



Short communication

Vertically aligned double-walled carbon nanotube electrode prepared by transfer methodology for electric double layer capacitor

Yuichi Honda^a, Masayuki Takeshige^a, Hideki Shiozaki^b, Takaharu Kitamura^b, Kenji Yoshikawa^b, Supriya Chakrabarti^c, Osamu Suekane^d, Lujun Pan^e, Yoshikazu Nakayama^{f,g}, Masaki Yamagata^a, Masashi Ishikawa^{a,*}

^a Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

^b Hitachi Zosen Corp., 2-11 Funamachi 2-Chome, Taisho-ku, Osaka 551-0022, Japan

^c Osaka Science & Technology Center, Innovation Plaza Osaka, 3-1-10 Techno-stage, Izumi, Osaka 594-1144, Japan

^d Osaka Science & Technology Center, Technology Research Institute of Osaka Prefecture, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan

^e Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

^f Department of Mechanical Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

^g Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

ARTICLE INFO

Article history:

Received 29 July 2008

Received in revised form 9 September 2008

Accepted 9 September 2008

Available online 18 September 2008

Keywords:

Double-walled carbon nanotube

Electric double layer capacitor

Vertically aligned DWCNT

Transfer

Rate capability

ABSTRACT

We successfully prepared a vertically aligned double-walled carbon nanotube (DWCNT) sheet by a transfer procedure from a silicon substrate as a DWCNT seedbed that was covered with catalyst grains to an aluminum sheet as a current collector for application to a high-performance electrode for an electric double layer capacitor (EDLC). The charge–discharge characteristics and EDLC performances of the aligned DWCNT electrode were evaluated and compared with those of a vertically aligned multi-walled CNT (MWCNT) electrode. The gravimetric capacitance of the DWCNT electrode was ca. four times larger than that of the MWCNT electrode. The rate capability of the DWCNT electrode was found to be excellent. This is mainly ascribed to our transfer technique.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

An electric double layer capacitor (EDLC) is composed of two non-faradic electrodes and an electrolyte. Its function stores charges at an electric double layer interface that consists of space charges in an electrode bulk and physical adsorption of counter ions in an electrolyte [1]. In general, activated carbon (AC) material with a high specific surface area, e.g., 800–3000 m² g⁻¹, has been utilized as electrode material for EDLC [2–10]. However, the grain boundary resistance between AC particles decreases the power density of EDLC.

To solve this problem, we observed that carbon nanotube (CNT) could potentially provide enough electronic conductivity and the order of nanoscale in an electrode [11–13]. The interlayer spacing of multi-walled CNT (MWCNT) [14] is generally smaller than the adsorption ion size [15], so no ions can penetrate the MWCNT inter-

layer to generate capacitance. Therefore, a gravimetric capacitance per MWCNT weight would decrease with increased MWCNT layers.

Considering this context, single-walled CNT (SWCNT) seems most suitable as an EDLC electrode material because it is composed of only a single carbon network layer. However, SWCNT has some undesirable physical properties for EDLC performance. For example, not all SWCNTs inevitably exhibit metallic high conductivity, because they have three chiral structures of a graphene sheet, two of which are semi-conductive [16]. Furthermore, the SWCNT diameter is usually smaller than that of MWCNT. When the diameter is smaller, the electronic conductivity depends more strongly on the chirality of a graphene sheet [17–19]. Thus here we focused on double-walled CNT (DWCNT) as an ideal CNT for EDLC electrode material. DWCNT should satisfy both reasonable electric conductivity and gravimetric capacitance because it is composed of the smallest number of walls among MWCNTs, which can exclude extra weight for generating high gravimetric capacitance.

Concerning electron pathways in the stack of DWCNTs for realizing high rate capability, the electric conductivity along the longitudinal direction of any CNT, i.e., the *a* axis direction of a basal

* Corresponding author. Tel.: +81 6 6368 0952; fax: +81 6 6368 0952.
E-mail address: masaishi@ipcku.kansai-u.ac.jp (M. Ishikawa).

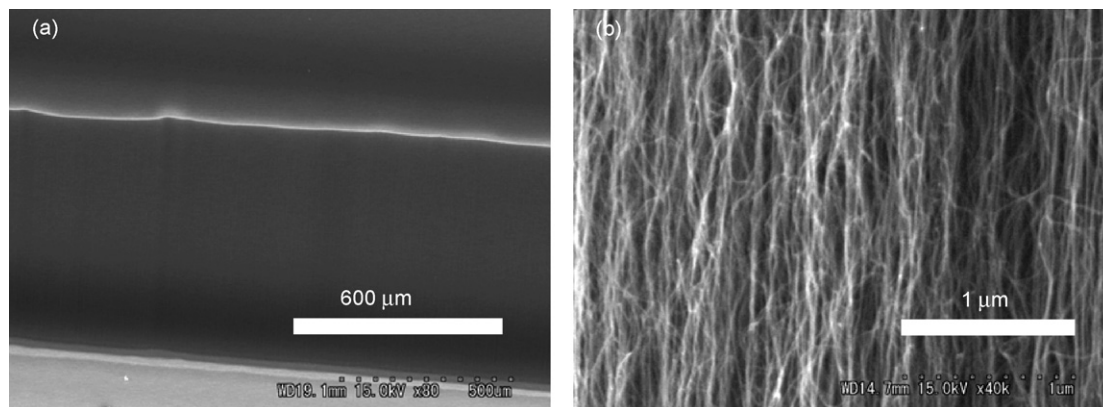


Fig. 1. SEM images of as-grown DWCNTs at (a) low and (b) high magnifications.

plane, is generally much higher than that between CNTs, i.e., the contact surfaces of the basal planes (along the *c* axis). Therefore, one optimal electrode structure would be that each DWCNT is vertically aligned on a current-collector substrate, i.e., each highly conductive sidewall of DWCNT must be directly connected to the current collector without any bundles. Recently, a novel preparation method for highly ordered SWCNTs with a long length (mm-scale) was reported and applied to an EDLC electrode [20]. Nonetheless, it is not clear that all SWCNTs were directly connected to a current collector, because SWCNTs appeared rather horizontally aligned along a current collector surface, judging from the reported photographs indicating the electrode structure.

In this work, we fabricated a vertically aligned DWCNT electrode by utilizing “transfer methodology” [21,22], that is, the transfer of brush-like CNT from a silicon substrate to a current collector coated by conductive cement to maintain the original brush morphology fabricated by a chemical vapor deposition (CVD) method. In particular, we successfully fabricated the aligned DWCNT electrode even with a nanotube 700 μm long. We found that the gravimetric capacitance of the aligned DWCNT electrode was about four times larger than that of the corresponding MWCNT electrode while maintaining excellent high rate performance.

2. Experimental

The vertically aligned DWCNTs were synthesized with a thermal catalytic CVD technique. The detailed process and synthesis conditions have been described elsewhere [23,24]. The morphology of the DWCNTs was observed by scanning electron microscopy (SEM: Hitachi S-4300) as well as high-resolution transmission electron microscopy (HR-TEM: Hitachi HF-2000). To evaluate the surface conditions of the DWCNT electrode, Raman spectroscopy of the synthesized DWCNT was performed using a monochromator (250IS-3) equipped with a detection device (cooling CCD camera DV401-FIS). The 632.8-nm laser line of a He-neon (Ne) laser (Seki Technotron) was used for excitation with output power of 15 mW.

The resulting vertically aligned DWCNT was transferred to an aluminum (Al) current collector sheet (thickness: 50 μm) coated homogeneously with a slight amount of electrically conductive cement, i.e., phenolic glue containing 5 wt.% graphitic carbon (thickness: less than 10 μm) to maintain the original vertical alignment on the Al sheet. Such a vertically aligned DWCNT sheet is hereinafter denoted as a “DWCNT sheet.” An MWCNT sheet (length: 300 μm , average diameter: ca. 14 nm, I_G/I_D : ca. 1.2) was also employed as a test electrode for comparison in the charge–discharge performance.

A test cell consisted of a pair of DWCNT or MWCNT sheet electrodes with a commercially available propylene carbonate (PC) electrolyte containing 1.96 M triethylmethylammonium tetrafluoroborate (TEMABF₄, Tomiyama Pure Chemical Industries). A separator applied to the cell was made of cellulose (Nippon Kodoshi TF4050). The electrodes and the separators were immersed in a 1.96 M TEMABF₄-PC solution for 5 min under reduced pressure immediately before their installation.

As for the galvanostatic discharge test, the cell was charged to 2.5 V and then discharged to 0 V at a constant current density in a range from 0.1 to 20 A g⁻¹ using the Battery Labo System (Keisokuki Center). Cyclic voltammetry was performed at a scan rate from 10 to 4000 mV s⁻¹ in a cell voltage range between -2.5 and 2.5 V using an electrochemical analyzer (BAS, ALS model 650B). Capacitor assembly was carried out in a dry room (dew point: -60 °C). All experiments were performed at room temperature (25 °C).

3. Results and discussion

Fig. 1(a) reveals that as-grown DWCNTs fabricated by the thermal catalytic CVD technique are uniform and macroscopically aligned vertically on a Si substrate. The thickness of the DWCNT bulk layer is ca. 700 μm . Although each DWCNT appears somewhat wavy with adjoining DWCNT parts, brush-like DWCNTs contain no hairball-like, bulky bundles, as shown in Fig. 1(b). Furthermore, substantial free spaces are found among the brush-like DWCNTs.

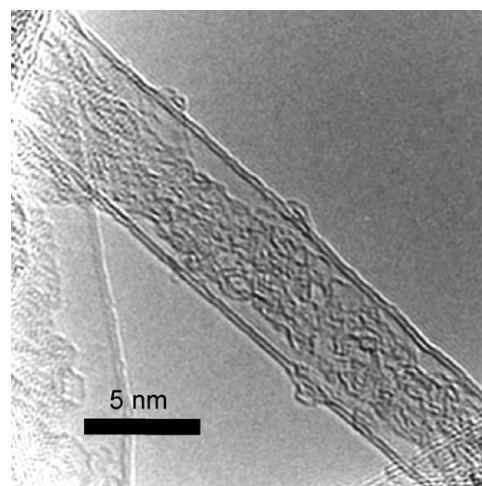


Fig. 2. HR-TEM image of an as-grown DWCNT.

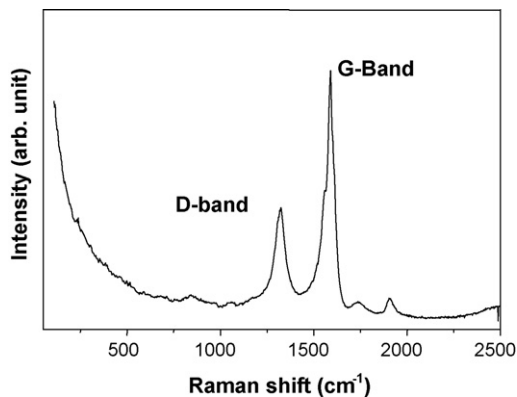


Fig. 3. Raman spectrum of as-grown DWCNTs.

Such open morphology of brush-like DWCNTs has the potential to provide easy access for ions to the spaces between DWCNTs and to the DWCNT surface.

Fig. 2 shows an HR-TEM image of an as-grown DWCNT. The tube wall is obviously composed of two graphene sheets, where the mean outer and inner diameters are ca. 4.9 and 4.2 nm, respectively. The outer surface of the sidewall appears partly covered with amorphous carbon. Detailed HR-TEM study revealed that most of the nanotubes (~80%) are DWCNTs, and the rest are MWCNTs with a very low percentage of SWCNTs. Raman spectroscopy was applied to an as-grown DWCNT sample to evaluate their crystallinity. The observed Raman spectrum is shown in Fig. 3. Since a D-band is clearly observed, DWCNTs would have defects to some extent. This clear D-band also indicates the existence of amorphous carbons, which are in good agreement with the observation by HR-TEM. A

radial breathing mode (RBM) is not observed in less than 200 cm^{-1} , probably because the inner and outer diameters of DWCNTs are large (ca. 4.2 and 4.9 nm, respectively) and coexistent MWCNTs (ca. 20% as mentioned above) should have no contribution to RBM.

The current response of the capacitor electrode in the operational cell voltages must be investigated. Fig. 4 shows the cyclic voltammograms (CVs) obtained for a symmetrical two-electrode cell. Here specific capacitance (C_s) was estimated from the following equation:

$$C_s = \frac{2I}{\nu m} \quad (1)$$

where I is the current, ν is the scan rate, and m is the mass of the active material at a single electrode. At the lowest scan rate, 10 mV s^{-1} (Fig. 4(a)), the obtained CV shows a butterfly shape, where the capacitance (or the current) increases with increasing cell polarization without ohmic distortion, suggesting that the internal series resistance is very low. The minimum capacitance is 31 F g^{-1} at 0 V while the maximum capacitance is 47 F g^{-1} at ca. 2.5 V at 10 mV s^{-1} . The present dependence of the capacitance on the voltage implies that the thickness of an electric double layer may be shrunk by a strong electric field, which is oriented vertically from the sidewall surface of the DWCNT, with an increase in the applied cell voltage. Other possibility is a contribution of a space charge layer at the DWCNT electrode, which might cause such voltage-dependent current [5,25].

To evaluate the high rate performance of the capacitor with the DWCNT electrodes, a test cell was also scanned at a rate from 100 to 4000 mV s^{-1} (Fig. 4(b)–(d)). Although some ohmic distortion appears at extremely high scan rates of 1000 and 4000 mV s^{-1} , note that such ultra-high rate scanning still generates considerable capacitance that dominates electronic and ionic resistance despite

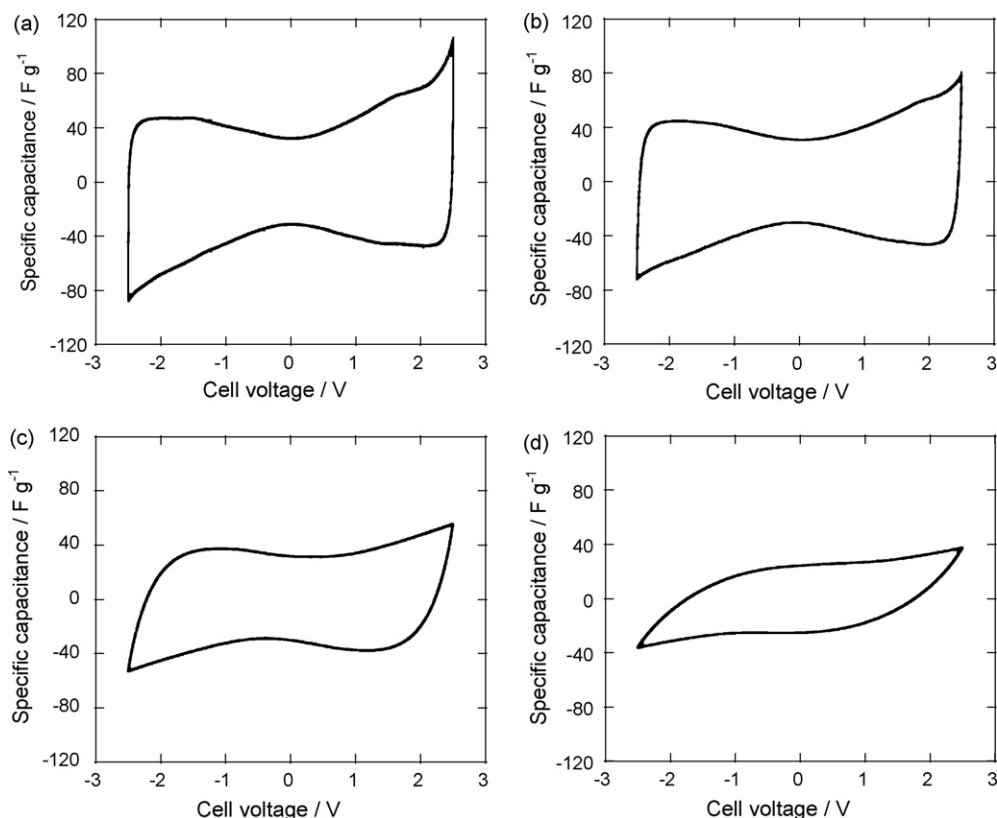


Fig. 4. Cyclic voltammograms for vertically aligned DWCNT sheet electrode at various scan rates: (a) 10 , (b) 100 , (c) 1000 , and (d) 4000 mV s^{-1} .

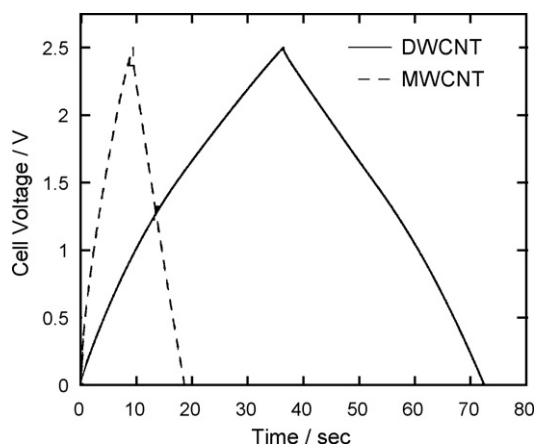


Fig. 5. Cell voltage profiles with galvanostatic (2 A g^{-1}) charge–discharge duration for EDLCs composed of MWCNT and DWCNT sheet electrodes.

the active material thickness of $700 \mu\text{m}$. This can be attributed to the following two origins: one is directly derived from our transfer methodology; each DWCNT is connected directly to the Al current collector, realizing continuous graphene layers of DWCNT as ideal electron pathways: the other is that ion transfer is quite facile due to the bundleless, open structure of the brush-like DWCNTs. The former should be an especially crucial factor providing ultra-high rate capability for aligned DWCNT electrodes. In fact, although other groups have researched the CV response of vertically aligned DWCNT electrodes, their CVs suffered significant distortion even at several 10 's of mV s^{-1} . The authors ascribed the behavior to the poor contacts of DWCNTs with a substrate, which were interfered by small catalyst particles [26]. More importantly, they directly utilized a low-conductive Si substrate as a current corrector for their electrode that should limit high rate capability. Therefore, our transfer methodology is highly beneficial for realizing extremely high rate capability of a DWCNT electrode.

To elucidate the practical performance as a storage device, a charge–discharge test was performed by applying a constant current. Fig. 5 depicts charge–discharge profiles in a galvanostatic condition at a high rate of 2.0 A g^{-1} . For comparison, an MWCNT sheet, which consists of MWCNTs with an average diameter of 14 nm , was used as an alternative EDLC electrode. The slope of the DWCNT electrode is clearly gentler than that of the MWCNT elec-

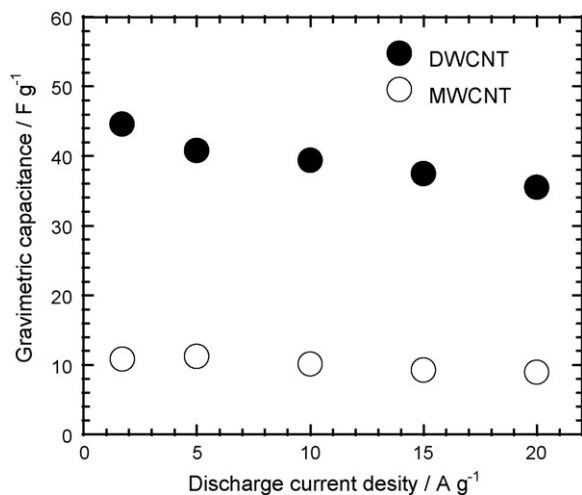


Fig. 6. Relationship between discharge current density and discharge capacitance of DWCNT and MWCNT sheet electrodes.

trode. Furthermore, as for the DWCNT electrode, its capacitance in the high voltage region is larger than that in the low voltage region, which corresponds well to the obtained voltammogram shape (see Fig. 4).

Fig. 6 indicates the relationship between the gravimetric capacitance and the current density in a range from ca. 2.0 to 20 A g^{-1} . The specific capacitance (C_s) was estimated by the following equation:

$$C_s = \frac{2I\Delta t}{\Delta Vm} \quad (2)$$

where I is the discharge current, Δt is the discharging time, ΔV is the change in cell voltage with Δt , and m is the mass of the active material at a single electrode. Note that the capacitance for DWCNT (ca. 44 F g^{-1}) is about four times larger than that for MWCNT (ca. 10 F g^{-1}). Since the interlayer distance of any CNT is generally smaller than the adsorption ion size, no ions can penetrate the CNT interlayer. Thus, the gravimetric capacitance for DWCNT should be much higher than that for MWCNT. Concerning their rate capability, both MWCNT and DWCNT can almost maintain their intrinsic capacitances even at an extremely high rate of 20 A g^{-1} . This result also suggests that each CNT (not only DWCNT but also MWCNT) is directly connected to an Al current collector to form an extremely facile electron pathway utilizing an intrinsic low-resistance bulk property based on excellent conduction along a axis of CNT. We conclude that a vertically aligned DWCNT sheet by the transfer methodology is an outstanding electrode material for EDLC among MWCNT materials.

4. Conclusion

Electrochemical measurements were performed for a highly oriented DWCNT sheet as an EDLC electrode. From the galvanostatic discharge test, gravimetric capacitance for the aligned DWCNT electrode was about four times larger than that of the tested MWCNT electrode. This result demonstrates that a decrease in the wall layer number of CNTs enhances the gravimetric capacitance. The rate capability of the aligned DWCNT electrode was excellent, similar to the MWCNT electrode, which indicates that the direct connection by the transfer methodology of each CNT to a conductive substrate provides an ideal electronic pathway along a basal CNT plane. The present results suggest that the aligned DWCNT sheet is a promising material for a high-performance EDLC electrode.

Acknowledgements

The authors gratefully acknowledge the foundation support from the Osaka Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence, JST (to all the authors), and partly from the Research and Development Organization of Industry–University Cooperation from the Ministry of Education, Culture, Sports, Science and Technology of Japan (to Ishikawa).

References

- [1] B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Publisher, New York, 1999.
- [2] D. Lozano-Castello, D. Cazorla-Amoros, A. Linares-Solano, S. Shiraishi, H. Kurihara, A. Oya, *Carbon* 41 (2003) 1765–1775.
- [3] S. Alvarez, M.C. Blanco-Lopez, A.J. Miranda-Ordieres, A.B. Fuertes, T.A. Centeno, *Carbon* 43 (2005) 866–870.
- [4] G. Gryglewicz, J. Machnikowski, E. Lorenc-Grabowska, G. Lota, E. Frackowiak, *Electrochim. Acta* 50 (2005) 1197–1206.
- [5] O. Barbieri, M. Hahn, A. Herzog, R. Kottz, *Carbon* 43 (2005) 1303–1310.
- [6] W. Xing, S.Z. Qiao, R.G. Ding, F. Li, G.Q. Lu, Z.F. Yan, H.M. Cheng, *Carbon* 44 (2006) 216–224.
- [7] E. Raymundo-Pinero, K. Kierzek, J. Machnikowski, F. Beguin, *Carbon* 44 (2006) 2498–2507.

- [8] B. Xu, F. Wu, S. Chen, C. Zhang, G. Cao, Y. Yang, *Electrochim. Acta* 52 (2007) 4595–4598.
- [9] M. Sevilla, S. Alvarez, T.A. Centeno, A.B. Fuertes, F. Stoeckli, *Electrochim. Acta* 52 (2007) 3207–3215.
- [10] C.-L. Liu, W. Dong, G. Cao, J. Song, L. Liu, Y. Yang, *J. Electrochem. Soc.* 155 (2008) F1–F7.
- [11] S. Iijima, *Nature (London)* 354 (1991) 56–58.
- [12] T.W. Ebbesen, H.J. Lezec, H. Hiura, H. Hira, J.W. Bennett, H.F. Ghaemi, T. Thio, *Nature (London)* 382 (1996) 54–56.
- [13] H. Dai, E.W. Wong, C.M. Lieber, *Science* 272 (1996) 523–526.
- [14] A. Peigney, Ch. Laurent, E. Flahaut, R.R. Bacsa, A. Rousset, *Carbon* 39 (2001) 507–514.
- [15] K. Ikeda, N. Yoshida, Y. Shinozaki, M. Kashihara, Y. Hozumi, T. Kawasato, K. Hiratsuka, *Reports Res. Lab. Asahi Glass Co., Ltd.*, 54 (2004) 33–39.
- [16] R. Saito, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, *Appl. Phys. Lett.* 60 (1992) 2204–2206.
- [17] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, 1996.
- [18] C.H. Olk, J.P. Heremans, *J. Mater. Res.* 9 (1994) 259–262.
- [19] J.W.G. Wildoer, L.C. Venema, M.S. Dresselhaus, A.G. Rinzler, R.E. Smalley, C. Dekker, *Nature (London)* 391 (1998) 59–62.
- [20] D.N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura, S. Iijima, *Nat. Mater.* 5 (2006) 987–994.
- [21] Y. Honda, T. Haramoto, M. Takeshige, H. Shiozaki, T. Kitamura, M. Ishikawa, *Electrochem. Solid-State Lett.* 10 (2007) A106–A110.
- [22] Y. Honda, M. Takeshige, H. Shiozaki, T. Kitamura, M. Ishikawa, *Electrochemistry* 75 (2007) 586–588.
- [23] S. Chakrabarti, T. Nagasaka, Y. Yoshikawa, L. Pan, Y. Nakayama, *Jpn. J. Appl. Phys.* 45 (2006) L720–L722.
- [24] S. Chakrabarti, H. Kume, L. Pan, T. Nagasaka, Y. Nakayama, *J. Phys. Chem. C* 111 (2007) 1929–1934.
- [25] S. Shiraishi, M. Kibe, T. Yokoyama, H. Kurihara, N. Patel, A. Oya, Y. Kaburagi, Y. Hishiyama, *Appl. Phys. A* 82 (2006) 585–591.
- [26] T. Iwasaki, T. Maki, D. Yokoyama, H. Kumagai, Y. Hashimoto, T. Asari, H. Kawarada, *Phys. Status Sol. (RRL)* 2 (No. 2) (2008) 53–55.