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Growth of Carbon Nanotubes on Carbon Fiber by Thermal CVD Using Ni Nanoparticles as Catalysts

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Abstract

Nickel nanoparticles and thin film on carbon fiber have been prepared through electroless deposition. Moreover, carbon nanotubes were grown on carbon fiber covered by nickel nanoparticles using thermal chemical vapor deposition. The effects of changes in the thickness of the nickel catalyst layer and the growth temperature of carbon nanotubes were studied systemically, and the results are discussed in the present work.

Keywords: Carbon nanotubes; carbon fiber; Ni nanoparticles; electroless deposition; CNT; CVD

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1. Introduction

Carbon nanotubes are promising candidates for applications ranging from nano-electronics to field emission displays, sensors, and electrochemical devices due to their unique electrical and scale-dependent physical properties [1–6]. The properties of carbon nanostructures and, consequently, their potential applications, strongly depend on their structural characteristics such as diameter, number of layers (in the case of nanotubes), length or presence of defects. Thus, a very strict control of the experimental parameters is required during the carbon nanotube fabrication. Carbon nanotubes with various properties can be produced by different techniques, including arc discharge [7], laser ablation [8], pyrolysis [9, 10], plasma enhanced [11, 12] and thermal chemical vapor deposition (CVD) [13, 14]. CVD methods have been preferred because of their versatility, low cost, high purity, controlled growth, and industrial scalability [15–17]. Fe, Co, and Ni have been widely reported to be the most effective catalysts for the CVD growth of carbon nanostructure [18, 19].

Carbon fibers have many excellent mechanical characteristics, including high tensile strength and elastic modulus as well as high thermal and electrical conductivities. Polymer-based advanced conductive composites filled with carbon fibers have great utility in adverse environments because of their excellent mechanical stability and durability over a wide range of temperature and pressures [20]. Hence, many conductive polymer composites have been produced with carbon fiber as conductive reinforcements. Incorporation of carbon nanostructures, such as carbon nanotubes can enhance the strength of the composite materials. Unfortunately, dispersion of carbon nanostructure is difficult due to their tendency to form agglomerates which reduces the load bearing capacity of the composite materials.

In the present work, we fabricated directly anchored carbon nanotubes on carbon fiber using thermal CVD method. Electroless deposited nickel nanoparticles and thin films on carbon fiber acted as catalyst for the growth of carbon nanotubes. The effects of modifying fabrication parameters of carbon nanotubes, such as nickel catalyst thickness and carbon nanotube growth temperature on the carbon nanotube length and width were investigated. Our results will contribute towards successful manufacture of composite materials composed of carbon fibers with incorporated carbon nanotubes.

2. Experimental

For the present investigation, PAN based continuous carbon fibers (Toray, TGP-H-030, 30x30 cm) was used. A Nickel sulphate bath (25 g/L) was used as a nickel source for the formation of the nickel catalyst layer. Tri-sodium citrate (50 g/L), sodium hypophosphite (25 g/L) and ammonium chloride (25 %) were used as stabilizer, reducing and complexing agents in the electroless deposition, respectively. Ammonia was used to maintain the pH of the solution. The reducing agent used in this work is sodium hypophosphite, whose chemical reaction consists of two simultaneous reactions: First, the cathodic reaction of Ni^{2+}, H^+, and $H_2PO_2^-$ for the deposition of Ni and the production of hydrogen [21–23], and the anodic oxidation of $H_2PO_2^-$.

The coating of carbon fiber was removed by immersing the fibers in an acetone solution for 1 hour and rinsing with deionized water prior to electroless deposition; desizing process. The cleaned fibers were heated in an oven at 80 ºC for 1 hour in order to dry the fiber surface. Next, the treated carbon fiber was activated by tin chloride (10 g/L) and palladium chloride (1 g/L) with a dipping time of 3 and 2 minutes at room temperature, respectively. Afterwards, the activated samples were dipped in the nickel solution (pH 11) bath at 60 ºC.

Nickel-coated carbon fiber samples (1x1 cm) were placed in the middle of a single zone quartz tube furnace with an inner tube diameter of 5 cm and heating zone length of 80 cm. Each sample was annealed at 500 ºC with H_2 stream at a flow rate of 200 sccm for 20 minutes. After annealing, the furnace was

heated with Ar and H_2 (50 and 150 sccm) to a reaction temperature of 550 ºC. Ar and H_2 were then replaced by C_2H_2 (10 sccm), H_2 (150 sccm), Ar (500 sccm) and N_2 (50 sccm) to initiate the synthesis of carbon nanostructures for 5 minutes. Finally, the sample was slowly cooled down to room temperature in Ar and N_2 (50 and 450 sccm) environments. The resulting carbon nanotubes were characterized by Field Emission Scanning Electron Microscopy (FE-SEM, JEOL, JSM-6700F).

3. Results and Discussion

The FE-SEM images of carbon fiber surfaces after deposition Ni catalysts are shown in Fig. 1. Nickel nanoparticles were deposited on carbon fiber using electroless methods with solutions of various nickel concentrations. As the nickel concentration increases, the nickel coating thickness increases significantly. At 0.5 % Ni concentration (Fig. 1a), nanoscaled nickel particles (< 20 nm) were deposited preferentially on the carbon surface, whereas at 1 % Ni concentration (Fig. 1b), very thin nickel film was homogenously deposited on carbon surface. At 30 % Ni concentration (Fig. 1c), initially, thin film type nickel was deposited on the surface and then more larger nickel clusters were deposited once more on the top of the nickel thin film. As a result, the higher concentration of nickel causes aggregation of nickel particles on the Ni thin film. However at 100 % concentration (Fig. 1d), thick Ni film with tiny Ni nanoparticles on the surface was homogenously deposited on the carbon fibers. These results suggest that the amount of nickel coating increases significantly as the nickel concentration increases. It seems that nickel catalysts cover the entire surface of the carbon fiber with 3D growth mode in sequence of nanoparticles (NPs) ->thin layer (TL) ->Hybrid NPs-TL->thick layer.
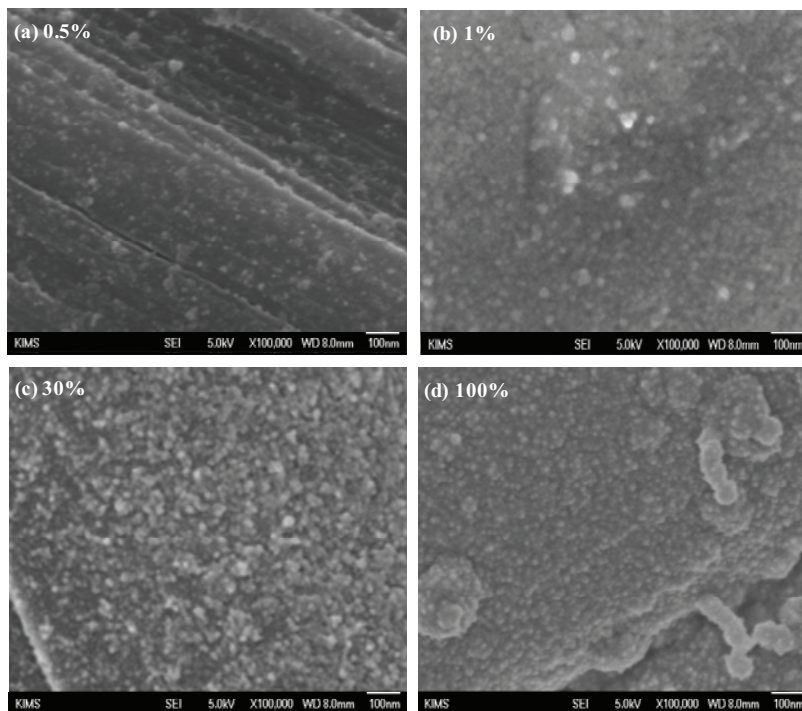

Fig. 1 FE-SEM images of carbon fiber surfaces covered with nickel catalysts (x100,000). Ni baths of different concentrations (plating time for 5 sec and temperature at 60 ºC) were used for preparing various samples, whose images are shown in this figure.

Based on these results, several important growth parameters such as types of Ni catalysts film and CNT growth temperature were systematically altered to determine the optimal growth conditions for carbon nanotubes growth. Electroless deposited nickel (0.5, 1, 30 and 100 %) samples were used to study the growth of carbon nanotubes on carbon fiber by thermal CVD.

In 0.5 % and 1 % Ni solution samples, granular carbon nanotubes were grown and randomly woven into each other on the carbon surface (Fig. 2a & b). Due to nickel catalyst thickness, high density of carbon nanotube was obtained from 1 % than that of the 0.5 % concentration. At 30 % concentration (Fig. 2c), granular and spring type of carbon nanotubes were generated on the surface. With increasing the catalyst thickness as 100 % concentration (Fig. 2d), lengthwise highly dense carbon nanotubes with more thick in diameter were grown on carbon fiber. These results strongly suggest that with increasing the nickel catalyst thickness, one can fabricate highly anchored carbon nanotubes with more longer and thicker on carbon fiber using CVD. Electroless Ni catalysts deposition method on carbon fiber is suitable method for structure controlled CNT growth and roll-to-roll fabrication of CNT.
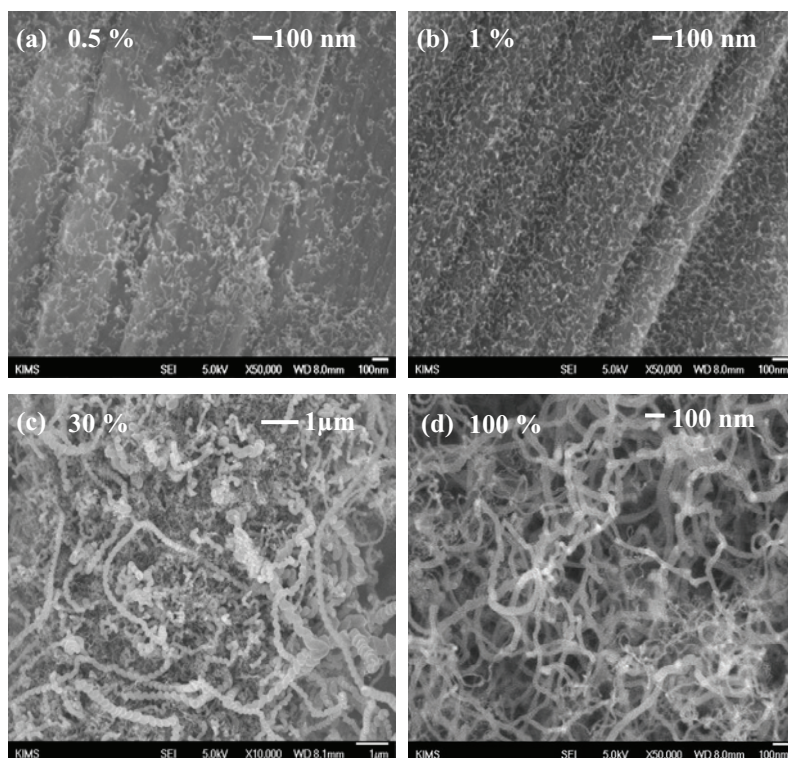

Fig. 2 CNTs grown on electroless-deposited Ni (0.5, 1, 30 and 100 %, respectively): pre-treatment for 20 min with H_2 (200 sccm) and synthesis with C_2H_2 (10 sccm), H_2 (150 sccm), Ar (500 sccm) and N_2 (50 sccm) at 550 ºC for 5 min, (x 50,000 for (a), (b) & (d) and x 10,000 for (c)).

The growth temperature plays an important role to control length and width of carbon nanotube through CVD. Hence, nickel catalysts coated carbon fiber sample (100 %) was used to optimize the growth behaviour of carbon nanotube depending on the reaction temperature. The FE-SEM images in Fig. 3, show carbon nanotubes grown on carbon fiber. The average length of carbon nanotube (8 um at 550 ºC and 10 um at 650 ºC and 750 ºC, respectively) increases as the growth temperature is increased. Whereas

the carbon nanotube width (100~120 nm at 550 ºC and 70~90 nm at 650 ºC and ~ 50 nm at 750 ºC, respectively) decreased with increasing the growth temperature. The comparison of nanotubes grown at 550 ºC with those grown at 650 ºC and 750 ºC, respectively indicated that thicker, shorter and less curved carbon nanotube at relatively lower reaction temperature ascribable to the reduced reaction rate. While the growth behaviour of CNT with more thinner in width and longer in length at high temperature can be understood by the fast reaction rate. In addition, nickel catalysts and induce carbon atoms can be rearranged and diffused into the carbon fiber surface at high temperature, results in the formation of tiny Ni nanoparticles on the surface and affect to the structure of carbon nanotube.
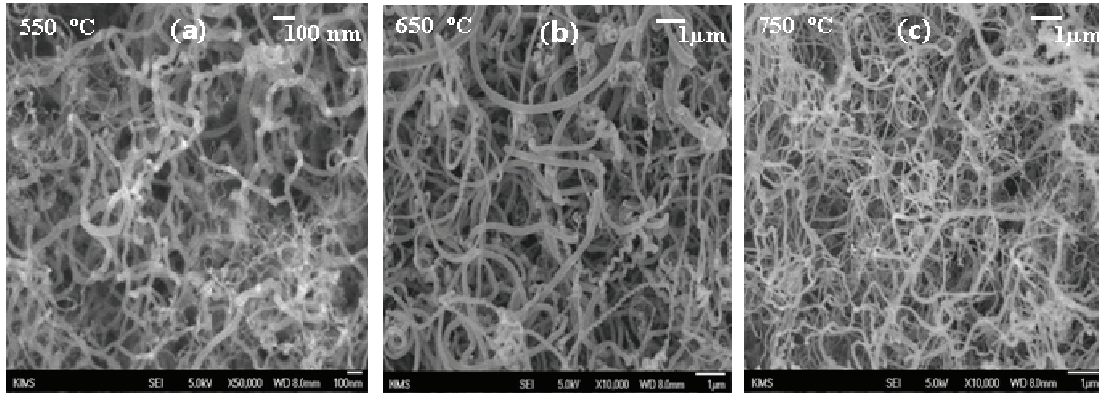

Fig. 3 FE-SEM images of carbon nanotubes growth on nickel plated carbon fiber by thermal CVD. Pre-treatment with H_2 (200 sccm) for 20 min. Synthesis with C_2H_2 (10 sccm), H_2 (150 sccm), Ar (500 sccm) and N_2 (50 sccm) for 5 min at 550, 650 and 750 ºC, respectively (x50,000 for (a) and x10,000 for (b & c)).

4. Conclusions

Directly anchored carbon nanotubes were achieved by using electroless deposited Ni catalysts and thermal CVD method. The thickness and particle size of Ni catalysts can be varied from few ten nm to hundred nm by adjusting the concentration of Ni plating solution. With increasing the film thickness of Ni catalysts, various types of carbon structures such as carbon nanotube, carbon filament and carbon spring were obtained. And also, depending on the growth temperature, one can adjust the density, shape, length and width of carbon nanotube. The optimal growth condition for directly anchored carbon nanotube on carbon fiber was pre-treatment time with H_2 (200 sccm) for 20 min and followed by 5 min growth time at 550 °C using a gas mixture of C_2H_2 (10 sccm), H_2 (150 sccm), Ar (500 sccm) and N_2 (50 sccm) under atmospheric pressure. Further studies need to be carried out for successful synthesis of composite materials based on carbon fiber with carbon nanotubes.

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