Pure Appl. Chem., Vol. 81, No. 12, pp. 2317–2325, 2009. doi:10.1351/PAC-CON-08-11-25 © 2009 IUPAC, Publication date (Web): 16 November 2009

Fabrication of a vertically aligned carbon nanotube electrode and its modification by nanostructured MnO₂ for supercapacitors*

Wei-De Zhang[‡] and Jin Chen

Nano Science Research Center, School of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510640, China

Abstract: Strongly bonded arrays of vertically aligned, multi-walled carbon nanotubes (MWNTs) have been successfully grown on Ta foils, and provide a convenient basis for fabricating electrodes with high conductivity and stability. The MWNT arrays were further coated by nanostructured MnO₂ through reacting with KMnO₄ solution at room temperature. The morphology of the MnO₂/MWNT nanocomposite was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was found that the MnO₂ is a beehive-like nanostructure that is homogeneously and densely coated on the surface of the MWNTs. The capacitance of the MWNT electrode was significantly increased from 0.14 to 6.81 mF cm⁻² after being modified with nanostructured MnO₂, that is, the mass-specific capacitance of the bare and MnO₂-modified MWNTs was about 33 and 446 F g⁻¹, respectively. The MnO₂/MWNT nanocomposite on Ta foils could be potential for developing a supercapacitor.

Keywords: carbon nanotubes; electrodes; manganese dioxide; nanocomposites; supercapacitors.

INTRODUCTION

Supercapacitors or electrochemical capacitors are charge-storage devices that have been extensively investigated and are being developed as new energy storage devices with the advantage of high energy density, great power density, and long cycle life [1]. According to different energy storage mechanisms, supercapacitors can be divided into two kinds: the electric double-layer capacitors using carbon with high specific surface area as the electrode material [2]; and the redox supercapacitors using certain metal oxides or conducting polymers with high capacitance as the electrode materials [3–5]. The high performance of supercapacitors usually comes from high specific surface area and high reversible redox reactions of the electrode materials. Carbon nanotubes (CNTs), including single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs), are considered as potential electrode materials for supercapacitors due to their excellent mechanical property, good electrical conductivity, unique pore structure, and chemical stability [6–9]. However, because of relatively low specific surface area, the capacitance of CNTs is smaller than that of the traditional activated carbon and mesoporous carbon [10,11], which limits their further practical applications.

^{*}Paper based on a presentation at the International Symposium on Novel Materials and their Synthesis (NMS-IV) and the 18th International Symposium on Fine Chemistry and Functional Polymers (FCFP-XVIII), 15–18 October 2008, Zhenjiang, China. Other presentations are published in this issue, pp. 2253–2424.

[‡]Corresponding author: E-mail: zhangwd@scut.edu.cn; Tel.: 86-20-87114099; Fax: 86-20-87112053

In order to improve the capacity performance of CNTs, metal oxide/CNT composites, such as $RuO_2/CNTs$ [4,12], $MnO_2/CNTs$ [5,13,16], and NiO/CNTs [14], have been prepared taking advantage of both the excellent electrical conductivity and chemical stability of CNTs and the high capacitance of metal oxides [15]. Among these metal oxides, RuO_2 shows the highest capacitance [4], so is its cost. MnO_2 is another candidate for supercapacitors because of its novel chemical and physical properties, high theoretical capacity together with natural abundance and environmental compatibility [2,5,13,16]. The supercapacitance of MWNT powder increased from 29.8 to 250.5 F g⁻¹ after modification with MnO_2 , which has recently been reported [16]. The significant increase in the capacitance of the $MnO_2/MWNT$ nanocomposite electrode is due to the pseudo-capacitance of MnO_2 .

In the present work, we grew vertically aligned MWNTs on Ta foils, which efficiently simplifies the fabrication of electrode for electrochemical applications. These high-density, well-aligned MWNTs with a large, electrochemically accessible surface area, high purity and high electrical conductivity, have been demonstrated to be high-performance electrode materials for supercapacitors with modifications [4,6]. Here we report coating of the vertically aligned MWNTs with nanostructured MnO_2 by a simple method of solution oxidation and deposition for electrode material to develop planar supercapacitors.

EXPERIMENTAL SECTION

Ta foils with thickness of 0.1 mm were purchased from Goodfellow. All other reagents were of analytical grade and used without further purification. All solutions for electrochemical measurements were prepared with high-quality deionized water (18.4 M Ω cm⁻¹).

A field-emission scanning electron microscope (SEM) (JEOL JSM 6700F) was used to observe the bare and MnO_2 -modified well-aligned MWNT arrays. Transmission electron microscopy (TEM) observations were performed with a Philips CM 300 FEG instrument operated at 300 kV. X-ray diffraction (XRD) profiles were recorded on a Bruker GADDS diffractometer with an area detector operating under a voltage of 40 kV and a current of 40 mA using Cu K α radiation ($\lambda = 0.15418$ nm).

Electrochemical measurements were performed using a CHI 660C electrochemical workstation (Shanghai Chenhua, China). A three-electrode system was employed with MWNT or MnO₂/MWNT electrode as working electrode, a Ag/AgCl (3 M KCl) electrode and a platinum wire served as reference electrode and counter electrode, respectively. All potentials were referred to the Ag/AgCl (3 M KCl) electrode.

Growth of vertically aligned MWNTs on Ta foils was conducted by catalytic chemical vapor deposition with ethylenediamine as a carbon source [17–19]. A thin film of cobalt (thickness about 10 nm) was firstly magnetron sputtering deposited on the Ta foils as the catalyst for the growth of MWNTs. The prepared MWNTs on the Ta foils were further modified with MnO₂ through reaction with KMnO₄ solution [20]. A typical preparatory procedure for MnO₂/MWNT nanocomposite was as follows: KMnO₄ (18 mg) was dissolved in aqueous 10 M HNO₃ (10 ml), and the vertically aligned MWNTs were immersed top-down in the solution for 30 min. The amount of MnO₂ deposited on the MWNT electrode was monitored by controlling the immersing time to get high capacitive performance. The resistance of the electrode will increase if the MnO₂ layer is too thick. Through testing, 30 min is chosen as the best reaction time. The resultant product was washed with deionized water to remove the remaining ions, and was then dried at 60 °C for 12 h. The MnO₂/MWNT nanocomposite attached to a Ta foil was thus obtained.

RESULTS AND DISCUSSION

Morphological characterization of the vertically aligned MWNTs and the ${\rm MnO}_2/{\rm MWNT}$ nanocomposite

We have successfully grown vertically aligned MWNT arrays with large area by catalytic CVD on silica or silicon surfaces with deposited metal thin film as a catalyst and ethylenediamine as a carbon source [17–19]. The MWNTs also grew on the metal substrate with vertical alignment (Fig. 1A). The structure characterization of the MWNTs by TEM shows that the nanotubes are in a bamboo-like structure (Fig. 1B). The inserts in Figs. 1A and B show the closer SEM and TEM observations on the broken roots of the nanotubes. It is worth pointing out that the tips of the nanotubes do not contain any metal nanoparticles (Fig. 1B), which is contrary to those grown on the silicon or silica substrates [17,18]. In addition, the MWNTs are adhesively grown on the Ta foils, and the MWNTs can be broken (Fig. 1A) by tweezers but the MWNT films cannot be peeled off as a whole. The growth of MWNTs on the Ta substrate follows the root-growth mechanism, which is because of the strong interaction between the catalyst nanoparticles (Co) and the metal substrate (Ta). On the other hand, those MWNTs grown on silicon or silica surface follow the tip-growth mechanism due to the weak interaction of the catalyst nanoparticles with the substrate, thus the MWNTs can be peeled off easily as a thin film.



Fig. 1 (A) SEM image of vertical CNTs grown on a Ta foil; (B) TEM image of the MWNTs.

W.-D. ZHANG AND J. CHEN

The vertically aligned MWNTs are very convenient for further modification by physical [4] or chemical [21–23] methods. In the present work, we deposited MnO_2 on the nanotubes through the reaction of MWNTs (as a reductive reagent) with $KMnO_4$ (as an oxidative reagent). The typical SEM images of $MnO_2/MWNT$ nanocomposite are shown in Fig. 2A (top view) and B (side view). It can be seen that the surface of the MWNTs is homogeneously coated and the MnO_2 -coated MWNTs keep good alignment. No isolated particle was found, that is, all the MnO_2 are tightly adhered on the nanotubes. The enlarged morphology (insert in Fig. 2A) shows very clearly that the surface of the $MnO_2/MWNT$ nanocomposite is very rough and has beehive-like structure on it. The insert in Fig. 2B depicts the cross-section of a broken nanotube, which indicates obviously the coating layer as a shell and the nanotube as a core, forming the tube-in-tube structure. TEM observations were carried out for a more detailed structural characterization. Figure 2C provides an overview of a modified nanotube, clearly showing that the nanotube is uniformly coated with a thick layer of MnO_2 with porous structure. This is in agreement with the observation by SEM. More importantly, we can also conclude from TEM observation that the adhesion of MnO_2 on the walls of the MWNTs is very strong even though the sample was ultrasonicated for preparation of the TEM sample in advance.



Fig. 2 SEM images of (A) top view and (B) side view of the $MnO_2/MWNT$ nanocomposite; (C) TEM image of a MWNT modified with MnO_2 ; (D) XRD pattern of the $MnO_2/MWNT$ nanocomposite on a Ta foil. The arrows indicate the diffraction patterns from MnO_2 , and the triangles indicate the diffraction patterns from the Ta substrate.

The crystal structure of the $MnO_2/MWNT$ nanocomposite was studied by X-ray diffraction (XRD) analysis, as shown in Fig. 2D. The XRD pattern shows diffractions of very strong peaks of the Ta substrate at 20 of 38.5°, 55.6°, 69.6°, 82.5°, 95.0° and a very weak peak at 20 of 26.2°, which is graphite structure of MWNTs [(002) planes]. In addition, two small peaks at about 20 of 58.9° and 60.0°, which belong to MnO_2 (600), (312) planes, respectively, also appeared in the XRD profile. The XRD result clearly indicates that MnO_2 was deposited on the surface of MWNTs.

Fabrication of the MWNTs and MnO₂/MWNT electrodes

The MWNTs adhered on metal substrates are favorable for direct application as electrode because of their strong combination and high conductivity as well. The growth of vertically aligned MWNTs on the Ta foils and the procedure for the fabrication of MWNT electrode were depicted in Fig. 3. Ta foils were firstly deposited with a thin film of Co as catalyst for CVD synthesis of MWNTs. A piece of Ta foil with MWNTs was connected to the surface of a glassy carbon (GC) electrode using conductive silver paint (Structure Probe, Inc., USA). The edges of the Ta substrate and the GC electrode were insulated by painting with nail enamel (Maybelline, NY, USA). These MWNTs connected to the GC electrode were used as the working electrode. The MnO₂-modified MWNT electrode can be fabricated in the same way.



Fig. 3 Schematic of details showing the fabrication of an MWNT electrode.

The electrochemical properties of the MWNT and $MnO_2/MWNT$ nanocomposite electrodes were evaluated by cyclic voltammetry (CV) in 5.0×10^{-3} M K₃Fe(CN)₆ containing 1.0 M KCl. The CV response of the MWNT and the MnO₂/MWNT nanocomposite electrodes are shown in Figs. 4A and B, respectively. The difference between the anodic and cathodic peak potentials (ΔE_p) is nearly 59 mV at



Fig. 4 CVs of (A) the bare MWNT electrode with scan rate of (a) 10, (b) 20, (c) 50, (d) 100, and (e) 150 mV s⁻¹, and (B) the MnO₂/MWNT electrode with scan rate of (a) 10, (b) 30, (c) 50, (d) 100, and (e) 150 mV s⁻¹, in a 5.0×10^{-3} M K₃Fe(CN)₆ solution with 1.0 M KCl; the relationship between the CV responding current and the square root of the scan rate (C) at the MWNT electrode and (D) at the MnO₂/MWNT electrode.

the MWNT electrode at all sweeping rates (Fig. 4A), suggesting ideal reversibility of the MWNT electrode [24]. The CV responding current at both MWNT and $MnO_2/MWNT$ electrodes depends linearly on the square root of the scan rate over the range of 10–150 mV s⁻¹, indicating a diffusion controlling kinetic reaction at the electrodes. On the other hand, both the response current and the value of ΔE_p increase with the increase of the scan rate at the $MnO_2/MWNT$ nanocomposite electrode (Fig. 4B). We conclude that the modification of MWNTs with nanostructured MnO_2 plays an important role in increasing the effective surface area, which results in the enhancement of capacitance of MWNTs, as discussed below.

Supercapacitive property of the MnO₂/MWNT nanocomposite electrode

The electrochemical capacitance of the MWNT and $MnO_2/MWNT$ electrodes was investigated by CV and chronopotentiometry in 1.0 M Na_2SO_4 aqueous solution and the corresponding results are shown in Figs. 5 and 6. It is well known that a large-current, rectangular-type CV and symmetry in anodic and cathodic directions are the indications of ideal capacitive behavior of the electrode materials. Figure 5 shows the typical CVs of the MWNT (curve a) and $MnO_2/MWNT$ nanocomposite (curve b) electrodes at a scan rate of 100 mV s⁻¹ in 1.0 M Na_2SO_4 aqueous solution under a potential ranging from 0 to



Fig. 5 CVs on (a) the bare MWNT electrode and (b) the $MnO_2/MWNT$ nanocomposite electrode in 1.0 M Na_2SO_4 solutions. Scan rate = 100 mV s⁻¹.



Fig. 6 (A) Chronopotentiograms of (a) the bare MWNTs electrode with an applied current of 0.01 mA, and (b) the $MnO_2/MWNT$ nanocomposite electrode with an applied current of 0.1 mA in 1.0 M Na_2SO_4 solutions between 0 and +1.0 V. (B) Cyclic life of the $MnO_2/MWNT$ nanocomposite electrode during a charge–discharge cycle at the charge–discharge current of 0.1 mA.

0.9 V. It can be seen that the $MnO_2/MWNT$ nanocomposite electrode has a nearly rectangular-shaped and symmetric CV and its CV response current is much larger than that of the MWNT electrode. This is a clear indication that the $MnO_2/MWNT$ nanocomposite electrode has excellent capacitive performance. The capacitive behavior of the $MnO_2/MWNT$ nanocomposite electrode is mainly caused by the existence of the nanostructured MnO_2 layer.

Figure 6A shows the galvanostatic charge–discharge behavior of the bare MWNT electrode with an applied current of 0.01 mA (curve a) and the $MnO_2/MWNT$ nanocomposite electrode with an applied current of 0.1 mA (curve b) in the potential range between 0 and +1.0 V in a 1.0 M Na₂SO₄ aqueous solution. The symmetry of the charge and discharge characteristics indicates that the $MnO_2/MWNT$ nanocomposite has excellent capacitive characteristics and a strongly reversible oxidation reaction. The specific capacitance (C_m) can be estimated according to the following equation:

$$C_{\rm m} = [(Idt)/dE]/A = i/[(dE/dt)A]$$
(1)

where *i* is the applied current and *A* is the planar surface area of the MWNT or the $MnO_2/MWNT$ nanocomposite. The calculated specific capacitance (C_m) of the bare MWNT and $MnO_2/MWNT$ nanocomposite electrodes, according to the physical surface area of the electrodes, is 0.14 and 6.81 mF cm⁻², respectively. The mass-specific capacitance of the bare MWNTs is found to be about 33 F g⁻¹ [6], and the capacitance of the MnO₂/MWNT nanocomposite with 70 wt % MnO₂ was about 446 F g⁻¹. The significant increase in the capacitance of the MnO₂/MWNT nanocomposite electrode is due to the 3D nanostructure of MnO₂ at the surface of the MWNTs, which enhances the accessible surface area to the electrolyte, and more importantly, the nanostructured MnO₂ provides Faradaic pseudo-capacitance. The above results indicate that the capacitive performance of the MnO₂/MWNT nanocomposite electrode.

The charge-discharge cycling stability of the MnO₂/MWNT nanocomposite electrode was also investigated by chronopotentiometry with an applied current of 0.1 mA in 1.0 M Na₂SO₄ and the corresponding result is shown in Fig. 6B. As can be seen in Fig. 6B, the specific capacitance of the nanocomposite electrode declined slightly during the first 500 cycles but remained almost constant thereafter. During the initial charge-discharge cycles, aggregation of the nano-MnO₂ decreases the active sites and hinders electrolyte penetrating into the electrode. Moreover, unreversible reaction and dissolution and/or detachment of MnO₂ from the MWNTs during charge–discharge cycles also result in the capacitance degradation. However, compared to the first cycle, 90 % value of the specific capacitance of the MnO₂/MWNT nanocomposite remained after 1000 cycles, which indicates that the MnO₂/MWNT nanocomposite electrode has excellent long-term cycling stability. The great enhancement of capacitance in the MnO₂/MWNT nanocomposite can be ascribed to the nanostructured MnO₂ on the surface of the MWNTs. Clearly, MnO₂ on the surface of the MWNTs with beehive-like nanostructure (Figs. 1 and 2) enhances the accessible surface area and active sites of the nanocomposite, in which MWNTs serve as double layer capacitance and MnO_2 as Faradaic pesudocapacitance [4]. The 3D nanostructured $MnO_2/MWNT$ nanocomposite is desirable for the penetration of electrolyte into the whole electrode matrix. Furthermore, for the MnO₂/MWNT nanocomposite, the bonding between MWNTs and MnO_2 is very strong, thus showing very high stability during the electrochemical process with excellent capacitive performance. Therefore, we conclude that the nanostructured MnO2-modified MWNT arrays can be used as a supercapacitor.

CONCLUSION

A method for fabrication of CNT electrodes with high mechanical stability has been developed by directly growing CNTs on metal substrate, such as Ta foils. The strong combination between the CNTs and the Ta foils, as well as the good conductivity, is favorable for making CNT electrodes with high performance. In addition, the vertically aligned nanotubes provide such a morphology that is convenient for further modification with metal or oxide nanoparticles. As an example, we have successfully pre-

pared $MnO_2/MWNT$ nanocomposite through the reaction of MWNTs with $KMnO_4$ in aqueous solution. Beehive-like nanostructured MnO_2 was adhesively grown on the surface of the vertically aligned MWNT arrays, thus forming a 3D $MnO_2/MWNT$ nanocomposite. The results of the electrochemical measurements show that the $MnO_2/MWNT$ nanocomposite has much higher capacitive performance than the bare MWNTs. The $MnO_2/MWNT$ nanocomposite may be a promising novel nanomaterial for the development of supercapacitors.

ACKNOWLEDGMENTS

The financial support of the work by the National Natural Science Foundation of China under grant 20773041 and the Research Fund for the Doctoral Program of Higher Education (RFDP) under grant 20070561008 is greatly acknowledged.

REFERENCES

- 1. A. Burke. J. Power Sources 91, 37 (2000).
- 2. J. K. Chang, C. T. Lin, W. T. Tsai. Electrochem. Commun. 6, 666 (2004).
- 3. C. C. Hu, W. C. Chen. Electrochim. Acta 49, 3469 (2004).
- 4. J. S. Ye, H. F. Cui, X. Liu, T. M. Lim, W. D. Zhang, F. S. Sheu. Small 1, 560 (2005).
- 5. Y. Chen, C. G. Liu, C. Liu, G. Q. Lu, H. M. Cheng. Mater. Res. Bull. 42, 1935 (2007).
- J. S. Ye, X. Liu, H. F. Cui, W. D. Zhang, F. S. Sheu, T. M. Lim. *Electrochem. Commun.* 7, 249 (2005).
- 7. J. H. Chen, W. Z. Li, D. Z. Wang, S. X. Yang, J. G. Wen, Z. F. Ren. Carbon 40, 1193 (2002).
- 8. P. M. Ajayan. Chem. Rev. 99, 1787 (1999).
- 9. G. H. Deng, X. Xiao, J. H. Chen, X. B. Zeng, D. L. He, Y. F. Kuang. Carbon 43, 1566 (2005).
- 10. F. C. Wu, R. L. Tseng, C. C. Hu, C. C. Wang. J. Power Sources 144, 302 (2005).
- 11. E. Mora, V. Ruiz, R. Santamaria, C. Blanco, M. Granda, R. Menendez, J. M. J. Galan, F. R. Reinoso. *J. Power Sources* **156**, 719 (2006).
- 12. X. Qin, S. Durbach, G. T. Wu. Carbon 42, 451 (2004).
- 13. Z. Fan, J. H. Chen, M. Y. Wang, K. Z. Cui, H. H. Zhou, Y. F. Kuang. *Diamond Relat. Mater.* 15, 1478 (2006).
- 14. J. Y. Lee, K. Liang, K. H. An, Y. H. Lee. Synth. Met. 150, 153 (2005).
- 15. G. Yuan, Z. Jiang, A. Aramata, Y. Gao. Carbon 43, 2913 (2005).
- 16. X. F. Xie, L. Gao. Carbon 45, 2365 (2007).
- 17. W. D. Zhang, Y. Wen, S. M. Liu, W. C. Tjiu, G. Q. Xu, L. M. Gan. Carbon 40, 1981 (2002).
- 18. W. D. Zhang, J. T. L. Thong, W. C. Tjiu, L. M. Gan. Diamond Relat. Mater. 11, 1638 (2002).
- 19. W. D. Zhang, F. Yang, P. Y. Gu. Nanotechnology 16, 2442 (2005).
- 20. X. B. Jin, W. Z. Zhou, S. W. Zhang, G. Z. Chen. Small 3, 1513 (2007).
- 21. W. D. Zhang. Nanotechnology 17, 1036 (2006).
- 22. J. S. Ye, Y. Wen, W. D. Zhang, H. F. Cui, G. Q. Xu, F. S. Sheu. Nanotechnology 17, 3994 (2006).
- 23. J. Chen, W. D. Zhang, J. S. Ye. Electrochem. Commun. 10, 1268 (2008).
- 24. J. M. Nugent, K. S. V. Santhanam, A. Rubio, P. M. Ajayan. Nano Lett. 1, 87 (2001).