



Ultrathin manganese dioxide nanosheets grown on partially unzipped nitrogen-doped carbon nanotubes for high-performance asymmetric supercapacitors



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ABSTRACT

In this work, N-doped carbon nanotubes (NCNTs) have been easily unzipped using a chemical oxidation method to obtain porous and multi-defective partially unzipped N-doped carbon nanotubes (PU-NCNTs), which are promising as negative electrode materials for supercapacitors and are also suitable substrate materials for the efficient loading of ultrathin manganese dioxide (MnO₂) nanosheets. Herein, the PU-NCNT/MnO₂ composite was synthesized through a simple microwave irradiation method. Moreover, we have fabricated an asymmetric supercapacitor (ASC) using PU-NCNT/MnO₂ composite as cathode, PU-NCNTs as anode and neutral aqueous Na₂SO₄ as electrolyte. Because of the synergistic effects of the PU-NCNTs electrode and the high capacitance as well as good rate performance of PU-NCNT/MnO₂ composite, the asymmetric cell exhibited good electrochemical performance. The optimized ASC can be worked stably in the voltage window of 0–1.8 V and exhibited a maximum energy density of 14.76 Wh kg⁻¹ at the current density of 1 A g⁻¹. Additionally, the PU-NCNT/MnO₂//PU-NCNT ASC exhibited long cycling stability with 80.5% specific capacitance retained after 1000 cycles at a current density of 1 A g⁻¹. These encouraging results show that PU-NCNT/MnO₂ could be promising materials for commercial use of supercapacitors.

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1. Introduction

Supercapacitors, a promising energy storage device with the properties of higher power density, longer cyclic life, faster charge-discharge rates but lower energy density (E) compared to batteries, have received much attention in the recent years [1–3]. According to equation $E = 0.5CV^2$, the key to improve energy density (E) is to enhance the specific capacitance (C) and improve the cell voltage (V). Fabricating asymmetric supercapacitors (ASCs) is a good way to increase the performance, ASCs can not only take the advantages of both supercapacitors and batteries for using different type electrodes (high power density and energy density), but also use the different potential windows of the two electrodes to increase the operating voltage of the cell, which can improve the specific capacitance and energy density significantly [4,5]. Besides, the

specific capacitance is generally related to the electrode/electrolyte interface. Therefore, the rational design of new electrode materials with optimized surface structures/functionality have become a major research focus in this field, including the development of materials with different morphology [6,7], the investigation of the effective surface area [8,9], and the introduction of heteroatoms into the electrode materials [10,11].

Electrode materials such as carbon materials, conducting polymers and Faradaic materials have been extensively investigated for supercapacitor applications. Carbon materials (e.g. activated materials (AC) graphene and carbon nanotubes (CNTs)) are commonly used as electrode materials commonly for electrical double-layer capacitors (EDLCs) because of their excellent electronic, mechanical and thermal properties. However, their specific capacitance is too low, which greatly restricts their application in supercapacitors. By contrast, pseudocapacitors can deliver much higher capacitance than EDLCs through the fast and reversible redox Faradaic reactions occurred on the surface of the electrode materials. Among various pseudocapacitor materials, manganese dioxide (MnO₂) has been attracted significant interest for supercapacitors because of its outstanding performance such as high theoretical capacitance

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(1370 F g⁻¹), low-cost and environmentally friendly [5,12]. Until now, MnO₂ with different structures and various crystallographic forms (α , β , γ , δ and λ) have been synthesized as electrode materials for supercapacitors. Unfortunately, due to the inherent low electrical conductivity and slow ion transport rate during cycling, the MnO₂ electrodes often display low specific capacitance and unsatisfactory cycling stability when used in the practical applications [13]. In order to improve the electrochemical performance of MnO₂, one effective strategy is to make composite of MnO₂ with carbon materials [14–17]. Among them, CNTs and graphene possess excellent properties such as good conductivity, large specific surface area, and good chemical stability, which are generally regarded as the promising substrates for the growth of the MnO₂. For example, Kathyayini et al. [18] reported the synthesis of the α -MnO₂/MWCNT composite, and the assembled ASC device showed an excellent cycle performance with a maximum energy density of 26.3 Wh kg⁻¹ in 1 M Na₂SO₄ aqueous solution. Zhang et al. [19] reported the synthesis of a N-doped graphene/MnO₂ nanosheet composite, and then fabricated a flexible solid-state asymmetric supercapacitors using the N-doped graphene/MnO₂ nanosheet composite as the cathode and the activated carbon as the anode, the device had a wide voltage window of 1.8 V and exhibited a high energy density of 3.5 mWh cm⁻³. However, there are still some shortcomings for these substrate materials. For two dimensional graphene, much of the surface area is lost due to restacking via the van der Waals interactions, and the side walls of CNTs are hydrophobic and inert, which suggests to few available active sites and a limited surface area, hindering their applications in supercapacitors [20–22]. Recently, it has been reported that “opening” the CNTs is a useful method to improve their electrochemical performance [23–26]. Partially unzipped carbon nanotubes (PUCNTs), obtained by unzipping CNTs using a chemical oxidation method, have been regarded as a combination of a tube and a nanoribbon. It has a CNTs' structure with few layers graphene at the edge to exhibit the synergistic effects, which is better than both CNTs and graphene, such as higher density of active sites, larger surface area, higher conductivity [27–29], and also beneficial to control and optimize the MnO₂ loading [30]. In addition, nitrogen-doping has been used in recent years to improve the properties of Cu₂O [31], CNTs and graphene. Among them, N-doping CNTs have been widely used in supercapacitors, since N-doping can generate vacancies and other defects on their edges (It can be analysed by Raman spectroscopy, as shown in Fig. S1), further enhancing the wettability and electroactive surface area of the electrode materials [32,33], and introduce pseudocapacitance into the system (for aqueous supercapacitors) [34]. Based on the above considerations, we assume that the PU-NCNTs should be an ideal negative electrode materials and could provide large surface for the growth of MnO₂ growing of nanoscale particles.

In this paper, we used the facile synthesis of the PU-NCNTs via chemical oxidation process, and then the PU-NCNTs were selected as the substrate for the growth of MnO₂. The PU-NCNT/MnO₂ composites was synthesized through a simple microwave irradiation method, where ultrathin MnO₂ nanosheets were uniformly grown on the PU-NCNTs substrate. The schematic illustration for the synthesis of the PU-NCNTs and synthesis of PU-NCNT/MnO₂ composite is shown in Scheme 1. Then, an ASC using PU-NCNT/MnO₂ composite as the positive electrode material and PU-NCNTs as the negative electrode materials was fabricated and the electrochemical performances were well studied. Attributing to the unique structure of the negative material and good performance of the positive and negative materials, the fabricated PU-NCNT/MnO₂//PU-NCNTs ASC had a large operating voltage of 1.8 V, and exhibited long cycling stability with 80.5% specific capacitance retained after 1000 cycles at a current density of 1 A g⁻¹.

2. Experimental

2.1. Synthesis of PU-NCNTs

PU-NCNTs were unzipped by oxidation using a method similar to that reported by Tour et al. [26]. Typically, 150 mg of NCNTs (Chengdu Organic Chemicals Co. Ltd., China) was stirred for 1 h in 36 mL of H₂SO₄. Then, 4 mL of H₃PO₄ was added for 15 min. Subsequently, 450 mg of KMnO₄ was slowly added about 30 min, and then stirred on a hot plate (65 °C) for 2 h. After this time, the reaction sample was slowly poured into a solution of 10 mL of H₂O₂ in 100 mL of cold water. Finally, the sample was filtered and washed several times with diluted HCl water by vacuum filtration. After freeze-drying, the PU-NCNTs were obtained.

2.2. Synthesis of PU-NCNT/MnO₂ composite

The PU-NCNT/MnO₂ composite was obtained by a redox reaction under microwave irradiation. First, 100 mg of PU-NCNTs was dispersed in deionized water and under ultrasonic treatment for 30 min. Then, KMnO₄ powder (200 mg) was added and stirred at 0 °C for 20 min. Subsequently, the solution was heated by a household microwave oven under the middle temperature mode for another 5 min. Finally, the black precipitate was obtained by vacuum filtration, washed with alcohol/distilled water, and collected by freeze-drying.

2.3. Synthesis of δ -MnO₂

For comparison, δ -MnO₂ was prepared by dissolving 3.6 g of KMnO₄ in 40 mL of distilled water at 85 °C. Then, 100 mL of 1:1 (v/v) HCl was added dropwise. Finally, the obtained solution was centrifuged, washed with distilled water, and dried in air at a temperature of 100 °C for 6 h.

2.4. Materials characterization

The microstructural morphologies of the materials were characterized by scanning electron microscopy (SEM, Supra55, Zeiss, Germany) and transmission electron microscopy (TEM, Tecnai G2F20 S-TWIN). The crystal structures were determined by an X-ray diffraction (XRD, D/max-UltimaIII, Rigaku, Japan) equipped with Cu K α radiation ($\lambda = 0.15418$ nm). The specific surface area of the materials were determined by Brunauer-Emmett-Teller (BET) method. The thermograms were studied using a thermal analyzer (TGA, SDT Q600, TA, USA) under air flow at the temperature from room temperature to 800 °C with the heating rate of 5 °C min⁻¹.

2.5. Electrochemical measurements

The positive electrodes were prepared by mixing 80 wt% PU-NCNT/MnO₂, 15 wt% acetylene black, and 5 wt% poly vinylidene difluoride (PVDF) dispersed in *N*-methyl-2-pyrrolidone (NMP) solvent. Then, the sample was coated on a Ni-foam grid (1 cm²) at a pressure of 10 MPa and dried at 65 °C for 10 h. The negative electrodes were prepared by the similar procedure. The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests of each electrodes were tested in a three-electrode system, which used 1 M Na₂SO₄ aqueous as the electrolyte and Pt foil and saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. To fabricate an ASC device, the active materials' mass ratio (PU-NCNT/MnO₂: PU-NCNTs) was estimated to be 0.6:1 from the specific capacitance in terms of their GCD curves in a three-electrode cell to keep the charge balance (see ESI) [35].

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