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## RAPID COMMUNICATION

# Facile synthesis and super capacitive behavior of SWNT/MnO<sub>2</sub> hybrid films

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#### Abstract

In this paper, facile and scalable single-walled carbon nanotubes with manganese oxide (SWNT/ $MnO_2$ ) hybrid films are presented and systematically studied. The hybrid films are synthesized by a modified chemical vapor deposition (CVD) method, followed by one-step simple precipitation process and then characterized in 1 M tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>)/propylene carbonate (PC) organic electrolyte. The electrochemical behavior of the SWNT/ $MnO_2$  hybrid films is discussed with regards to specific capacitance, energy density, power capability and cycle life, by means of cyclic voltammetry measurements, electrochemical impedance analysis and galvanostatic charge/discharge analysis. The SWNT/ $MnO_2$  hybrid electrode delivers highest specific capacitance of 150 F g<sup>-1</sup>, energy density of 70 Wh kg<sup>-1</sup>, and power density of 79 kW kg<sup>-1</sup>. It exhibits excellent stability of 98.5% retention at current densities of 50 A g<sup>-1</sup> and 2 A g<sup>-1</sup>, after 15,000 cycles and 1000 cycles, respectively. It also shows ultra-high frequency response with a knee frequency of 2043 Hz. The hybrid films are binderfree, robust, with pre-formed electrical pathways and excellent electrode structures for supercapacitor applications.

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### Introduction

Of recent energy storage devices, electrochemical supercapacitors (ECs) [1] have moderate energy density and high power density. ECs typically can be divided into two groups: (i) electrical double layer supercapacitors (EDLCs), which store the energy using reversible adsorption of ions from the

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electrolyte onto the high accessible surface area of the carbon materials, such as activated carbon (AC) [2], activated carbon fabrics (ACF) [3,4], carbon nanotubes (CNTs) [5,6], and graphene [7,8]. (ii) Redox pseudocapacitors, which utilize fast and reversible faradaic reaction occurring at the electrode-electrolyte interface, typically based on conductive polymers (CPs), such as polyaniline (PAN) [9] and polypyrrole (PPy) [10], or transition metal oxides (TMOs), such as  $RuO_2$  [11] and  $MnO_2$  [12].

Compared with CP<sub>s</sub> which typically suffer from swelling/ shrinking during charge/discharge, TMOs have a better stability, thus are more widely pursued [13]. Among the TMOs,

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 $RuO_2$  has superior specific capacitance (SC) of 720 F g<sup>-1</sup> [14], but MnO<sub>2</sub> is more attractive owing to low cost, environmental friendliness and natural abundance [15]. In general, the low electrical conductivity of MnO<sub>2</sub> electrode material usually leads to low power performance. In order to improve the performance of MnO<sub>2</sub> electrode, CNTs are often used as a backbone for MnO<sub>2</sub> deposition, because of their high electrical conductivity, chemical stability and high mechanical strength. Many different approaches to synthesize CNT<sub>s</sub>/MnO<sub>2</sub> nanocomposites have been developed, such as physical mixing [16], thermal decomposition [17], hydrothermal method [18], and electrodeposition [19]. However, most of these routes are complicated and require long reaction time, limiting their industrial implementation. Therefore, it is of great interest to develop a facile and efficient method to synthesize nanostructure MnO2 as electrode materials.

In previous study, we used precipitation method to reduce  $KMnO_4$  with ethanol to synthesize  $MnO_2$  and showed its excellent performance with SWNT composite in the aqueous electrolyte [20]. Similar approach was also demonstrated by Jiang et al. [21]. For the above electrode systems, however, one drawback is that inactive binder material and conductive carbon are still needed. Another drawback is that aqueous electrolytes only provide 1 V voltage window, limiting the energy density.

Here we report a new and facile approach to make SWNT/ MnO<sub>2</sub> hybrid films, which is binder-free, robust, and with pre-formed electrical pathways. The approach has following merits: (i) facile synthesis with a short reaction time at room temperature, (ii) simple control of the coated MnO<sub>2</sub> mass on SWNTs by adjusting the precipitation time, (iii) large voltage window by employing organic electrolyte, (iv) binder-free and no need to add electric conductor materials, and (v) industrial scalablility. The entangled structure of SWNT films provides excellent electron path, significantly lowers the electrical resistivity of the nanostructured MnO<sub>2</sub>, and improves the power density of the hybrid films. The SWNT/  $MnO_2$  electrodes have the highest SC of 150 F g<sup>-1</sup>, energy density of 70 Wh kg<sup>-1</sup>, and power density of 79 kW kg<sup>-1</sup> with excellent cycling stability of 98.5% retention after 15,000 cycles at 50 A  $g^{-1}$  and 1000 cycles at 2 A  $g^{-1}$ , respectively.

#### Materials and methods

#### Preparation of pristine SWNT films

The SWNTs macrofilms were fabricated using a chemical vapor deposition (CVD) technique in a tube furnace [22]. A mixture of ferrocene as carbon feedstock/catalyst and sulfur as an additive to promote SWNTs growth at an atomic ratio of Fe:S=10:1 was heated (1140 °C), while a mixture of argon and hydrogen (1500 and 150 mL min<sup>-1</sup>, respectively) gas was flowed into the tube furnace. After 30 min reaction, the furnace was cooled to room temperature. In order to eliminate the contamination, and introduce surface functional groups, the as-synthesized SWNT macrofilm was heat treated in the air at 430 °C for 30 min and then rinsed with diluted hydrochloric acid. After that, the SWNT macrofilms were extensively washed with deionized water to pH 7.

#### Preparation of SWNT/MnO<sub>2</sub> hybrid films electrodes

SWNT/MnO<sub>2</sub> hybrid film electrodes were prepared by modified simple precipitation [23]. Briefly, an SWNT film electrode on copper foil was immersed in ethanol, while 0.1 M KMnO<sub>4</sub> aqueous solution was dropwise added. A thin layer of nanostructured MnO<sub>2</sub> was deposited on the surface of the SWNT bundles in 30 min. The resulting SWNT/MnO<sub>2</sub> electrode was rinsed excessively in deionized water and ethanol and finally dried at room temperature for 24 h.

#### **Electrochemical measurements**

Electrochemical measurements were carried out using symmetric coin cells, for both SWNT/MnO<sub>2</sub> supercapacitors and SWNT supercapacitors (control samples). A 1 M tetraethylammonium tetrafluoroborate (TEABF₄) (Alfa Aesar) dissolved in battery-graded propylene carbonate (PC) (Alfa Aesar) solvent was used as the organic electrolyte. A Wattman glass microfiber paper was used as the separator. The supercapacitors were assembled in an Ar-filled Unilab glove-box. The cyclic voltammograms were performed with an EG&G PARSTAT 2273 potentiostat/galvanostat with various scan rates. The electrochemical impedance spectroscopy (EIS) was conducted at frequency range from 100 kHz to 10 mHz. The EIS data fitting program ZVIEW was used to obtain the equivalent circuit parameters. The galvanostatic charge-discharge measurements were performed on an Arbin BT4+ test system. All electrochemical measurements were performed at room temperature.

#### Structural characterization

The transmission electron microscopy (TEM) and the scanning electron microscopy (SEM) images were taken with a JEOL JEM-2010F microscope and a JEOL JSM-7400F microscope, respectively.

#### MnO<sub>2</sub> loading measurement

In order to ensure the accuracy of the MnO<sub>2</sub> loading measured, a Mettler Toledo microbalance XP6 with 0.001 mg readability was used. The weight was measured following the standard procedure: 3 copper foils punched from the same piece foils for SWNT coating were measured to get the average weight of copper foil substrates; the copper foils coated with SWNT films were punched and weighted; after MnO<sub>2</sub> reaction coating, the SWNT/MnO<sub>2</sub> composite electrodes were weighted to calculate the mass of the precipitated MnO<sub>2</sub>. The weight difference of SWNT electrode before and after coating MnO<sub>2</sub> shows average 20 wt% mass loading of MnO<sub>2</sub> precipitated on the surface of SWNT bundles.

#### **Results and discussion**

Scheme 1 depicts the precipitation process of  $MnO_2$  on a punched SWNT film electrode. In this process, hydrophilic functional groups [22] on the surface of the SWNT bundles act as nucleation sites for  $MnO_2$  anchoring. During about 30 min synthesis, brown precipitates were deposited onto



Scheme 1 Schematic illustration of the synthesis process of nano- $MnO_2$  on the surface of SWNTs macro-film and the corresponding snapshots of the process taken with a camera.



**Figure 1** SEM images of (a) SWNT film as synthesized before coating MnO<sub>2</sub> layer. (b) SWNT/MnO<sub>2</sub> electrode material as-synthesized. (c) SWNT/MnO<sub>2</sub> electrode material after 15,000th cycles.

the SWNT film, while purple color of the solution gradually disappeared. In this reaction,  $CH_3CH_2OH$  is oxidized into  $CH_3COOH$  and  $MnO_4^-$  is reduced into  $MnO_2$  with the formation of KOH, then KOH is neutralized by  $CH_3COOH$ , to form  $CH_3COOK$  and  $H_2O$  [23,24].

Figure 1a presents the typical SEM image of the pristine SWNT films. It can be seen that the SWNT bundles are entangled and interconnected with a combination of mesoporous and macroporous structures, providing excellent electrical conductivity. Figure 1b illustrates the morphology of the SWNT/MnO<sub>2</sub> hybrid films. The  $MnO_2$  nanoparticles uniformly deposited on the surfaces of the SWNT bundles. Since the spontaneously coated layer is not perfectly smooth, it could provide a larger surface area for better electrode/ electrolyte interfacial contact. After long charge/discharge cycling (15,000 cycles) in 1M TEABF<sub>4</sub>/PC electrolyte, the coin

cell supercapacitor was disassembled to examine the surface morphology of the cycled SWNT/MnO<sub>2</sub> electrode (Figure 1c). Compared to Figure 1b, it seems that the SWNT/MnO<sub>2</sub> are aggregated after cycling, which is actually caused by unremoved residues from the electrolyte salts, confirmed by X-ray energy dispersive spectroscopy (XEDS). Except the electrolyte residues observed, the MnO<sub>2</sub> thin layer remains the similar morphology after the long cycling, indicating a strong bonding between SWNT and MnO<sub>2</sub>.

The electrochemical performance of the SWNT/MnO<sub>2</sub> and SWNT electrodes (control samples) in 1 M TEABF<sub>4</sub>/PC electrolyte were evaluated using the cyclic voltammograms (CVs), with a wide potential window from -1.5 to 1.5 V. Figure 2a displays the *CV* curves of SWNT/MnO<sub>2</sub> electrode with various scan rates (from 50 to 2000 mV s<sup>-1</sup>), with the current response normalized with respect to the electrode



**Figure 2** (a) *CV* curves of SWNT/MnO<sub>2</sub> electrode measured at different scan rates (50 mV s<sup>-1</sup> to 2000 mV s<sup>-1</sup>). (b) Comparative *CV* curves of SWNT/MnO<sub>2</sub> and SWNT at scan rate of 500 mV s<sup>-1</sup>. (c) TEM image of SWNT/MnO<sub>2</sub> electrode material before cycling. (d) TEM image of SWNT/MnO<sub>2</sub> electrode material after the 15,000th cycles cycling.

mass. It shows that with a higher scan rate of 2000 mV  $s^{-1}$ the normalized current is higher than that of  $200 \text{ mV s}^{-1}$ . This can be understood that the charging process takes shorter time (i.e. 1.5 s at 2000 mV s<sup>-1</sup> scan rate to increase from -1.5 V to 1.5 V, compared with 15 s for 200 mV s<sup>-1</sup> to increase from -1.5 V to 1.5 V) for enough amount of ions to be attracted to the two electrodes to build the same potential. Figure 2b presents the CV curve comparison of the SWNT/MnO<sub>2</sub> electrode and the SWNT electrode at the scan rate of 500 mV s<sup>-1</sup>. It shows the normalized current increased dramatically for the SWNT/MnO2 electrode, owing to the redox reaction of MnO2. Compared with the SWNT electrode (black curves), a slightly distortion is observed for the SWNT/ MnO<sub>2</sub> electrode, which is attributed to the relatively high resistance of the coated nano-MnO2 and relatively low conductivity of the 1 M TEABF<sub>4</sub>/PC organic electrolyte  $(13 \text{ mS cm}^{-1})$  [25]. The SWNT/MnO<sub>2</sub> electrode has redox peak from 0.6 to 1.2 V. The intercalation/deintercalation of the tetraethylammonium cation(TEA<sup>+</sup>) from TEABF<sub>4</sub>/PC electrolyte leads to the reversible redox transition of Mn<sup>4+</sup> from/to  $Mn^{3+}$ , which can be described as Eq. (1):

$$MnO_2 + TEA^+ + e^- \rightleftharpoons (MnOO)TEA \tag{1}$$

In order to further ensure the strong bonding and the anchoring stability of the  $MnO_2$  nanoparticles on SWNTs, TEM images were recorded before and after the long charge/discharge cycling (Figure 2c and d). Lattice structures can

clearly be seen in the SWNT/MnO<sub>2</sub> hybrids, showing the polycrystalline feature of  $MnO_2$  (marked with red square), both in as-synthesized SWNT/MnO<sub>2</sub> electrode and the electrode after long charge/discharge cycling. The ultra-thin  $MnO_2$  layer (approximately 3 nm) is loaded on SWNT bundles and the stability of the  $MnO_2$  layer is not affected by the electrochemical testing. The merit of the ultra-thin layer of the  $MnO_2$  grown on SWNT bundles is that it greatly shortens the diffusion paths of the electrolyte ions during the fast charge/discharge process, and ensures the high utilization of the  $MnO_2$  nanoparticles, contributed by the surface pseudo-capacitive reaction of  $MnO_2$  [26].

The specific capacitances of the electrodes with different scan rates are summarized in Figure 3a, according to Eq. (2):

$$C_{\rm s} = \frac{A}{{\rm SR} \times V \times M} \tag{2}$$

where  $C_s$ , A, SR, V, and M denote the SC, the integral areas of the cyclic voltammogram loops, the scan rate, the potential window, and the mass of electrodes, respectively. The SCs of SWNT/MnO<sub>2</sub> (based on total mass of the electrode, and based on mass of MnO<sub>2</sub>) and SWNT electrode are plotted as a function of scan rates (from 2 to 2000 mV s<sup>-1</sup>).

It should be pointed out that, the total weight of the SWNT/ $MnO_2$  electrode is contributed by approximately 80% of the SWNT film and 20% of loaded  $MnO_2$ . In order to estimate the SC based on  $MnO_2$ , the capacitance contribution of SWNT



**Figure 3** (a) Comparison of specific capacitances of SWNT/MnO<sub>2</sub> electrode (blue line: based on mass of MnO<sub>2</sub>; black line: based on total mass of SWNT/MnO<sub>2</sub>) and SWNT electrode at different scan rates. (b) Ragone plots of SWNT/MnO<sub>2</sub> electrode and SWNT electrode at different current densities (0.1 A g<sup>-1</sup> to 100 A g<sup>-1</sup>). Green and orange transparent regions indicate the Ragone plot of Ni-MH and Li-ion batteries extracted from Ref. [28]. (c) Galvanostatic charge/discharge curves of SWNT/MnO<sub>2</sub> at different current densities (from 5 A g<sup>-1</sup> to 100 A g<sup>-1</sup>).

from total capacitance of  $SWNT/MnO_2$  composite is deducted using Eq. (3) [27]:

$$C_{s-Mn} = \frac{C_{s-com} - C_{s-NT} \times (1 - 20\%)}{20\%}$$
(3)

where  $C_{\text{s-Mn}}$  is the SC based on MnO<sub>2</sub> (blue line in Figure 3a);  $C_{\text{s-com}}$  is the SC based on SWNT/MnO<sub>2</sub> hybrid film electrode, and  $C_{\text{s-NT}}$  is the SC based on the SWNT films.

In order to better illustrate the SWNT/MnO<sub>2</sub> electrode performance, the black curve in Figure 3a shows the specific capacitance of the pure SWNT film electrodes (as the control sample), which is insensitive to the scan rate compared to the SWNT/MnO<sub>2</sub> electrodes. This is because of the rapid formation of the double layers in the pure SWNT film electrodes. For SWNT/MnO<sub>2</sub> electrodes, a dramatic increase of the specific capacitance is observed at small scan rates below 10 mV  $s^{-1}$ , indicating a strong scan rate dependence of the specific capacitance. The increase of the specific capacitance is largely contributed from the redox reaction which would take a relatively longer time, compared to the pure electrical double layer formation within the pure SWNT electrodes. It should be noted however, at a fast scan rate above 500 mV s<sup>-1</sup>, the specific capacitance of SWNT/MnO<sub>2</sub> electrode still outperforms the SWNT electrode, showing excellent rate capability owing to the pre-formed fast electron path in the SWNT network.

At 2 mV s<sup>-1</sup> scan rate, the SC based on the total mass of SWNT/MnO<sub>2</sub> is 151 F g<sup>-1</sup>, and the SC of the MnO<sub>2</sub> in the SWNT/MnO<sub>2</sub> hybrid films is evaluated as high as 596 F g<sup>-1</sup>.

Compared to the theoretical SC of  $MnO_2$  (1370 F g<sup>-1</sup>), the degree of electrochemical utilization is ~44% for  $MnO_2$  in the SWNT/MnO<sub>2</sub> electrode. The reason of such high SC of  $MnO_2$  is probably owing to the deeper diffusion of electrolyte ions into the thin  $MnO_2$  layer to contribute to redox reaction. While at a high scan rate of 2000 mV s<sup>-1</sup>, the SC based on the total mass of SWNT/MnO<sub>2</sub> electrode is 38 F g<sup>-1</sup>, and the SC based on the mass of  $MnO_2$  is 109 F g<sup>-1</sup>, indicating a low capacitance contribution from  $MnO_2$  (less than 10%). The relatively decreased value of SC is attributed to the intrinsic low conductivity of the  $MnO_2$  layer.

Ragone plot in Figure 3b exhibits the high energy and power density feature of the SWNT/MnO2 electrode. In consistent with the SC plots, the SWNT/MnO<sub>2</sub> electrodes delivered a much higher energy density while keeping equally high power density, compared with the SWNT electrodes in TEABF<sub>4</sub>/PC electrolyte. To be specific, at current density of 100 A  $g^{-1}$ , the SWNT/MnO<sub>2</sub> based supercapacitor delivered an energy density of  $6.2 \text{ Wh kg}^{-1}$  at an extremely high power density of 79 kW kg<sup>-1</sup>, in contrast with the 3.6 Wh kg<sup>-1</sup> at the power density of  $82 \text{ kW kg}^{-1}$  of the SWNT electrode. The slight decrease (3%) of the power density of SWNT/MnO<sub>2</sub> electrode could be attributed to the longer electrolyte ion diffusion paths caused by the thin MnO<sub>2</sub> layer. However, compared with the 72% increase of the energy density, the decrease of 3% power density becomes negligible, because of the presence of the highly-conductive SWNT film that facilitates the kinetics of electron transport path. At this ultra high current density, the SWNT/MnO2 electrode finishes one cycle within one second, indicating excellent power capability. At a small current density (0.1 A  $g^{-1}$ , one full cycle takes approximately 4 h in total), the energy density of the SWNT/MnO<sub>2</sub> electrode reached 70 Wh kg<sup>-1</sup> at the power density of 77.3 W kg<sup>-1</sup>, providing seven times higher energy density at the same power density, compared to the SWNT electrode (10 Wh kg<sup>-1</sup> at the power density of 77.7 W kg<sup>-1</sup>).

It should be noted that the energy density of the present SWNT/MnO<sub>2</sub> electrode outperformed the Ni-MH rechargeable battery [28], which is highlighted in green belt part of Figure 3b, although it is not competitive with the Li-ion battery indicated in orange belt part. At  $1 \text{ A g}^{-1}$  current rate, the cell performs one full charge in approximately 180 s, which is 20 C rate in terms of the current rate for an Li-ion battery during charging/discharging. At this high current rate, the SWNT/MnO<sub>2</sub> electrode provides power density of 0.8 kW kg<sup>-1</sup>, and energy density of 20 Wh kg<sup>-1</sup>, which is very

competitive to the performance of Li-ion batteries. In addition, 20 C current rate is extremely detrimental to the cycling stability of Li-ion batteries. So for high power and relatively low energy density applications, the SWNT/MnO<sub>2</sub> electrode is a very promising alternative to complement the current Li-ion battery systems. At a high energy density over 30 Wh kg<sup>-1</sup>, however, lithium batteries have a higher power density than the SWNT/MnO<sub>2</sub> electrode, probably because the faster Li-ion intercalation/extraction contributed by the smaller ion size of Li<sup>+</sup>, compared to the slower redox reaction limited by the larger ion size of TEA<sup>+</sup>.

Figure 3c presents the galvanostatic charge/discharge curves of SWNT/MnO<sub>2</sub> electrode at various current densities. It should be noted that the slightly unsymmetric charge/discharge curves for the current densities below 20 A g<sup>-1</sup> is due to contribution from the pseudocapacitance of MnO<sub>2</sub> because a redox reaction typically takes more time than



**Figure 4** Cycle performance comparison of SWNT/MnO<sub>2</sub> electrode and SWNT electrode in TEABF<sub>4</sub>/PC electrolyte. (a) 15,000 cycles at current density of 50 A g<sup>-1</sup>. (b) 1000 Cycles at current density of 2 A g<sup>-1</sup>. (c) Randomly-picked continuous 6 charge-discharge cycle profile of SWNT/MnO<sub>2</sub> electrode at current density of 2 A g<sup>-1</sup>. (d) Galvanostatic charge/discharge curves from the 1st to the 1000th cycles for SWNT/MnO<sub>2</sub> and SWNT electrode at 2 A g<sup>-1</sup> (arrow indicates the direction where cycle number is increasing).

pure EDL formation. The small IR drops [20] are observed at the high charge current densities, which decrease with lowering the current density, as marked in Figure 3c.

In addition to the high energy and power density, the SWNT/MnO<sub>2</sub> hybrid films exhibited excellent long cycle stability. We performed the cycling test for 15,000 cycles at current density of 50 A g<sup>-1</sup> (Figure 4a), and for 1000 cycles at 2 A g<sup>-1</sup> (Figure 4b). At the current density of 50 A g<sup>-1</sup>, one charge-discharge cycle finishes in 2 s. The SC of both the SWNT/MnO<sub>2</sub> electrode and the SWNT electrode slightly increased and then stabilized at around the 3000th cycle. This is attributed to more accessible porous surfaces to the electrolyte ions after numbers of cycles. Thus, the effective surface area increased and the capacitance improved.

It should be noted that the SC fluctuation is attributed to the overshoots [29], observed at the higher current density of 50 A g<sup>-1</sup>, contributing to the variation of the SC  $(41\pm3 \text{ F g}^{-1})$ . The overshoot is also observed at 100 A g<sup>-1</sup> shown in Figure 3c. However, the overshoots do not degrade the stability of the cells, because of the high operation window of 2.5 V for TEABF<sub>4</sub>/PC electrolyte [25].

As demonstrated in Figure 4b, overshoots are avoided for the SWNT/MnO<sub>2</sub> electrode at a small current density of  $2 \text{ A g}^{-1}$ , resulting in a high and narrow columbic efficiency (from 98.5% to 99%). The SC is very stable in the range from 118 to 121 F g<sup>-1</sup>, 3 times of that for the SWNT electrode (from 38.6 to 40 F g<sup>-1</sup>), providing a much higher capacitance and remaining an excellent cycling stability. Figure 4c shows a randomly-picked, continuous 6 charge-discharge cycle profile, which exhibits very good stability of the SWNT/MnO<sub>2</sub> electrode.

To better illustrate the stability and comparison, chargedischarge curves of the SWNT/MnO<sub>2</sub> and the SWNT electrode are given in Figure 4d at the current density of 2 A g<sup>-1</sup>. The charge-discharge profiles of the SWNT/MnO<sub>2</sub> electrode exhibited a slightly distorted triangular symmetry, indicating pseudocapacitive behavior, as discussed above. The SWNT electrode exhibited almost a linear curve, suggesting an ideal EDLC behavior. Compared with the SWNT electrode, both charge and discharge time increased to 3 times for the SWNT/MnO<sub>2</sub> electrode, consistent with the increased energy density. From the 1st to the 1000th cycles, the charge discharge curves at different cycle numbers almost overlap with each other, for both the SWNT/MnO<sub>2</sub> and the SWNT electrodes, which again proves excellent cycling stability. The IR drops of both electrodes are from 1.5 V to 1.44 V at the initial cycle, and there is no significant difference after long cycles (At 100th cycle, both IR drops are from 1.5 V to 1.42 V). This also indicates the good stability, compared with previous research [20,24].

In order to evaluate the frequency response of the SWNT/ MnO<sub>2</sub> and SWNT electrodes and better understand the possible change of these two different electrodes before and after long cycling, EIS was performed in the frequency ranging from 100 kHz to 0.1 Hz at open circuit potential (Figure 5). Two different equivalent circuit models were used to simulate the capacitive and resistive elements of the two cells. For the SWNT electrode, the elements in the equivalent circuit include the series resistance ( $R_s$ ), the double-layer capacitance ( $C_{dl}$ ), the charge transfer resistance ( $R_{ct}$ ), the Warburg diffusion element ( $W_o$ ), the leakage resistance ( $R_{leak}$ ), and the mass capacitance ( $C_L$ ) [29]. For the SWNT/MnO<sub>2</sub> electrode, the pseudocapacitance element ( $C_{pseud}$ ) is associated with the redox capacitance. The curve fitting values are summarized in Table 1.

Theoretically, the Nyquist plot for supercapacitor consists of a high-frequency semicircle arc and a low-frequency straight line. The high-frequency semicircle is corresponding to  $R_{ct}$  at the electrode/electrolyte interface, and the lowfrequency straight line is corresponding to ion diffusion in the electrode material.  $R_s$  is determined by the first intersection point on the real axis of the Nyquist spectrum in the high-frequency region, which is mainly contributed from the electrolyte resistance, the ionic resistance of ions moving through the separator, the intrinsic resistance at the interface of active material, and the contact resistance at the interface of active material/current collector.  $R_{ct}$  shown as the second intersection point of the semicircle on the real axis is mainly contributed by the resistance at the



Figure 5 Nyquist plots of (a) SWNT/MnO<sub>2</sub> and (b) SWNT electrode before and after 1000 cycles with the electrical equivalent circuits used for fitting impedance spectra.

SWNT	$R_{\rm s}~(\Omega)$	$R_{\rm ct}~(\Omega)$	$W_{ m oR}$ ( $\Omega$ )	C <sub>dl</sub> (μF)		$R_{\text{leak}}$ (k $\Omega$ )	<i>C</i> <sub>L</sub> (mF)
Before cycle	3.13	0.75	1100	7.95		19.98	1.30
After cycle	3.06	0.83	734	7.11		19.30	1.30
SWNT/MnO <sub>2</sub>	$R_{\rm s}~(\Omega)$	$R_{\rm ct}~(\Omega)$	$W_{ m oR}$ ( $\Omega$ )	$C_{pseud}$ ( $\mu$ F)	C <sub>dl</sub> (μF)	$R_{\text{leak}}$ (k $\Omega$ )	<i>С</i> <sub>L</sub> (mF)
Before cycle	2.71	0.97	7322	1500	12.6	0.61	3.80
After cycle	2.48	1.24	4027	2500	24.7	0.63	10.50

Table 1 Impedance curve fitting results of the SWNT/MnO<sub>2</sub> and the SWNT electrodes, before and after long cycling, in TEABF<sub>4</sub>/PC using ZVIEW.

electrode/electrolyte interface [5]. As shown in Figure 5, the low frequency straight line is almost vertical, indicating a good capacitive behavior. With SWNT films acting as preformed electric pathways, the  $R_s$  of SWNT/MnO<sub>2</sub> electrode is similar to that of the SWNT electrode, with slightly higher  $R_{ct}$  than SWNT electrode due to the redox reactions. Both SWNT/MnO<sub>2</sub> electrode and SWNT electrode have very small arc region, indicating a good conductivity of the active materials and current collector. For comparison, we also measured the MnO<sub>2</sub> directly deposited on the current collector (copper substrate), which exhibited a much higher series resistance and charge-transfer resistance (20  $\Omega$ ), due to the poor electrical conductivity of the MnO<sub>2</sub> cell.

To characterize the frequency response, the knee frequency is usually examined, representing the maximum frequency the energy stored can fully access [30]. In this work, the knee frequency is as high as 3562 Hz and 2043 Hz, for the SWNT electrode and the SWNT/MnO<sub>2</sub> electrode, respectively. This ultra-high knee frequency indicates superior frequency response, compared with literature [5,31-33].

As shown in Table 1, the value of  $R_s$  slightly decreased after cycling for both the SWNT electrode and the SWNT/ MnO<sub>2</sub> electrode, believably owing to an improved wetting of the separator and electrode/electrolyte interfaces. The  $R_{ct}$ of both SWNT/MnO<sub>2</sub> and SWNT electrodes increased slightly after long cycling, which could be attributed to the corrosion of the current collector by the dissolved oxygen in electrolytes during the cycling [34]. The similar phenomenon of increasing  $R_{ct}$  after long cycling was also observed by other groups [34,35]. Compared with the recently reported graphene/MnO<sub>2</sub> composite [34], which showed significantly increased  $R_{ct}$  (from 1.7 to 4.2  $\Omega$ ), the increment in the current experimental results is much lower (from 0.97 to 1.24  $\Omega$ ), in consistent with the excellent stability of the SWNT/MnO2. The Warburg diffusion element after long cycling is decreased due to the easier accessibility of the electrolyte into the electrode materials for both SWNT and SWNT/MnO<sub>2</sub>, where SWNT/MnO<sub>2</sub> has a higher Warburg diffusion resistance due to the thin MnO<sub>2</sub> layer. Compared with the SWNT, the SWNT/MnO<sub>2</sub> electrode has two components to contribute to the capacitance,  $C_{dl}$  and  $C_{pseud}$ . The fitting values show that the pseudocapacitance contributes in a much higher ratio than the double layer capacitance. It is interesting to notice that both  $C_{dl}$  and  $C_{pseud}$  increased after cycling, probably owing to the increasing functional porous area and/or better wetting of the electrolyte/ electrode interfaces.

#### Conclusions

In summary, we have successfully fabricated binder-free SWNT/MnO<sub>2</sub> hybrid films as supercapacitor electrodes using a facile precipitation method. The performance of the SWNT/ MnO<sub>2</sub> electrodes in 1 M TEABF<sub>4</sub>/PC organic electrolyte demonstrates a much improved energy density and equally high power density, as well as an ultra-high frequency response (knee frequency of 2043 Hz) and an excellent long cycle stability. High specific capacitance of 596 F  $g^{-1}$  indicates very high MnO2 utilization owing to the much improved the electrical conductivity. In addition, the functional groups on CNTs ensure the strong bonding and excellent stability of the MnO<sub>2</sub> thin layer, revealed by the microscopic observations and electrochemical performance. The power density of 79 kW kg<sup>-1</sup> (with energy density of 6.2 Wh kg<sup>-1</sup> at current density of 100 A  $g^{-1}$ ) shows its great potential to be used in high power applications, such as harbor lifting crane and laser power sources. The energy density of 70 Wh  $kg^{-1}$  (with power density of 77.3W kg<sup>-1</sup> at current density of 0.1 A g<sup>-1</sup>), shows its high competitiveness compared with the current Ni-MH battery systems, thus makes it very promising to be implemented as the electric energy storage devices for hybrid vehicles. The facile synthesis of the SWNT/MnO<sub>2</sub> electrode is cost-efficient, easily controlable and highly scalable to be implemented in energy storage industry.

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