Hierarchical carbon nanotube membrane with high packing density and tunable porous structure for high voltage supercapacitors

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ARTICLE INFO

ABSTRACT

We reported the fabrication of a hierarchical carbon nanotube (CNT) membrane by using the 90% granulated double- or triple-walled CNTs and 10% 100 μm long multiwalled CNTs as the linker. The membrane with packing density of 420 kg/m^3, excellent electrical conductance and good mechanical strength, functioned as both the electrode and current collector and allowed the weight ratio of CNTs increased up to 45–50% based on the weight of CNT, electrolyte and separator. The granulated double or triple walled CNTs, by the aggregation at high temperature etching using CO_2, simultaneously exhibited high surface area and tunable pore structure and high pore volume, and were favorable for the ion transport of organic electrolyte, due to the effect of opening cap or side wall by the CO_2. The CNT membrane electrode, exhibited the capacitance of 57.9 F/g and the energy density of 35 W h/kg, as operated at 4 V.

1. Introduction

Supercapacitor has advantage of high power density, rapid charging and discharging, without the loss of efficiency, and very long cycling stability [1–13], and therefore, found applications in initializing the wind turbine or heavy vehicles. However, the energy density based on supercapcitor cell is only 5–6 W h/kg as using activated carbon (AC) as the electrode, which is unable to meet the use in battery–supercapacitor combination system for future pure electrical or hybrid vehicles. Carbon nanotubes (CNTs) [2,3,6,7,10,12,13] represented one of the most promising candidates of AC, since CNTs have higher chemical stability than AC as operated above 3 V and the predominant exohedral surface of CNTs [4] favors the quick accumulation and transport of electrolyte ions so as to increase the performance of quick charge and discharge under high currents [2,3,9,14]. But the randomly packed network of CNTs had a porosity of 90% or above, which resulted in the lower packing density (100–250 kg/m^3) of CNTs [11,15] as compared to that (400–650 kg/m^3) of AC powders. In this case, the weight ratio of CNT in supercapacitor did not exceed 10–20%, which is unfavorable to increase its volume energy density as using CNTs in large amounts in practical supercapacitor. Densification of single-walled CNT (SWCNT) array by vaporizing the solvent is effective to increase the packing density [7]. But it was not a cross-linked structure and tended to expand and became loose again if wetted by the electrolyte. The volume expansion of CNT electrode membrane, in turn, arise the potential risk of shortcut in practical application. Apparently, it is essential to design a stacking structure of CNTs with high packing density, excellent mechanical strength, better electrical conductance, and the pores mostly accessible to ions of electrolytes [8].

In the present work, we proposed the densification of CNTs by the high temperature aggregation under CO_2 atmosphere. The used DWCNTs and TWCNTs with inner diameter of 2–3 nm were transformed into particles with average size of 0.2–2 μm. The CNT particles have a packing density of 420 kg/m^3, close to that of AC. Meanwhile, the etching using CO_2 is effective to open the cap or sidewall of these tubes to give a rational distribution of micropore, mesopore and macropore, and an increased surface area and pore volume. Further, these CNT particles are cross-linked by 10% MWCNTs (100 μm long) to fabricate an electrical conducting membrane with higher mechanical stability in electrolyte (Fig. 1) than the paralleled CNT array [7]. Detailed structure characterization and the capacitance performance test were made for the better understanding the effect of the new hierarchical CNT membrane electrode on the performance of supercapacitor. These results are useful to fabricate next generation supercapcitor with the energy density 2–3 folds that of AC based supercapaictor.

2. Experimental

2.1. Carbon nanotube purification

Pristine DWCNTs/TWCNTs were prepared by the decomposition of methane over Fe/Mo/MgO catalyst at 850 °C in a fluidized bed reactor [16]. Considering MgO support doesn't contribute to the capacitance and the Fe–Mo metals have negative effect on the stability of supercapacitor [18], a multistep method was used here to remove these impurities [19–23]. Firstly, pristine CNTs were directly etched by the CO_2 (96% purity) at 200–900 °C, in an instrument of thermogravimetric analysis (TGA, TA, 5 °C/min) in situ, which is effective to remove amorphous carbon, to open the cap or sidewall of tubes [2], and, to probably destroy some carbon capsules outside the Fe-Mo nanoparticles [22]. Second, samples after CO_2 etching were washed by the use of 1 mol/L HCl at 35 °C for 24 h to remove all MgO support, most Fe metals on MgO support, and some Fe/Mo metals pristine inside the carbon capsule, but exposure to acid after CO_2 etching. Third, the acid-washed sample was washed further by de-ion water for five times and dried at 110 °C for 12 h. Fourth, the dried sample was annealed in Ar/H$_2$ atmosphere (90% Ar and 10% H$_2$) at 1000 °C for 2 h, to remove about 99% oxygen-containing functional groups. Thus, the purity of tubes is high up to 99%. Some impurities still remained in CNTs, e.g. Fe/Mo metals inside the thick carbon capsule, do not influence the performance of supercapacitor in short time.

Note here that the CO_2 etching at high temperature directly resulted in the aggregation of CNTs to become particles with average size of 0.2–2 μm. The granulated structure doesn't change in the subsequent processing steps of acid wash and drying.

2.2. Fabrication of carbon nanotube-based supercapacitor

Supercapacitor was fabricated by the steps as follows. Granulated DWCNTs/TWCNTs were mixed with 10% aligned MWCNTs (12 nm in diameter, 100 μm in length) [17] and then were dispersed uniformly in N-methyl-2-pyrrolidone (Pure chemical, Beijing, China) solution. CNT membrane with 40 mm in diameter and 200 μm in thickness was made by filtration. After drying, the membrane was cut to round sheet with a diameter of 13 mm, which was used as both the electrode and current collector [10], since the CNT membrane has high strength and excellent electrical conductance. Coin-size (2025) capacitor cells were assembled in a glove-box (MIKRO-UNA, Shanghai, China, [O$_2$] < 1 ppm, [H$_2$O] < 1 ppm). One supercapacitor unit cell was comprised of two electrodes (each is 16 mg in weight) that were electrically isolated by a celgard porous membrane. The electrolyte was 1 M Et$_4$NBF$_4$/propylene carbonate (Pure chemical, Zhangjiagang, China).

2.3. Characterization

The pristine and purified CNT sample were characterized by scanning electronic microscope (SEM, JSF7401, 3–20 kV), transmission electronic microscope (TEM, JEOL2010, 200 kV), Raman spectroscopy (Horiba JY, 633 nm laser), TGA (TA, elevating heat rate: 5 °C/min, CO_2 atmosphere), and nitrogen adsorption instrument (ASAP2010, 77 K).
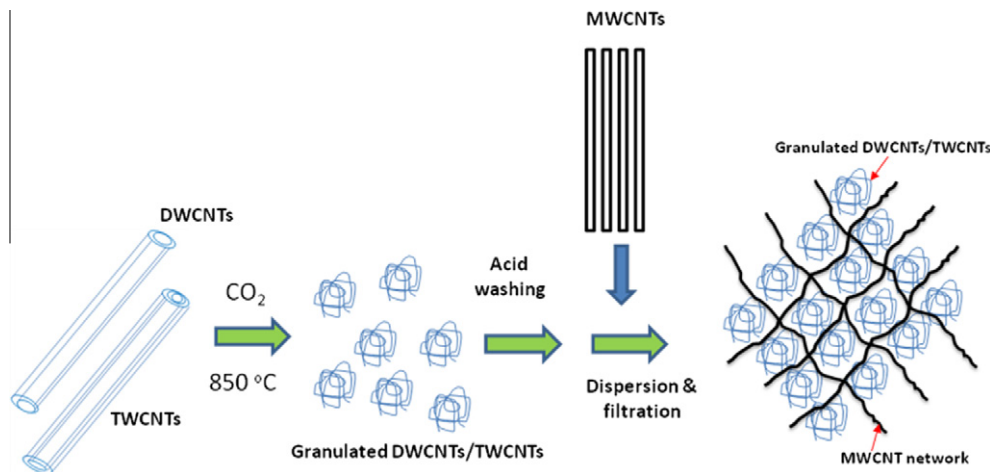

Fig. 1 – Illustration of fabrication of carbon nanotube membrane consisted of dominant granulated DWCNTs/TWCNTs and long MWCNTs as backbone.

The electrochemical performance such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of CNT-based supercapacitor was characterized by using a Solartron 1470E electrochemical station equipped with a 1455AFRA module. The CV curve and specific capacitance under different scan rate of 0–200 mV/s between 0–3.5 and 0–4 V, the cycling ability was tested under 100 mV/s and in the range of 0–4 V for 5000 cycles.

3. Result and discussion

Fig. 2a showed the SEM image of pristine CNT product grown densely on very thin MgO nanosheets [16]. After removing the MgO support by acid washing, the carbon product is dominant DWCNTs and TWCNTs (Fig. 2b). Typically TWCNTs and DWCNTs in the product were shown in Fig. 2c and d, respectively. Their outer diameter and inner diameter is in the range of 3–5 and 2–4 nm, respectively. After measuring about 240 tubes on 50 TEM images, it is estimated that the product contains about 3% 1.5 nm tube (SWCNTs or DWCNTs), 60% DWCNTs (2–2.5 nm in diameter, 3–4 nm in outer diameter), 35% TWCNTs (2–2.5 nm in inner diameter, 3.5–5 nm in outer diameter) and about 2% impurities (graphene with 3–6 layers and carbon encapsulated metal nanoparticles). The inner diameter of these tubes is suitable for the transport of electrolytes ions (Et_4NBF_4/PC) inside, but the closed cap of pristine tubes should be opened in advance.

The experiment of opening the cap or the side wall of these tubes was carried out in a TGA instrument, using CO_2 as the carried gas. The temperature elevating rate was intentionally tuned to be 5 °C/min, significantly lower than that (10 °C/min) in the normal test, in order to determine the content of amorphous carbon and DWCNTs/TWCNTs. A very small peak at 400 °C is assigned to amorphous carbon. In the range of 400–800 °C, CNT sample remained quite stable and no weight loss was observed. Significant weight loss of sample occurred above 800 °C. The temperature is lower than that for etching pure CNTs, since the presence of metal catalyst in the carbon product helped the oxidation of CNTs at relatively low temperature. The weight loss was 45% when temperature was approaching to 1000 °C. Thus, the etching temperature was fixed at 850 °C to avoid the serious weight loss of carbon at higher temperature. It is found that, the loss of carbon increase linearly with the etching time. At different times, we sampled the CNTs and measured the content of Fe solvable in HCl acid. The content of Fe, originally inside the carbon capsule but now is solvable in HCl, approached to 50% and did not increase when the etching time is 10 min. It suggested that the thin carbon capsule (which may be assigned to 1–3 carbon shells) was destroyed by CO_2 etching, but the thick carbon capsule (larger than three carbon shells) did not. The total loss of carbon at that time is about is about 3–5%. The value (weight loss of carbon) is far smaller than those (about 30–50%) in previous reports for opening the cap
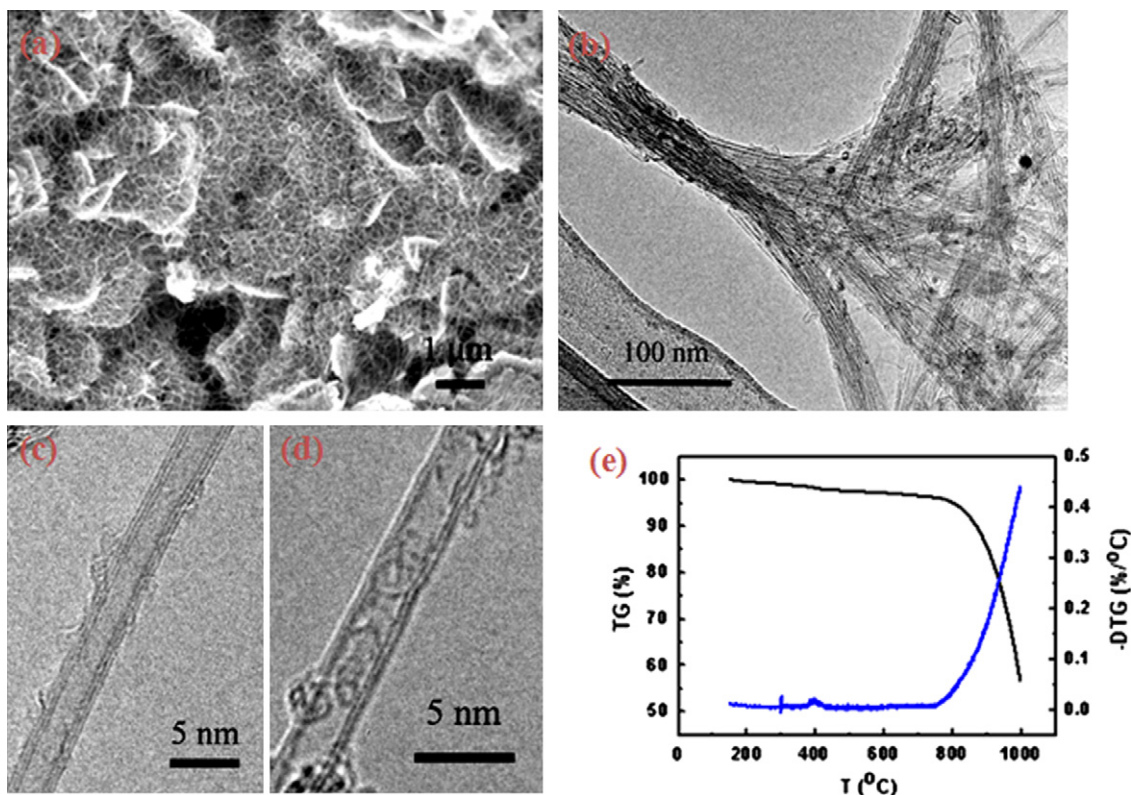

Fig. 2 – Morphologies and in situ thermogravimetric analysis of DWCNTs/TWCNTs. (a) SEM image of CNTs grown on MgO nanosheets, (b) TEM image of the purified DWCNTs/TWCNTs bundles at low magnification, (c and d) HR-TEM images of TWCNTs and DWCNTs, respectively, and (e) in situ thermogravimetric analysis of DWCNTs/TWCNTs at CO_2 atmosphere with heating-rate of 5 °C/min.

of SWCNTs [2] or removing other carbon impurities inside CNT product [22]. The etching condition of 850 °C for 10 min, assisted by the metal catalyst in the present work, is an optimal one to just open the cap or side wall of tubes, but not to decrease the yield of tubes seriously.

Fig. 3 showed TEM images of tubes by the etching of CO_2. Many TWCNTs (Fig. 3a) and DWCNTs (Fig. 3c) with cap opening were observed. The connected part of nanotube and metal catalyst is most easily opened, as suggested in the previous work for detaching CNT array from the substrate [24]. However, except this, we also found the side wall of nanotubes can be opened. 3–4 nm long slits on the side wall were observed on a SWCNT with diameter of 6.8 nm (Fig. 3a) and on a DWCNT with inner diameter of 2.5 nm (Fig. 3b), respectively. Moreover, the outer wall of a DWCNT was destroyed, but its inner shell remained perfect (Fig. 3d), suggesting that the CO_2 etching firstly affect the outer shell, then the inner shell

of DWCNTs, similar to that using CO_2 to etch CNT array [25]. The opened cap or side-wall of tubes allows the access of electrolyte ions to the inner channel of tubes and the quick the transport of them inside, which is crucial to increase its supercapacitor performance discussed below.

Raman characterization (Fig. 4a and b) revealed clearly the effect of CO_2 etching on the tube structure. Firstly, some peaks at 25–300 cm^{-1}, assigned to the radial breathing mode (RBM) of tubes (Fig. 4b), became weakening or disappeared. It suggested some small-diameter tubes, with larger surface energy as compared to large-diameter tubes [26], was destroyed by the CO_2 etching. The increased intensity of peaks at 150 and 225 cm^{-1} is probably due to the contribution of inner shell of some DWCNTs or TWCNTs when its outer shell was etched off (as in Fig. 3d). In addition, the intensity ratio of D band ($\sim$1340 cm^{-1}) to G band ($\sim$1580 cm^{-1}) (I_D/I_G value) was increased from 0.17 to 0.35 after CO_2 etching (Fig. 4a).
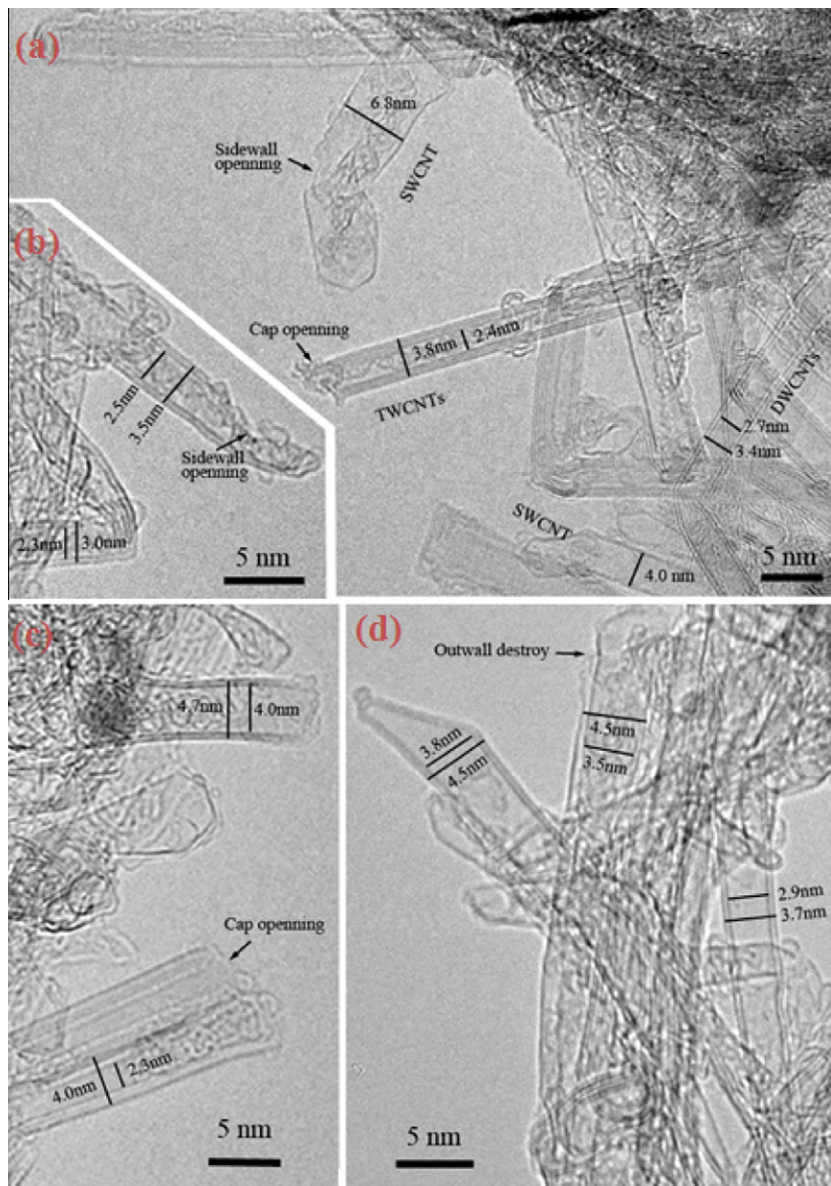

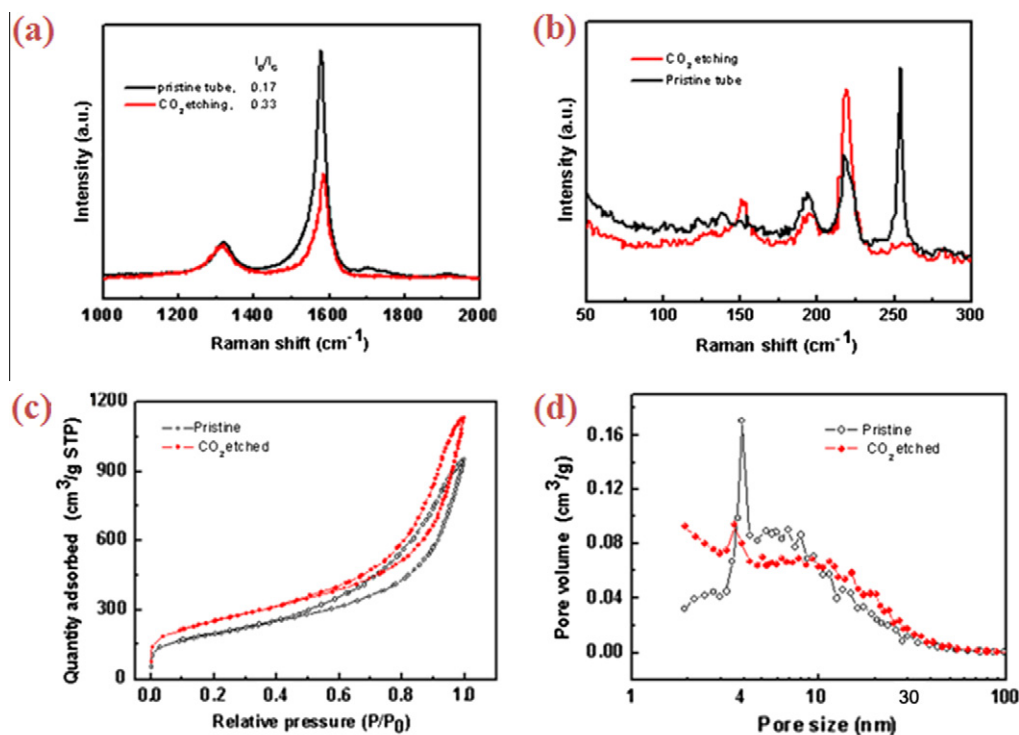Fig. 3 – HR-TEM images of DWCNTs/TWCNTs etched with CO_2 at 850 °C.

Fig. 4 – (a and b) Raman spectra of DWCNTs/TWCNTs in the range of 100–300 cm^{-1}, and 1000–2000 cm^{-1}, respectively, (c) N$_2$ adsorption and desorption isotherms at 77 K for pristine (black), etched DWCNTs/TWCNTs (red), and (d) BJH pore size distribution of non-etched (black) and etched (red) DWCNTs/TWCNTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Note that the amorphous carbon was totally removed at 400 °C, and the oxygen-containing functional groups were removed at 1000 °C, which should both contribute to the decrease in the defective degree of the sample [27]. In this case, the increased defect degree of sample after CO$_2$ etching is apparently due to the increased the ratio of sp^3 hybridized carbon near the opened cap or opened side-wall of CNTs (Fig. 2) and implied that the cap or side wall of most tubes was effectively opened by the CO$_2$ etching.

The effect of CO$_2$ etching on tubes was further understood by the experiment of the nitrogen adsorption. The BET specific surface area of tubes was increased from 670 to 871 m^2/g after CO$_2$ etching (Fig. 3c). The value (871 m^2/g) is among the highest one for DWCNT samples and even higher than that of some SWCNTs if containing carbon impurities, such as MWCNTs or carbon encapsulated metal nanoparticles [1,13,17,22]. T-plot curve was effective to determine the contribution of external surface area of the sample (see Supplementary materials). For pristine tube, micropores contributed to the surface area of 51 m^2/g, while the external surface area was 619 m^2/g. In contrast, for CO$_2$-etched tubes, micropores contributed to the surface area of 76 m^2/g, while the external surface area was increased to 795 m^2/g. The significantly increased external surface area of electrode was easily accessible to ions of electrolyte. Detailed pore size distribution (Fig. 4d) indicated that the percentage of mesopores of 3–10 nm was significantly decreased after CO$_2$ etching, and the percentage of pores of 10–30 nm was slighted increased. The result confirmed that the granulated DWCNTs/TWCNTs were more compact than

the pristine sample. In addition, the absolute pore volume between 1.7 and 300 nm of the sample was increased from 1.43 to 1.66 ml/g and the average pore size was enlarged from 8.72 to 9.12 nm by the etching using CO$_2$. It clearly suggested that the granulated tubes still have sufficient channel allowing the quick transport of electrolyte ions [5,10]. In addition, the percentage of micropores at 1–2 nm was increased, due to the effect of opening cap or side wall of most tubes.

As follows, we made the CNT membrane by using the granulated DWCNTs/TWCNTs (TEM image in Fig. 5a) and long MWCNTs, followed the steps shown in Fig. 1. SEM image revealed that long MWCNTs formed a network to hold or wrap the granulated DWCNTs/TWCNTs (Fig. 5b). And the size of these small particles did not change much in the subsequent processing. No leakage was found on this kind of CNT membrane with the diameter of 4 cm and the area of 12 cm^2 (Fig. 6a). Apparently, the mechanical strength of CNT membrane in the present work depends mostly on the MWCNT network. Adding more long MWCNTs would further increase the mechanical strength of the CNT membrane, but reduce the BET surface area of total electrode and consequently, give a small capacitance [29]. Note that such kind of membrane is significantly different from pure SWCNT film or pure DWCNT buckypaer [28]. The loosely packed pure SWCNT or DWCNT membrane tended to expand as wetted by electrolyte and may have potential risk in destroying the structure of supercapacitor cell. As follows, the membrane is cut to a round sheet with the diameter of 1.3 cm and is used to make a coin-like supercapacitor device (Fig. 6b), using 1 M Et$_4$NBF$_4$/
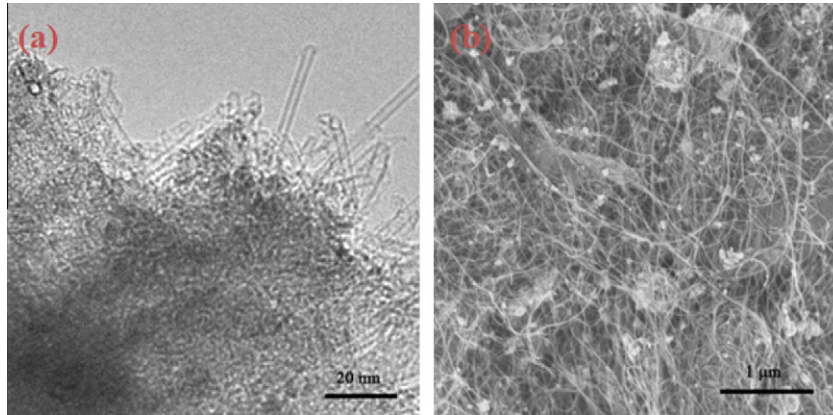
Fig. 5 – (a) TEM image of granulated DWCNTs/TWCNTs, (b) SEM image of CNT membrane consisted of 90% DWCNTs/TWCNTs (white spots or large powder) and 10% aligned MWCNTs (network).
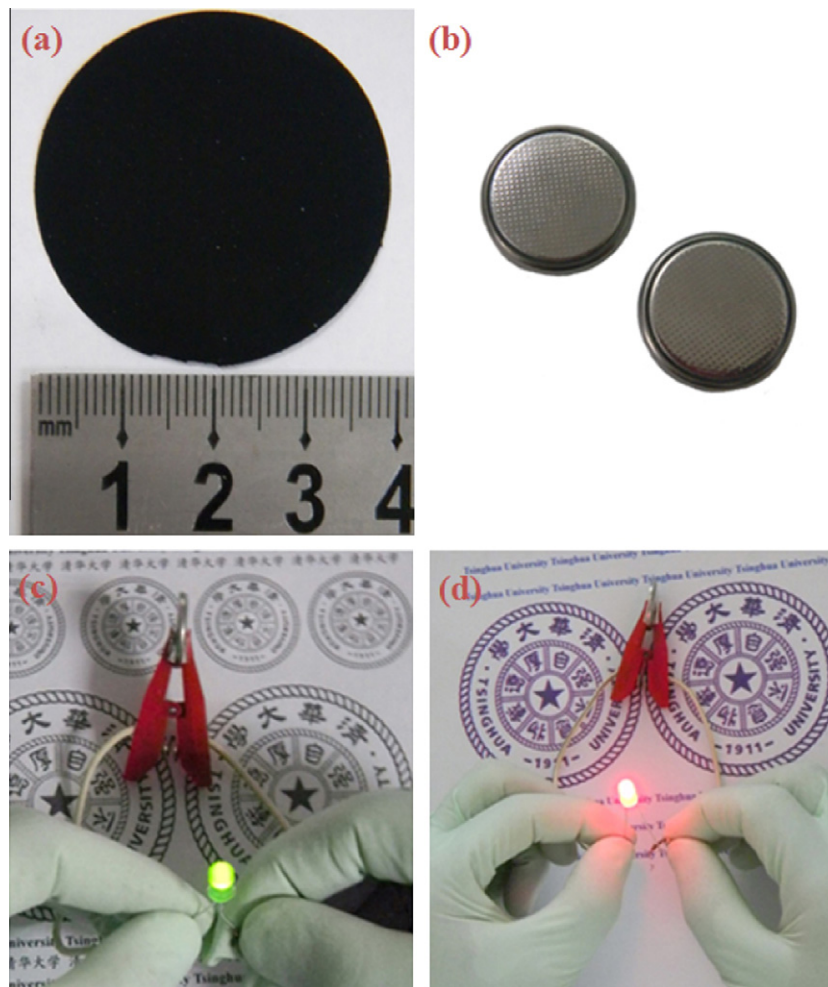

Fig. 6 – (a) Macroscopic photographs of DWCNT/TWCNT membrane, (b) assembled coin-size supercapacitors, (c) a supercapacitor lights a light-emitting-diode when operated at 3.5 V and (d) a supercapacitor lights a light-emitting-diode when operated at 4 V.

PC as the electrolyte. Such small size supercapacitor is effective to light a diode operated at 3.5 V (Fig. 6c) and 4 V (Fig. 6d), respectively. When the CNT supercapacitor was operatezd at 4 V, the diode emitted very strong white light for long times (Fig. 6d). Our method is very simple to make the membrane with uniform thickness (deviation is less than 3%) and con-

trollable surface density (420 kg/cm^3). Thus, the performance of coin-like supercapacitor using different parts of a large membrane or made at different times is nearly the same.

Fig. 7 presented the detailed supercapacitor performance of DWCNT/TWCNT electrode operated at 4 V. They exhibited nearly the identical symmetric trapezoid-shaped cyclical voltammograms (CVs, Fig. 7a). As expected, the area of CV curve became larger for samples after CO_2 etching. Note that, the triangle area in the upper-right region of CV curve is relatively small, confirming the high purity of our sample. Note that, electrolyte is apt to decompose in the presence of impurities such as metal or oxygen-containing functional groups [18]. It is difficult to elevate the operating voltage above 3 V if the amount of impurities is large [18]. These results also confirmed that our CNT product is of high purity and the residue Fe/Mo metals inside thick carbon capsule do not influence the performance of supercapacitor [2]. Further, the capacitance of CNT electrode after CO_2 etching was obviously higher than that of without CO_2 etching in the scanning rate range of 1–50 mV/s (Fig. 7b). Quantitatively, the value increased from 47.7 to 59.1 F/g under the scanning rate of 10 mV/s. However, in the scanning rate range of 100–200 mV/s, two capacitance lines overlapped, suggesting the effect of CO_2 etching became insignificant. The ESR value is about 1.19 and 1.45 Ω for the membrane contained 90% long pristine tube or 90% granulated tube by CO_2 etching, respectively (Fig. 7c). The result suggested that, although CO_2 etching made DWCNTs/

TWCNTs granulated, the linkage of them by long MWCNTs ensured nearly the same electrical conductance of the CNT membrane, compared to that of the pristine. Thus, the decrease of capacitance with the scanning rate (Fig. 5b) is a natural phenomenon due to the diffusion limitation of ions of electrolyte into small pores of electrode under high current [2,3,10]. However, even though, our membrane using CO_2 etched DWCNTs/TWCNTs still exhibit an energy density of 35 W h/kg in very wide range of power density, which value is 34.6% higher than that (26 W h/kg) of membrane using pristine tube (Fig. 7d). Considering the excellent electrical conductance of CNT membrane [28,30], it probably served as electrode and current collector simultaneously. The weight ratio of CNT membrane is 45–50% based on the weight of CNT, electrolyte and separator. In this case, if future technology allows the no use of organic binder but with the acceptable structural stability, it is possible to fabricate a supercapacitor with gross energy density of 10–12 W h/kg.

Moreover, our new CNT membrane electrode exhibited the sustainably constant ability for 5000 cycles (Fig.8). Nearly no loss was found compared to the initial value. In comparison, few impurities inside the pristine tube influence its cycling ability in 1–1000 cycles. Only after that, its performance became relatively stable. It suggested the importance of removing Fe or other impurities on the electrochemical stability of the electrode material as operated at high voltage [2,18]. The excellent retention of its capacitance of the high purity
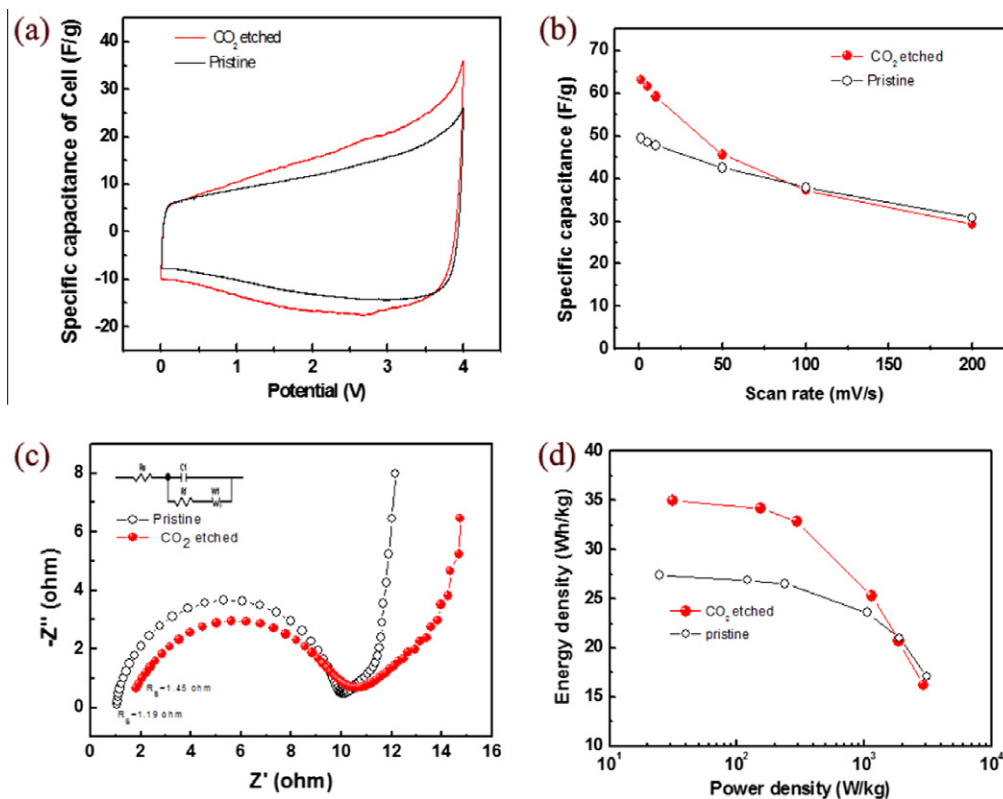

Fig. 7 – (a) CV curve of DWCNT/TWCNT electrode with and without CO_2 etched, (b) dependent relationship between the capacitance value of DWCNT/TWCNT electrode with and without CO_2 etched and the scanning rate in the test, (c) Nyquist plots of DWCNT/TWCNT electrodes with and without CO_2 etched, and (d) Ragone plots of DWCNT/TWCNT electrode with and without CO_2 etched.
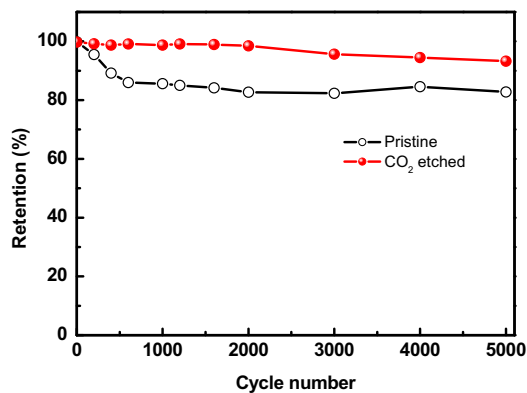
Fig. 8 – Comparison of the cycling ability of supercapacitor cell by the use of pristine DWCNT/TWCNT sample and CO$_2$ etched DWCNT/TWCNT sample at the scan rate of 100 mV/s. Retention is the relative capacitance value of the electrode to the initial value.

DWCNTs/TWNCTs is similar to that of SWCNTs with high purity [2]. But the relatively higher yield of DWCNTs/TWCNTs [16,28,29] compared to that of SWCNTs [27] made our electrode the low cost for the commercialization.

In addition, the comparison of the capacitance of DWCNTs at the monodispersed state [13] and aggregated state here suggested that the energy density of tubes decreased with the densification of CNTs. Apparent, the ion transport became more and more difficult with the increase of the packing density of electrode material [1,2,13,14]. Also aligned SWCNT array provided a channel allowing quick transport of ions of electrolyte, and consequently, gave a better performance under high currents [5,7]. To point of this view, the design of stack housing structure of electrode materials is always a balance between its weight ratio and its surface area which really effects, as well as its mechanical strength for safety operation. Further investigation is needed to optimize such kind of hierarchical structure of CNT membrane for a much better performance.

4. Conclusions

DWCNTs/TWCNTs with large inner diameter were granulated by CO$_2$ etching in the present work to become compact particles with size of 0.2–2 μm. Meanwhile, their surface area is increased up to 871 m^2/g by CO$_2$ etching due to the effect of opening cap or side wall. Granulated DWCNTs/TWCNTs were linked by 100 μm long MWCNTs to form a membrane with high mechanical stability and excellent electrical conductance. The supercapacitor based on the CNT membrane, with high surface area, high packing density, and sufficient mesopores and macropores, exhibited high energy density and high stability.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2012.06.058.

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