Journal of Ceramic Processing Research. Vol. 12, No. 3, pp. 343~347 (2011)

J O U R N A L O F
Ceramic Processing Research

Electrical impedance properties of a nanoweb electrode embedded carbon nanotube for a bio-chemical sensor

Dae-Sup So[a], Hoon Huh[b], Heon Ham[c], Kwang Bo Shim[c], Hyoun Woo Kim[c] and Inpil Kang[d,*]

[a]*National Nanotechnology Policy Center, Korea Institute of Science and Technology Information, 130-741, Seoul, Korea*
[b]*Cleaner Production Center, Korea Institute of Industrial Technology, 330-825, Cheonan, Korea*
[c]*Division of Material Science and Engineering, Hanyang University, 133-791, Seoul, Korea*
[d]*Mechanical and Automotive Engineering Department, Pukyong National University, 608-739, Busan, Korea*

In this study, carbon nanotube (CNT) based nanoweb electrodes were fabricated and their electrical impedance properties were investigated to develop chemical sensors and biosensors. The nanoweb electrodes were fabricated with multi-wall CNT (MWCNT) based on PAN using an electrospinning technique. The morphology of the nanoweb electrode was investigated utilizing SEM and TEM. With various amounts of buffer solution, the electrical impedance of the composite electrodes was measured using an LCR meter. The capacitance values showed drastic increments while the resistance values only changed within a few percent range. It is found that the addition of CNTs to a nanofiber web can improve not only the sensitivity but also the linearity of a nanoweb compared to a no-CNT web electrode. Since CNTs have excellent electrochemical properties, the electrical impedance of nanoweb embedded CNTs may be remarkably changed by the ions produced by a buffer solution, and this improves the sensing response of the nanoweb electrode consequently.

Key words: Carbon nanotube, Bio-chemical sensor, Nanoweb, Electrospinning.

Introduction

Having a huge surface area, high mechanical strength but light weight, excellent electrical properties, and well-defined chemical characteristics, carbon nanotubes (CNTs) have received much attention as promising materials for sensors [1, 2]. CNTs are electrically conductive and their electrical properties are extremely sensitive when they are bonded to molecules. Since a CNT composite electrode serves as a "reservoir" of target chemical, in general, cyclic voltametric, amperometric, and conductance measurements have been studied to measure the sensing characteristics of CNTs for chemical and bio oriented applications [3-7]. However, from the viewpoint of engineering applications, there are many huddles to the utilization of individual nanotubes as sensor electrodes. It is challengeable to locate a nanotube to the desired spot to achieve a nano-electrode by means of dielectrophoresis or nano-manipulation techniques.

It is required to develop a feasible sensor electrode fabrication process for the mass production of CNT sensors. The nano composite process can be a simple and effective way to develop CNT electrodes with mass-production capability.

The nanoweb may be a promising fabrication methodology for sensor electrodes even though the process is rather more complicated than that of screen printing. Nanowebs fabricated with nanofibers by means of electrospinning have huge bioengineering applications including as drug release membranes, high efficiency filter media, protective clothing materials, bio-transplant materials, etc. Electro spinning is a relatively promising approach to produce bulk material using nanofibers with simple equipment and this process gives nonwoven fabric made up of 100-500 nm diameter fibers, using an electrical field applied to a polymer solution and melt. Electrospinning can fabricate nanowebs having a huge surface area and flexibility, and this can possibly improve the sensitivity of a sensor with a larger surface area-to-unit mass ratio of the bulk electrode [8, 9]. An electrospun non-CNT based nanoweb was demonstrated to be a sensitive sensory material. Wang *et al.* [10, 11] developed an electrospun nanofiber membrane sensor for detecting metal ions and showed that the sensitivity of the nanofiber sensor is almost three orders of magnitude higher than that of thin films of the same material.

The addition of CNTs to a nanoweb has been reported to improve the mechanical and electrical properties of an electrospun nanoweb. Ahn *et al.* [12] fabricated functionalized MWCNT/Poly(ethylene terephthalate) (PET) nanowebs by electrospinning and they reported that the addition of MWCNT produced an electrical conductivity in the electrostatically dissipative range and also increased their tensile strength and modulus. Choi *et al.* [13] fabricated carbon-CNT embedded nanocarbon fiber webs by electrospinning and tested the electrochemical properties of these

*Corresponding author:
Tel : +82-51-629-6167
Fax: +82-51-629-6150
E-mail: ipkang@pknu.ac.kr

webs. They reported that the electrical conductivity and specific surface area increased as the embedded CNT ratio increased. However, CNT application engineering still involves many potential problems in its fabrication process to achieve superior properties at the nano scale to macro scale. In particular considerable huddles such as dispersion and uniform mixing with the matrix polymer should be overcome.

We fabricated CNT-based bulk electrodes for chemical and biosensor applications. In order to, somehow, translate the superior sensing properties of CNTs for industrial sensor applications, CNT- based bulk electrodes were fabricated using electrospinning techniques. Although, nanowebs involving CNTs to improve material properties have been reported, their application for bio and chemical sensor nanowebs has not been reported as yet. Furthermore, a simple and effective measurement for engineering-oriented applications of CNTs has been developed for a bio chemical sensor. Electrochemical based measurements have been widely used for the analysis of bio and chemical sensing, which are rather more complicated than electrical-based measurements in most engineering applications. Electrical impedance (R-C) based measurements were studied since it is simple to develop an electrical circuit for signal processing. Thus, the sensing properties of fabricated CNT nanowebs were tested by means of their electrical impedance change. The electrical impedances were measured under various amount of a buffer solution. An electrical impedance measurement provides a rapid and simple sensing measurement to develop a chemical sensor and bio sensors with bulk nano electrodes. It is anticipated that CNT embedded electrospun nanoweb electrodes based on electrical impedance measurements may provide a feasible fabrication process for mass production of CNT sensors.

Experimental Section

Preparation of CNT based bulk nanoweb electrodes

The nanoweb electrodes were fabricated with MWCNT based on polyacrylonitrile (PAN) using an electrospinning technique. PAN (150,000 g/mol) and N, N-dimethyl formamide (DMF) were purchased from Aldrich Co. MWCNTs (purity of 90% and O.D. 10-15 nm, I.D. 2-6 nm, length of 0.1-10 μm, Aldrich Co.) were used to make a MWCNT-PAN/DMF composite solution. The PAN was dissolved in the DMF to make a spinning solution with a concentration of 12 wt.%. MWCNTs were added to the mixture with DMF to disperse it into the solvent and then sonicated at 20 kHz for ~8 hours to produce a black suspension. Several key parameters such as voltage, gap distance and flow rate were controlled to fabricate uniform electrospun nanofibers. The recipe and the optimum conditions for electrospinning are summarized at Table. 1.

Fig. 1 shows a schematic illustration of the electrospinning equipment.

Since an electrical property is basically required for a sensing electrode, we improved the property by means of embedded MWCNTs into the nanofiber and carbonized the nanoweb through a burning process. The carbonized nanoweb was expected to be electrically conductive after

Table 1. Electrospinning conditions

Variable	Concentration (wt.%)		Viscosity (cP)	Voltage (kV)	Needle diameter (ID Size, mm)	Gap distance (cm)	Flow rate (ml/minute.)
	PAN/DMF	CNT/PAN					
Concentration (CNT/PAN)	12	0	120	16	0.33	15	0.005
		0.5	124				
		1.5	129				
		3	134				

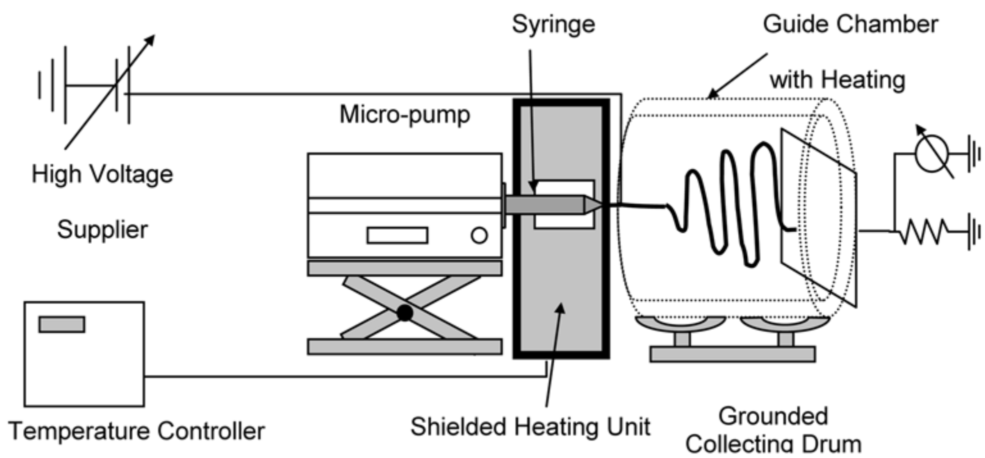

Fig. 1. Schematic illustration of the electrospinning equipment.

this process and the CNT embedded nanoweb can more easily absorb the target chemical in a solution rather than the pure PAN based nanoweb. Because the chemical absorption property of the nanoweb can be significantly improved by adding CNTs to the composite, carbonized and CNT embedded nanowebs were produced in a furnace by the carbonizing process. The MWCNT/PAN-based nanoweb was carbonized through a burning process. The carbonization process seems to improve both the electrical and chemical absorption properties of MWCNT/PAN based nanoweb. To optimize the carbonization process, CNT nanofiber webs were heated to 270 °C with a speed of 1 °C/minute and then stabilized for 1 hour at 270 °C. In a second step, they were heated again to 900 °C with a rate of 5 °C/minute.

Finally, in order to fabricate sensor electrodes, the carbonized nanowebs were cut into proper sizes and two electrodes were connected onto them with silver conducting epoxy to measure the electrical impedance and to reduce the contact resistance as shown in Fig. 2.

Electrical impedance property test

Being a nano-porous and electrical conductive material, an electrically analogues sensor model of CNTs and their composite are represented by a parallel circuit consisting of a resistance and capacitance from electrical impedance spectroscopy (EIS) test [14]. Each electrical impedance component varies under specific physical and chemical conditions. The capacitance value of the sensor shows a very sensitive response under chemical exposure [15]. Based on the preliminary study, the characteristics of CNT bulk electrodes were investigated by varying the amount of buffer solution. A pH 7 buffer solution (Sigma-Aldrich) was applied to each electrode to emulate a biochemical analysis with an amount of 2 μl/drop using a micro pipette. The electrical impedance properties were measured using an LCR meter (HIOKI 3522 LCR HiTESTER) at 1 kHz after fully soaking the electrodes with the buffer solution.

Results and Discussion

The morphology of carbonized nanofibers in the CNT nanoweb was investigated by FE-SEM and TEM. FE-SEM (JEOL, JES-6701F) and FE-TEM (Philips, TecnaiTM, G2F30) were used to measure the morphology of the resulted fibers. Fig. 3 and 4 show the morphology of carbonized nanofibers in CNT nanowebs.

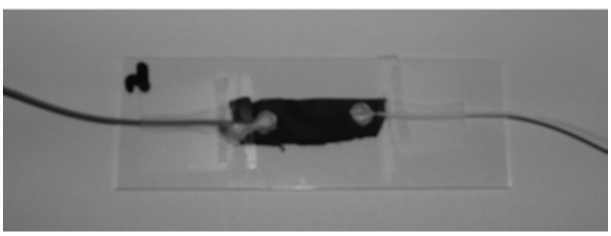

Fig. 2. Carbonized electrospun MWNT/PAN (1 wt.%) nanoweb electrode (18 × 48 mm, R_0=658 Ω, C_0 = 7.17 mF).

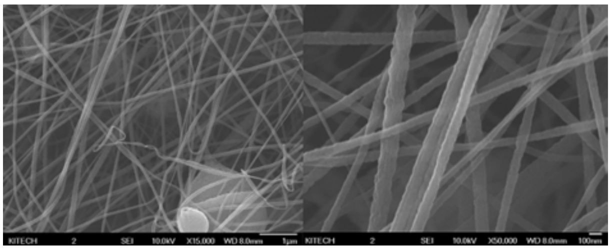

Fig. 3. FE-SEM images of PAN-MWNT/DMF (10 wt.%) nanoweb electrode sample: (a) × 15,000 image, (b) × 50,000 image.

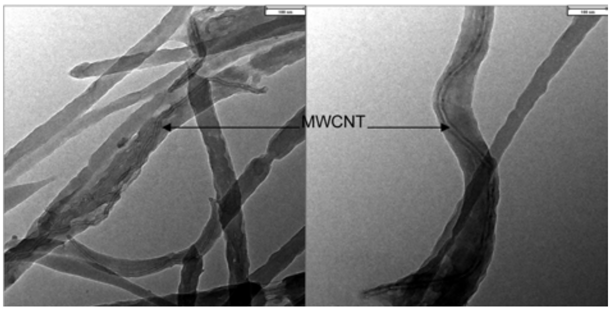

Fig. 4. TEM images of the nanoweb electrode sample showing MWNTs in nanofibers.

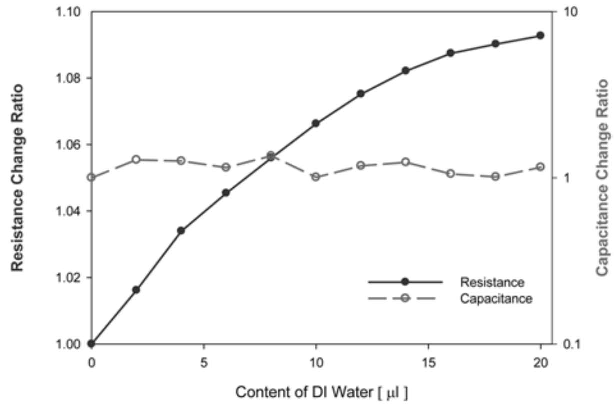

Fig. 5. Electrical impedance changing patterns of a CNT nanoweb (1.5 wt.%) electrode under DI water.

It was found that the MWCNTs were located in nanofibers along the fiber direction in the web from the TEM images and a fine fabrication of nanofibers containing well-aligned MWCNTs similar to that in a literature survey [16] was demonstrated.

The electrical impedances of the CNT nanowebs (1.5 wt.%) were measured with an LCR meter after dropping onto it deionized (DI) water. Fig. 5 shows a DI water test of a nanoweb electrode to find the chemical sensing characteristics of the electrodes.

Having no chemicals in the DI water, this test is expected to give the dopping effect of the electrodes. When DI water droplets were applied to the electrode, the resistance property shows a gradual increment while the capacitance property only shows a small variation in a limited range. The electrical conductivity of the electrode was decreased after dropping the DI water onto it owing to its electrically insulating property. By contrast the capacitance of the electrode was little changed by the DI droplets due to the absence of chemicals in them.

Fig. 6 shows a test of electrical impedances of a CNT nanoweb electrode containing the same amount of CNT (1.0 wt.%).

Because the buffer solution is electrically insulating, the electrical conductivity of the electrode is decreased after dropping the solution on it as well. However because the buffer solution involves some chemicals, the capacitance of the electrode is drastically changed with respect to the concentration of droplets. From the results of the above tests, it is deduced that the capacitance variation of nano electrodes strongly depends on the doping effect caused by chemicals in the solution. The resistance change patterns of nanoweb electrodes are shown in Fig. 7.

The electrical resistance property does not show a distinct sensing characteristic according to the buffer solution concentrations. It is approximately concluded that the electrical resistance property may not be eligible to find chemical targets due to a lower sensitivity. The capacitance change patterns of nanoweb electrodes are shown in Fig. 8. The nanoweb electrodes show a similar impedance changing pattern to film type electrodes under the buffer solution test [17].

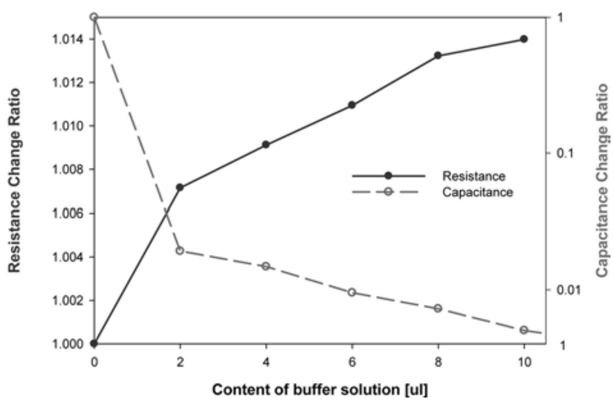

Fig. 6. Electrical impedance change pattern of a CNT nanoweb (1.0 wt.%) electrodes under pH 7 buffer solution.

The capacitance property is drastically changed by more than 50% with respect to its original value according to the buffer solution concentration. In addition, the changing tendency shows linearity in some cases, below 3 wt.% of CNTs, which is desirable to develop new sensory materials for biochemical applications. It has been reported that CNTs improve the electrical and mechanical properties of nanowebs but their effects on nanowebs have rarely been studied for application as bio sensors and chemical sensors. It is found that the addition of CNTs to a nanofiber web can improve the sensitivity of the nanoweb from a comparison with a no CNT sample.

The measured resistance values vary like a drift of other conventional sensors. It is reported that the change of resistance of bulk CNTs can be induced by absorbed molecules on their surfaces and this changes the carrier concentration in the outer graphene layer of the CNTs [5]. However, the capacitance value appears comparatively stable with little variation. The changing patterns of resistance and capacitance show distinct differences over the CNT electrodes. The capacitance values show drastic changes while the resistance values only change within a few percent. An amount of 2 μCl/drop up to 10 droplets was applied to the electrodes and the impedance values show saturated responses after 2-3 drops.

The ions in the solution penetrate into the electrode surfaces and form a double layer charge on the nanotube surfaces. The diffused ions also change the electrical parameters of the electrodes much like a doping effect. Because absorbed molecules on CNT surfaces can act as dopants, the electrical conductivity and the capacitance of the electrodes will change when chemicals in the buffer solution contact the CNTs. This chemical doping may change the impedance of the CNTs and this can be detected by a change in the electrodes' electrical properties.

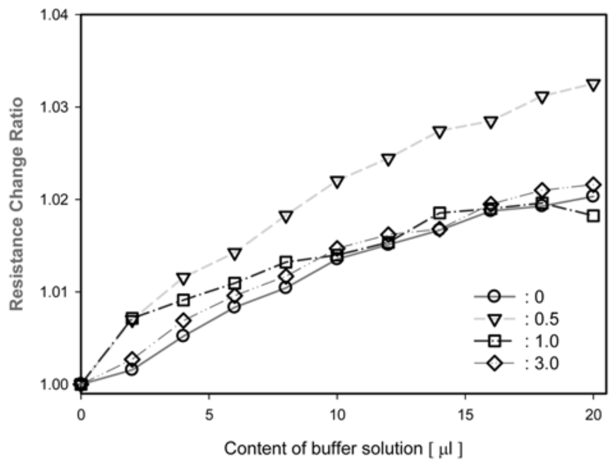

Fig. 7. Electrical resistance change pattern of CNT nanoweb electrodes with variations of CNT contents under a pH 7 buffer solution.

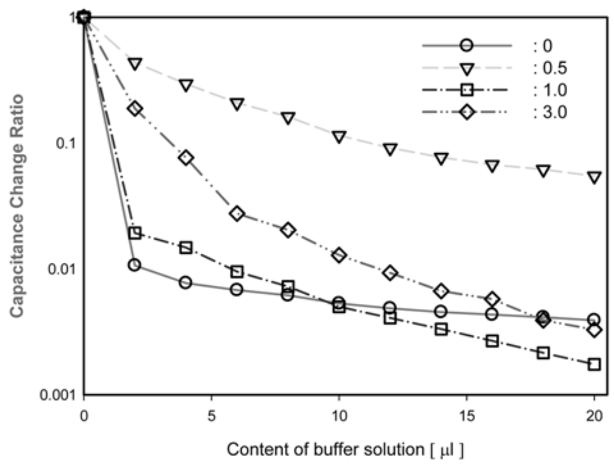

Fig. 8. Electrical capacitance change pattern of CNT nanoweb electrodes with variations of CNT contents under a pH 7 buffer solution.

Having a large surface area, the capacitance of the CNT can be changed remarkably by the ions produced by a buffer solution, and the resistance will be changed as well. A CNT embedded electrospun nanofibrous web improves the electrochemical properties of the web by means of increasing both the specific surface area and electrical conductivity and this is available to develop a promising sensor electrode for bio chemical applications.

In order to develop biochemical sensors, the following topics need to be considered for further study. The CNT based nanoweb electrodes should be functionalized to have a chemical selectivity to absorb targeted chemicals through the surface modification of nanotubes. The efficacy of the diffuse layer caused by the host matrix PAN is necessary to study further. An electrical conversion circuit is required to convert the change of electrical impedances into an analogue or digital output for the signal processing system of biochemical sensor. The variation of the capacitance can be converted into a voltage or digital output using commercial circuits. Eventually, the capacitance response of a CNT nanoweb electrode can be expected to develop as a novel biochemical sensor with high linearity and sensitivity. It is anticipated that CNT based nanoweb electrodes based on electrical impedance measurements may provide a feasible fabrication process for mass production of CNT sensors.

Conclusions

CNT-based bulk electrodes were fabricated and their electrical impedance properties were investigated under a chemical solution test to develop chemical and biosensors. Bulk composite electrodes were fabricated with multi-wall carbon nanotubes based on PAN using an electrospinning technique.

A simple and effective measurement for engineering oriented applications of CNTs has been investigated for the bio chemical sensor as well. The capacitance values show drastic changes while the resistance values only change within a few percent range. Having a large surface area, the capacitance of CNTs can be changed remarkably by the ions produced by a buffer solution, and the resistance was changed as well. It is found that the addition of CNTs to a nanofiber web can effectively improve the sensitivity of nanoweb compared to a no-CNT web electrode and the CNT composite nanoweb can be a promising novel nanoelectrode for sensors.

In order to develop biochemical sensors, bulk CNT electrodes should be functionalized to have a chemical selectivity to absorb target chemicals through the surface modification of nanotubes. An electrical conversion circuit is required to convert the change of electrical impedance into an analogue or digital output for the signal processing system of a biochemical sensor.

Eventually, the capacitance response of a CNT nanoweb electrode can be expected to develop as novel biochemical sensors with high linearity and sensitivity. It is anticipated that CNT nanocomposite bulk electrodes based on electrical impedance measurements may provide a feasible fabrication process for mass production of CNT sensors.

Acknowledgement. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2008-331-D00032).

References

1. S. Iijima, Nature 354 (1991) 56-58.
2. W. Yang, P. Thordarson, J.J. Gooding, S.P. Rigner and F. Braet, Nanotechnology 18 (2007) 1-12.
3. S.H. Lim, J. Wei, J. Lin, Q.T. Li and J.K. You, Biosensors & Bioelectronics 20 (2005) 2341-2346.
4. Y.C. Tsai and C.C. Chiu, Sensors and Actuators B 125 (2007) 10-16.
5. K. Kordas, T. Mustonen, G. Toth, H. Jantunen, M. Lajunen, C. Soldano, S. Talapatra, S. Kar, R. Vajtai and P.M. Ajayan, Small 2 (2006) 1021-1025.
6. J. Wang and M. Mushama, Analyst 129 (2004) 1.
7. S. Sanchez, M. Pumer, E. Cabruja and E. Fabregas, Analyst 132 (2007) 142-147.
8. Y. Zhang, C.T. Lim, S. Ramakrishna and Z.M. Huang, Journal of Materials Science: Materials in Medicine 16 (2005) 933-946.
9. D.R. Chang, E.Y. Jeong and H.S. Kim, Kor. J. Mater. Res., 17[5] (2007) 278-282.
10. X. Wang, C. Drew, S.H. Lee, K.J. Senecal, J. Kumar and L.A. Samuelson, Nano Letters 2 (2002) 1273-1275.
11. X. Wang, Y.G. Kim, C. Drew, B.C. Ku, J. Kumar and L.A. Samuelson, Nano Letters 4 (2004) 331-334.
12. B.W. Ahn, Y.S Choi and T.J. Kang, Journal of Applied Polymer Science 110 (2008) 4055-4063.
13. G.R. Choi, Y.W. Ju, H.R. Jung, C. Kim, K.S. Yang and W.J. Lee, Theories and Applications of Chem. Eng. 11 (2005) 911-914.
14. I. Kang, M.J. Schulz, J.H. Kim, V. Shanov and D. Shi, Smart Materials and Structures 15 (2006) 737-748.
15. I. Kang, M.J. Schulz, J.W. Lee, G.R. Choi, J.Y. Jung, J.B. Choi and S.H. Hwang, Solid State Phenomena 120 (2007) 289-296.
16. H. Hou, J.J. Ge, J. Zeng, Q. Li, D.H. Reneker, A. Greiner and S.Z.D. Cheng, Chem. Mater. 17 (2005) 967-973.
17. D.S. So, I. Kang, H. Huh and H. Lee, Journal of Nanoscience and Nanotechnology 10 (2010) 3449-3452.