Carbon/MnO₂ Double-Walled Nanotube Arrays with Fast Ion and Electron Transmission for High-Performance Supercapacitors

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Supporting Information

ABSTRACT: The novel carbon (C)/MnO₂ double-walled nanotube arrays (DNTAs) are designed and fabricated via template-assisted electrodeposition. The unique DNTA architectures of C/MnO₂ composites with high weight fraction of MnO₂ allow high electrode utilization ratio and facilitate electron and ion transmission. In the half-cell test, the hybrid C/MnO₂ DNTAs as electrodes show a large specific capacitance (Csp) of 793 F/g at the scan rate of 5 mV/s, high energy/power densities, and much enhanced long-term cycle stability. After 5,000 cycles, the Csp retention of C/MnO₂ DNTAs keeps ~97%, which is much larger than 69% of the MnO₂ nanotube arrays (NTAs). The symmetrical supercapacitors (SSCs) composed of C/MnO₂ DNTAs also show the predominant performance, such as large Csp of 161 F/g and high energy density of ~35 Wh/kg, indicating that the C/MnO₂ DNTAs is a potential electrode for supercapacitors. The high order pore passages, double-walled structures, hollow structures, and high conductivity are responsible for the superior performance of C/MnO₂ DNTAs. Such hybrid C/MnO₂ DNTAs may bring new opportunities for the development of supercapacitors with superior performance.

KEYWORDS: electrodeposition, hybrid material, nanotube array, supercapacitor

INTRODUCTION

Recently, the energy storage and conversion have attracted wide interest because of the growing demands for energy and increasing concerns with air pollution. Among various energy storage systems, supercapacitors (SCs) have been considered as excellent potential candidates for energy storage because of their higher power density and longer cycle stability than batteries and greater energy density than the conventional electrical double layer capacitors.1−3 Up to now, the carbonaceous materials,4,5 metal oxides or hydroxides,6,7 and conducting polymers8 as major types of electrode materials have been widely reported for SCs: Carbonaceous materials have long cycle stability and high power density, nevertheless, the low energy density greatly limits their application.9 By contrast, the conducting polymers, metal oxides, and metal hydroxides enable high energy density, but they are usually kinetically unfavorable.10,11 Recently, it has inspired attempts to develop novel hybrid electrodes via the coupling of various materials for SCs because of the inherent limitations of above single material.12−22

Among the various supercapacitive materials, MnO₂ has been widely thought to be one of the most promising materials for SCs because of its low cost, high abundance, and large theoretical specific capacitance (Csp) and being environmentally-friendly. However, MnO₂ owns the poor conductivity (10⁻⁶−10⁻⁸ S/cm) that limits rate capability for high power performance and still remains a major challenge, thus preventing its wide energy storage applications.23 To effectively use MnO₂, various MnO₂/conductive matrix hybrid materials, such as MnO₂/Zn₂SnO₄,24 MnO₂/Au,25,26 MnO₂/SnO₂,27 MnO₂/conducting polymers,28 and carbon (C)/MnO₂,29 were widely studied. Among them, the C/MnO₂ hybrid materials showed a great potential for the next generation SCs because carbon is light and has high conductivity and good capacitive property.30,31 At present, in the above various cases, MnO₂ is low weight ratio in hybrid electrodes, and in general it has remarkable cycling and rate performance; however, the power and energy densities are often reduced.30,32−34 To date, as before it remains a challenge to develop the orderly MnO₂-carbon hybrid electrodes with high weight fraction of MnO₂ and large specific surface area for high energy and power densities demand such as electric vehicles.

Based on the above consideration, here we designed novel C/MnO₂ double-walled nanotube arrays (DNTAs) with high weight fraction of MnO₂ for SCs. The aligned DNTAs show high orderly pore structures. The design of such C/MnO₂ DNTAs shows the following aims: (i) As the high electrical conductivity of carbon layers, the fast charge storage and delivery can be realized on carbon layers, and this will help to overcome the limited electric conductivity of MnO₂. In addition, the carbon layers are thin and light, so the weight fraction of MnO₂ in electrodes will be obviously enhanced (~98.94 wt %), and high energy and power densities will be easily achieved. (ii) The C/MnO₂ DNTAs will relax ion transport because of the short ion diffusion paths and provide reversible, fast faradic reactions. (iii) The DNTAs will improve

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the utilization rates of electrode materials because of the special double-walled nanotube arrays. (iv) The C/MnO2 DNTAs will let each nanotube can available take part in electrochemical reactions because of excellent electrical contact with current collectors. The results in this study prove that the fabricated C/MnO2 DNTAs exhibit high Csp superior rate capability, and great long-term cycle life, and are potential electrode materials for SCs with high performance.

## EXPERIMENTAL SECTION

**Synthesis of ZnO/C NRAs.** ZnO nanorod arrays (ZnO NRAs) were electrodeposited on a Ti substrate in 0.01 M Zn(NO3)2 + 0.05 M H3BO3 + 0.05 M CH3COONH4 by galvanostatic electrodeposition at 0.8 V at 50°C for 90 min at 70°C. Then the fabricated ZnO NRAs were electrodeposited on a Ti substrate in 0.01 M Zn(NO3)2 + 0.05 M H3BO3 + 0.05 M CH3COONH4 by galvanostatic electrodeposition at 0.1 mA cm⁻² at 70°C for 30 min. The C/MnO2 double-walled nanotube arrays (DNTAs) and MnO2 nanotube arrays (NTAs) were synthesized via dissolving ZnO nanorods from the ZnO/C/MnO2 NRAs in 0.25 M NaOH solution, respectively. Sample Characterizations. The surface morphologies of the fabricated samples were characterized using an environmental SEM (scanning electron microscope, FEI Quanta 400) and the transmission electron microscope (TEM, JEM-2010HR). The fabricated samples were also analyzed by XRD (power X-ray diffraction, Bruker, D8). EDS (X-ray energy dispersive spectroscopy), XPS (X-ray photoelectron spectroscopy, ESCA-LAB 250), and laser micro-Raman spectroscopy (Renishaw inVia) were used to study the chemical compositions and structures of the products.

**Electrochemical Characterizations of the C/MnO2 DNTAs and Symmetrical Supercapacitors (SSCs) Composed of C/MnO2 DNTAs.** Electrochemical measurements of the C/MnO2 DNTAs were performed in a three-electrode electrolytic cell (The specific mass loading is 0.22 mg/cm²). A Na2SO4 solution (1.0 mol/L) was used as electrolyte. The counter electrode used a Pt foil, and the reference electrode used an Ag/AgCl electrode. Before measurement, the working electrodes of C/MnO2 DNTAs and MnO2 NTAs were impregnated with electrolyte to let them thoroughly wet for 30 min. A CHI 660C electrochemical workstation (Shanghai Chenhua Instruments Co.) was utilized to measure the electrochemical properties of samples at room temperature. Cyclic voltammetry was measured in the potential range of 0–0.8 V at 5–100 mV/s. EIS (electrochemical impedance spectroscopy) was also measured to study the conductivity of C/MnO2 DNTAs in 1.0 M Na2SO4 solution in a three-electrode cell. The EIS was measured at an open-circuit potential of 0.32 V over the frequency range of 1–10 kHz by applying an alternating-current perturbation of 10 mV. The symmetrical supercapacitors (SSCs) were built with two identical C/MnO2 DNTAs electrodes that were separated with a separator. Before assembling, the two electrodes and the separator were impregnated with electrolyte for 30 min to make them thoroughly wet. The cyclic voltammetry and galvanostatic charge-discharge curves were measured by a two-electrode test to determine the electrochemical performance of SSCs.

## RESULTS AND DISCUSSION

Scheme 1 shows the procedures utilized to fabricate the C/MnO2 DNTAs, and they are described in detail in the Experimental Section. ZnO NRAs, ZnO/C NRAs, and ZnO/C/MnO2 NRAs are sequentially fabricated, and finally the C/MnO2 DNTAs were synthesized by dissolving ZnO from the ZnO/C/MnO2 NRAs. Figures 1a and 1b show SEM images of the ZnO NRAs and ZnO/C NRAs, respectively. From Figure 1b–d, it is clearly observed that the carbon shells are uniformly coated on the ZnO NRAs surfaces with thicknesses of about 30–50 nm. XRD of ZnO/C NRAs is shown in Figure 1c(2), which is similar to the XRD of pure ZnO nanorods. Besides the peaks of ZnO nanorods and Ti substrate, no carbon peak is observed. This means the carbon shells are amorphous. Raman spectrum of ZnO/C NRAs shows two peaks at 1368 and 1602 cm⁻¹ as shown in Figure 1f, which corresponds to sp³ and sp² carbon, respectively, indicating the existence of carbon shells. Figure 2a shows SEM image of the ZnO/C/MnO2 core-shell NRAs, and it shows MnO2 shells are uniformly coated on the surfaces of ZnO/C NRAs. The typical SEM image of the fabricated C/MnO2 DNTAs is shown in Figure 2b, which clearly shows that the large-scale and orderly C/MnO2 DNTAs are successfully fabricated. The diameters and lengths of C/MnO2 DNTAs are about 650 nm and 3.0 μm, respectively. The hollow nanotube arrays and large open space between the neighboring nanotubes in C/MnO2 DNTAs will allow facile electrolyte diffusion throughout the film electrode as shown in Figure 2f.

More structure details are examined by TEM, and Figure 2c shows the typical TEM image of C/MnO2 DNTAs. The thicknesses of carbon and MnO2 layers are about 35 and 100 nm, respectively. The high-resolution transmission electron microscopy (HRTEM) image measured from MnO2 layer is shown in Figure 2d, and the SAED pattern is present in Figure 2e, which both show the amorphous structures of MnO2 layers. Figure 2g shows XPS spectrum in the energy region of Mn 2p for C/MnO2 DNTAs. Two detected peaks at 642.3 eV and 654.1 eV correspond to Mn 2p 3/2 and 2p 1/2, respectively, and this result indicates that the element Mn is present in Mn(IV), which corresponds to MnO2 in deposits. Figure 2h shows XPS spectrum in the energy region of C 1s for C/MnO2 DNTAs. The peak at 284.8 eV shows the existence of carbon in products. Based on the above analyses, the C/MnO2 DNTAs were successfully fabricated. TGA and DTG curves of the C/MnO2 DNTAs and MnO2 NTAs are shown in Figure S2, which shows the weight fraction of MnO2 in the C/MnO2 DNTAs is about ∼98.94 wt %. Figure S3 shows the EDX and XRD results of C/MnO2 DNTAs. The element of Zn is not seen in Figure S3a. The ZnO peak is not observed in C/MnO2 double-walled nanotube structures as shown in Figure
Figure 1. SEM images of (a) ZnO NRAs and (b) ZnO/C NRAs; (c–d) TEM images of a ZnO/C nanorod with different magnifications; (e) XRD and (f) Raman spectra of (1) ZnO NRAs and (2) ZnO/C NRAs.

Figure 2. (a) SEM image of ZnO/C/MnO$_2$ NRAs; (b) SEM image of C/MnO$_2$ DNTAs; (c–d) TEM images and (e) SAED pattern of C/MnO$_2$ DNTAs; (f) Schematic illustration for the advantage of C/MnO$_2$ DNTAs. (g) XPS spectrum of Mn 2p; (h) XPS spectrum of C 1s.
The limit pseudocapacitor, smaller performance. In addition, the high conductibility of C/MnO2 rate capability for the fast charge-discharge and high power advantages will be provided: (i) The C/MnO2 DNTAs with anisotropic morphology, hollow nanotube structure, and large surface area will create fast diffusion paths for ions, which will obviously enhance ion transmission and electrode utilization rate as shown in Figure 3a. (ii) The weight fraction of supercapacitive MnO2 in C/MnO2 DNTAs is high (~98.94%) because the carbon layer is thin and light, so high energy and power densities will be achieved because of the high Csp of C/MnO2 DNTAs. (iii) The conductive networks will be well-built in the electrode since the MnO2 layers are attached tightly on the Ti substrate with superior electrical contact as shown in Figure 3a. Here the conductivity of C/MnO2 DNTAs is studied by EIS measurement. The Nyquist plot of C/MnO2 DNTAs between 1 Hz and 10 kHz is shown in Figure 3b. The equivalent circuit of Nyquist plots of C/MnO2 DNTAs is shown in Figure S5, where Cdl is the double-layer capacitor, Cie is the limit pseudocapacitor, Rs is the solution resistance, RWP is the Warburg impedance, and Rct is the charge transfer resistance. Based on the results in Figure 3b, the C/MnO2 DNTAs shows smaller Rct, indicating that the carbon nanolayers can obviously reduce the charge transfer resistance, thus improving the transport and collection of electrons in electrode. The higher conductibility of C/MnO2 DNTAs than MnO2 NTAs will favor rate capability for the fast charge-discharge and high power performance. In addition, the high conductibility of C/MnO2 DNTAs will enhance the utilization rate of the electrode because of the slight polarization.

To explore the performance of C/MnO2 DNTAs for SCs, cyclic voltammetry measurements were performed in an aqueous solution of 0.5 M Na2SO4 by the half-cell test (a three-electrode configuration). Cyclic voltammograms (CVs) of C/MnO2 DNTAs among 0~0.8 V at sweep rates of 5~50 mV/s are shown in Figure 4a. It is seen that the CVs exhibit rectangular-like shapes, which indicate well supercapacitative behaviors. The Csp of C/MnO2 DNTAs is obtained to be 793 F/g at current density of 1.5 A/g, which is much higher than 319 F/g of MnO2 NTAs at the same scan rate (SEM image of MnO2 NTAs is shown in Figure S6c). Figure 4b shows the dependences of Csp of C/MnO2 DNTAs and MnO2 NTAs on scan rates. With the scan rate increasing, the Csp usually shows decay because of ion diffusion limitation in solution.39 Here the C/MnO2 DNTAs show Csp decay of about 17.3% with the scan rate increasing from 5 to 50 mV/s. Even at 50 mV/s, the Csp of C/MnO2 DNTAs still obtain 659 F/g. Nevertheless, compared with C/MnO2 DNTAs, the MnO2 NTAs show a serious Csp decay of 41.4% with the scan rate increasing from 5 to 50 mV/s and a small Csp of 178 F/g at 50 mV/s. Therefore, the above results in Figure 4b show the C/MnO2 DNTAs have a much larger Csp and a much better rate capability than MnO2 NTAs at various scan rates.

Figure S7a shows galvanostatic charge-discharge curves of the C/MnO2 DNTAs in the half-cell at different current densities, and a symmetric nature in charging/discharging curves is seen, indicating superior reversible redox reactions and good supercapacitive characteristic. Figure 4c shows the summary plot of Csp vs current density, which also demonstrates the C/MnO2 DNTAs exhibit significantly enhanced supercapacitive performance comparing with MnO2 NTAs. With current density increasing from 1.0 to 10 A/g, the C/MnO2 DNTAs show ~25.5% Csp loss, which is much smaller than ~54.4% Csp loss of MnO2 NTAs, so this result also demonstrates the C/MnO2 DNTAs have a much better rate capability than MnO2 NTAs.

In the half-cell test, the C/MnO2 DNTAs also show excellent long-term cycle life, which is highly important for practical SC operations. Figure 4d shows the Csp variation of C/MnO2 DNTAs as a function of cycle number at 5 mV/s, and it shows no any significant decrease in Csp after 5000 cycles. The Csp retention of C/MnO2 DNTAs still keep ~97%. However, the MnO2 NTAs only show the Csp retention of ~69% after 5000 cycles, which is much smaller than 97% of C/MnO2 DNTAs. The above results demonstrate that the C/MnO2 DNTAs as electrode materials are much higher stability than MnO2 NTAs.

Herein, the advantages of C/MnO2 DNTAs as electrodes for SCs were further investigated in the half-cell test. Figure 5 shows cycling performance of the C/MnO2 DNTAs at progressively increased and decreased current density, and it indicates that the fabricated C/MnO2 DNTAs still own high cycle stability after the electrode suffered from sudden current density change. Therefore, the synthesized C/MnO2 DNTAs own both superior rate capability and excellent long-term cycle life, which are very important for the practical utilizations in the supercapacitors.

To show the feasibility of C/MnO2 DNTAs for SCs, a simple symmetrical supercapacitor (SSC) based on two small pieces of thin films (1.0 cm2) of C/MnO2 DNTAs was presented for a demo as shown in Figure 6 (the electrolyte is 1.0 mol/L Na2SO4 solution, and it was dripped on the surfaces of thin films). Here we found that this device could power a red light-
emitting diode (LED) for about 8 min after charging at 1.0 mA/cm² for 30 s.

Cyclic voltammetry measurements of the SSC based on C/MnO₂ DNTAs were performed in 0.5 M Na₂SO₄ solution on a two-electrode test configuration as shown in Figure 7a. The $C_{sp}$ of the SSC of C/MnO₂ DNTAs is obtained to be 161 F/g at 5 mV/s, which is much higher than 66 F/g of the SSC of MnO₂ NTAs at the same sweep rate. The SSC of C/MnO₂ DNTAs shows a $C_{sp}$ decay of about 20.87% with the scan rate increasing from 5 to 100 mV/s as shown in Figure 7b. Even at a scan rate as large as 100 mV/s, the SSC of C/MnO₂ DNTAs still achieves a value as high as 127 F/g. However, compared with the SSC of C/MnO₂ DNTAs, the SSC of MnO₂ NTAs shows a serious $C_{sp}$ decay of 55.73% with the scan rate increasing from 5 to 100 mV/s and a small $C_{sp}$ of 29 F/g at 100 mV/s. Figure S8 shows galvanostatic charge-discharge curves of the SSC of carbon/MnO₂ DNTAs and SSC of MnO₂ NTAs at different current densities. Figure 7c shows the summary plot of $C_{sp}$ vs current density, which demonstrates the SSC of C/MnO₂ DNTAs exhibit significantly enhanced supercapacitive performance comparing with that of MnO₂ NTAs. The SSC of C/MnO₂ DNTAs shows the improved long-term cycle life. The $C_{sp}$ variation as a function of cycle number of the SSC of C/MnO₂ DNTAs at 0.75 A/g is shown in Figure 7d, which shows the SSC of C/MnO₂ DNTAs almost can undergo more than 10,000 cycles without an obvious decrease in $C_{sp}$. After 10,000 cycles, the $C_{sp}$ retention of SSC of C/MnO₂ DNTAs still keeps ~85%. However, the MnO₂ NTAs only show the $C_{sp}$ retention of ~62% after 10,000 cycles, indicating a much worse cycle stability. The above results demonstrate that the SSC of C/MnO₂ DNTAs is much higher stability than the SSC of MnO₂ NTAs during the long-term cycling test.

Figure 8a shows the cycling performance of the SSC of C/MnO₂ DNTAs on a two-electrode test configuration at progressively increased and decreased current density. The SSC of C/MnO₂ DNTAs still shows high cycle stabilities at
various current densities after the electrode suffered from sudden current density change. The energy and power densities of the SSC of C/MnO₂ DNTAs are also studied because they are highly important for electrochemical devices. Figure 8b shows the Ragone plot, and it indicates the SSC of C/MnO₂ DNTAs can provide a high energy density of ∼40 Wh/kg, much superior to the SSC of MnO₂ NTAs and the conventional SSCs. In addition, the C/MnO₂ DNTAs also can provide the highest power density of 16 KW/kg, which is higher than the power demand of PNGV (Partner-ship for a New Generation of Vehicles), 15 KW/kg, indicating the superior capability of the SSC of C/MnO₂ DNTAs.

The volumetric performance of the SSC of C/MnO₂ DNTAs on a two-electrode test configuration is also investigated, and it is shown in Figure 9. The volumetric Cᵥp of SSC of C/MnO₂ DNTAs at 5 mV/s is calculated to be 177 mF/cm³, which is much larger than 72 mF/cm³ of the SSC of MnO₂ NTAs at the same scan rate. The dependence of volumetric Cᵥp of the SSC of C/MnO₂ DNTAs and MnO₂ NTAs on the scan rate is shown in Figure 9a. With the scan rate increasing from 5 to 100 mV/s, the volumetric Cᵥp of the SSC of C/MnO₂ DNTAs shows a decay of about 21.47%. However, compared with C/MnO₂ DNTAs, the SSC of MnO₂ NTAs shows a serious Cᵥp decay of 55.56% with the scan rate increasing from 5 to 100 mV/s and a small volumetric Cᵥp of 32 F/cm³ at 100 mV/s. With current density increasing from 0.2 to 2.0 mA/cm², the SSC of C/MnO₂ DNTAs shows a much larger volumetric Cᵥp than MnO₂ NTAs as shown in Figure 9b, and they only show...
10.31% volumetric C\textsubscript{sp} loss, which is much smaller than ~53.39% C\textsubscript{sp} loss of MnO\textsubscript{2} NTAs. In addition, the SSC of C/MnO\textsubscript{2} DNTAs shows much larger volumetric power density and energy density than the SSC of MnO\textsubscript{2} NTAs as shown in Figure 9c.

**CONCLUSIONS**

In conclusion, the novel hybrid C/MnO\textsubscript{2} DNTAs as electrodes were designed for SC applications. The unique DNTA architectures of C/MnO\textsubscript{2} composites permit a high utilization ratio of electrode with the facilitated ion and electron transmission. The designed C/MnO\textsubscript{2} DNTAs show superior supercapacitive performance, such as large C\textsubscript{sp} high energy/power densities, and superior long-term cycle life. The hollow nanotube structures, double-walled structures, orderly pore passages, and high conductivity are mainly responsible for the much improved supercapacitive performance of the C/MnO\textsubscript{2} DNTAs. The SSCs composed of C/MnO\textsubscript{2} DNTAs also show the predominant performance, indicating the C/MnO\textsubscript{2} DNTAs are promising materials for SCs. The design and synthesis strategy of electrode materials reported in this study can be used for other metal oxides, such as Co\textsubscript{3}O\textsubscript{4}, NiO, and V\textsubscript{2}O\textsubscript{5}, to build carbon-based hybrid DNTAs and other double-walled hollow nanostructures that will be very promising for various electrochemical devices, such as batteries and sensors.

**ASSOCIATED CONTENT**

Supporting Information
SEM, TG, DTG, EDS, XRD, adsorption-desorption isotherms, and galvanostatic charge-discharge curves. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES**