into the mixture with vigorous stirring. Afterward, the mixture was mechanically stirred for 30 min to obtain a uniform suspension. Then an aqueous solution (10 mL) of APS (2.28 g) was introduced drop by drop into the above mixture instantly to start the oxidative polymerization at 0 °C. The reaction was performed under mechanical stirring at 0 °C for 24 h. During the polymerization process, the color changed to dark green. The resulting precipitates were centrifuged and washed with distilled water and ethanol till the filtrate became colorless. Finally, the product was dried in vacuum at 60 °C for 24 h to obtain the desired SA-MWCNTs/PANI coaxial tubular nanocomposites as a dark green powder.

The MWCNTs without SA was reacted with aniline following the procedure described above to produce control composites for comparison, which is denoted as MWCNTs/PANI nanocomposites. Meanwhile, pure PANI was also synthesized without any MWCNTs component or other additive under the same condition, which was more like the oligoaniline and considered as the control product for the comparative study.

2.4. Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) were carried out on a CHI660D electrochemical workstation (Shanghai, China) with a three-electrode system. The SA-MWCNTs/PANI composite electrodes were prepared as follows. A mixture containing 80 wt% active materials (8 mg), 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) were well mixed in ethanol until they formed a slurry with a proper viscosity. Then the slurry was