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Wearable Carbon Nanotube Fibers for Energy Storage

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Wearable electronics are new developing technologies for energy storage in modern society, and they represent a new class of materials with an array of novel functionalities, such as flexibility, stretchability, and lightweight. We report the use of Carbon nanotube (CNT) fiber as weaved fabric electrodes for this kind of wearable energy storage applications. This CNT fabric is composed by all pure CNTs. The weaved CNT fabric offers many advantages such as large active specific surface areas, high electrical conductivity, improved electron transfer as well as high chemical stability, and the capacitance of our CNT fabric is about 60-80 F g^{-1} whose value is the highest in the same kind of CNT fabrics. Our CNT fabric can adapt to wearable electronics such as wearable solar cells and batteries, high-performance sportswear, wearable displays, new classes of portable power etc.

Keywords: Multilayers; Nanostructures; Electrochemical techniques; Electron microscopy

1. INTRODUCTION

Wearable electronics are new developing technologies for energy storage in modern society, and they represent a new class of materials with an array of novel functionalities, such as flexibility, stretchability, and lightweight [1]. All these electronic applications require energy storage materials which have above properties. Carbon nanotube (CNT) fibers fabricated by chemical vapor deposition (CVD) spinning process are macroscopic continuous yarns with a length of over several kilometers and a quality close to conventional textile yarns [2]. They combine lightweight, flexible, high specific surface area, superior electrical conductivity and mechanical properties, and can be weaved into electronic textiles for energy storage devices [3]. All these particular properties of CNT fibers are perfectly met the demands of wearable electronic applications.

We report novel weaved CNT textiles for flexible fibred supercapacitors. The CNT textiles worked as supercapacitor electrodes are weaved by macroscopic continuous CNT bundles which are stacked by several nano-diameter CNT fibers. This CNT fiber has four unique advantages which are suit for supercapacitor materials. First, the CNT fibers have high electrical conductivities of 5.0×10^5 S m^{-1} and this value is two orders of magnitude higher than that other CNT fibers for electrochemical applications (1-2) $\times 10^3$ S m^{-1} [4, 5]. Second, the CNT fibers have large specific areas of 500-1000 m^2 g^{-1}, allowing for a large storage of electric charges in surpercapacitor devices [6]. Third, the CNT fibers exhibit favorable mechanical properties, such as elastic behavior and resistance to cyclic stretching [7, 8]. The CNT fibers are tough enough to be not fractured, which can keep the electronic transport free. Fourth, the CNT fibers are continuous macroscopic yarns and their length and quality can be controlled in synthesis and spinning process to meet the need of electronic devices.

2. EXPERIMENTAL

These CNT fibers fabricated by the CVD spinning method are continuous, concentric, and discrete. Millions of these CNT fibers can self-assemble into a multilayered CNT bundles in the gas flow when a mixture of acetone and ethanol is used as the carbon source during fabrication. The details of CNT fibers fabrication have been reported in other papers [3].

A three-electrode electrochemical cell coupled to a CHI 660C electrochemical workstation (Chenhua Instrument Corp., Shanghai, China) was used for the cyclic voltammetry (CV) at a scan rate of 25 $mV \cdot s^{-1}$ on the potential interval -0.2~0.8 V vs. Ag^+/Ag in 2 M NaCl (Kewei Chemical Reagent Corp., Tianjin, China) aqueous solution. The weaved CNT fiber fabrics were used as the working electrode with an Ag/AgCl reference electrode (Leici Instrument Corp. Shanghai, China) and a Pt wire counter electrode.

Scanning electron microscopy (SEM) was performed on a XL30ESEM, Philips Corp. Holland. Transmission electron microscopy (TEM) was performed on a Tecnai G2 F20, Philips Corp. Holland.

3. RESULTS AND DISCUSSION

Macroscopic CNT bundles are flexible like human hairs, as seen in fig. 1a. The bundle can be clear seen from optical microscope in fig. 1b. The CNT bundles can be enwound or spun on a spool as shown in fig. 1c. We enwind the CNT bundles on a glass rod. To study the electrochemical capacitance properties, the CV experiments are conducted in an electrochemical work station with a conventional three-electrode system in a 2 mol dm^{-3} NaCl aqueous solution. As fig. 1d and fig. 1e shown, here the CNT fibers act as the working electrode and the end of enwound CNT bundle is connected to a termination of the electrochemical work station. An Ag/AgCl reference electrode as the reference electrode and a Pt wire as counter electrode, respectively. Fig. 1f is the CV curve of this CNT fiber electrode. The wide and close symmetric shape of the CV curve indicates a good capacitive behavior. Electrochemical capacitance was calculated from the area of the rectangle as the reversible charge-discharge section, divided by the weight of the CNT fiber in the fabric (0.60 mg), which gave a capacitance of 60.4 $F \cdot g^{-1}$. The mass capacitance in F g^{-1} of the supercapacitor was calculated from the integral area of the dashed rectangle as the reversible charge-discharge section in CV curves (figure 1f, 2d and 3d) according to the equation: $C = \frac{A_c + A_d}{\nu \times \Delta V \times m}$, where A_c and A_d represent the integral charge area and the discharge area, respectively. ν is the scan rate in V s^{-1}, ΔV is the potential widow of the dashed rectangle and *m* is the average mass of the CNT fibers [9, 10] . Commercial carbon fibers were also measured as a reference which exhibited negligible capacity, indicating the capacitance for the fabric only came from the CNTs in the fibers and their surface areas.

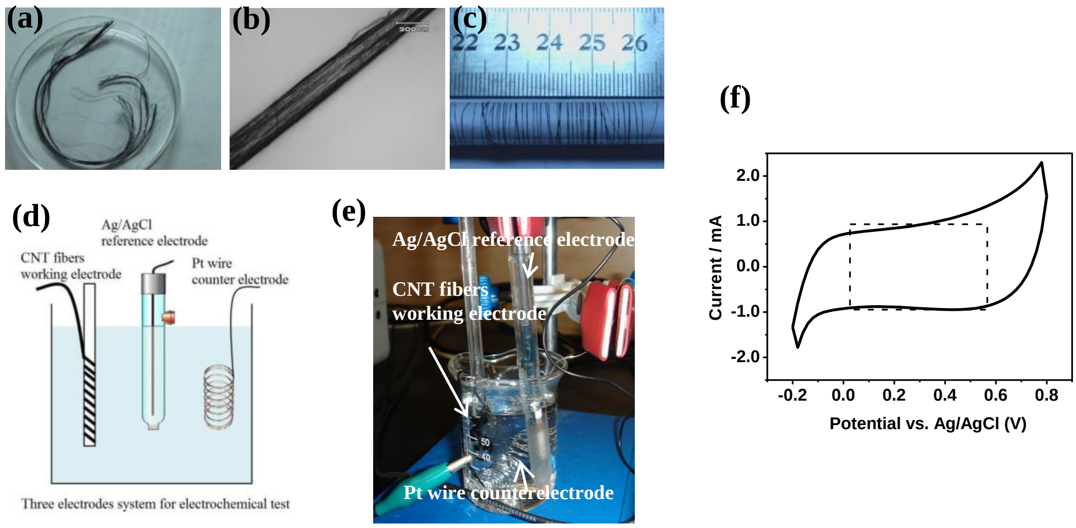

Figure 1. The photographs of CNT fibers and electrochemical test for CNT fibers. **(a)** The photographs of CVD synthesized CNT fibers; **(b)** The optical microscope image of a CNT fiber bundle; **(c)** CNT fibers spun on a spool, showing the CNT fibers is continuous, uniform, and reelable; **(d)** The schematic illustration of three electrodes system for CNT fibers electrochemical test. (CNT fibers as working electrode, Ag/AgCl as reference electrode, and pure Pt wire as counter electrode); **(e)** The photographs of three electrodes system of CNT fibers for electrochemical tests; **(f)** The CV curve of CNT fibers.

Using three electrodes system as fig. 1e shown, the CNT fibers, as a working electrode, were enwound on a glass rod and connected to the termination of the electrochemical workstation to employed CV test at a scan rate of 10, 25, 50 and 100 mV·s^{-1} on the potential interval -0.2~0.8 V vs. Ag^+/Ag in 2 M NaCl aqueous solution. From CV curses in fig. 2, we can see the CNT fibers has no typical supercapacitor rectangle shape in CV graph at the scan rate of 50 and 100 mV s^{-1}. This mainly because at fast scan rate, the electrons transfer in CNT fibers is not fast enough to complete the charge and discharge process. At 10 and 25 mV s^{-1}, the CV graph of the CNT fibers exhibits the typical supercapacitor properties. Therefore, at the low scan rate (≤ 25 mV s^{-1}), it is appropriate to do the supercapacitance measurement. In the work in this paper, we choose 25 mV s^{-1} scan rate to conduct CV test for weaved CNT fibers.

As for fabricate the weaved CNT fibers, we stitched several meter-long continuous CNT fiber (0.64 mg) into a single jersey fabric by 13×10 lines to form a cross-linked weaved fabric in the dimension of 23×18 mm, shown in fig. 3a and fig. 3b. To making good conjunction with the electrochemical instrument, the end of weaved fiber was connected to a copper wire with Sn paste as shown in fig. 3a.

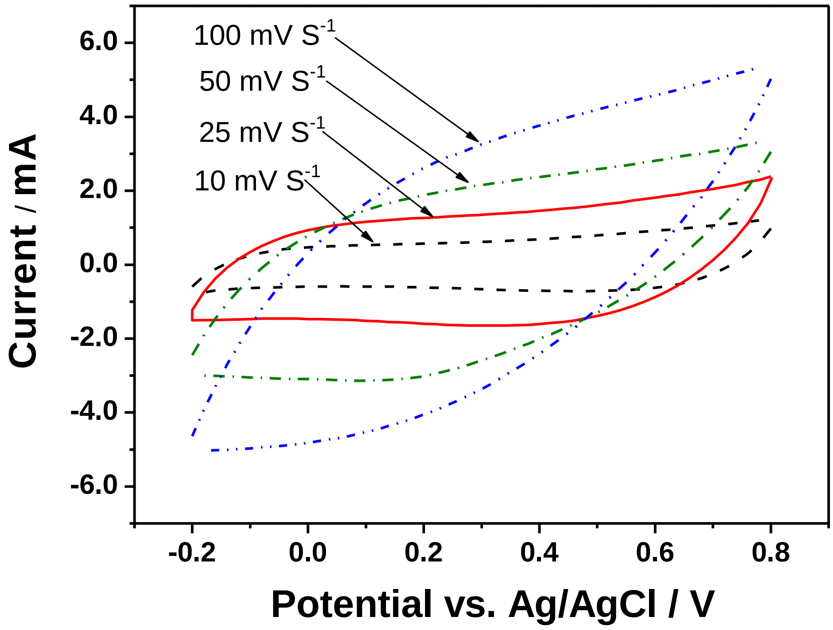

Figure 2. CV curves of CNT fibers at scan rate of 10, 25, 50 and 100 mV s^{-1}.

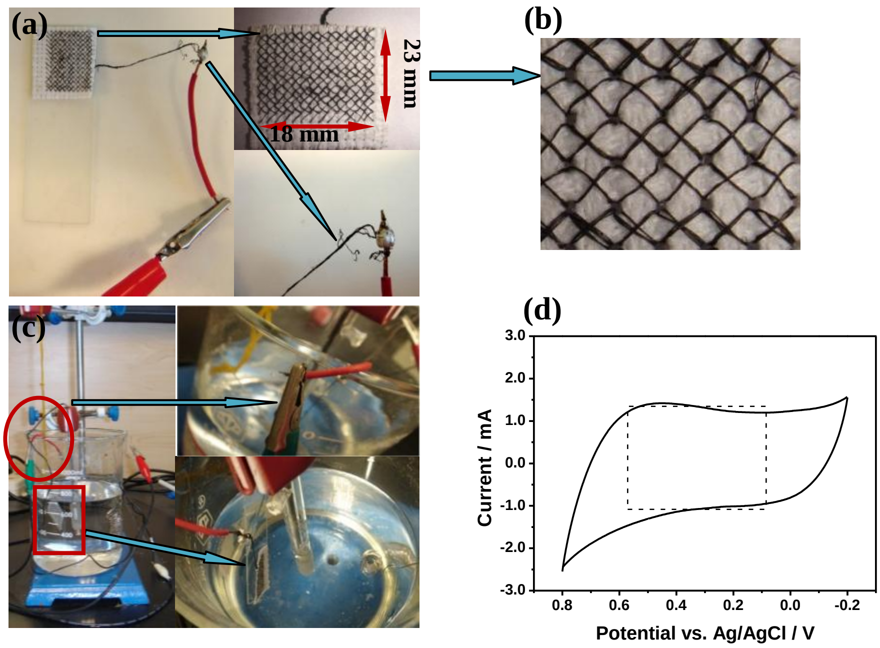

Figure 3. The photographs of weaved CNT fibers on a cloth and the electrochemical test for this weaved CNT fiber cloth. **(a)** The weaved CNT fiber cloth electrode; **(b)** The large image of CNT fiber weaved on a cloth; **(c)** The photographs of three electrodes system of weaved CNT fiber cloth for electrochemical tests; **(d)** The CV curve of weaved CNT fiber cloth.

The copper wire was coated with a polymer and the Sn paste was coated with epoxy resin as the insulators. Fig. 3c is the photographs of three electrode system for electrochemical test of weaved CNT fiber cloth and fig. 3d is the CV result of it. The wide and close symmetric shape of the CV curve indicates a good capacitive behavior. Electrochemical capacitance was calculated as 76.4 F g^{-1}. The same area jersey fabric with no CNT fibers was conducted with CV test under the same condition to investigate the background capacitance and the blank jersey fabric employed no electrochemical capacity properties, so the 76.4 F g^{-1} is only the capacitance of CNT fibers.

To further remove the background disturbance and investigate the pure electrochemical properties of the CNT fibers, we make a pure-weaved CNT fabric as one fabric, which here we call it a pure-weaved CNT fabric.

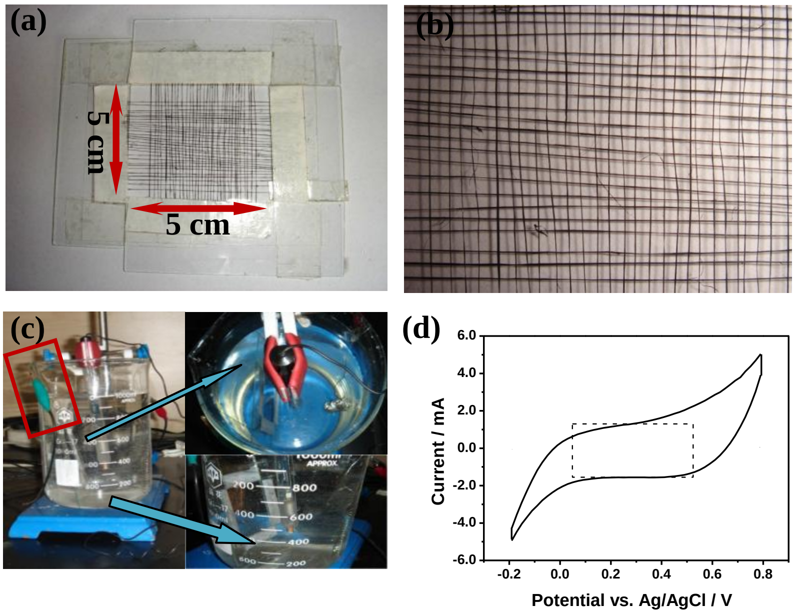

Figure 4. The photographs of a pure-weaved CNT fabric and the electrochemical test for this CNT fabric. **(a)** The pure-weaved CNT fabric; **(b)** The large image of self-weaved CNT fabric; **(c)** The photographs of three electrodes system of self-weaved CNT fabric for electrochemical tests; **(d)** the CV curve of self-weaved CNT fabric.

As shown in fig. 4a, this CNT fiber fabric was weaved by five meter-long continuous CNT fibers (0.71 mg). These fibers were manipulative weaved into 33×29 pieces of cross-linked CNT strands in the dimension of 5×5 cm. The CNT strands in this fabric intervened by each other to make the structure most like a fishing net as fig. 4b shown. The ends of all CNT strands were gathered to one 'last' strand by hand twisting. The whole CNT fabric adhered on four glass patches which were acted as supporting brackets. This CNT fabric and its glass bracket were all immersed in the NaCl solution as a working electrode as fig. 4c shown. The 'last' one strand was directly connected to the terminator of electrochemical workstation. As the CV curve shown in fig. 4d, the capacitance of this CNT fiber was 80.9 F g^{-1} whose value is the highest in the same kind of CNT fabrics.

All though above three kind of weaved CNT fibers have different weaved method, they all exhibit high electrochemical capacitances which can be attributed to the high electrical conductivity and the multiple-layered structure of the fibers that allow for an effective contact with the electrolyte. As shown in fig. 5a, SEM images of CNT fibers, there are hollow and multilayer microstructures insert the CNT fibers. From fig. 5d, TEM observation confirms that the layered yarn consists of high-purify CNTs. Thereby, these multilayer CNT fibers hold a large active specific surface area in the electrolyte. It can be seen from fig. 5b and fig. 5c, CNT bundles are densely packed together to form a CNT yarn surface. Additionally, the CNT bundles oriented in order, aligned along the fiber axis. The ordered orientation of these CNT bundles enhances electron transfer which benefits the electrical conductivity.

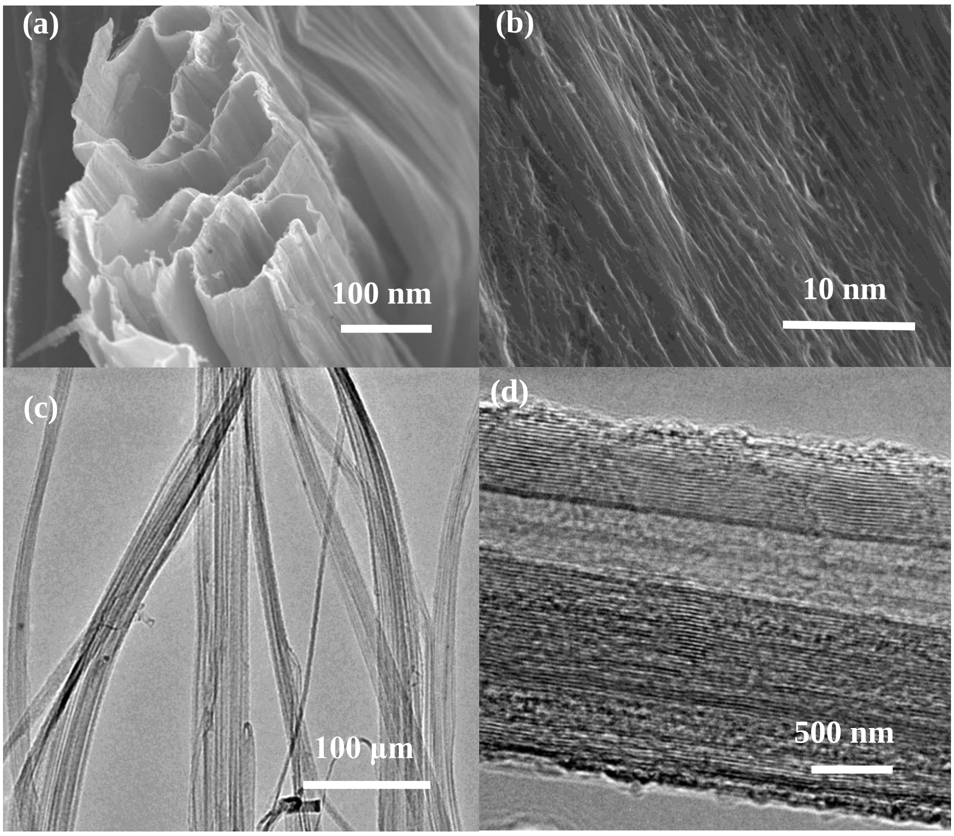

Figure 5. Microstructures of the multilayered CNT fibers observed by SEM **(a, b)** and TEM **(c, d)**. **(a)** Cross-sections of a group of as-spun CNT fibers, showing the hollow, multilayer microstructures insert; **(b)** A CNT yarn surface showing densely packed CNT bundles aligned along the fiber axis; **(c)** The CNT bundles observed by TEM; **(d)** High-resolution TEM images of a CNT fiber.

The supercapacitances of these three woven CNT fibers are all between the extents of 60-80 F g^{-1}, because the woven CNT cloth or fabric is all from a same CNT synthesized by the same CVD spinning. However, there are some differences of capacitance value (~ 20 F g^{-1}) among these three woven CNT fabric because of the different weave technique. Among the three weaved fibers, the pure-weaved CNT fabric (fig. 4d) exhibits the highest capacitance, which almost attributes to the best contact with the electrolyte. As figure 5b shown, the CNT fabric is good ordered, uniform, and tightly cross-linked together. When it immerses into the NaCl solution, this fabric structure keeps the almost

CNT surface contacts with the electrolyte, allowing for excellent charge transfer at the solid-liquid interface. Moreover, the pure CNT fabric (fig. 4) is directly connected with the termination of electrochemical workstation without the assistants of Sn paste and Cu wire. At this circumstance, the capacitance is still high which indicated the electrical conductivity of the CNT fiber is extraordinary.

Our weaved fabric CNT fibers have especially electrochemical performances compared to pioneering work by Poulin [11] and Baughman [12]. They have established processing methods for preparing continuous fibers of CNTs and CNT composites that are ideal for electronic textiles. However, the electrochemical capacity of their CNTs fibers is very low. Baughman et al [12] weaved the CNTs onto a cloth and its capacity is only 5 F g^{-1} which is far lower than our weaved CNTs fabrics in this report. The capacitances of our CNT fabrics are about 60-80 F g^{-1}, whose value is the highest in the same kind of CNT fabrics (5-50 F g^{-1}) [11-16]. Nevertheless, CNT composites usually have higher capacitances according to some reports [17-20], which are about 100-600 F g^{-1}. But these CNT composites are not the pure weaved fabric CNT fibers which are mentioned in this report, and they have no comparability with our fabric CNT fibers.

The electrochemical performances of CNT fibers own to their producing mechanically robust, high conductivity and high surface area. Therefore, to improve the electrochemical performances of these weaved CNT fibers, the proper way focus on the preparation process. Furthermore, using CNT fibers as woven carrier, the other electrochemical active molecule can combine on the surface of CNT fibers, which will further improve the energy storage properties of the wearable electronic devices. Overall, we believe these wearable CNT fabrics will find a wide range of applications.

4. CONCLUSIONS

We report the use of CNT fibers as weaved fabric electrodes for energy storage device applications. The weaved CNT fabric offers many advantages such as a large active specific surface area, high electrical conductivity, enhanced electron transfer as well as high chemical stability, suitable for supercapacitor devices. The capacitances of our CNT fabrics are about 60-80 F g^{-1}, whose value is the highest in the same kind of CNT fabrics. The CNT fabrics are flexibility, stretchability, and lightweight, so they can be weaved into kinds of textiles for energy storage application, which will significantly benefit the development of wearable and stretchable electronics.

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References

1. L. B Hu, M. Pasta, F. L. Mantia, L. F. Cui, S. M. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han, Y. Cui. *Nano Lett.* 10 (2010) 708.

2. Y. L. Li, A. Kinloch, A. H. Windle. *Science* 304 (2004) 276.
3. X. H. Zhong, Y. L. Li, Y. K. Liu, X. H. Qiao, Y. Feng, J. Liang, J. Jin, L. Zhu, F. Hou, J. Y. Li. *Adv. Mater*. 22 (2010) 692.
4. S. W. Lee, B. S. Kim, S. Chen, Y. Shao-Hor, P. T. Hammond. *J. Am. Chem. Soc.* 131 (2009) 671.
5. S. R. Shin, C. K. Lee, I. So, J. H. Jeon, T. M. Kang, C. W. Kee, S. I. Kim, G. M. Spinks, G. G. Wallace, S. J. Kim. *Adv. Mater.* 20 (2008) 466.
6. X. L. Feng, Y. Y. Liang, L. J. Zhi, A. Thomas, D. Q. Wu, I. Lieberwirth. *Adv. Funct. Mater.* 19 (2009) 2125.
7. A. E. Aliev, J. Oh, M. E. Kozlov, A. A. Kuznetsov, S. L. Fang, A. F. Fonseca, R. Ovalle, M. D. Lima, M. H. Haque, Y. N. Gartstein, M. Zhang, A. A. Zakhidov, R. H. Baughman. *Science* 323 (2009) 1575.
8. W. J. Ma, L. Q. Liu, R. Yang, T. H. Zhang, Z. Zhang, L. Song, Y. Ren, J. Shen, Z. Q. Niu, W. Y. Zhou, S. S. Xie, *Adv. Mater.* 21 (2009) 603.
9. L. J. Ci, N. Punbusayakul, J. Q. Wei, R. Vajtai, S. Talapatr, P. M. Ajayan. *Adv. Mater.* 19 (2007) 1719.
10. C. Masarapu, H. F. Zeng, K. H. Hung, B. Q. Wei. *ACS Nano* 3 (2009) 2199.
11. B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, P. Poulin. *Science* 290 (2000) 1331.
12. A. B. Dalton, S. Collins, E. Muñoz, J. M. Razal, V. H. Ebron, J. P. Ferraris, J. N. Coleman, B. G. Kim, R. H. Baughman. *Nature* 423 (2003) 703.
13. S. W. Lee, B. S. Kim, S. Chen, Y. Shao-Horn, P. T. Hammond. *J. Am. Chem. Soc.* 131 (2008) 671.
14. J. Wang, R. P. Deo, P. Poulin, M. Mangey. *J. Am. Chem. Soc.* 125 (2003) 14706.
15. T. Iwasaki, T. Maki, D. Yokoyama, H. Kumagai, Y. Hashimoto, T. Asar, H. Kawarada. *Phys. Stat. Sol. (RRL)* 2 (2008) 53.
16. M. Jung, H. G. Kim, J. K. Lee, O. S. Joo, S. I. Mho. *Electrochimica Acta* 50 (2004) 857.
17. H. S. Park, B. G. Choi, S. H. Yang, W. H. Shin, J. K. Kang, D. Jung, W. H. Hong. *Small* 5 (2009) 1754.
18. S. B. Ma, K. W. Nam, W. S. Yoon, X. Q. Yang, K. Y. Ahn, K. H. Oh, K. B. Kim. *J. Power Sources* 178 (2008) 483.
19. S. R. Sivakkumar, W. J. Kim, J. A. Choi, D. R. MacFarlane, M. Forsyth, D. W. Kim. *J. Power Sources* 171 (2007) 1062.
20. E. Frackowiak, V. Khomenko, K. Jurewicz, K. Lota, F. Béguin. *J. Power Sources* 153 (2006) 413.

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