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Flexible of multiwalled carbon nanotubes/manganese dioxide nanoflake textiles for high-performance electrochemical capacitors

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ABSTRACT

In this paper, an ultrathin layer of acid treated multiwalled carbon nanotubes (CNTs) are conformally wrapped on everyday cotton textiles for subsequently controlled electrodeposition of MnO_2 nanoflakes. The general morphology and detailed microstructure of the as-prepared composites are characterized and the formation mechanism is investigated by time-dependent experiments. Such conductive textiles show outstanding flexibility and strong adhesion between the CNTs and the textiles of interest. Supercapacitors made from these ternary conductive textiles show high specific capacitance up to 247 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$. A capacity retention of 94.7% can be maintained at 2000 continuous charge-discharge cycles, after which the textiles electrode essentially maintained its whole structural integrity. The discharge curves remain unchanged with a slight capacitance decrease even under vertical folding condition. All these demonstrate that hybrid flexible electrode of MnO_2 and conductive textile is an effective strategy towards high-energy supercapacitors and may provide a promising design direction for optimizing the electrochemical performance of insulating metal oxide based on electrode materials.

1. Introduction

Electrochemical capacitors (ECs), also known as supercapacitors or ultracapacitors, have received much attention due to their high power density (1–2 orders of magnitude higher than that of batteries), fast charging and discharge within seconds (i.e., fast response time), long cycle life (2–3 orders of magnitude better than that of batteries), excellent reversibility and good safety [1–3]. ECs can be used either alone as primary power source or as auxiliary power source with rechargeable batteries for high power applications, and have been used in a variety of applications ranging from portable consumer electronics, hybrid electric vehicles, to large industrial scale power and energy management. On the basis of electrode materials used and the charge storage mechanisms, ECs are typically classified as electrical double-layer capacitors (EDLCs) and Faradic redox reaction pseudocapacitors [4]. The pseudocapacitance of the electrochemical capacitors have been attracting tremendous attention because that their energy density is usually many times greater than that of carbon-based materials using double layer charge storage [5–7]. For this purpose, there is so much attention now on the RuO_2, NiO and MnO_2 [8–11] as candidates for active pseudocapacitive materials of supercapacitor. Among all these materials, manganese dioxide is one of the most promising electrode materials due to its high energy density, low cost, environmental benignity and natural abundance [12–14].

To meet requirements of energy storage systems with low-cost and appropriate performance characteristics, one should incorporate earth-abundant capacitive carbon materials with low-cost and high theoretical specific capacitance metal oxides such as MnO_2. In addition, from the perspective of fabrication process, highly scalable approaches to make functional flexible electrodes will be of great importance for large-scale and low-cost energy storage devices with excellent mechanical stability and superior cycle lifetime.

Electronic textiles represent a developing new kind of materials with an array of novel characteristics, such as flexibility, lightweight and stretchability, which allow for many applications and designs previously impossible with traditional electronics

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technology. For instance, solution-based coating and printing techniques have been exploited to make conductive carbon nanotubes (CNTs) or graphene-based papers and textiles as electrodes and/or current collectors for batteries and supercapacitors [15–17]. However, direct conversion of cotton textiles into electrically active textiles for constructing supercapacitors remains a great challenge. The electrical conductivities of the textiles reported are many orders of magnitude lower than the commercial Al foil or Ni foam current collector based electrodes [18]. The other drawbacks are tendency towards detachment of coating conductive CNTs or graphene thin films from textile fabrics, and mechanical expansion of transition metal oxides during ion insertion/desertion process, which may induce aged decay of electrochemical stability of the fabric composites.

Inspired by traditional activation of cellulose textiles into activated carbon textiles (ACT) with a low sheet resistance by a simple chemical route [19], we demonstrate a novel CNTs/ACT/MnO_2 nanostructured textile for energy storage applications. In our approaches, an ultrathin layer of acid treated multi-walled carbon nanotubes were conformally wrapped from N–methyl–2–pyrrolidone (NMP) solution on three-dimensional [3D], porous woven cotton support structures for subsequent controlled electrodeposition of MnO_2 nanoflakes. After such functionalization, the textile features were well reserved and the obtained ACT was highly conductive and flexible. The CNTs wrapping approach not only provides an additional electron transport path besides the carbonaceous textile fibers but actively participates in the charge storage process as both can contribute to the energy storage of the whole film via electric double layer capacitance or pseudocapacitance. Moreover, such 3D porous networks not only permit high mass loading of active electrode materials but facilitate easy access of electrolytes to those materials. The CNTs/ACT/MnO_2 yielded greatly enhanced specific capacitive (247 $F{\cdot}g^{-1}$) at high current density (1 $A{\cdot}g^{-1}$) in aqueous electrolyte. This work demonstrates that CNTs/ACT/MnO_2 is an effective strategy towards high-energy supercapacitors and can be used as working electrode directly for flexible energy storage device applications. It would also provide a promising design direction for optimizing the electrochemical performance of insulating metal oxide based on electrode materials and could be generally applicable to many promising but challenging energy storage electrode materials in which the electron transport limits the device performances.

2. Experimental

2.1. Cotton textiles coating with carbon nanotubes

Firstly, as-purchased acid treated multi-walled carbon nanotubes (CNTs, 100 mg, Sigma Aldrich) were mixed in 50 mL NMP solution under constant stirring for 1 h. Then, 50 mg sodium dodecylbenzenesulfonate (SDBS) was added into the above suspension. A stable dispersed CNTs suspension was obtained after 30 min bath ultrasonication (DL-360D, 40 KHz, 360 W).

CNTs coating of cotton textiles was performed by a simple dipping, drying and annealing process. Firstly, a piece of commercial cotton textile with ≈300 μm thickness was dipped into 1 M NaF solution and kept for 1 h. Then it was dried in oven at 120 °C for 3 h to remove the water. Then, the NaF-treated cotton textile was dipped into the CNTs suspension about 5 min and remained into oven for 15 min drying at 120 °C to remove the solvent. This simple 'dip and dry' process was repeated for 5 times to increase the CNTs loading. The annealing of the textiles coating with CNTs was done in a horizontal tube furnace and heated at 900 °C for 10 min with 300 mL min^{-1} continuous flow of nitrogen gas. After cooling, the as-obtained CNTs coated active carbon textiles (denoted as CNTs/ACT) were washed with deionized (DI) water to remove the remained NaF and dried at 60 °C to remove the water.

2.2. Electrochemical deposition of MnO_2 nanoflakes

The electrodeposition of MnO_2 on CNTs/ACT was performed by a CHI 660 C workstation (China) with a three-electrode system with Pt foil as counter electrode, CNTs/ACT as working electrode, and saturated calomel electrode (SCE) as reference electrode at room temperature. Typically, a piece of CNTs/ACT was cut with size of 1 cm × 2 cm, and 1 cm × 1 cm was immersed into the mixed aqueous solution of 0.05 M $Mn(CH_3COO)_2$ and 0.1 M Na_2SO_4. The MnO_2 nanoflakes were synthesized by potentiostatic method under 0.6 V (*vs.* SCE) with various deposition time (1∼3 h) to conformally coat MnO_2 nanostructures on CNTs/ACT fibers. After electrodeposition, the CNTs/ACT/MnO_2 were taken out and carefully washed with DI water to remove excessive electrolyte, and then dried in an oven at 80 °C for 3 h. The mass of MnO_2 nanostrucutres can be obtained by the weight difference before deposition and after drying of the textiles.

2.3. Structural characterization of nanostructured MnO_2

The CNTs/ACT and CNTs/ACT/MnO_2 hybrid composite were characterized by X-ray diffraction (XRD, Rigaku D/max-2550V, Cu Kα radiation), FT-IR spectra (AVATAR370FT-IR), SEM (JEOL, JSM-6700F) and energy dispersive X-ray spectrometer (EDS).

2.4. Electrochemical characterization

Cyclic voltammogram (CV) and Galvanostatic (GV) charge/discharge measurements of the CNTs/ACT and CNTs/ACT/MnO_2 hybrid electrodes were performed with a standard three-electrode cell in the potential range of 0–1 V (*vs.* SCE) using a CHI 660 C workstation (China). The synthesized samples, Pt foil and saturated calomel electrode (SCE) were served as working electrode, counter electrode and reference electrode, respectively. 1 M Na_2SO_4 aqueous solution served as electrolyte at room temperature. The capacitance values were calculated based on the mass of electrodeposited MnO_2 nanoflakes.

3. Results and discussion

In our experiment, clean, white, plain woven cotton fabrics were chosen as the substrate of the textiles electrode. An optical photograph of a piece of textile is shown in Fig. 1 a. The textile fibers usually display a hierarchical structure with complex surface morphology, functional surface groups such as hydroxyl groups, and high microscopic porosity. Scanning electron microscopy (SEM) characterization of the textiles reveals that the textiles consists of interwoven cellulose fibers with diameters about 10∼20 μm (as shown in Fig. S1(a)). We know that acid treated CNTs have carboxyl functional groups on the surfaces and the ends, which can form strong hydrogen bonds with the hydroxyl groups in the cellulose fibers. Thereupon, when the cotton fabrics are dipped into the CNTs suspension, they are quickly coated with CNTs because of mechanical flexibility of CNTs and high surface area of cellulose fibers, together with large van der Waals forces and/or hydrogen bonding between CNTs and cellulose fibers [17]. The compatibility and strong interaction would greatly enhance the dispersion as well as the interfacial adhesion and thus bind the CNTs very tightly to the cellulose matrix. It has also been reported that the electrical properties, elastic modulus and mechanical strength could be remarkably enhanced after blending cellulose with small amount of CNTs [20]. As the dipping cycles progressed, a large number of CNTs were loaded onto the fibers to give a black