

## Electrophoretic Deposition for the Growth of Carbon nanofibers on Ni-Cu/C-fiber Textiles

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In this study, Ni, Ni-Cu and Ni/Cu catalysts were deposited onto C-fiber textiles *via* the electrophoretic deposition method, and the growth characteristics of carbon nanofibers on the deposited catalyst/C-fiber textiles were investigated. The catalyst deposition onto C-fiber textiles was accomplished by immersing the C-fiber textiles into Ni or Ni-Cu mixed solutions, producing the substrate by post-deposition of Ni onto C-fiber textiles with pre-deposited Cu, and passing it through a gas mixture of N<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> at 700 °C to synthesize carbon nanofibers. For analysis of the characteristics of the synthesized carbon nanofibers and the deposition pattern of catalysts, SEM, EDS, BET, XRD, Raman and XPS analysis were conducted. It was found that the amount of catalyst deposited and the ratio of Ni deposition in the Ni-Cu mixed solution increased with an increasing voltage for electrophoretic deposition. In the case of post-deposition of Ni catalyst onto substrates with pre-deposited Cu, both bimetallic catalyst and carbon nanofibers with a high level of crystallizability were produced. Carbon nanofibers yielded with the catalyst prepared in Ni and Ni-Cu mixed solutions showed a Y-shaped morphology.

**Key Words :** Carbon nanofibers, Electrophoretic deposition, Nickel and copper catalyst, CVD, C-fiber textiles

### Introduction

Carbon nanofiber is defined as a fibrous material containing over 90% carbon element with a diameter of less than 1 μm. Nanofibers can be applied to various fields of study, such as materials for hydrogen storage, electromagnetic interference, fuel cells, and secondary batteries to biomaterial. This is possible because carbon nanofibers may possess thermal resistance, chemical stability, high electrical conductivity, mechanical strength, high specific surface area, pliability, and high solidity and elasticity due to sp, sp<sup>2</sup> and sp<sup>3</sup> hybridization, in terms of chemical structure.<sup>1-5</sup>

The methods of synthesis of carbon nanofibers vary, including electrospinning, laser, chemical vapor deposition (CVD) and others. Among the various types, the CVD method was utilized in this investigation. In the CVD method, hydrocarbon gas is thermally decomposed in the presence of a catalyst at high temperatures to synthesize the carbon nanofibers. This method has the advantages of reduced time and cost for production of the carbon nanofibers.<sup>6-10</sup>

In order to facilitate the CVD method, preparation of the catalyst to be used in the thermal decomposition process is

important, and various methods can be used, including coprecipitation, plasma deposition, electroless plating, electrophoretic deposition, *etc.* Although the electrophoretic deposition method using reduction potential difference may experience reduced deposition uniformity compared to that of other methods, it has the merits of simplicity and economic feasibility, which can be achieved since the pre-activation process and preparation of complicated solutions is not necessary, unlike the electroless deposition method.<sup>11-15</sup>

In this study, three experimental conditions of deposition, Ni catalyst deposition onto C-fiber textiles, Ni-Cu catalyst deposition onto C-fiber textiles, and Ni catalyst deposition onto C-fiber textiles with pre-deposited Cu, were performed to prepare the substrates. The prepared substrates were subsequently treated with ethylene as a carbon source to synthesize carbon nanofibers *via* the CVD method, and the characteristics of the synthesized carbon nanofibers were investigated.

### Experimental

**Reagents and Materials.** The reagents and gases used in

**Table 1.** Reagents used in the growth of carbon nanofibers

Reagents	Molecular formula	Specification	Manufacturer
C-fiber textiles	C		SGL Carbon Group, Germany
Nickel(II) acetate tetrahydrate	Ni(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	97%	Duksan, Korea
Copper(II) acetate monohydrate	Cu(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	98%	Duksan, Korea
Nitric acid	HNO <sub>3</sub>	65%	Duksan, Korea

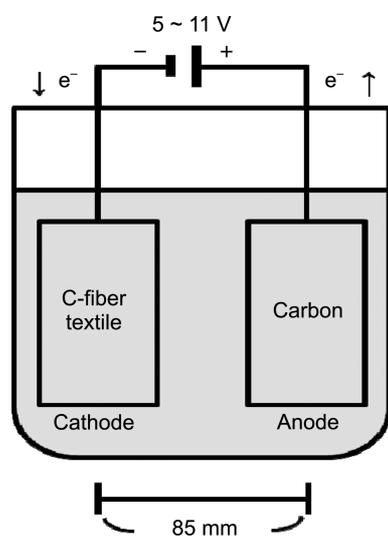
**Table 2.** Gases used in the growth of carbon nanofibers

Gas	Molecular formula	Specification	Manufacturer
N <sub>2</sub> gas	N <sub>2</sub>	99%	Korea Standard gas
H <sub>2</sub> gas	H <sub>2</sub>	20%	Korea Standard gas
Ethylene gas	C <sub>2</sub> H <sub>2</sub>	20%	Korea Standard gas

this experiment are tabulated in Tables 1 and Table 2. The C-fiber textiles for the substrate were purchased from SGL Carbon Group in Germany.

**Deposition of Catalysts.** Ni and Cu catalysts were deposited onto C-fiber textiles as per the electrophoretic deposition method, and a schematic diagram of the experimental apparatus is demonstrated in Figure 1. In this method, a carbon electrode was treated as the anode, and C-fiber textiles as the cathode, with a distance of 85 mm between each electrode. Three experimental conditions were deliberated to deposit catalyst onto the C-fiber textiles. Ni was deposited onto the C-fiber textiles within a Ni aqueous solution, or Ni and Cu were deposited onto the C-fiber textiles within a Ni-Cu mixed aqueous solution. For the last condition, Cu was pre-deposited onto the C-fiber textiles, and Ni was subsequently deposited onto that C-fiber textile in a Ni aqueous solution.

For the first condition, a 0.025 M nickel (II) acetate tetrahydrate aqueous solution was used, with a 5 minute deposition time at various voltages of 5, 8 and 11 V. For the second condition, catalyst deposition onto C-fiber textiles was conducted within a mixed solution of 0.025 M nickel (II) acetate tetrahydrate and 0.001 M copper (II) acetate monohydrate, with a deposition time of 5 minutes at 5, 8 and 11 V. Ni deposition onto Cu pre-deposited C-fiber textiles within a Ni aqueous solution was carried out for 10 minutes at 8 V in 0.001 M copper(II) acetate monohydrate and, then transferred into a nickel(II) acetate tetrahydrate solution and treated with 8 V for 10 or 20 minutes to prepare the substrate.

**Figure 1.** Electrophoretic deposition apparatus used in the deposition of catalysts.

**Reduction.** A reduction step was applied, in order to convert iron hydroxides and oxides attached to the surface of the C-fiber textiles into elemental nickel and copper, by using a tube furnace. Hydrogen balanced with nitrogen gas was used for the reduction process, and the flux of the reaction gas was controlled by an MFC (Mass Flow Controller). The reactor temperature was raised at the rate of 12 °C/min, until reaching 700 °C, and only pure nitrogen gas was flowed while the temperature was being raised.

Once the temperature reached 700 °C, nitrogen gas balanced with 20% hydrogen gas was flowed into the reactor, and the reduction process was carried out for 2 h.

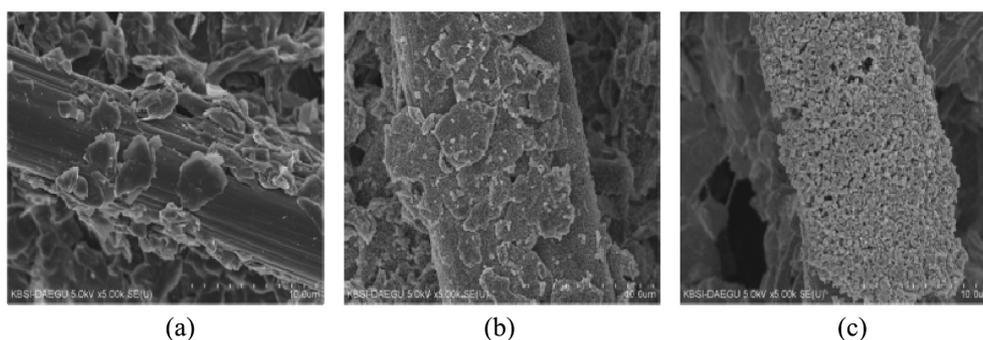
**Growth of Carbon Nanofibers.** Carbon nanofibers were grown on the C-fiber textiles by CVD in a horizontal quartz tube reaction apparatus, after completion of the reduction process. The reaction apparatus was manufactured as a metal heating element, and the horizontal quartz reaction tube of 80 mm (diameter) × 1400 mm (length) was divided into 3 zones, to get a uniform temperature profile. The flux of the reaction gas was controlled by an electronic MFC. Ethylene gas (C<sub>2</sub>H<sub>4</sub>) was used to grow the carbon nanofibers as a carbon source, and hydrogen was used to eliminate the remaining hydroxyl group after the reduction process, while nitrogen was used to stabilize the reaction.

A prepared metal catalyst was evenly spread on a quartz boat, which was placed into the reactor under a nitrogen atmosphere, and the reactor temperature was raised at 12 °C/min. Once the temperature reached 700 °C, it was maintained for 30 minutes. Nitrogen gas and 20% hydrogen (N<sub>2</sub> balance) gas were flowed into the reactor together, then, hydrogen (N<sub>2</sub> balance) gas and 20% ethylene (N<sub>2</sub> balance) gas were flowed into the reactor, for 3 h. The flow of ethylene and hydrogen gases was cut off after the completion of the reaction. Nitrogen was passed through for cooling to room temperature, under an inactive reactor atmosphere.

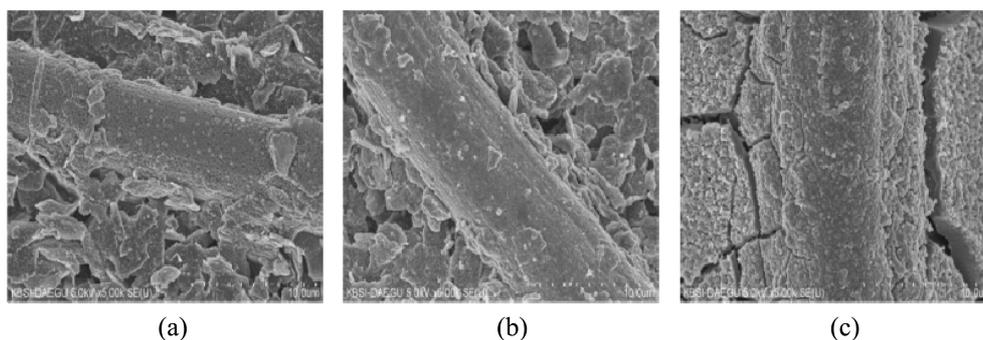
**Analysis.** Synthesis of carbon nanofibers and conditions of the deposited catalysts on the surface of the substrates were observed by Scanning Electron Microscopy (SEM, Hitachi, S-4800) for the various voltages catalysts applied. The amounts of two of the catalysts and their compositions on the surface were investigated through Energy Dispersive Spectroscopy (EDS, Thermo ARL, ARL-3460). Brunauer Emmett Teller (BET, Quantachrome, Quadrasorb) measured the specific surface area of the synthesized carbon nanofibers. Raman spectroscopy (Horiba Jobin Yvon, LabRAM HR-800) indicated the ratio of intensities of the G-band and D-band, and the crystallizability of the carbon nanofibers. X-ray diffraction (XRD, PANalytical, X'pert PRO-MPD) was used to study the crystallizability of the carbon nanofibers and catalysts. Bonding patterns were analyzed with measurement of the bonding energy of carbon using X-ray Photoelectron Spectroscopy (XPS, Thermo Fisher Scientific, Multilab-2000).

## Results and Discussion

### SEM Images of Catalysts. Ni, Ni-Cu and Ni/Cu catalysts



**Figure 2.** SEM images of Ni catalysts on C-fiber textiles, deposited in Ni aqueous solution at different voltages for 5 min. (a) 5 V. (b) 8 V. (c) 11 V.



**Figure 3.** SEM images of Ni-Cu catalysts on C-fiber textiles deposited in Ni-Cu mixed aqueous solution at different voltages for 5 min. (a) 5 V. (b) 8 V. (c) 11 V.

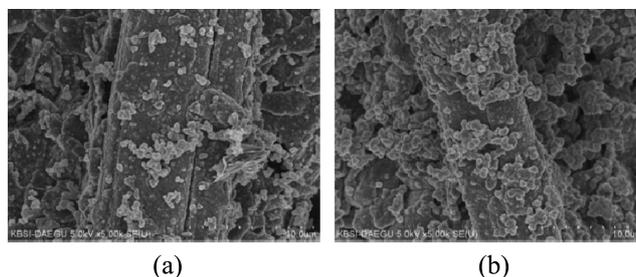
were deposited onto C-fiber textiles under various voltages, using the electrophoretic deposition method. The reason for the introduction of the Ni/Cu system onto the C-fiber textiles is because the self-diffusion coefficient of Cu is  $3.05 \times 10^{-11} \text{ cm}^2/\text{s}$ , which is greater than that of Ni,  $2.88 \times 10^{-14} \text{ cm}^2/\text{s}$ . As Cu atoms spread toward the outer Ni layer with a simple thermal treatment, it was expected to generate carbon nanofibers with different properties from the Ni or Ni-Cu catalyst system.<sup>16</sup>

Figure 2 displays the SEM images of the catalyst deposited in Ni aqueous solution for 5 minutes at 5 V (a), 8 V (b) and 11 V (c). As seen in Figure 2, only a small amount of Ni was deposited at 5 V (a), and it was found that the amount of Ni catalyst deposition was proportional to the voltage. In Figure 2(c), an excessive amount of Ni deposition onto the C-fiber textile was observed.

The SEM images of catalyst deposition of the Ni-Cu combined solution for 5 minutes at 5 V (a), 8 V (b) and 11 V (c) are shown in Figure 3. It was stipulated that the amounts of deposition of Ni-Cu particles were raised with the voltage increment, and excessive amounts of Ni catalyst with partial fractures were found at 11 V (c).

In Figure 4, the SEM images of Ni deposited onto Cu pre-deposited C-fiber textiles at a voltage of 8 V for 10 minutes (a) or 20 minutes (b) are shown. As can be observed in this figure, deposited Ni catalyst was present on the Cu catalyst layer, while the size of the catalyst grew bigger with an increasing time of deposition.

**EDS of Catalysts.** In order to investigate the compositions

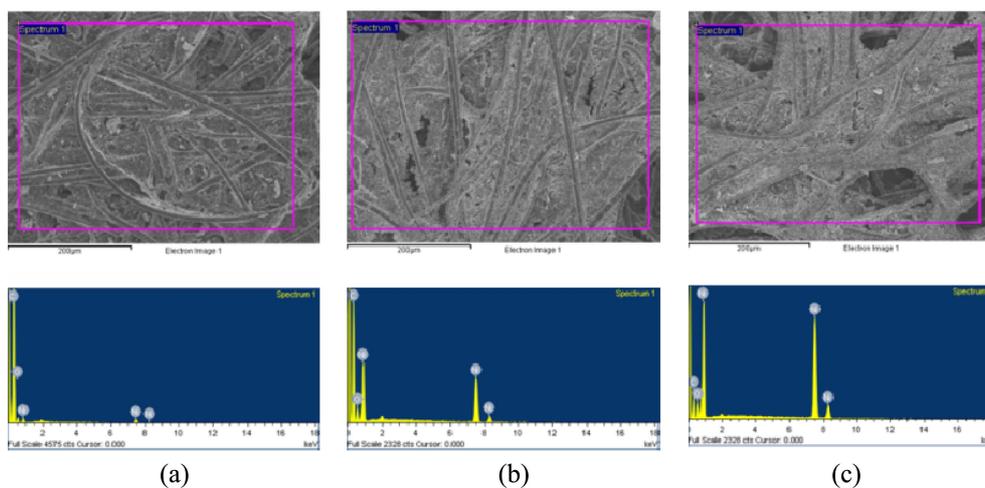


**Figure 4.** SEM images of Ni catalysts on the Cu pre-deposited C-fiber textiles in Ni aqueous solution at 8 V for varying times. (a) 10 min. (b) 20 min.

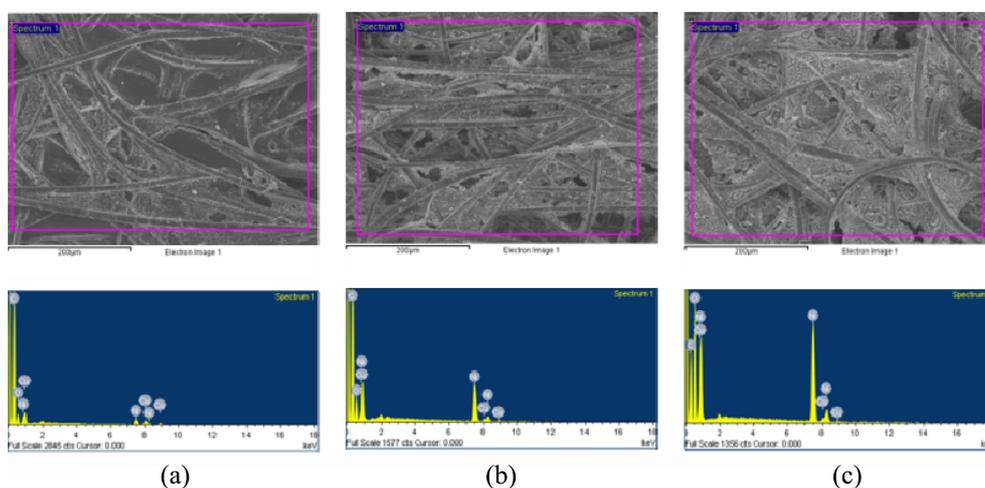
of the deposited catalysts, EDS measurement was performed. Figure 5 displays the EDS results in Ni aqueous solution for 5 minutes at 5 V (a), 8 V (b) and 11 V (c). As can be seen in the figure, the ratio of Ni increased with increasing voltage.

EDS results for experiments performed in Ni-Cu combined aqueous solution for 5 minutes at 5 V (a), 8 V (b) and 11 V (c) are shown in Figure 6. As the deposition voltage was increased, the composition of Cu decreased while that of Ni increased. EDS results of the deposition onto Cu pre-deposited C-fiber textiles at a voltage of 8 V for 10 minutes (a) or 20 minutes (b) are shown in Figure 7. With an increase in the deposition time, the Ni content increased, while Cu decreased. The EDS results of the above three conditions are summarized in Table 3.

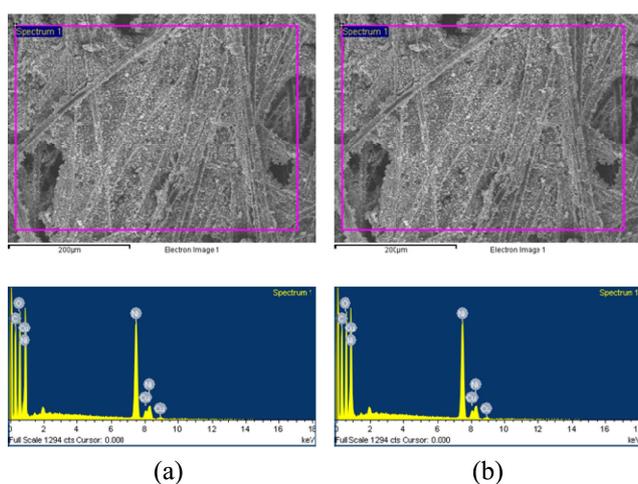
**SEM Images of Carbon Nanofibers.** To study the growth



**Figure 5.** EDS results for the catalysts deposited in Ni aqueous solution at different voltages for 5 min. (a) 5 V. (b) 8 V. (c) 11 V.



**Figure 6.** EDS results for the catalysts deposited in Ni-Cu mixed solution at different voltages for 5 min. (a) 5 V. (b) 8 V. (c) 11 V.



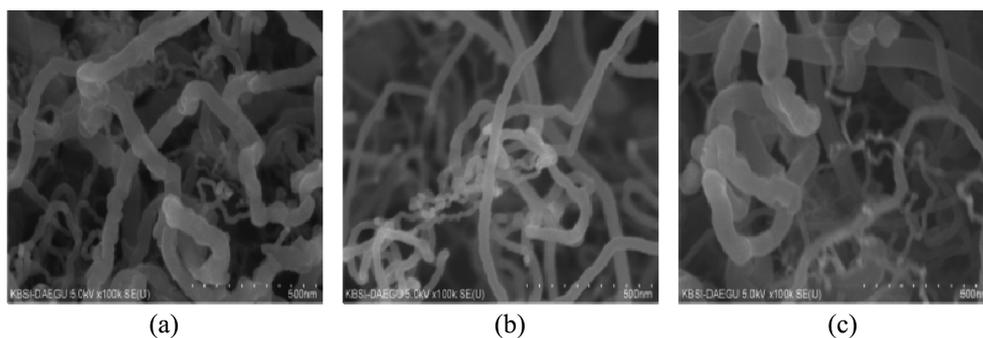
**Figure 7.** EDS results of Ni catalysts on the Cu pre-deposited C-fiber textiles in Ni aqueous solution at 8 V for varying times. (a) 10 min. (b) 20 min.

conditions of synthesized carbon nanofibers, SEM images were observed after synthesis in the presence of the catalysts

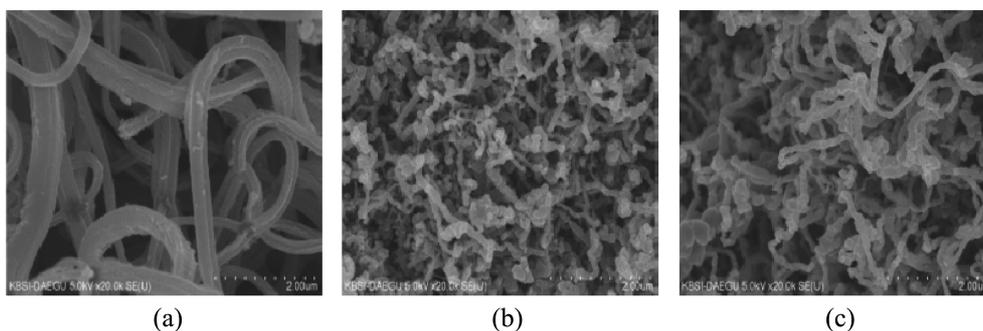
**Table 3.** Combined EDS results for the electro-deposited substrates of 3 different compositions; 1) Ni solution 2) Ni-Cu solution 3) Ni solution after Cu deposition

Name	Voltage (V)	Time (min)	C (at%)	O (at%)	Ni (at%)	Cu (at%)
Ni	5		90.22	8.87	0.91	0
	8	5	82.78	10.15	7.06	0
	11		57.20	12.82	29.97	0
Ni-Cu	5		84.61	12.91	1.29	1.19
	8	5	80.57	14.35	4.79	0.29
	11		49.42	38.39	11.77	0.43
Ni/Cu	8	10	54.95	33.30	10.84	0.91
	8	20	57.35	30.27	12.10	0.28

produced from the aforementioned three conditions. Figure 8 shows SEM images of the carbon nanofibers synthesized exclusively with Ni catalyst. As shown in the figure, carbon nanofibers with Y-shaped morphology were formed regardless of the voltage. However, an average diameter of 40 nm was observed at 8 V for 5 minutes (b), which was relatively



**Figure 8.** SEM images of carbon nanofibers grown on the catalysts/C-fiber textiles deposited in Ni aqueous solution at different voltages for 5 min. (a) 5 V. (b) 8 V. (c) 11 V.



**Figure 9.** SEM images of carbon nanofibers grown on the catalysts/C-fiber textiles deposited in Ni-Cu mixed solution at different voltages for 5 min. (a) 5 V. (b) 8 V. (c) 11 V.

consistent and straight compared to the other voltages (a, c).

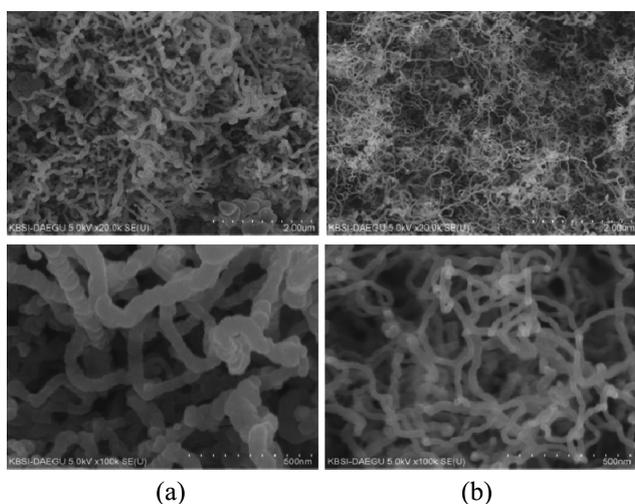
Figure 9 shows the SEM images of carbon nanofibers synthesized in the presence of catalyst produced in Ni-Cu mixed aqueous solution. Rough surfaces of hydrocarbon clustered carbon nanofibers were observed at higher voltages (b, c), but the nanofibers synthesized at 5 V (a) displayed a Y-shaped morphology which was similar in shape to Figure 8, but with a much larger diameter of 300 nm.

As the synthesis of carbon nanofibers shown in Figure 8

can be considered as Y-shaped carbon nanofibers with different branches and two growth directions, the one shown in Figure 9 was considered to be Y-shaped CNF, originating from a single catalyst with multiple growth directions, disclosing a possible relationship between the diameter of the carbon nanofibers and the size of the source catalyst.

Figure 10 shows the SEM images of the carbon nanofibers synthesized with Ni catalyst deposited onto Cu pre-deposited C-fiber textiles. No Y-shaped was observed for samples at any time of deposition; however, Figure 10(b) displayed coil-shaped carbon nanofibers with a diameter of 33 nm, produced at 8 V for 20 minutes. It was thought that the deposition pattern of the catalyst particles and the introduction of Cu may affect the growth mechanism of carbon nanofibers.

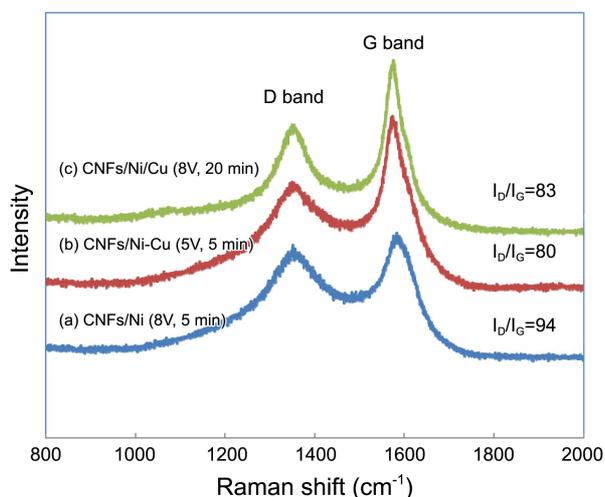
**BET.** To investigate the specific surface area of the synthesized carbon nanofibers,  $N_2$  sorption measurements were obtained, and the results are presented in Table 4. BET experiments against the substrate of the synthesized carbon nanofibers included the following conditions: 1) 8 V for 5



**Figure 10.** SEM images of carbon nanofibers grown on the Ni/Cu pre-deposited C-fiber textiles at 8 V for varying times. (a) 10 min. (b) 20 min.

**Table 4.** BET results for carbon nanofibers grown under 3 different deposition conditions

Name	Voltage (V)	Time (min)	Surface Area ( $m^2/g$ )
Ni	8	5	20
Ni-Cu	5	5	44
Ni/Cu	8	20	57

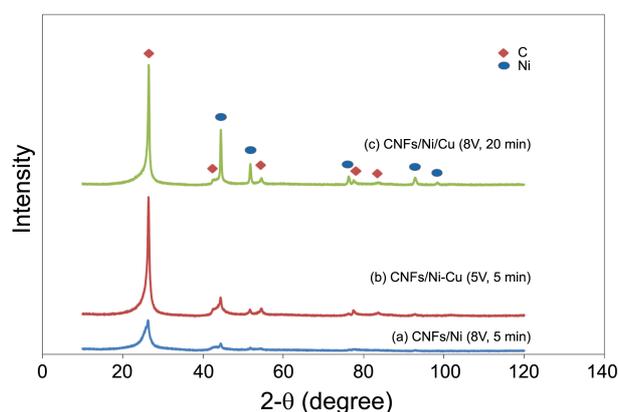


**Figure 11.** Raman spectra of carbon nanofibers grown under 3 different deposition conditions.

minutes in Ni aqueous solution, 2) 5 V for 5 minutes in Ni-Cu combined aqueous solution, 3) 8 V for 20 minutes in Ni deposition onto Cu pre deposited C-fiber textiles.

As Table 4 indicates, the greatest value of specific surface area of the carbon nanofibers was obtained under the third experimental condition, since the diameter of the synthesized carbon nanofibers was the most consistent and uniform, as can be seen in the SEM images of Figure 10(b).

**Raman.** Raman analysis, Figure 11, was obtained for the above three experimental conditions. In Figure 11, the D-band at  $1350\text{ cm}^{-1}$  was due to disordered graphite, and the G-band at  $1590\text{ cm}^{-1}$  was caused by ordered graphite. The D-band reveals the structural defects due to impurities and graphitized carbon nanofibers, other than carbon nanofibers that have  $sp^3$  hybridization. An increase in the ratio of the D-band intensity to G-band intensity indicates a high level of impurities and structural defects, and low crystallizability of carbon nanofibers. It was found that the intensity of the G-band in Figure 11(a) was relatively lower than that in (b) and (c), but had a higher value of D-band/G-band intensity (0.94), compared to those in (b) (c) (0.80 and 0.83, respectively). The ratios of the D-band/G-band intensity in Figure 11(b) and (c) were quite close to each other while being lower than (a), indicating the higher crystallizability of (b)

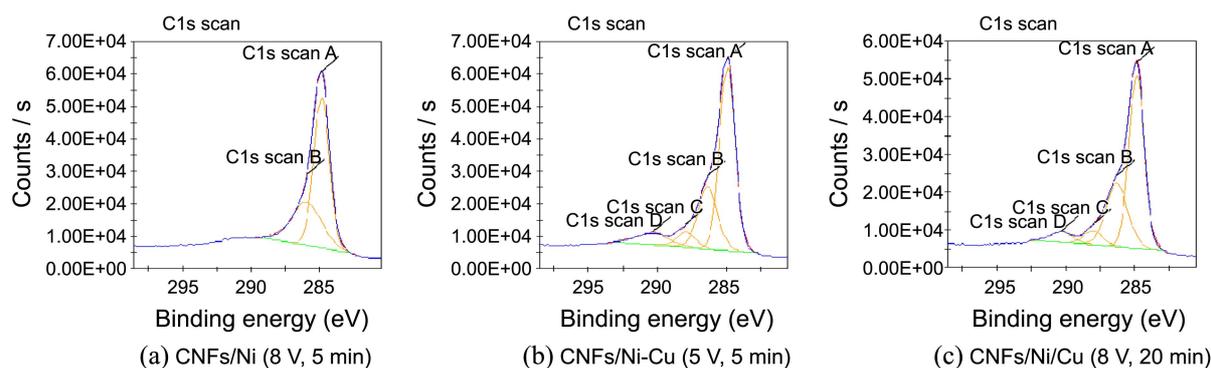


**Figure 12.** X-ray diffraction patterns of carbon nanofibers grown under 3 different deposition conditions.

and (c), and the higher graphitization level in (a) for the synthesized carbon nanofibers.

**XRD.** Figure 12 demonstrates the XRD results for the substrates generated from the above 3 experimental conditions. As seen in the figure, only peaks of Ni deposition onto C-fiber textiles and those of carbon bonded in carbon nanofiber synthesis were observed in the X-ray patterns. The intensity of the deposition system with the Ni-Cu mixed solution (b) and Ni/Cu system (c) was greater than that of the catalyst prepared in Ni solution. As Cu, the co-catalyst, was involved in the reaction, the efficiency of Ni and its crystallizability were improved, resulting in the production of highly crystallizable carbon nanofibers. The ratio of D-band to G-band in the Raman spectra also supports this phenomenon. The Ni/Cu system (c) yielded enhanced crystallizability of the catalyst, likely because Cu formed a stable catalyst layer as it was deposited onto the C-fiber textiles to keep the bulk phase of pre-deposited Ni.

Copper addition has been found to increase the thermal stability of supported Ni catalysts by enhancing the ability of the Ni catalyst to accumulate carbon, resulting in high crystallinity with longer catalytic lifetimes. In the case of (b) and (c), while the catalyst layers showed different crystallizability, crystallizability of the synthesized carbon nanofibers was similar. The domain sizes of catalysts are measured as  $163.8\text{ \AA}$  (Ni, 8 V, 5 min),  $167.229\text{ \AA}$  (Ni-Cu, 5 V, 5 min) and



**Figure 13.** X-ray photoelectron spectra of carbon nanofibers grown under 3 different deposition conditions.

**Table 5.** The results of X-ray photoelectron spectra for the carbon nanofibers grown

Element	Component	Name	Binding energy	Chemical bonding
C	CNFs	C1s Scan A	284.88-284.95	C-C(sp <sup>2</sup> )
		C1s Scan B	285.99-286.37	C-C(sp <sup>3</sup> )
		C1s Scan C	287.93-288.00	C=O
		C1s Scan D	290.31-290.32	COO

285.5 Å (Ni/Cu, 8 V, 20 min) respectively.

**XPS.** In order to investigate the chemical bonding structure, composition of elements and functional groups on the surface of the carbon nanofibers synthesized under the above 3 deposition conditions, they were subjected to XPS analysis. Results are tabulated in Figure 13. The bonding energy of C1s, at the range of 280-299 eV, was measured for carbon nanofibers synthesized by the CVD method with each of the 3 catalysts. As indicated in Figure 13(a), peaks at 284.9 eV and 285.9 eV were observed, corresponding to sp<sup>2</sup> and sp<sup>3</sup> hybridized bonding, respectively, but no functional group was found. On the other hand, peaks at 287.9 eV and 290.3 eV in (b) indicated the presence of C=O and COO bonding, along with sp<sup>2</sup> and sp<sup>3</sup> hybridization. Despite a reduction in intensity, these peaks were also found in (c), for which data are tabulated in Table 5.

Generally, the introduction of functional groups containing oxygen onto carbon nanofibers enhances its reactivity for the attachment of organic or inorganic materials. This fact is a significant factor for synthesis of carbon nanofibers/organic-inorganic composite, meaning that oxygen-containing functional groups are introduced without an additional oxidation process.

### Conclusions

With Ni/Cu/C-fiber textile systems as the substrate produced by electrophoretic deposition under three different deposition conditions, carbon nanofibers were synthesized through the CVD method by passing the coated textiles through N<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> gas mixtures. For substrate production, Ni aqueous solution, Ni-Cu mixed aqueous solution, and Ni aqueous solution with pre-deposited Cu on C-fiber textiles were used, and the following conclusions were made:

1. As voltage and time of deposition increase, the amount of catalyst deposited on the C-fiber textiles increase, with elevated Ni contents but reduced Cu contents.

2. Carbon nanofibers grown on Ni/C-fiber textiles deposited in Ni aqueous solution at 8 V for 5 minutes were synthesized with a diameter of 40 nm, and had consistent Y-shaped branch morphology.

3. Carbon nanofibers grown on Ni-Cu/C-fiber textiles deposited in Ni-Cu mixed aqueous solution at 5 V for 5 minutes were synthesized with a diameter of 300 nm, and had multi-directional Y-shaped branch morphology.

4. The substrate using Ni deposited on C-fiber textiles with pre-deposited Cu yielded the most uniform carbon nanofibers, with a diameter of 33 nm, and showed the highest specific surface area of 57 m<sup>2</sup>/g based on BET results.

5. According to XRD analysis, the catalyst deposited on C-fiber textiles had a higher crystallizability during the catalyst deposition process with the system including Cu, compared to that including only Ni deposition.

6. Raman analysis revealed that the carbon nanofibers synthesized on Ni-Cu or Ni/Cu bimetallic catalysts had similar ratios of D-band/G-band intensity, at 0.80 and 0.83 respectively, which were lower in value than the exclusive Ni catalyst, but had a higher composition of sp<sup>2</sup> hybridization.

7. XPS analysis revealed that carbon nanofibers synthesized in Cu-containing catalyst systems had oxygen functional groups without any additional oxidation process.

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