



Synthesis and electrochemical capacitance of core–shell poly (3,4-ethylenedioxythiophene)/poly (sodium 4-styrenesulfonate)-modified multiwalled carbon nanotube nanocomposites

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ABSTRACT

A noncovalent method was used to functionalize multiwalled carbon nanotubes with poly (sodium 4-styrene sulfonate). And then, the core–shell poly (3,4-ethylenedioxythiophene)/functionalized multiwalled carbon nanotubes (PEDOT/PSS-CNTs) nanocomposite was successfully realized via *in situ* polymerization under the hydrothermal condition. In the process, PSS served for not only solubilizing and dispersing CNTs well into an aqueous solution, but also tethering EDOT monomer onto the surface of CNTs to facilitate the formation of a uniform PEDOT coating. Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM) were used to characterize the resultant PEDOT/PSS-CNTs. In addition, the PEDOT/PSS-CNTs nanocomposite (50 wt.% PEDOT) had a specific capacitance (SC) of 198.2 F g^{-1} at a current density of 0.5 A g^{-1} and a capacitance degradation of 26.9% after 2000 cycles, much better than those of pristine PEDOT and PEDOT/CNTs (50 wt.% PEDOT). The enhanced electrochemical performance of the PEDOT/PSS-CNTs nanocomposite (50 wt.% PEDOT) should be attributed to the high uniform system of the nanocomposite, resulting in the large surface easily contacted by abundant electrolyte ions through the three-dimensional conducting matrix.

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1. Introduction

Electrochemical capacitors (ECs), known as supercapacitors, have attracted great interest as promising energy storage devices for many applications, such as in electric vehicles, support for fuel cells, uninterruptible power supplies, memory protection of computer electronics and cellular devices, due to their higher power density, larger energy density and longer cycle performance than conventional dielectric capacitors [1–5]. Traditionally, different forms of carbon (active carbon, carbon fiber and carbon nanotubes), metal oxides (RuO_2 , IrO_2 and so on) and conducting polymers (PANI, PPy, PTH and their derivatives) have been widely used as the electrode materials for ECs applications [6–11].

In contrast to others, conducting polymers (COPs) based ECs represent an interesting class, thanks to the combination of high capacitive energy density and low material cost [12–15]. Among the COPs, poly (3,4-ethylenedioxythiophene) (PEDOT), as a member of polythiophene family, has drawn a wide interest in ECs application because of its fast charge/discharge ability, wide potential

window, and environment-friendly feature as well as high room temperature conductivity (easily up to 500 S cm^{-1}) [16–18]. Furthermore it also has been demonstrated that thick PEDOT films can exhibit the SC increasing linearly with the film deposition charge, approaching 5 F cm^{-2} [19]. However, PEDOT also has some inevitable shortcomings, that is, relatively small “theoretic SC” and mechanical deterioration during long-term cycling, which is a great challenge to overcome the above problems. It has been reported that a maximum SC value of 56 F g^{-1} for PEDOT can be obtained during electrochemical redox processes [20]. Hence, the carbon nanotubes (CNTs) with mesoporous structure can be exploited due to the ultra high mechanical strength, good electrical conductivity, high specific area and high aspect ratios. Because of their complementary electrical, electrochemical and mechanical properties, PEDOT and CNTs, if combined, may offer the improved performance for ECs [21,22]. For example, Lota et al. [23] have revealed that the PEDOT/CNTs nanocomposite electrode can possess an excellent electrochemical performance operating in acidic, alkaline and organic media, respectively. However, ordinary CNTs are large molecules with thousands of carbon atoms and inert surface nature limited by the strong van der Waals, consequently, they are practically insoluble in all solvents and difficult to handle [24]. Therefore, functionalization of CNTs is expected to play a vital role in tailoring the structure and properties of CNTs. Many

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research groups have focused on functionalizing CNTs with various organic and organometallic materials to improve the solubility and compatibility of CNTs [25,26]. In terms of the modified CNTs with their striking properties for wide applications, Wang et al. [27] recently have synthesized the PEDOT/functionalized SWNTs composites by the electrochemical method. Ham et al. [28] have also concentrated on the combination of PEDOT and three types of the modified SWNTs to improve electrical conductivity and flexibility of pristine PEDOT.

To date, one of the most successful approaches to modify CNTs have involved in wrapping linear polymers polystyrene sulfonate (PSS) around the CNTs. The strategy through noncovalent sidewall functionalization of CNTs with negatively charged PSS essentially creates active sites onto the surface of the nanotube as the anchorage centers, and thereby improves the process-ability of CNTs [29,30]. Herein, the aim of this study is to systematically investigate the electrochemical properties of PEDOT/PSS-CNTs nanocomposite with a uniform core-shell structure synthesized via *in situ* polymerization under the hydrothermal condition. To our knowledge, the studies undertaken here have not been reported so far and the demonstrated combination of functionalizing CNTs and hydrothermal method is facile and effective, which could be developed for a large-scale synthesis of structurally uniform COPs/CNTs nanocomposite as the potential electrodes in supercapacitors. In this article, it is also revealed that the core-shell morphology of the PEDOT/PSS-CNTs nanocomposite (50 wt.% PEDOT) has a remarkable effect on the capacitive behavior, which can be attributable to the fact that the PSS-CNTs as a support is helpful to provide the larger SC and better electrochemical stability.

2. Experimental

2.1. Chemicals and materials

CNTs (diameter, 20–40 nm) were purchased from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China) and purified by refluxing the as-received CNTs in nitric acid for 12 h before use. 3,4-Ethylenedioxythiophene (EDOT, 99%) and poly (sodium 4-styrene sulfonate) (PSS, MW, 500–60000) were both obtained from Aldrich. Ammonium persulfate (APS), sodium chloride (NaCl) and sulfuric acid (H₂SO₄) were purchased from Shanghai Chemical Reagent Co. Ltd. Aqueous solution was prepared with doubly distilled water.

2.2. Experimental procedure

50 mL NaCl solution (1.0 M) containing 30 mg CNTs was sonicated at room temperature for 2–3 h. 100 mg PSS was mixed into the above solution under stirring for 6 h, followed by centrifuged and washed with deionized water. Then, PSS-CNTs were obtained.

The PEDOT/PSS-CNTs nanocomposite was synthesized by the following process. 0.026 mL of EDOT monomer was dissolved in 30 mL of H₂SO₄ solution (0.2 M) and stirred at room temperature for 1 h. The 50 wt.% of PSS-CNTs with respect to EDOT was then dispersed into the solution and sonicated for 30 min to facilitate the EDOT adsorption on the sidewall of CNTs, followed by adding the oxidant APS (0.056 g). After another 2 h of stirring, the mixture was placed in a 50 mL Teflon-lined stainless steel autoclave, subsequently sealed with plumbing pliers and transferred quickly into the oven and maintained at 150 °C for 5 h. The product of PEDOT/PSS-CNTs (50 wt.% PEDOT) were washed with distilled water and dried at 60 °C under vacuum. Finally parallel experiments were carried out just by changing the amount of PSS-CNTs support in the starting mixture to obtain other

PEDOT/PSS-CNTs nanocomposites with different mass ratio of PEDOT.

For comparison, the pristine PEDOT and PEDOT/CNTs (50 wt.% PEDOT) nanocomposites were both prepared by the same procedure as described above except that the precursor solution was monomer EDOT and the mixture of monomer EDOT and bare CNTs, respectively.

2.3. Morphology characterization and electrochemical measurements

Fourier transformation infrared spectroscopy (FT-IR) patterns of the synthetic samples were recorded on a model 360 Nicolet AVATAR. Transmission electron microscope (TEM) observations of the synthetic powder were carried out on TECNAI-20.

The working electrodes were prepared by mixing the electroactive materials (5 mg) with acetylene black (AB) and polytetrafluoroethylene (PTFE) with the weight ratio of 80:15:5. The mixture was ground to make a more homogeneous slurry, which was pressed on a graphite current collector (area: 1 cm²) and dried at room temperature. Electrochemical performance was determined mainly by the cyclic voltammogram (CV) and galvanostatic charge–discharge using a CHI660B electrochemical analyzer system (Chenhua, Shanghai China) in 0.5 M H₂SO₄ solution. A three-electrode system was equipped with the as-prepared graphite electrode as a working electrode, a platinum plate counter electrode and a saturated calomel electrode (SCE) reference electrode. And the quasi-capacitor was fabricated by two identical graphite electrodes face to face in 0.5 M H₂SO₄ solution. Moreover, the SC of the active materials in the electrode ($C_{m, electrode}$, Fg⁻¹) could be calculated from the galvanostatic charge–discharge curves in a three-electrode beaker-type cell based on the following equation:

$$C_{m, electrode} = \frac{q_{electrode}}{\Delta V \times m} \quad (1)$$

where $q_{electrode}$ was the average of anodic and cathodic charges integrated from the charging and the discharging, ΔV was the potential window, m was the loading of the electrode. And the SC of PEDOT in the PEDOT/CNTs or PEDOT/PSS-CNTs nanocomposite system ($C_{m, PEDOT}$, Fg⁻¹) could be estimated from the following equation.

$$C_{m, PEDOT} = \frac{C_{m, electrode} - (1 - w_{PEDOT})C_{m, CNTs(or PSS-CNTs)}}{w_{PEDOT}} \quad (2)$$

where $C_{m, electrode}$ was the SC of the PEDOT/CNTs (or PEDOT/PSS-CNTs) nanocomposite electrode, $C_{m, CNTs (or PSS-CNTs)}$ was the SC of CNTs (or PSS-CNTs) electrode, w_{PEDOT} was the weight fraction of PEDOT in the composite system.

3. Results and discussion

3.1. Structural characterization and morphology analysis

The FT-IR spectrum of commercial PSS is depicted as curve 1 in Fig. 1a. The relatively sharp bands at 2930 and 2851 cm⁻¹ are assignable to stretching vibrations of C–H and –CH₂– groups, and one at 1455 cm⁻¹ is due to their bending mode. The peak at 1607 cm⁻¹ for stretching of C=C and 1007 cm⁻¹ for bending of C–H are attributable to the aromatic rings in PSS. The band at 1228 and 1152 cm⁻¹ are representative of asymmetric and symmetric vibrations of –SO₃ group, respectively [31]. In addition, the as-synthesized PSS-modified CNTs powder (see curve 2 in Fig. 1a) exhibits the characteristic absorption bands of all the mentioned peaks of commercial PSS, suggesting that CNTs are suc-

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