



Macromolecular Nanotechnology

Significant enhancement of electrochemical behaviour by incorporation of carboxyl group functionalized carbon nanotubes into polyaniline based supercapacitor

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ABSTRACT

The innovative sea cucumber like polyaniline/carbon nanotube-COOH (PANI/CNT-COOH) composite material achieves enhanced electrochemical properties, due to the carboxyl group functionalization on the surface of carbon nanotubes generates unique microstructure, conductivity and excellent electrical properties. Cyclic voltammetry and galvanostatic charge/discharge tests are carried out to investigate the electrochemical properties. The PANI/CNT-COOH material exhibits higher capacitance (381 F g^{-1} at 1 A g^{-1}) than PANI/CNT (without carboxyl group functionalization, 238 F g^{-1} at 1 A g^{-1}) and pure PANI (186 F g^{-1} at 1 A g^{-1}). PANI/CNT-COOH also exhibits fast reflect of oxidation/reduction at high current density and good long-term cycling stability with capacity retention ratio of 92% after 1000 cycles. The three-dimensional (3D) structure provides a high electrode/electrolyte contact area and a short path length for electrons and electrolyte ions transport.

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1. Introduction

Energy storage is unquestionably one of the great challenges the world facing today [1,2]. Supercapacitors attract researchers from both the industry and the scientific community. Comparing to conventional capacitors and batteries, they not only obtain relative higher energy density and faster power density, but also own a longer cycle life [3–5]. In addition, supercapacitors are operational safer when charged and discharged at high rates, which is mainly due to physical rather than chemical energy storage [6]. Supercapacitors coupled with fuel cells or batteries have already been applied on electric vehicles [7]. A major shortcoming of current supercapacitors is their low energy density [8]. We could imagine that supercapacitors possess similar energy density to that of lithium ion batteries, coupled with inherent short recharge time, will make great progress in energy technology.

Polyaniline (PANI) attracted extensive attention in view of its high theoretical specific pseudocapacitance, low preparation cost, good environmental stability, and fast faradaic reaction [9–12]. However, its low rate capability and poor cycling stability arising from continuous volume expansion/shrinkage during repeated charging and discharging process restrict its practical applications in supercapacitors [13–16]. However, carbon nanotubes (CNTs) displayed high aspect ratio, electrical conductivity, chemical stability, extraordinary mechanical strength and Young's modulus [33,34], making them capable of constructing multifunctional nanocomposites with excellent electronic and mechanical properties. The composite based

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on PANI and carbon materials could effectively solve the problem and achieve an enhanced capacitance due to the synergetic combination of the excellent mechanical properties of carbon materials and high pseudocapacitance of PANI [12,17]. Ramana et al. fabricated PANI/CNT nanocomposite with core-shell structure by the self-assembly with capacitance of 368.4 F g^{-1} at a discharge rate of 0.5 A g^{-1} [30]. Zhu et al. produced PANI/graphite oxide nanocomposites via interfacial polymerization with capacitance 68.3 F g^{-1} at a discharge rate of 0.2 A g^{-1} [31]. Therefore, the combination of PANI and CNTs with 3D sea cucumber like morphology will endow the nanocomposites large capacitance of PANI and high conductivity and mechanical strength of CNTs and ensure them to retain remarkably enhanced electrochemical properties [32].

In this paper, carboxyl group functionalized carbon nanotube is decorated with PANI by chemical oxidative polymerization (PANI/CNT-COOH). We found that, PANI/CNT-COOH material based supercapacitor electrode material exhibits higher capacitance (381 F g^{-1} at 1 A g^{-1}) than that of PANI/CNT (without carboxyl group functionalization on CNT, 238 F g^{-1} at 1 A g^{-1}) and pure PANI (186 F g^{-1} at 1 A g^{-1}) electrode material.

2. Experimental

2.1. Materials and methods

Multi wall carbon nanotubes (CNT and CNT-COOH) were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, and used as received (length: $0.5\text{--}2 \mu\text{m}$; diameter: $20\text{--}30 \text{ nm}$; purity $>95 \text{ wt}\%$). Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and used as received, except aniline which was distilled under reduced pressure before use. All the solutions were prepared using deionized (DI) water.

2.2. Synthesis of PANI, PANI/CNT and PANI/CNT-COOH electrodes

PANI was synthesized by chemical oxidative polymerization from a dispersion prepared with 0.47 g of aniline in 50 ml of hydrochloric acid solution. A solution of ammonium persulfate (1.14 g APS dissolved in 50 ml 1 M hydrochloric acid) as an oxidizing agent was added dropwise to the above solution. The polymerization process was carried out for 24 h in an ice water bath under vigorous stirring. PANI/CNT nanocomposite materials were synthesized applying the same above procedure with the addition of 0.6 mg/ml ($50 \mu\text{l}$) of carbon nanotubes with and without carboxyl functional group to the initial aqueous dispersion. Finally, the resulting products were collected by centrifugal cleaning several times with deionized water and ethanol, then drying completely at $50 \text{ }^\circ\text{C}$ before any characterizations.

2.3. Material characterization

The morphologies of the products were examined by a field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, and Japan) at 5 kV . The crystallinity of the composites were analysed by X-ray powder diffraction (XRD, SHIMADZU XRD-6000) on a Ni-filtered $\text{Cu K}\alpha$ radiation at 40 kV and 200 mA with the 2θ ranging from 10° to 60° and a step scan rate of $15^\circ \text{ min}^{-1}$. Thermogravimetric analysis (TGA) was carried out on TGA analyzer (STA 449 F3 Jupiter). Fourier transform infrared spectrometer (FT-IR, AVATAR360, Nicolet) were used to analyse the ingredients of the nanocomposites. The Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore width of the samples were characterized by nitrogen adsorption using a surface area and porosity analyser (Gemini VII) and the mesoporous volume and the mesoporous radius were obtained by the Berret-Joyner-Halenda (BJH) method.

Electrochemical experiments were carried out in a three electrode system with a CHI660D electrochemical workstation. $1 \text{ M H}_2\text{SO}_4$ aqueous solution was used as electrolyte. Platinum sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The working electrode was assembled as follows. Firstly, PANI, PANI/CNT and PANI/CNT-COOH powders were dispersed in pure isopropanol (1 mg ml^{-1}); then, a suitable amount of Nafion solution was added. Afterwards, the dispersion was transferred with a micropipette on a mirror polished glassy-carbon electrode. The Nafion content in the final mixture was $5 \text{ wt}\%$. The cyclic voltammetry (CV) was carried out in a potential range of $0\text{--}1.4 \text{ V}$ at varying scan rates. Galvanostatic charge/discharge (GCD) curves were measured at step increasing current densities of $1\text{--}8 \text{ A g}^{-1}$ from 0 to 1 V . The battery testing system (Neware) was used to measure the cycle life of the sample with the cycle times of 1000 .

3. Results and discussion

The morphologies and structures of CNT-COOH, PANI, PANI/CNT and PANI/CNT-COOH were characterized using SEM. The results are shown in Fig. 1. The carbon nanotubes shown in Fig. 1a have uniform nanofiber morphology in diameter with about 30 nm . The pure PANI fibers with narrow size distribution in diameter about 40 nm are shown in Fig. 1b. The carbon nanotubes aggregate randomly as a result of their strong van der Waals interactions. However, as shown in Fig. 1c, the uniform PANI/CNT composite (CNT without carboxyl group decoration) presents a well extended network with the nanofiber diameter of $50\text{--}80 \text{ nm}$. The PANI uniformly coated on the surface of CNT. For the PANI/CNT-COOH composite, Fig. 1d clearly shows that the ordered PANI nanowires align vertically on the surface of CNTs and form a coaxial structure. The structure of

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