

Electrochemistry of Carbon Nanotubes and their Applications in Batteries and Supercapacitors

J. H. Chen, W. Z. Li, Z. P. Huang, D. Z. Wang, S. X. Yang, J. G. Wen, Z. F. Ren*

Department of Physics, Boston College & NanoLab, Inc.

ABSTRACT

Carbon nanotubes are grown on graphite sheet, carbon cloth and other materials by chemical vapor deposition (CVD) method. The electrochemical behavior of carbon nanotubes has been investigated by cyclic voltammetry in $1.0M\ H_2SO_4$ aqueous solutions. High "effective capacitance" and rectangular-shaped cyclic voltammograms at high scan rate ($100\ mV/s$) have been observed, which makes these carbon nanotubes of great interest as electrodes in supercapacitors. The material is very stable on cycling and no significant difference has been seen after continuous cycles over 30.

INTRODUCTION

Carbon nanotubes are very interesting materials in the sense of their structure and their size in the nanometer range, which leads to that they have highly accessible surface area, low resistivity, and high stability [1-3]. These features are ideally desired for carbon nanotubes to be used as electrodes in supercapacitors [4].

EXPERIMENTAL

Carbon nanotubes were grown directly on several substrates: graphite sheet, carbon cloth and graphite sheet covered with activated carbon by chemical vapor deposition (CVD) method using acetylene (C₂H₂) and ammonia (NH₃) [5-7]. Ni particles were deposited on the substrates and used as catalyst. Before the measurement of cyclic voltammogram, samples were immersed into 15% wt. HNO₃ aqueous solution for 30 minutes in order to remove the metallic particle (catalyst) and increase the wettability of the surface of the carbon nanotubes in aqueous solution. PC4 Potentiostat/Galvanostat (Gamry Instruments Inc. Warminster, PA 18974) was employed for the cyclic voltammetric (CV) measurements in 1.0M H₂SO₄ aqueous solutions. A platinum wire served as the counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode.

_

^{*} To whom correspondence should be addressed. Email address: renzh@bc.edu. Telephone: 617-552-2832. Fax: 617-552-8478.



RESULTS and DISCUSSION

Carbon nanotubes were grown on three kinds of substrates: activated carbon-coated graphite foil, bare graphite foil, and carbon cloth. The SEM images of the carbon nanotubes are shown in Fig.1, Fig.2 and Fig.3 respectively. Nanotube bundles can be found in Fig.1 and Fig.3.

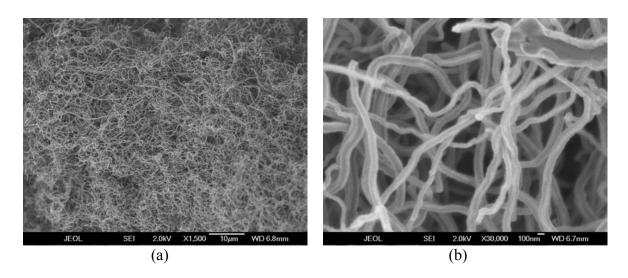


Figure 1. SEM images of carbon nanotubes grown directly on activated carbon-coated graphite foil. (a) low magnification to show the uniformity in large area and length; (b) high magnification to show the diameter.

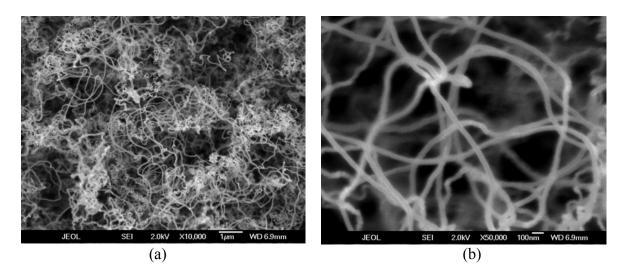
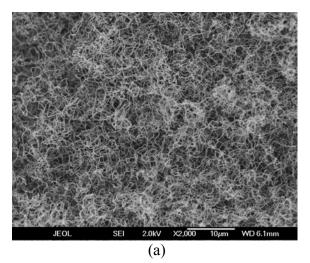


Figure 2. SEM images of carbon nanotubes grown directly on the graphite foil. (a) low magnification to show the uniformity in large area and length; (b) high magnification to show the diameter.





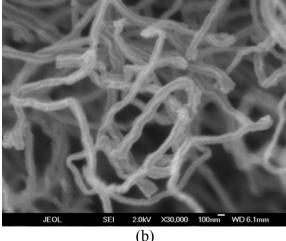


Figure 3. SEM images of carbon nanotubes grown directly on carbon cloth substrate. (a) low magnification to show the uniformity in large area and length; (b) high magnification to show the diameter.

The electrochemical properties of these nanotube electrodes were studied by cyclic voltammetry in 1.0M H_2SO_4 aqueous solution. The typical cyclic voltammograms (CVs) are shown in Fig.4, Fig.5, Fig.6 and Fig.7. These CVs are featureless voltammograms and no Faradic peaks can be observed between 0 to 0.9 V (vs. SCE). This result has also been observed for the single-

walled carbon nanotubes [4]. Rectangular-shaped cyclic voltammograms over a wide range of scan rates is the ultimate goal in electrochemical double-layer capacitors. This behavior is very important for practical applications. In Fig.4, Fig.5, Fig.6 and Fig.7, These carbon nanotube electrodes can retain the rectangular shape of CVs up to a high scan rate (100mV/s). This means the charge and discharge processes are very fast at the interface between the nanotube electrode and electrolyte

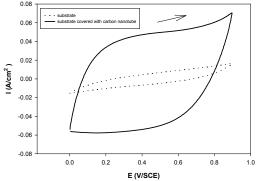


Figure 4. Cyclic voltammogram of sample #1 in 1.0M $\rm H_2SO_4$ aqueous solution. Sample #1: carbon nanotubes were grown directly on the graphite sheet substrate covered with activated carbon. Scan rate: 100mV/s.

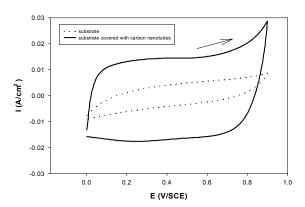


Figure 5. Cyclic voltammogram of sample #1 in 1.0M H₂SO₄ aqueous solution. Sample #1: carbon nanotubes were grown directly on the graphite sheet substrate covered with activated carbon. Scan rate: 25mV/s.



solution. The featureless CVs and high speeds of charge and discharge suggest a possible application of this kind of multi-walled carbon nanotubes to supercapacitor. The material

is stable on cycling and no significant difference can be seen after continuous cycles over 30 cycles.

The results in Fig.4, Fig.5, Fig.6 and Fig.7 show that the electrochemical capacitance of the electrode increases obviously when carbon nanotubes are grown on the substrates. The mass of carbon nanotubes grown on the substrate is obtained from the difference of total weight of the electrode before and after the growth of carbon The nanotubes. capacitance calculated from the CV curves, with $C = \int idt/\Delta V$, where i is the current. The increases of the effective capacitance per unit weight of carbon nanotubes can be calculated, for example, at the scan rate of 25mV/s, are 98.6 F/g and 140 F/g for sample #1 and sample #2, respectively.

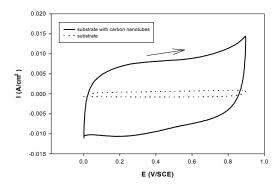


Figure 6. Cyclic voltammogram of sample #2 in 1.0M $\rm H_2SO_4$ aqueous solution. Sample #2: carbon nanotubes were grown directly on the graphite sheet. Scan rate: 100mV/s

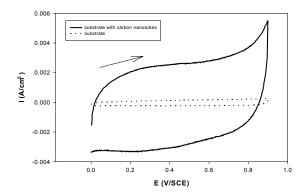


Figure 7. Cyclic voltammogram of sample #2 in 1.0M H₂SO₄ aqueous solution. Sample #2: carbon nanotubes were grown directly on the graphite sheet. Scan rate: 25mV/s

ACKNOWLEDGEMENTS

*The work is partially supported by US Army Natick Soldier Systems Center under a grant DAAD16-00-C-9227 and Biosource, Inc.

REFERENCES

- 1. H. Dai, E.W. Wong and C.M. Lieber, Science 272, 523 (1996).
- 2. T. W. Ebbesen, H.J. Lezec, H. Hiura, J.W. Bennett, H.F. Ghaemi ad T.Thio, *Nature* **382**, 54 (1996).
- 3. Y. Saito, K. Hamaguchi, K. Hata, K. Uchida, Y. Tasaka, F. Ikazaki, M. Yumura, A. Kasuya and Y. Nishina, *Nature* **389**, 554 (1997).
- 4. Chong-yang Liu, Allen J. Bard, Fred Wudl, Iris Weitz and James R. Heath, *Electrochemical and Solid-State Letters* **2** (11), 557 (1999).



- 5. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, "Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass", *Science* **282**, 1105 (1998).
- 6. Z. F. Ren, Z. P. Huang, J. W. Xu, D. Z. Wang, J. G. Wen, J. H. Wang, L. Calvet, J. Chen, J. F. Klemic, and M. A. Reed, "Growth of a Single Freestanding Multiwall Carbon Nanotube on Each Nanonickel Dot", *Appl. Phys. Lett.* **75**, 1086 1088 (1999).
- 7. Z. F. Ren, Z. P. Huang, J. W. Xu, D. Z. Wang, J. H. Wang, L. Calvet, J. Chen, J. F. Klemic, and M. A. Reed, "Large Arrays of Well-Aligned Carbon Nanotubes", *Proceedings of 13th International Winter School on Electronic Properties of Novel Materials*, Pages 263 267, (1999).