

Electrodeposition of MnO₂ on Carbon Nanotube Thin Films as Flexible Electrodes for Supercapacitors

Q. Cheng^{1),2)}, J. Ma¹⁾, H. Zhang¹⁾, N. Shinya¹⁾, L.-C. Qin³⁾, J. Tang^{1),2)*}

¹⁾ National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

²⁾ Doctoral Program in Materials Science and Engineering, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, 305-8577, Japan

³⁾ Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3255, USA

* tang.jie@nims.go.jp

Carbon nanotubes (CNTs) are a promising new material for electrodes of supercapacitors, owing to their unique internal structure, high surface area, remarkable chemical stability, and electrical conductivity. In this study, CNTs films with nanoporous structure were made by a filtration method. A nanostructured manganese dioxide layer was electrodeposited on a thin CNT film to form a flexible CNT/MnO₂ film electrode for supercapacitors. The morphology of the CNT/MnO₂ electrode was examined by SEM and TEM. Compared with a pure CNT film, the CNT/MnO₂ electrode shows a higher specific capacitance. The CNT network in the CNT/MnO₂ electrode acted as a substrate of good conductivity and high surface area. The nanostructured MnO₂ not only increased the surface area, but also has enhanced reactions with the cations in the electrolyte to increase specific capacitance.

Key words: Supercapacitor, MnO₂, Carbon nanotube, Electrodeposition

1. INTRODUCTION

Climate change and limited availability of fossil fuels have greatly affected the world economy and ecology. As a result, we are observing an increase in the production of renewable energy from the sun and wind, as well as in development of electric vehicles or hybrid vehicles with low CO₂ emissions. Because the sun does not shine in the night and the wind does not blow as we wished, energy storage systems, such as batteries and supercapacitors, are starting to play a larger part in our life. Supercapacitor, which is also called ultracapacitor or electrochemical double layer capacitor, is a kind of energy saving unit that can provide a huge amount of energy in a short period of time, making it indispensable for power delivery^[1]. Supercapacitors are more suitable for energy storage because of their excellent cyclability and power performance. However, supercapacitors often suffer from low energy performance which is usually evaluated by specific capacitance and energy density. Therefore we need to improve their energy performance to meet the higher requirements of future systems, ranging from portable electronics to hybrid vehicles and large industrial equipment. In development of this kind of energy devices, nanostructured electrode materials have attracted great attention. Nanostructured electrode materials are key components in the advancement of future energy technologies, as they show not only higher capacities but also better response rates than traditional materials^[2-3].

Carbon nanotubes (CNTs) are promising materials for the electrodes of supercapacitors, owing to their unique internal structure, high surface area, low mass density,

remarkable chemical stability, and electrical conductivity. CNTs can be classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), both of which have been widely explored as a choice for high power electrode materials because of their good electrical conductivity and readily accessible surface areas. Moreover, their high mechanical resilience and open tubular network make them an ideal support for active materials. But the energy density is, however, a concern due to their relatively small surface area^[4].

Nowadays, much research on supercapacitor is aimed at increasing power and energy densities as well as lowering fabrication cost and using environmentally friendly materials. For example, it has been found that RuO₂ exhibited prominent capacitive properties as a supercapacitor electrode material. However, its high cost prohibits it from wide applications. Instead, low cost materials such as MnO₂ and NiO₂ have been developed as the electrode materials, but their power performance need be enhanced^[5-6]. MnO₂ can form many polymorphs such as α -, β -, γ - and δ -type, offering distinctive properties and wide applications as catalysts, ion-sieves, and especially as electrode in Li/MnO₂ and Zn/MnO₂ batteries^[7-9]. On the other hand, MnO₂ is a promising material for pseudocapacitors due to its superior electrochemical performance, environmentally friendliness, and lower cost in production^[10-14]. Over the past years, several nanostructured MnO₂, including nanocrystals of different shapes, nanowires, nanotubes, nanobelts, and nanoflowers, have been synthesized^[15-16].

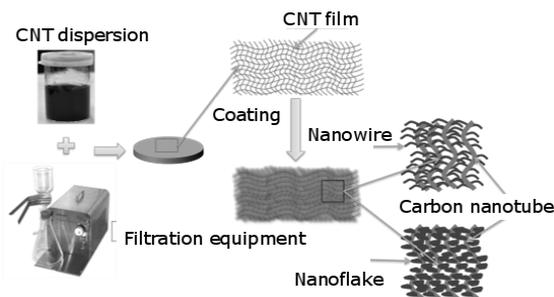


Fig. 1 Procedure for preparation of nanostructured electrode using carbon nanotubes.

We combine both CNTs and MnO_2 to form an electrode of high power density and enhanced energy density. The MnO_2 needs to be made into nanostructures because only the surface or near-surface areas (a few nanometers) can participate in the redox reactions with the cations in the electrolyte. The bulk form of MnO_2 may lead to poor power performance due to the relatively poor conductivity of MnO_2 . Our research strategy is shown schematically in Fig. 1. We first make an entangled CNT network which can act as the substrate for MnO_2 . This conductive substrate can provide a high path for electrical conduction. What's more, the CNT film can provide a porous structure for ion absorption and hosting MnO_2 . Most important of all, the entangled CNT film has a very large surface area which is a crucial performance parameter for supercapacitors. We synthesized nanostructured MnO_2 on CNTs (or CNT bundles) by electrodeposition. On one hand, the nanostructured MnO_2 would increase the surface area to improve the electrochemical double layer capacitance. On the other hand, the nanostructured MnO_2 would also enhance the redox reactions with the protons or cations in the electrolyte which would in turn increase capacitance.

2. EXPERIMENTAL

2.1 Synthesis of CNT Film and Manganese Dioxide

The SWCNT samples were purchased commercially (Cheap Tube Inc. (purity > 90%, amorphous carbon content < 3wt%). The specific area of the SWCNTs is $407 \text{ m}^2/\text{g}$, the electrical conductivity is 100 S/cm , and their length is about $5\text{--}30 \mu\text{m}$. The carbon nanotubes were used without any further treatment. For a conventional filtration, the SWCNTs would disperse in solutions. We used sodium dodecyl sulfate as the surfactant to help SWCNTs disperse in distilled water. Then the SWCNTs were filtrated to form a glassy filter paper (bucky paper).

Manganese dioxide was deposited onto the as-prepared SWCNT film by using a triple-electrode electrodeposition method. Before coating, the prepared SWCNT electrode was washed with ethanol and distilled water before dried at $60 \text{ }^\circ\text{C}$ for 12 hours. An Ag/AgCl electrode was used as the reference electrode and a Pt plate electrode was used as the counter electrode. The electrolyte consists of $0.1 \text{ M N}_2\text{SO}_4$ and $0.1 \text{ M Mn}(\text{CH}_3\text{COO})_2$ at $\text{pH} = 5.5$ for avoiding production of $\text{Mn}(\text{OH})_2$ in the electrolyte. We also used a potentialstatic technique for 5 min for activation and then used cyclic voltammetry to synthesize MnO_2 by

cycling for 200, 500, and 700 cycles under the scan rate of 250 mV/s on the CNT film^[17].

2.2 Characterization

Morphologies of the CNT film and manganese dioxide were examined by scanning electron microscopy (SEM, JSM-6500). The nanostructure of MnO_2 was examined using transmission electron microscopy (TEM, JEM-2100). Characterization of the crystal structure of manganese oxide was based on x-ray diffraction (XRD, RINT-2500). Electrochemical measurements in an aqueous electrolyte (1 M KCl) were conducted by a triple-electrode cell where Ag/AgCl is used as a reference electrode and a Pt plate is used as a counter electrode.

3. RESULTS AND DISCUSSION

3.1 Microstructure of CNT/ MnO_2 Electrode

The proposed electrode is a three-dimensional structure, including a CNT network and a nanostructured manganese oxide coating. Fig. 2(a) shows the cross-sectional morphology of the prepared CNT network by filtration. The thickness of the CNT network is about $10 \mu\text{m}$. Fig. 2(b) shows typical plan-view morphology of the CNT network. We can see that the carbon nanotubes entangled into bundles and form a rather smooth web with a three-dimensional nanoporous network structure which is desired for ion absorption. Fig. 2(c) shows a high magnification SEM image after MnO_2 coating, where the MnO_2 nanocactuses were deposited quite uniformly on the SWCNT bundles. Fig. 2(d) shows a low magnification image after MnO_2 coating.

An XRD pattern of the MnO_2 deposited on a gold coated glass slide is shown in Fig. 3(a) indicating the formation of $\gamma\text{-MnO}_2$. Despite the poor crystallinity of the sample, we could still observe the (110) and (002) Bragg reflections, confirming that the as-prepared products are $\gamma\text{-MnO}_2$ ^[18]. The x-ray diffraction pattern is strongly affected by three factors: 1) lattice parameters of $\gamma\text{-MnO}_2$; 2) concentration of De Wolff defects; and 3) the amount of microtwinning. The (110) peak with a d -spacing of 4.072 \AA in ramsdellite is shifted to higher 2θ by De Wolff disorder. The $\gamma\text{-MnO}_2$ prepared by electrochemical methods has some different features in the x-ray diffraction pattern which are governed by two

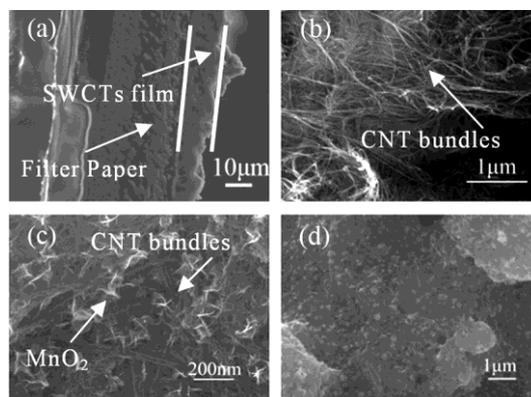


Fig. 2 SEM image of CNT film. (a) cross-sectional view; (b) Top view of CNT film; (c) High magnification image after MnO_2 coating; and (d) Low magnification image after MnO_2 coating.

kinds of defects that modify both the shape and the position of most diffraction peaks. For our case, we observed a broadened peak at $2\theta = 25^\circ$ since the microcrystal growth on the crystal faces, which includes the De Wolff defects, causes a small increase of 2θ . There is also a sharp peak of (110)-type that is located beside the broadened one indicating that there is some γ - MnO_2 with good crystallinity^[18]. In addition, we see Bragg reflections from of gold and copper because MnO_2 was deposited on a gold coated glass slide and copper tape was used for fixation.

γ - MnO_2 has been widely used in aqueous Zn/ MnO_2 cells that dominate the primary battery market and also in primary Li/ MnO_2 cells^[18-19]. The reflection intensities are very low due to the poor crystallinity the γ - MnO_2 structure synthesized by electrodeposition in solution. Fig. 3(b) shows a TEM image of the MnO_2 structure.

Figs. 4(a) and (b) show denser MnO_2 nanostructures on the CNT network prepared under different experimental conditions. There are two types of microstructures. One is nanowire (Fig. 4(a)) and the other is nanocactus (Fig. 4(b)). Both structures have very uniform morphologies that will benefit the electrochemical performance. We also found the element of both Mn and O from the Energy-dispersive x-ray spectrum (EDS).

3.2 Electrochemical Properties

Cyclic voltammetry (CV) tests were performed to investigate the electrochemical properties of both the CNT film and the CNT/ MnO_2 electrode in an aqueous electrolyte, which is shown in Fig. 5. It can be seen from Fig. 5(a) that both the CNT film and CNT/ MnO_2 show the typical rectangular CV curves at the scan rate of

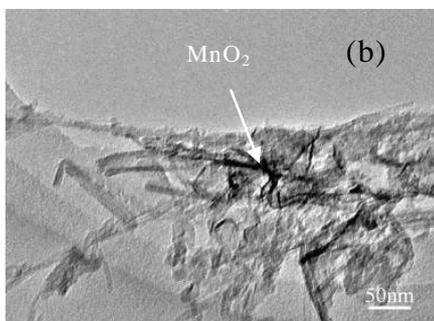
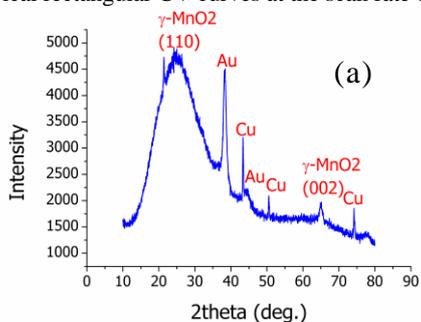


Fig. 3 (a) XRD pattern of the as prepared MnO_2 . (b) TEM image of the MnO_2 structure.

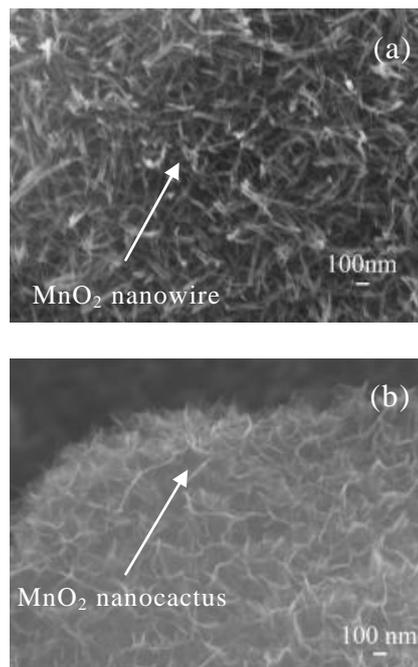


Fig. 4 SEM analyses of MnO_2 prepared under different conditions. (a) MnO_2 made by CV at the scan rate 250 mV/s for 500 cycles; (b) MnO_2 made by CV at the scan rate 250 mV/s for 700 cycles.

10 mV/s indicating an ideal electrochemical behavior of the two electrodes. We also observed that the specific capacitance and energy density which are in proportion to the current is increased by about three times with the MnO_2 coating. The specific capacitance and energy density are calculated by Equation (1) and Equation (2) given below, respectively. Figs. 5(c) and (d) are the cyclic voltammetry results of the CNT film and CNT/ MnO_2 electrode, respectively. They were measured at different scan rates ranging from 10 to 100 mV/s in a 1 M KCl aqueous electrolyte. The CNT/ MnO_2 electrode shows a very good rectangular form which indicates very fast current responses even at high scan rates. It is attributed to a high electron conduction of the CNT substrate with a large surface area. We also calculated the specific capacitance under different scan rates as shown in Fig. 5(b). The specific capacitance improved significantly under every scan rate. The MnO_2 coating on CNTs is therefore a very effective modification to increase the energy performance of the supercapacitor.

$$C = \frac{I}{dv/dt} \tag{1}$$

$$E_{density} = \frac{1}{2} CV^2 \tag{2}$$

4. CONCLUSIONS

γ - MnO_2 nanostructures have been electrochemically deposited on a single-walled carbon nanotube film

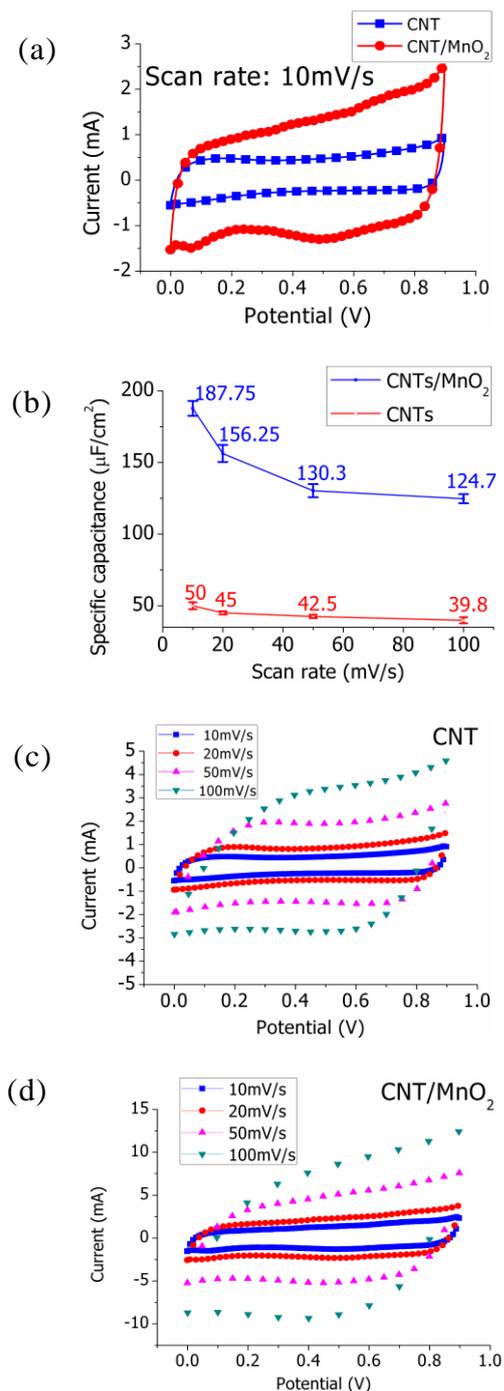


Fig. 5 (a) CV curves of the CNT network and CNT/MnO₂; (b) specific capacitance vs. scan rate of CNT and CNT/MnO₂ electrode; (c) CV curves of CNT film under different scan rate; and (d) CV curves of CNT/MnO₂ under different scan rate.

substrate with a three-dimensional nanoporous structure. Through a comparative study of CNT film and CNT/MnO₂ electrodes in 1M KCl aqueous electrolyte, the CNT/MnO₂ electrode shows a much higher specific capacitance than the pure CNT electrode and it exhibits a very good current response at high scan rate. This is attributed to the construction of a three-dimensional

nanoporous structure that consists of tiny MnO₂ nanostructures on CNT film substrate. This study indicates that nano-architected electrode is very useful in high performance supercapacitors. This kind of nanostructured hybrid electrodes has great potentials to lead to a new class of light, flexible, and wearable charge storage devices.

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