Research Article

The Preparation of Carbon Nanotube/MnO₂ Composite Fiber and Its Application to Flexible Micro-Supercapacitor

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In recent years, flexible electronic devices pursued for potential applications. The design and the fabrication of a novel flexible nanoarchitecture by coating electrical conductive MWCNT fiber with ultrathin films of MnO₂ to achieve high specific capacitance, for micro-supercapacitors electrode applications, are demonstrated here. The MWCNT/MnO₂ composite fiber electrode was prepared by the electrochemical deposition which was carried out through using two different methods: cyclic voltammetry and potentiostatic methods. The cyclic voltammetry method can get “crumpled paper ball” morphology MnO₂ which has bigger specific capacitances than that achieved by potentiostatic method. The flexible micro-supercapacitor was fabricated by twisting two aligned MWCNT fibers and showed an area specific capacitance of 2.43 mF/cm². The flexible micro-supercapacitors also enable promising applications in various fields.

1. Introduction

In the past several years, rapid progress in flexible technology applied a large number of innovative products such as skin sensors, wearable displays, electronic paper, organic light-emitting diode (OLED) [1–3]. The flexible and transparent electrode is becoming one of the most interesting research topics in the field of materials science and technology. The conventional rigid electronics are difficult to satisfy these applications. Most of flexible electrodes use both polymers and thin films of inorganic oxides as the conducting layers. The electrical properties of these oxides can be good; nevertheless, there was a significant deficiency for the low tensile fracture strains of mechanical characteristics which were not optimally suitable for use in flexible devices. At the same time, this kind of flexible electrode is not easily manufactured. In order to play the features of flexible devices in a better way, which includes shapes from foldable or deformable to complex curvilinear, their energy management (such as batteries and supercapacitors) should be flexible at best [4, 5]. Therefore, the development of the energy storage devices with the superiority of lightweight, flexibility,

and environmental protection becomes a strong demand. In the past several years, because of their unique structures which provide them with intriguing chemical and physical performances, for example, excellent electronic properties, carbon nanotubes have been vastly researched for broad types of applications [6–10].

Here, we demonstrate the design and the fabrication of a novel flexible nanoarchitecture by coating the electrical conductive multiwalled carbon nanotubes (MWCNTs) fiber with ultrathin films of MnO₂ to achieve high specific capacitance for micro-supercapacitors electrode applications.

2. Experimental Section

2.1. Growth of Spinnable MWCNT Arrays and Spin of Fiber. Carbon nanotube arrays were synthesized by a chemical vapor deposition in a quartz tube furnace using Fe (1 nm)/Al₂O₃ (10 nm) on silicon wafer as the catalyst, ethylene (40 sccm) as carbon sources, and a mixture of Ar (560 sccm) and H₂ (40 sccm) gases as carrying gas. The reaction was typically performed at 750°C for 20 min. MWCNT

FIGURE 1: Characterizations of a CNT array. (a) SEM image by side view at low magnification. (b) High resolution TEM image. (c) Photograph of spinning carbon nanotube fiber. (d) SEM image of carbon nanotube fiber.

fibers were spun from MWCNT arrays with a spindle rotating at 2000 rpm and drawing at 10 cm/min^{-1} .

2.2. Composite Electrode Production. The $\text{MnO}_2/\text{MWCNT}$ fiber composite electrode was prepared by the electrochemical deposition which was carried out through using two different methods: cyclic voltammetry and potentiostatic method. With the method of cyclic voltammetry, the MnO_2 nanoparticles were electrochemically deposited on MWCNT fibers in an aqueous solution including $0.05 \text{ M Mn}(\text{CH}_3\text{COO})_2$ and $0.10 \text{ M Na}_2\text{SO}_4$ at a potential range from -0.2 to 0.8 V (versus Ag/AgCl) through an electrochemical analyzer system (CHI 660D). The potentiostatic deposition performed at the optimum conditions obtained in this work was 0.6 V applied potential and 200 seconds of deposition time.

2.3. Fabrication of Supercapacitor Cells and Electrochemical Measurement. Two $\text{MnO}_2/\text{MWCNT}$ nanocomposite fibers were immersed in the H_2SO_4 -PVA (either content $10 \text{ wt } \%$) aqueous solution for 10 min and picked out. For two bare MWCNT or $\text{MWCNT}/\text{MnO}_2$ composite fibers, one end of each fiber was firstly fixed and combined to a copper wire by silver paint. After twisting the two fibers, a supercapacitor wire was produced. One was functioned as the working electrode and the other as both counter and reference electrodes.

2.4. Characterization. The structures of nanotubes were characterized by scanning electron microscopy (SEM, Hitachi FE-SEM S-4800 operated at 1 kV) and transmission electron microscopy (TEM, JEOL JEM-2100F operated at 200 kV). TEM samples were prepared by drop casting N,N-dimethyl formamide solutions of nanotubes onto copper grids in the open air. Raman spectra were shown in Figure 2 analysis by Raman spectroscopy (Dilor LabRam-1B, He-Ne laser of 4 mW , excitation wavelength of 632.8 nm).

3. Results and Discussion

Figure 1(a) shows SEM images of vertically aligned CNTs obtained under CVD conditions by side way. The array thickness ranged from tens of micrometers to millimeters mainly through the control of the growth time. The optimum CVD conditions were ethylene (40 sccm), Ar (560 sccm), and H_2 (40 sccm). The reaction was typically performed at 750°C for 20 min. Figure 1(b) shows high resolution transmission electron microscopy (TEM) image of a typical multiwalled CNT with diameter of about $8\text{--}10 \text{ nm}$. The CNTs synthesized by this approach are all multi-walled with the interlamellar distance of 0.34 nm . The well-defined lattice fringes in TEM images of the MWNTs indicate that the as-grown nanotubes have a high degree of local crystalline order. Figure 1(c) was a photograph of spanning carbon nanotube fiber. The fiber diameter can be controlled from 3 to 30 mm and lengths up to 200 m , mainly depending on the initial ribbon width during the spinning. Figure 1(d) shows a typical SEM image of a CNT fiber with a uniform diameter along the axial direction. Under higher magnifications, many CNT strands would wind together to form the fiber. These strands consist of highly aligned individual CNTs assembled from the arrays [11, 12].

Figure 2(a) shows the Raman spectra of the CNT fiber. Raman spectroscopy of the CNT fiber is beneficial to evaluate the structure integrity of carbon-based nanotubes. It is popular that two characteristic peaks of D-band and G-band arise from defects or disorder of graphene sheets and C-C stretching (E_2g) model of graphite, respectively, and intensity ratio of D-band to G-band reflects crystallinity degree. Here, D-band and G-band were observed at 1355 and 1580 cm^{-1} , respectively [13]. The intensity ratios of D-band to G-band are gradually calculated to be 0.72 . This result agrees with TEM and SEM observations. Figure 2(b) displays the typical stress-strain curve of a CNT fiber with a tensile strength of 0.39 GPa . Note that the mechanical strength of the fiber greatly relies on and increases with the CNT length. This is logical considering

FIGURE 2: (a) Raman spectra of the CNT fiber. (b) A typical stress-strain curve.

FIGURE 3: (a), (b), and (c) SEM image of a typical CNT fiber with conformal coating of MnO_2 nanostructures by cyclic voltammetry method and (d), (e), and (f) by potentiostatic method.

that CNTs are connected at the ends in a fiber. Due to the flexibility of the nanotube, it will not break after being bent, folded, or even tied many times [3, 14].

The MnO_2 loading on the CNT fiber can be controlled by tuning the electrochemical deposition methods and deposition time. Figures 3(a), 3(b), and 3(c) show the morphology and microstructure of a representative composite by cyclic voltammetry and Figures 3(d), 3(e), and 3(f) by potentiostatic method. As can be seen in Figures 3(a), 3(b), and 3(c), a unique hierarchical MnO_2 architecture has been successfully grown on CNT fiber. Figures 3(b), and 3(c) show no aggregations of MnO_2 nanoparticles, and the MnO_2 exhibited an architecture with uniform “crumpled paper ball” morphology

[15]. Remarkably, the architecture provides huge surface areas with effective electrolyte transport and active-site accessibility. Evidently, Figures 3(d), 3(e), and 3(f) indicate that MnO_2 nanosphere shows a tendency to aggregation. Although, by this way, the MnO_2 nanosphere can provide active site, the efficiency is lower than that of the cyclic voltammetry way for the surface areas which cannot achieve the degree of cyclic voltammetry way.

Two bare MWCNT fibers or two MWCNT/ MnO_2 composite fibers were then adopted as parallel electrodes to prepare wire-shaped micro-supercapacitors. Figure 4 presents CV curves at different scan rates of micro-supercapacitors fabricated by bare MWCNT fiber

FIGURE 4: (a) CV curves at different scan rates of micro-supercapacitors fabricated by bare MWCNT fiber and (b) MWCNT/MnO₂ composite fiber by cyclic voltammetry method. (c) Schematic illustration of fabrication processes of the wire-shaped micro-supercapacitors. (d) Dependence of specific capacitance in the supercapacitor wire on the current. (a) Twisting two bare MWCNT fibers. (b) Twisting two MWCNT/MnO₂ composite fibers by potentiostatic method and (c) by cyclic voltammetry method.

(Figure 4(a)) and MWCNT/MnO₂ composite fiber (Figure 4(b)). Figure 4(c) shows the illustration of fabrication processes of the wire-shaped micro-supercapacitors. Two MnO₂/CNT nanocomposite fibers were immersed in the H₂SO₄-PVA aqueous solution for 10 min and picked out. The surface covered by H₂SO₄-PVA gel electrolyte can separate the two electrodes when fibers were twisted. Then, the twisted two fibers were packaged by polydimethylsiloxane (PDMS) to fabricate the flexible micro-supercapacitors. The average specific capacitance of supercapacitor was calculated by the following equation: $C = 2i_0/[m(\Delta V/\Delta t)]$, where i_0 , $\Delta V/\Delta t$,

and m correspond to the discharge current, average slope of the discharge curve, and mass of the active material in the electrode, respectively. The galvanostatic charge-discharge potential range is during 0–1.0 V. Figure 4(d) has compared the dependence of specific capacitances on current between 5×10^{-4} and 3×10^{-3} mA for the bare and the composite fibers. The specific capacitances were reduced with the increasing current in the three cases, that is, C from 2.43 to 2.06 mF/cm² and B from 2.39 to 2.01 mF/cm². Due to the potentiostatic method, the MnO₂ can have a bigger specific surface area than that obtained by cyclic voltammetry method. And

the bare fiber was from 2.27 to 1.95 mF/cm². However, the reduced degrees for the composite fibers were lower than those for the bare fiber. It is rational considering that MnO₂ nanoparticles have performed higher pseudocapacitances than MWCNTs [16, 17]. The charging mechanism of MnO₂ is described by the following reaction:

where B⁺ = Li⁺, Na⁺, K⁺, H⁺. Equation (1) displays that the large surface area and high ionic and electronic conductivity of the electrode material are essential in order to utilize the high theoretical specific capacitance (SC) (1380 F g⁻¹) of MnO₂ [18].

4. Conclusion

In conclusion, we have successfully prepared MWCNT fibers and MWCNT/MnO₂ composite fibers. By comparing the two ways of preparing the MWCNT/MnO₂ composite fibers, the cyclic voltammetry method can get “crumpled paper ball” morphology MnO₂ which has bigger specific capacitances than those obtained by potentiostatic method. The flexible micro-supercapacitors also enable promising applications in various fields.

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