Studies on CNTs–MnO_2 nanocomposite for supercapacitors

MEIGEN DENG*, BANGCHAO YANG, ZHIAN ZHANG, YONGDA HU
School of Microelectronics and Solid State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China
E-mail: dengmeigen@163.com

Due to their narrow distribution size, highly accessible surface area, low resistivity and high stability [1], carbon nanotubes (CNTs) have been regarded as suitable materials for electrodes in supercapacitors since they were discovered in 1991 [2]. However, pure CNTs possess a very moderate surface area from ca. 120 to 400 $m^2 \cdot g^{-1}$, so specific capacitance of supercapacitors based on pure CNTs is fairly low and therefore enhancement of CNTs specific capacitance is of great interest for supercapacitor application. An improvement of capacitance can be realized by increase of electrode surface area of CNTs or by pseudofaradaic effects obtained by additive of special oxides or conducting polymers [3–6]. Here we report the preparation of CNTs–MnO_2 nanocomposite and its performance as electrode material for supercapacitors.

CNTs were produced catalytically with Ni particles as the catalyst. Nitric acid treatment was employed to remove the catalyst particles before use. For the preparation of CNTs–MnO_2 nanocomposite, CNTs were added into a solution of 0.1 $mol \cdot L^{-1}$ $KMnO_4$ with polyvinylpyrrolidone used as surfactant. The CNTs suspension was stirred for 2 hr so that the $KMnO_4$ was sufficiently absorbed on the CNTs. A solution of 0.15 $mol \cdot L^{-1}$ $Mn(CH_3COO)_2$ is slowly added and the mixed solution was stirred violently for 12 hr. The CNTs–MnO_2 nanocomposite was obtained by filtering and rinsing the suspension with deionized water followed by drying of the remaining powder at a temperature of 120 °C.

Electrodes for supercapacitors were formed by pressing a mixture of CNTs or CNTs–MnO_2 nanocomposite (95 wt.%) + polytetrafluoroethylene (5 wt.%) onto nickel foam current collectors. Two electrode capacitors were built by sandwiching a glass-fiber between two electrodes. The aqueous electrolytes was 2 $mol \cdot L^{-1}$ KCl. The values of specific capacitance was estimated by galvanostatic charge–discharge cycling.

Fig. 1 illustrates the transmission electron microscope (TEM) images of pure CNTs and CNTs–MnO_2 nanocomposite. As shown in Fig. 1a, the diameter of the CNTs is in the range of 30–40 nm and no catalyst particle is visible after nitric acid treatment. Fig. 1b reveals that the surface of CNTs was quite uniformly coated with MnO_2.

Fig. 2 shows the galvanostatic charge–discharge of the pure CNTs and CNTs–MnO_2 nanocomposite supercapacitors. Capacitance of each cell can be deduced from the slope of the $V(t)$ curves: $C_{cell} = I/(dV/dt)$. Specific capacitance of the active materials can be calculated as follows: C_{cell} being the total capacitance of the cell, m the amount of active material in one electrode, the specific capacitance of the active material is then $C = 2C_{cell}/m$. The measured specific discharge capacitance for pure CNTs and CNTs–MnO_2 nanocomposite were 49 $F \cdot g^{-1}$ and 146 $F \cdot g^{-1}$, respectively. Specific energy can be calculated by formula $E = (CU^2)/2$, where C is capacitance of the capacitor cell, and U working voltage. The measured specific energy for the pure CNTs and CNTs–MnO_2 nanocomposite supercapacitors were 1.7 and 5.1 $Whr \cdot kg^{-1}$, respectively.

For the pure CNTs supercapacitor, the capacitance was mainly derived from the charge accumulated in the electric double layer formed at the interface between the CNTs electrodes and electrolyte solution. However, in the case of CNTs–MnO_2 nanocomposite electrode supercapacitor, except for the electric double layer capacitance, pseudo-capacitance arose from redox reaction of MnO_2 also contributed to the electrode capacitance.

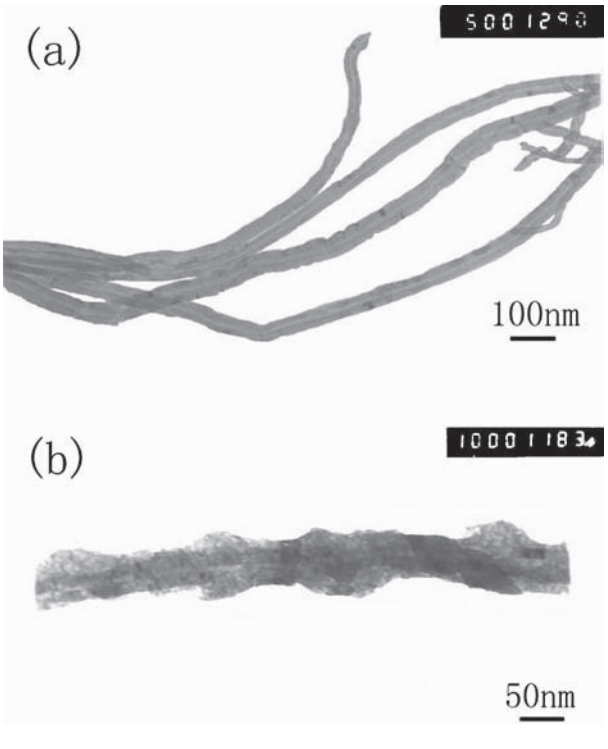

Figure 1 TEM images of: (a) pure CNTs and (b) CNTs-MnO_2 nanocomposite.

*Author to whom all correspondence should be addressed.

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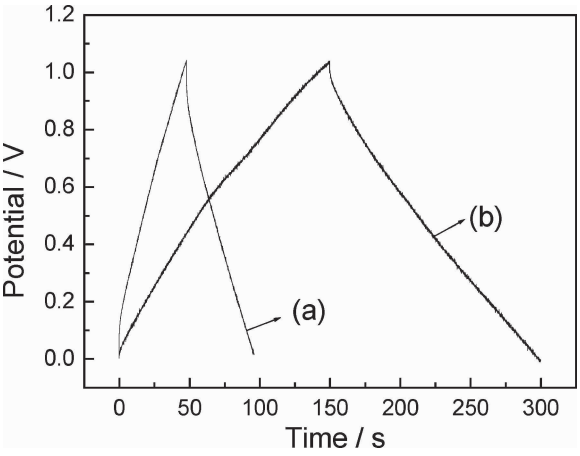

Figure 2 Galvanostatic charge–discharge of: (a) pure CNTs and (b) CNTs–MnO_2 nanocomposite supercapacitors.

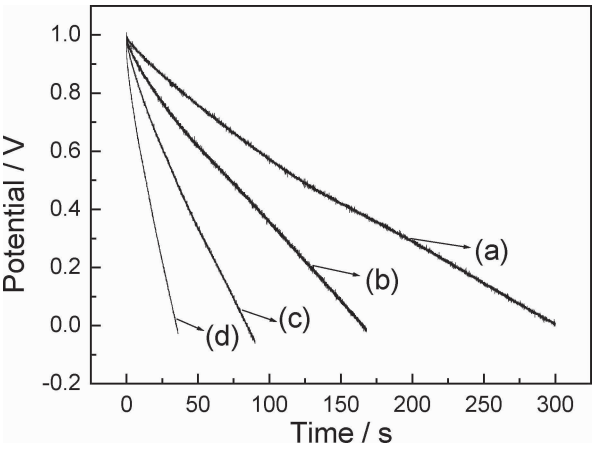

Figure 3 Constant current discharge of CNTs–MnO_2 nanocomposite supercapacitor at current densities of: (a) 5, (b) 10, (c) 20, and (d) 40 $mA \cdot cm^{-2}$.

The principal reaction involved in the charging and discharging process of MnO_2 in neutral electrolytes [7] can be presented as

$$MnO_2 + H^+ + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} MnOOH$$

The specific capacitance of pure MnO_2 prepared using this method can reach 203 $F \cdot g^{-1}$ [8], which is much higher than that of CNTs. So the deposition of MnO_2 on CNTs can increase the specific capacitance of CNTs effectively. What is more, the redox reaction of MnO_2 is primarily surface mechanism and is hence highly dependent on the surface area of the electrode material. The uniform coating of MnO_2 on the surface of CNTs can increase effectively the active sites of MnO_2 and thus was also helpful to enhance the specific capacitance.

Fig. 3 illustrates the performance of the CNTs–MnO_2 nanocomposite supercapacitors under constant current discharge. The potential-time response of the curves indicates that the nanocomposite possessed typical capacitor characteristic. The specific capacitance of the nanocomposite under different current densities were evaluated from Fig. 3. The values at current densities of 5, 10, 20 and 40 $mA \cdot cm^{-2}$ were 146, 134, 128 and 124 $F \cdot g^{-1}$, respectively. We can see when the discharge current density increased from 5 to 40 $mA \cdot cm^{-2}$, the specific capacitance decreased from 146 to 124 $F \cdot g^{-1}$, only a decrease of 15% was observed. This indicates that the nanocomposite supercapacitor had an outstanding power performance.

In conclusion, CNTs–MnO_2 nanocomposite was prepared by coating MnO_2 on the surface of CNTs. The deposition of MnO_2 made the specific capacitance of the CNTs increased from 49 to 146 $F \cdot g^{-1}$. Supercapacitors based on the CNTs–MnO_2 nanocomposite had an outstanding power performance and an energy density of 5.1 $Whr \cdot kg^{-1}$.

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