



# Carbon fabric-aligned carbon nanotube/MnO<sub>2</sub>/conducting polymers ternary composite electrodes with high utilization and mass loading of MnO<sub>2</sub> for super-capacitors

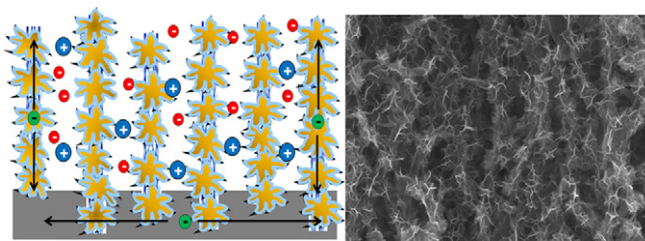
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## HIGHLIGHTS

- ▶ Carbon fabric-aligned carbon nanotube (CF-ACNT) acted as a unique substrate.
- ▶ MnO<sub>2</sub> and poly(3,4-ethylenedioxythiophene) (PEDOT) were deposited on CF-ACNT.
- ▶ The ternary composites showed a high MnO<sub>2</sub> utilization of 77.7%.
- ▶ The 3D porous ternary system allowed large MnO<sub>2</sub> mass loading up to 3.11 mg cm<sup>-2</sup>.
- ▶ A reasonable area-normalized capacitance of 1.3 F cm<sup>-2</sup> was achieved.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 24 March 2012

Received in revised form

22 July 2012

Accepted 25 July 2012

Available online 4 August 2012

### Keywords:

Aligned carbon nanotube

Carbon fabric

Manganese oxide

Poly(3,4-ethylenedioxythiophene)

Ternary composite

Super-capacitor

## ABSTRACT

3D porous ternary composite electrodes have been prepared by electrodepositing MnO<sub>2</sub> and poly(3,4-ethylenedioxythiophene) (PEDOT) successively on carbon fabric-aligned carbon nanotube (CF-ACNT) hybrids for the super-capacitors. MnO<sub>2</sub> petal-like nano-sheets are deposited on the ACNT surface with PEDOT uniformly encapsulated and interconnected MnO<sub>2</sub> nano-sheets and ACNTs. Cyclic voltammetry shows the MnO<sub>2</sub> utilization of ternary composites up to 77.7%, which far exceeds that of MnO<sub>2</sub>/CNT-based materials reported recently. Moreover, the 3D porous ternary system allows large mass loading of MnO<sub>2</sub>. And the ternary composites can remain a high MnO<sub>2</sub> utilization of 36% with the MnO<sub>2</sub> mass loading up to 3.11 mg cm<sup>-2</sup> while achieve a reasonable area-normalized capacitance of 1.3 F cm<sup>-2</sup> at 0.1 mV s<sup>-1</sup>. The ternary composites with substantially high mass loading exhibit an excellent rate capability and cycling stability, retaining over 95% of its initial charge after 1000 cycles. The excellent electrochemical performances are attributed to the synergetic effect of each component with unique properties and structures: high porosity and interconnectivity of CF, aligned ion diffusion channels along ACNTs, ultrathin MnO<sub>2</sub> nano-sheets and the improved conductivity by PEDOT.

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## 1. Introduction

Super-capacitors or electrochemical capacitors have attracted much attention due to high power density, fast charging and

discharging within seconds, superior cycle life time, and high reliability. A variety of materials with specific properties have been investigated to explore the great potential and applicability for advanced super-capacitors with high capacity performance, such as carbon-based materials, transition-metal oxides and conducting polymers [1–4]. However, previous attempts showed that the electrochemical properties of each material separately for super-

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capacitors were limited by their intrinsic structural shortcomings. For example, although carbon nanotubes (CNTs) exhibit excellent properties including high conductivity, large surface area, good mechanical properties and chemical stability [5–7], CNT-based electrodes act only as a stable high-surface-area support without redox properties, thus showing relative low specific capacitance [8–10]. Conducting polymers have high flexibility, but the huge capacity loss during successive charge/discharge cycles restricts their application for super-capacitors [11,12]. In addition,  $\text{MnO}_2$  as an important family member of transition-metal oxides is generally considered to be one of the most promising pseudocapacitive materials due to high theoretical specific capacitance, low cost, environmental friendliness and natural abundance [6,13,14]. Nevertheless, the electrochemical performances of  $\text{MnO}_2$  are basically limited by poor electronic conductivity and dense morphology of the oxide [15,16].

To overcome the limitation of each potential material, the design of specific composites prepared by the complementary combination of highly pseudocapacitive  $\text{MnO}_2$ , conductive CNTs or flexible conducting polymers is regarded as a powerful candidate for outstanding electrode materials [17,18]. Based on this structure, many binary composites, such as  $\text{MnO}_2/\text{CNT}$  [19–23] and  $\text{MnO}_2/\text{conducting polymers}$  [24,25], have been studied for high electrochemical performances. However,  $\text{MnO}_2/\text{conducting polymer}$  composites suffer from the mechanical instability and poor cycle-ability [26,27]. In contrast, binary composites of  $\text{MnO}_2/\text{CNT}$  exhibit advanced electrochemical performances, such as high specific capacitance, enhanced electrical conductivity and good cycling stability, which are attributed to the improved conductivity and mechanical property by CNTs [28–30].

Despite great potential, the low utilization of  $\text{MnO}_2$  at high mass loading is still a significant drawback of  $\text{MnO}_2/\text{CNT}$  binary composites. It is well known that the high transition-metal oxide concentration and large mass loading of active materials are essentially important for the high energy density of electrochemical applications [31]. However, dense morphology and poor conductivity of the binary composite electrodes due to high mass loading lead to the limited kinetics of charge transfer reaction and the difficulty in penetration of electrolyte into the bulk  $\text{MnO}_2$  [30,32]. Thus, the challenge with  $\text{MnO}_2/\text{CNT}$ -based composites lies in maximizing their electrochemical utilization. The approaches considered to efficiently improve the utilization can be concluded to two kinds: assembly of ternary composites and formation of a 3D porous structure. On the basis of the former method, ternary composites of  $\text{CNT}/\text{MnO}_2/\text{PEDOT-PSS}$  [18,33],  $\text{CNT-PSS}/\text{MnO}_2/\text{PPY}$  [31,34] and  $\text{CNT}/\text{MnO}_2/\text{PANI}$  [35] have been prepared with the outstanding electrochemical properties due to a synergetic effect from the combination of three components. The contact resistance of the electrodes is minimized effectively by conducting polymers due to the good interparticle connectivity between  $\text{MnO}_2$  and CNTs. In case of the later method, various carbon-based substrates, such as carbon nanofiber [36], carbon cloth [37,38], and CNT-textile [10,20] with a 3D porous network structure have been used for the controlled deposition of nano-structured  $\text{MnO}_2$ . The 3D porous architecture not only permits large loading of  $\text{MnO}_2$  but facilitates easy access of electrolytes to the electrodes, resulting in high specific capacitance and good rate capability [39–41].

To further improve the electrochemical performances of  $\text{MnO}_2/\text{CNT}$ -based composite electrodes, especially the high utilization and mass loading of  $\text{MnO}_2$ , we intend to combine the two concepts to form a 3D porous ternary system, which should have large specific surface area (SSA), high porosity and low internal resistance. In the present work, the carbon fabric-aligned carbon nanotube (CF-ACNT) hybrids prepared by chemical vapor deposition (CVD) are used as a porous substrate for electrode materials. The CF-ACNT

hybrids show high porosity, interconnected network, ordered porous structure and good electrical conductivity. The strategy of fabricating a 3D porous ternary composites is shown schematically in Fig. 1, where  $\text{MnO}_2$  and poly(3,4-ethylenedioxythiophene) (PEDOT) are successively deposited on CF-ACNT hybrids. The electrochemical properties of the 3D porous ternary composites with specific nano-structure and synergetic effects are measured in comparison with those reported in previous studies.

## 2. Experimental

### 2.1. Preparation of CF-ACNT hybrids

The growth of ACNTs on CF was performed by CVD in a reactor corundum tube furnace. The furnace was firstly purged with 300 sccm argon and heated to  $850^\circ\text{C}$  at  $5^\circ\text{C min}^{-1}$ . A feeding solution of catalyst precursor (ferrocene,  $0.025\text{ g mL}^{-1}$ ) and hydrocarbon source (xylene:ethanol:ethylene diamine = 49:49:2) were injected to the chamber during 60 min growth by a syringe pump. By measuring the weight difference of CF with and without CNTs, the mass of about 1~1.3 mg was obtained for CNTs on CF with a geometric surface area of about  $1\text{ cm}^2$ .

### 2.2. Preparation of CF-ACNT/ $\text{MnO}_2$ binary composites

$\text{MnO}_2$  was deposited onto CF-ACNT hybrids by a galvanostatic method with a three-electrode setup, where CF-ACNT, Pt foil and Ag/AgCl were used as working, counter and reference electrodes, respectively. A aqueous precursor solution with 0.1 M  $\text{Mn}(\text{CH}_3\text{COO})_2$  and 0.01M  $\text{Na}_2\text{SO}_4$  was used as the electrolyte, and the deposition was performed at a constant current of  $1\text{ mA cm}^{-2}$ . To ensure the conformal deposition of  $\text{MnO}_2$  uniformly on CF-ACNT surface, the precursor solution was introduced into CF-ACNT hybrids by 10 min vacuum impregnation before the deposition. Typically, the area of the hybrids was  $2\text{ cm}^2$  and only  $1\text{ cm}^2$  was immersed in the electrolyte for deposition. A small piece of Pt was used to connect the hybrids and the alligator clip to avoid side reactions. After the deposition, the working electrodes were washed with distilled water and then dried under vacuum at  $100^\circ\text{C}$  for 1 h. The  $\text{MnO}_2$  mass loading was evaluated by calculating the weight difference of the working electrodes.

### 2.3. Preparation of CF-ACNT/ $\text{MnO}_2$ /PEDOT ternary composites

PEDOT was continuously deposited onto CF-ACNT/ $\text{MnO}_2$  binary composites with the galvanostatic method as described in section 2.2. Aqueous solution consisting of 0.01 M EDOT and 0.005 M SDS was used for the deposition of PEDOT at a current of  $0.5\text{ mA cm}^{-2}$ . And the pH value of aqueous solution was adjusted by slowly adding  $p$ -toluenesulfonic acid to pH = 1. The mass loading of the electrodes was evaluated same to section 2.2. The PEDOT was also deposited onto the CF-ACNT under the same condition for electrochemical comparison.

The composites were defined based on the various deposition time, for example, the composite of CF-ACNT/ $\text{MnO}_2(10)/\text{PEDOT}(1)$  was prepared by the deposition of  $\text{MnO}_2$  for 10 min and subsequently the deposition of PEDOT for 1 min. The details of the deposition time and weight fraction of different composites were presented in Table S1.

### 2.4. Material characterization

The chemical structure of composites was characterized by X-ray photoelectron spectroscopy (XPS), which was performed with a PHI 1600 spectroscopy using Mg  $K\alpha$  X-ray source for excitation.

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