http://dx.doi.org/10.5012/bkcs.2014.35.6.1687

Synthesis and Characterization of Carbon nanofibers on Co and Cu Catalysts by Chemical Vapor Deposition

Eun-Sil Park, Jong-Won Kim,† and Chang-Seop Lee*

*Department of Chemistry, Keimyung University, Daegu 704-701, Korea. *E-mail: surfkm@kmu.ac.kr*
Received January 3, 2014, Accepted February 11, 2014

This study reports on the synthesis of carbon nanofibers *via* chemical vapor deposition using Co and Cu as catalysts. In order to investigate the suitability of their catalytic activity for the growth of nanofibers, we prepared catalysts for the synthesis of carbon nanofibers with Cobalt nitrate and Copper nitrate, and found the optimum concentration of each respective catalyst. Then we made them react with Aluminum nitrate and Ammonium Molybdate to form precipitates. The precipitates were dried at a temperature of 110 °C in order to be prepared into catalyst powder. The catalyst was sparsely and thinly spread on a quartz tube boat to grow carbon nanofibers *via* thermal chemical vapor deposition. The characteristics of the synthesized carbon nanofibers were analyzed through SEM, EDS, XRD, Raman, XPS, and TG/DTA, and the specific surface area was measured *via* BET. Consequently, the characteristics of the synthesized carbon nanofibers were greatly influenced by the concentration ratio of metal catalysts. In particular, uniform carbon nanofibers of 27 nm in diameter grew when the concentration ratio of Co and Cu was 6:4 at 700 °C of calcination temperature; carbon nanofibers synthesized under such conditions showed the best crystallizability, compared to carbon nanofibers synthesized with metal catalysts under different concentration ratios, and revealed 1.26 high amorphicity as well as 292 m^2g^{-1} high specific surface area.

Key Words : Carbon nanofiber, Co catalyst, Cu catalyst, Chemical vapor deposition

Introduction

Carbon fiber, a carbon material which has recently come into the spotlight, is a fibrous carbon material with more than 90% carbon content. It has high tensile strength and high thermal and electrical conductivity, and it shows adequate mechanical stability and durability under various temperature and pressure ranges in extreme environments.[2-5] Carbon nanofibers (CNFs), a type of material further developed from such carbon fibers, have been extensively researched by Baker and his colleagues since 1970.[9-11] According to their growth mechanism theory, adsorption and decomposition of hydrocarbons occur on the surface of the metal catalysts to form carbon materials which diffuse through catalysts and deposit on the opposite side, forming CNFs.

CNFs are very short in diameter (tens to hundreds of nm) compared to carbon fibers and can appear in a grass-like structure plus a variety of spiral, branched, and twisted structures. Due to the diversity of these structures, CNFs can have diverse physical properties. They can come arranged in a variety of lengths, numbers of layer, or diameters, and they are promising nano-materials. Among other things, they are expected to play a great role in development of hydrogen and secondary battery technologies to overcome the energy crisis due to fossil fuel exhaustion and environmental pollution.[4-8]

CNFs with such characteristics can be produced by various techniques including arc discharge, laser ablation, chemical vapor deposition (CVD), and plasma-enhanced CVD. CVD is much preferred due to various criteria including low cost, high purity, growth control, easy industrialization, *etc.*

Metal catalysts mainly used for CVD are transition metals like iron, cobalt, and nickel.[4-6] Particles of these metal catalysts are embedded in the middle or at the end of fibers, and it is possible to adjust the diameter of the CNFs depending on the size of the particles of the metal catalysts. In addition, selective control is possible with respect to the characteristics of carbon nanofibers if conditions, such as decomposition temperature, catalyst preparation, or reaction gas,[1-3,11-19] are regulated. Therefore, strict control of these variables is required during synthesis of CNFs.

In this study, using CVD based on a Co-Cu bimetallic catalyst, we synthesized homogeneous CNFs with high purity and surface area by adjusting the concentration ratios of Co and Cu.

Experimental

Materials. For preparing of catalysts to synthesize carbon nanofibers, transition metal catalysts as Cobalt nitrate ($Co(NO_3)_3{\cdot}9H_2O$, DAEJUNG C&M Co, purity 97.0%) and copper nitrate ($Cu(NO_3)_3{\cdot}9H_2O$, DAEJUNG C&M Co, purity 99.0%) were used; aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, DAEJUNG C&M Co, purity 98.0%) was used as a supporter to support transition metal catalysts; ammonium molybdate ($(NH_4)_6Mo_7O_{24}$, DAEJUNG C&M Co, purity 98.0%) to regulate cohesion between particles during reaction of transition metals at high temperature; and also ammonium carbonate ($(NH_4)_2CO_3$, DAEJUNG C&M Co, purity 30.0%)

of precipitant was used. Nitrogen N_2, (Korea Standard Gas Co, purity 99.9%) was used as carrier gas for synthesis of carbon nanofiber, and hydrogen (H_2/N_2, Korea Standard Gas Co, purity 20%) was used as promoting gas for gas phase reaction, while ethylene (C_2H_4/N_2, Korea Standard Gas Co, purity 20%) was used as a precursor for synthesis of carbon nanofibers.

Preparation of Catalysts. In this study, we prepared cobalt to copper metal catalysts through co-precipitation method and then used them for synthesis of carbon nanofibers. In order to investigate catalyst activity suitable for growth of carbon nanofibers first, catalytic materials were prepared at the rate of 10:0, 8:2, 6:4, 4:6, 2:8, and 0:10 of Cobalt nitrate and Copper nitrate based on mass ratio. This was dissolved in distilled water together with Aluminum nitrate and Ammonium Molybdate; ammonium carbonate was slowly added into solution dissolved by distilled water to have precipitate of metal particles and stirred for stabilization for 1 h. Then precipitate obtained through filtering was dried in a 110 °C oven for more than 24 h to evaporate moisture of solution and finally metal catalyst power was prepared, which was used as reaction catalyst for synthesis of carbon nanofibers.

Synthesis of Carbon Nanofiber. Carbon nanofibers were synthesized by Chemical Vapor Deposition in horizontal quartz pipe reaction device. The reaction apparatus was manufactured as metal heating element and horizontal quartz reaction pipe in 80 mm (diameter) × 1400 mm (length) and was divided into 3 zones to get uniform temperature profile.

Flux of reaction gas was controlled by electronic MFC (Mass Flow Controller); ethylene gas (C_2H_4) was used to grow carbon nanofibers; and hydrogen was used as as promoting gas for gas phase reaction while nitrogen was used for stabilization of reaction. Following are conditions of synthesis reaction; 500 mg of synthesized metal catalyst was evenly spread in quartz tube boat and put into a reactor and then, temperature was increased to 10 °C/min in steady nitrogen atmosphere.

Hydrogen atmosphere was maintained for 30 minutes if target synthesis temperature reached; ethylene and hydrogen gas were passed for 1 h; and ethylene and hydrogen gas were shut off upon completion of reaction. Next, nitrogen gas was put into; reactor atmosphere was kept as inert and was cooled up to room temperature of 10 °C/min.

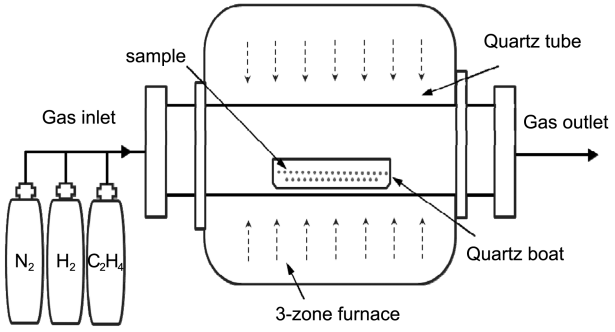

Figure 1. Schematic diagram of CVD apparatus for the preparation of CNFs.

Analysis. The surface morphology and composition of carbon nanofibers were characterized by Scanning Electron Microscope (Hitachi, S-4800) and Energy Dispersive Spectroscopy (ThermoARL, ARL 3460). The crystal quality of synthesized carbon nanofibers was analyzed by Raman spectroscopy (Horiba Jobin-Yvon, LabRam HR) and X-ray Diffractometry (PANalytical, X'pert PRO-MPD). XRD patterns were measured under the condition of 20-80° of Bragg angle and 1°/min of scanning speed with Cu target and Co Filter. The chemical state of the surface was investigated by X-ray Photoelectron Spectroscopy (Thermo Fisher Scientific, Multilab-2000). N_2 sorption experiments were performed to measure the specific surface area of prepared metal catalysts and carbon nanofibers by BET (Micromeritics, ASAP-2010). Thermal analyses were performed to investigate thermal properties of carbon nanofibers synthesized by CVD under air atmosphere of 45 °C to 1200 °C using by Thermogravimetry and Differential Thermal Analysis (TG/DTA, Stanton Redcroft Co. STA). Each sample was measured under the condition of 40 mL/min of reaction gas velocity and 10 °C/min of heating rate.

Results and Discussion

Synthesis of Carbon Nanofibers by Metal Catalysts. Carbon nanofibers were synthesized by using chemical reaction promoted by metal catalysts. Final carbon nanofibers obtained through such absorption reaction made by such catalysts are known to have close relationships with preparing of catalysts. Therefore, in order to investigate influences over synthesis of carbon nanofibers according to concentration ratio of Co and Cu, this study synthesized carbon nanofibers using ethylene gas (C_2H_4) as carbon source at 700 °C synthesis temperature under CVD.

SEM. Microstructure of synthesized carbon nanofibers was observed by SEM and shown in Figure 2. Carbon nanofibers shown in (a) of Figure 2 were grown by only using cobalt catalyst, and most of the fibers were long and straight with a variety of thickness of 20 nm-35 nm in diameter; on the other hand, those grown under cobalt and copper concentration ratio of 8:2 as shown in (b) had relatively regular diameters with 30 nm, mostly in the shape of carbon nanocoils. Unlike straight shaped-fiber, those in (c) grown under cobalt and copper ratio of 6:4 were evenly grown in winding shape with 27 nm in diameter; those in (d) grown under cobalt and copper ratio of 4:6, which means the amount of copper was more increased than that of cobalt, were raised unevenly with irregular diameters and length of fibers. With respect to (e) under cobalt and copper ratio of 2:8, fiber shapes were uneven, and fibers did not well grow; with respect to the case using only copper as metal catalyst, carbon nanofibers did not grow at all. Such inactivation of catalysts is deemed that pure copper without activation of chemical reaction was used so that copper helped activation of main catalyst cobalt but did not get involved in growth of carbon nanofibers.

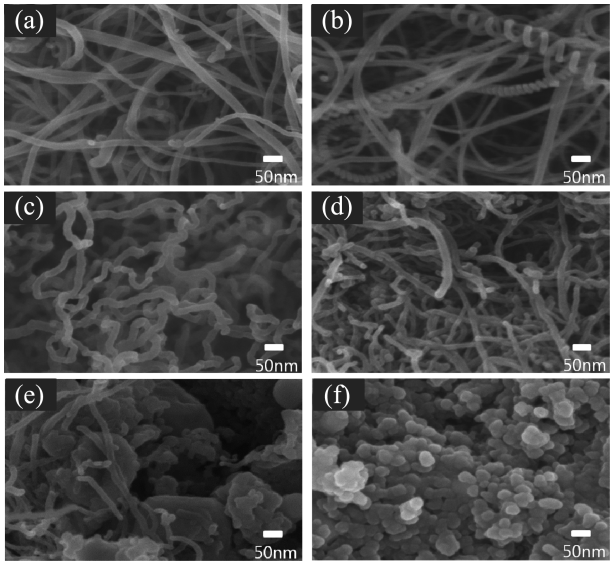

Figure 2. SEM images of CNFs synthesized from ethylene at 700ºC under different concentration of Co and Cu catalysts; (a) Co:Cu=10:0, (b) Co:Cu=8:2, (c) Co:Cu=6:4, (d) Co:Cu=4:6, (e) Co:Cu=2:8, (f) Co:Cu=0:10.

EDS. Qualitative and quantitative analysis was conducted on specific parts of carbon nanofibers using EDS, and kinds as well as average values of carbon elements shown in Table 1 according to concentration ratio of Co and Cu. If Co : Cu ratios are 10:0, 8:2, 6:4, 4:6 and 2:8, average values of each element are 89.41%, 91.48%, 90.92%, 88.55% and 76.73% respectively. When comparing results of SEM and EDS, average values of carbon element were generally high if carbon nanofibers well grew as in (a), (b), (c) and (d) of Figure 2; on the other hand, average values of carbon element were shown lower than other Co: Cu ratios if carbon nanofibers did not well grow as in (e) of Figure 2.

Raman. Most carbon nano-materials have various carbon nano-structures such as Diamond, Graphite, CNT (Carbon nanotube), CNF (Carbon nanofiber) according to carbon allotrope, and the carbon nano-structures are synthesized of C-C bondings with different directions only. Such direction of C-C bondings can be verified through a Raman analysis. Therefore, a Raman analysis was conducted in order to verify crystallizability of carbon nanofibers synthesized according to Co and Cu concentration ratio. Results of Raman measurement to verify crystallizability of carbon nanofibers synthesized according to Co and Cu concentration ratio are indicated on Figure 3. As can be seen on Figure 3, D-peak

Table 1. EDS results of CNFs synthesized based on different concentration of Co and Cu catalysts (atomic%)

Sample	Carbon	Oxygen	Cobalt	Copper	Aluminum
Co:Cu = 10:0	89.41	9.91	0.28	0	0.40
Co:Cu = 8:2	91.48	7.04	0.63	0.12	0.73
Co:Cu = 6:4	90.92	7.24	0.78	0.28	0.78
Co:Cu = 4:6	88.55	9.73	0.41	0.26	1.05
Co:Cu = 2:8	76.73	20.5	0.43	1.13	1.22

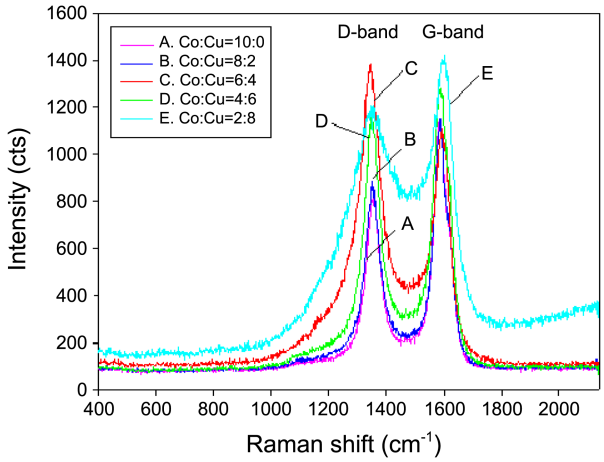

Figure 3. Raman spectra of CNFs synthesized from ethylene at 700 ºC under different concentration of Co and Cu catalysts.

discovered in 1340 cm^{-1} and G-peak discovered in 1580 cm^{-1} were observed in Raman spectra. D-peak is the one due to carbonaceous impurities or graphite structural defect while G-peak is the peak of carbon nanofibers graphitized to graphite crystal. Accordingly, amorphicity of carbon material can be calculated according to the rate of D-peak height/G-peak height (hereinafter "D/G"). As can be seen in Table 2, when concentration ratio of cobalt and copper was 6:4 rather than when only cobalt was used as metal catalyst, D/G value increased from 0.63 to 1.26; and D/G decreased to 0.76

Table 2. Raman D/G ratio of CNFs synthesized based on different concentration of Co and Cu catalysts

Sample	D/G
Co:Cu = 10:0	0.63
Co:Cu = 8:2	0.93
Co:Cu = 6:4	1.26
Co:Cu = 4:6	0.88
Co:Cu = 2:8	0.83

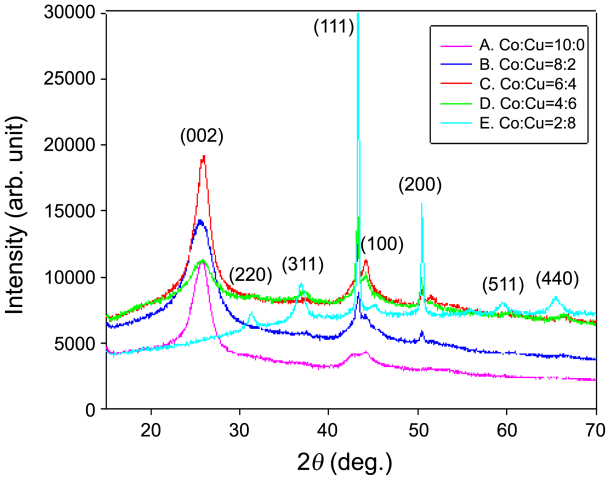

Figure 4. XRD patterns of CNFs synthesized from ethylene at 700 ºC under different concentration of Co and Cu atalysts.

again as concentration of copper increased comparing to that of cobalt.

XRD. Figure 4 shows XRD analysis result of carbon nanofibers synthesized according to concentration ratio of Co and Cu. If we compare the SEM result above and the XRD analysis result in Figure 4, except carbon nanofibers (e) which did not well grow under 2:8 Co and Cu ratio, it is seen that carbon nanofibers had carbon peak which showed all the peaks (002) and (100) even though there are some differences according to catalyst concentration ratios. According to evaluation method of crystallizability of carbon material by X-ray Diffraction, crystallizability of carbon nanofibers generally improves as cobalt concentration becomes higher; especially, in the case of (c) where ratio of Co and Cu is 6:4 same as Raman analysis result, it can be confirmed that carbon nanofibers with excellent and pure crystallizability were synthesized judging from narrower width peaks and bigger intensity than other carbon nanofibers. On the other hand, if concentration ratio of copper increases, intensity of carbon peak becomes low but intensities of copper peak which are shown in the peaks (111) and (200) become increased. The peaks which appeared at (220), (311), (511) and (440) were identified to be the peaks of $CuAl_2O_4$ produced from Copper and alumina used as support. As shown in XRD and Raman analysis results, crystallizability of carbon nanofibers are greatly influenced by concentration ratio of Co and Cu catalyst; as seen in the Table 2, carbon nanofibers with the most excellent and purest crystallizability were synthesized where concentration ratio of Co and Cu was 6:4.

XPS. XPS spectra to carbon nanofibers grown on Co and Cu catalysts are shown in Figure 5 and analysis results associated with the binding energies of carbon and oxygen are displayed in Table 3. Carbon nanofibers synthesized at the 6:4 concentration ratio of Co and Cu under which the largest crystallizability appeared in Raman and XRD analysis results, were used as example. According to XPS analysis results, XPS spectra identified binding energy of carbon in C1s scan A as C-C combination and binding energy of carbon in C1s scan B as C-Co Combination. The binding energy of Co-bonded carbon is lower than that of carbon-carbon, because carbon is more electronegative than Cobalt to pull more electrons. The binding energies of carbon in C1s scan C and scan D were identified to be the binding energies of C=O and C-O combinations.

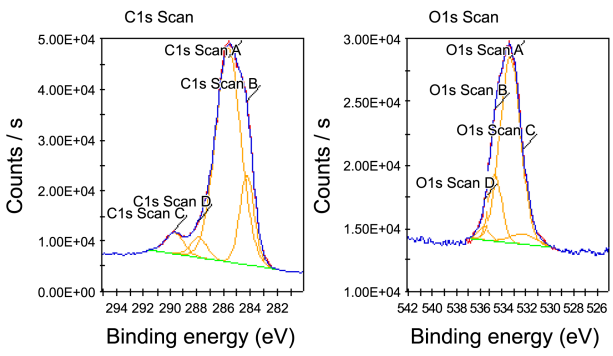

Figure 5. XPS spectra of CNFs (Co:Cu=6:4) synthesized from ethylene at 700 ºC.

Table 3. XPS results of CNFs (Co:Cu=6:4) synthesized from ethylene at 700 ºC

Name	Peak BE (eV)	Analysis
C1s scan A	285.64	C-C of CNF
C1s scan B	284.24	C-Co combination
C1s scan C	289.65	C=O combination
C1s scan D	287.82	C-O combination
O1s Scan A	533.33	C=O combination
O1s Scan B	534.61	C-O combination
O1s Scan C	532.24	Al_2O_3 combination
O1s Scan D	535.6	N_2O-Alcombination

BET. Table 4 shows changes in pore size, volume and specific surface area of carbon nanofibers measured according to concentration ratio of Co and Cu. As seen in Table 4, specific surface area more increased at the concentration ratio of Co and Cu of 8:2 than 10:0, and afterwards, specific surface area also decreased as Co concentration decreased. Consequently, carbon nanofibers synthesized at the 8:2 concentration ratio of Co and Cu revealed the highest BET value of 306 m^2g^{-1}, and this is verified that high BET value was achieved because a lot of carbon nano-coil shapes were made during synthesis of carbon nanofibers. This result shows that carbon nanofibers synthesized by Co-Cu binary system generally had high specific surface area of 178-306 m^2g^{-1}; and specific surface area of electrode active material is the most important factor to decide energy capacity of capacitor and therefore, it is expected that manufactured

Table 4. BET results of CNFs synthesized based on different concentration of Co and Cu catalysts

Sample	Surface area (m^2g^{-1})	Pore volume (ccg^{-1})	Pore size (nm)
Co:Cu = 10:0	245	0.491	4.1
Co:Cu = 8:2	306	0.535	3.4
Co:Cu = 6:4	292	0.462	3.8
Co:Cu = 4:6	232	0.558	3.1
Co:Cu = 2:8	178	0.391	3.8

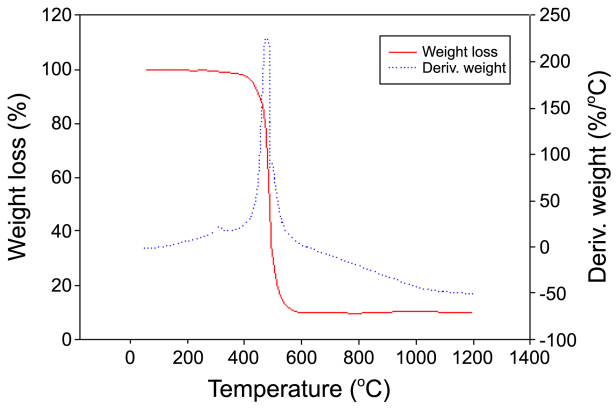

Figure 6. TG/DTA curves of CNFs (Co:Cu=6:4) synthesized from ethylene at 700 ºC.

electrode capacitance will be very large if carbon nanofibers synthesized in this study are applied as electrode material.

TG/DTA. In order to investigate mass change and thermal characteristics according to temperature of synthesized carbon nanofibers, TG/DTA analysis was made in air atmosphere by selecting carbon nanofibers synthesized at the 6:4 concentration ratio of Co and Cu under which the largest crystallizability appeared in Raman and XRD analysis results, and the result was shown in Figure 6. TG/DTA analysis was conducted as follows; less than 50 mg samples were collected in air atmosphere of temperature ranging from 45 °C to 1200 °C; respective reaction gas flow velocity and heating rate were adjusted to 40 mL/min and 10 °C/min. Mass decrease of carbon nanofibers by air oxidation started from 45 °C and ended at 600 °C, and mass rapidly decreased between 400~500 °C.

Conclusions

Carbon nanofibers are materials with wide applicable extent and abundant applicability including composite material, hydrogen storage, electromagnetic wave shield and super capacitor. Using chemical vapor deposition technique based on Co-Cu bimetallic catalysts, we synthesized carbon nanofibers in this study and drew the following conclusions;

1) According to SEM measurement, it is observed that the growth of carbon nanofibers in various shapes with 20 nm-35 nm diameters depending on concentration ratio of Co-Cu bimetallic catalysts.

2) According to EDS analysis for qualitative and quantitative analyses, average values of Carbon elements in carbon nanofibers showed relatively high values of 91.48%-76.73%.

3) According to Raman analysis to verify crystallizability of carbon nanofibers, D-peak discovered in 1340 cm^{-1} and G-peak discovered in 1580 cm^{-1} were observed; amorphicity of carbon material were calculated as 0.63 to 1.26 according to the rate of D-peak height/G-peak height.

4) According to XRD analysis, except carbon nanofibers (e) which did not well grow under 2:8 Co and Cu ratio, carbon nanofibers had characteristic peaks showing carbon peak (002) and (100) at almost of catalysts concentration ratios.

5) According to XPS analysis results, XPS spectra identified binding energy of carbon in C1s scan A as C-C combination and binding energy of carbon in C1s scan B as C-Co Combination.

6) BET measurement results showed carbon nanofibers synthesized by Co-Cu catalysts had high specific surface area of 178-306 m^2g^{-1}.

7) Characteristics of carbon nanofibers grown were greatly influenced by concentration ratio of metal catalysts; especially, uniform carbon nanofibers in 27 nm diameter grew when concentration ratio of Co and Cu was 6:4. It is revealed that carbon nanofibers synthesized under such conditions had the best crystallizability comparing to carbon nanofibers synthesized with metal catalysts of different concentration ratio and that they had 1.26 high amorphicity as well as 292 m^2g^{-1} high specific surface area.

Acknowledgments. This research was financially supported by the Ministry of Education, Science Technology (MEST) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation (No. 2012026209).

References

1. Chambers, C.; Park, R. T.; Baker, K.; Rodriguez, N. M. *J. Phys. Chem. B* **1998**, *102*, 4253.
2. Fun, Y.-Y.; Liao, B.; Liu, M.; Wei, Y.-L.; Lu, M.-Q.; Cheng, H.-M. *Carbon* **1999**, *37*, 1649.
3. Rodriquez, N. M. *J. Mater. Res*. **1993**, *8*, 3233.
4. Dresselhaus, M. S.; Dresselhaus, G.; Sugihara, K.; Spain, I. L.; Goldberg, H. A. *Graphite Fibers and Filaments*; Springer Press: 1988.
5. Ahn, C. C.; Ye, Y.; Tatnakumar, B. V.; Witham, C.; Bowman, R. C., Jr.; Fultz, B. *Appl. Phys. Lett.* **1998**, *73*, 3378.
6. Bartholomew, C. H. *Catal Rev. Sci. Eng*. **1982**, *24*, 67.
7. Seo, G. Y. *Understanding Nano Technology*; SNU Press: 2011.
8. Trimm, D. L. *Catal Rev. Sci. Eng*. **1977**, *16*, 115.
9. Baker, R. T. K.; Harris, P. S.; Thomas, R. B.; Waite, R. J. *J. Catal.* **1973**, *30*, 86.
10. Endo; M.; Kim, Y. A.; Hayashi; T.; Nishimura, K.; Matusita, T.; Miyashita, K.; Dresselhaus, M. S. *Carbon.* **2000**, *1287*, 1297.
11. Kim, M. S.; Rodrigues, N. M.; Baker, R.T. K. *J. Catal*. **1991**, *131*, 60.
12. Shu-ping, Z. *New Carbon Materials* **2010**, *25*, 9.
13. Li, D.; Xia, Y. *Nano Letters* **2004**, *4*, 933.
14. Bognitzki, M.; Czado, M.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H. *Adv. Mater.* **2001**, *13*, 70.
15. Tzeng, S. S.; Yang, T. C. *Composite Interfaces* **2005**, *12*, 259.
16. Jarrah, N. A.; Li, F.; Van Ommen, J. G.; Lefferts, L. *J. Mater. Chem.* **2005**, *15*, 1946.
17. Stemmet, C. P.; Meeuwse, M.; Van der Schaaf, J. B.; Kuster, F. M.; Schouten, J. C. *Chem. Eng. Sci.* **2007**, *62*, 5444.
18. Van Der Lee, M. K.; Van Dillen, A. J.; Geus, J. W.; De Jong, K. P.; Bitter, J. H. *Carbon* **2006**, *44*, 629.
19. Kim, T. Y.; Mees, K.; Park, H. S.; Willert-Porada, M.; Lee, C. S. *J. Nanosci. Nanotechnol.* **2013**, *13*, 7337.
20. Lee, S. W.; Mees, K.; Park, H. S.; Willert-Porada, M.; Lee, C. S. *Advanced Materials Research* **2013**, *750-752*, 280-292.