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The effect of carbon microfiber substrate pretreatment on the growth of carbon nanomaterials

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ABSTRACT

The floating catalyst method was used to obtain carbon nanotubes, carbon submicrotubes and other carbon nanomaterials by changing the pretreatment conditions of carbon microfiber substrate. The morphology and microstructure of the obtained products were characterized by field emission scanning electron microscopy, high-resolution transmission electron microscopy and Raman spectroscopy. The results showed that on untreated carbon microfiber surface, only some carbon particles and several carbon nanotubes were deposited. However, after carbon microfibers were boiled in the solution of H_2SO_4/HNO_3 and were immersed in the solutions of $Fe(NO_3)_3$/xylene, $Fe(NO_3)_3$/acetone, ferrocene/acetone and $Fe(NO_3)_3$/ferrocene/acetone, the obtained products were a high-density carbon nanotubes, carbon nanotubes with many carbon particles, carbon submicrotubes and a mixture of carbon nanomaterial, respectively. Thus the pretreatment of the carbon microfiber substrate greatly influenced the morphology and microstructure of the synthesized products.

1. Introduction

Carbon-based materials have attracted considerable attention and interest owing to their unique physical and chemical properties. For example, carbon nanotubes (CNTs), diamonds, carbon fibers and carbon submicrotubes and so on, they are good candidates for field emission electron source materials, absorption-wave materials, electrode materials and composites supports and so on [1–4]. Especially, since the paper about CNTs was reported by Iijima in 1991 [5], many studies have shown the exceptional mechanical, electrical and thermal properties of this new form of carbon [6–8]. Similar to CNTs, carbon submicrotubes are hollow and are composed of graphitic structure. Carbon submicrotubes have shown the same exceptional properties as CNTs. However, some problems are present about the synthesis of carbon nanomaterials on carbon microfiber substrate: catalyst was easily diffused into carbon microfiber substrate and other carbonaceous byproducts (including diamond, diamond-like and amorphous carbon) were also easily brought [9,10]. Therefore, by far, only few studies have been reported about the synthesis of CNTs on carbon microfiber substrate [11–17]. The synthesis of carbon nanomaterials (including CNTs and carbon submicrotubes) on carbon microfiber substrate can further improve the

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properties of carbon microfibers. Moreover, the composite materials of carbon micro- and nanomaterials probably have potential applications in many fields.

In this paper, we report the synthesis and characterization of different carbon nanomaterials on carbon microfibers by changing the pretreatment conditions of carbon microfiber substrate. We study the morphology and microstructure of the obtained products by field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. Finally, we obtain the optimum pretreatment conditions of carbon microfiber substrate for the growth of carbon nanomaterials, and discuss the effect of carbon microfiber substrate pretreatment on the growth of carbon nanomaterials.

2. Experimental

Before the growth of carbon nanomaterials, carbon microfibers were pretreated under different experimental conditions, which were shown in Table 1. The carbon microfibers used in the experiment were polyvinyl alcohol – based and polyacrylonitrile – based activated carbon fibers with a diameter range from 3 to 10 μm. First, carbon microfibers were ultrasonically cleaned in acetone and ethanol for about 10 min, respectively, and were dried at the room temperature. Then the carbon microfibers were boiled in the solution of H_2SO_4/HNO_3 for about 30 min and were immersed into the different solutions for about 12 h, respectively. Finally, the carbon microfibers needed to be taken out from the solutions and were dried at the room temperature before the deposition of carbon nanomaterials.

The growth of carbon nanomaterials was carried out in a tubular furnace with a horizontal quartz tube at the atmospheric pressure by floating catalyst method. The schematic diagram of the experimental setup was shown in Fig. 1. First, the obtained carbon microfibers were placed at the center and the catalyst was placed at the front of the quartz tube with different quartz boats. The two temperature zones were, respectively, controlled by different temperature controllers. Then the quartz tube was heated under N_2 ambient with a flow rate of 50 sccm to remove oxygen in it. When the temperature in the middle of the quartz tube was increased to 1023 K, C_2H_2/ferrocene mixtures were introduced into the tube. The flow rate ratio of C_2H_2/N_2 was shown in Table 1. The carbon nanomaterials were grown on the carbon microfibers when C_2H_2/ferrocene mixtures were introduced. After about 20 min, C_2H_2 gas and power supply were shut off. Finally, the quartz tube was cooled down to the room temperature in N_2 ambient with a flow rate of 50 sccm. The purities of both C_2H_2 and N_2 employed in the experiment are higher than 99.5%.

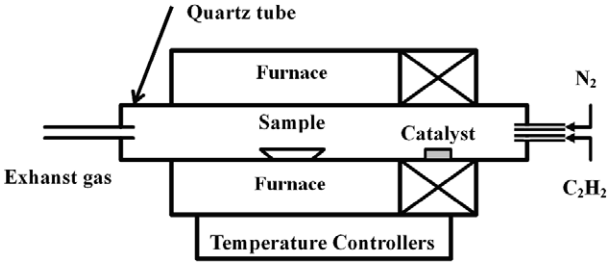

Fig. 1 – The schematic diagram of the floating catalyst setup for the growth of carbon nanomaterials.

Based on the different experimental conditions shown in Table 1, samples A, B, C, D and E were obtained, respectively. The morphology and microstructure of the obtained products were characterized by field emission scanning electron microscope (Hitachi S-4800) operated under an accelerating voltage of 15 kV, high-resolution transmission electron microscope (FEI Tecnai F 30) operated under an accelerating voltage of 300 kV and Raman spectrometer (Jobin Yvon HR800) with the laser wavelength of 488.0 nm by an Ar^+ laser.

3. Results and discussion

Fig. 2 shows the low-resolution SEM images of obtained products on carbon microfiber substrate with different experimental conditions. As seen in Fig. 2a, the surface of the carbon microfiber without immersion treatment is not entirely covered by the product, only some carbon particles and a few CNTs are grown on the surface of the carbon microfiber. In the inset of Fig. 2a, it can be clearly observed that a single CNT is surrounded by many carbon particles. However, after the carbon microfibers are immersed in the solution of $Fe(NO_3)_3$/xylene, the obtained product is a high-density CNTs. As shown in Fig. 2b, the CNTs on the surface of the carbon microfibers are not straight, and the length of CNTs is smaller than 2 μm. After the carbon microfibers are immersed in the solution of $Fe(NO_3)_3$/acetone, the obtained product is CNTs with carbon particles. As seen in Fig. 2c, the surface of the carbon microfibers is entirely covered by carbon particles and carbon clusters. Some CNTs are adsorbed on the carbon particles, and the CNTs are long in length. After the carbon microfibers are immersed in the solution of ferrocene/acetone, a submicroscale tubular structural product – carbon submicrotubes are grown on the carbon microfibers. As shown in Fig. 2d, the carbon submicrotubes are basically ver-

Table 1 – The experimental parameters for the growth of different carbon nanomaterials on carbon microfiber substrate

Samples	C_2H_2:N_2 (sccm)	$V_{H_2SO_4}$:V_{HNO_3}	Immersion condition	Deposition time (min)	Deposition temperature (K)	Products
A	50:200	1:3	–	20	1023	Carbon particles
B	30:150	1:3	$Fe(NO_3)_3$/xylene	20	1023	CNTs
C	50:200	1:3	$Fe(NO_3)_3$/acetone	20	1023	CNTs with particles
D	50:200	1:3	Ferrocene/acetone	20	1023	Carbon submicrotubes
E	50:200	1:3	$Fe(NO_3)_3$/ferrocene/acetone	20	1023	A mixture of carbon nanomaterials

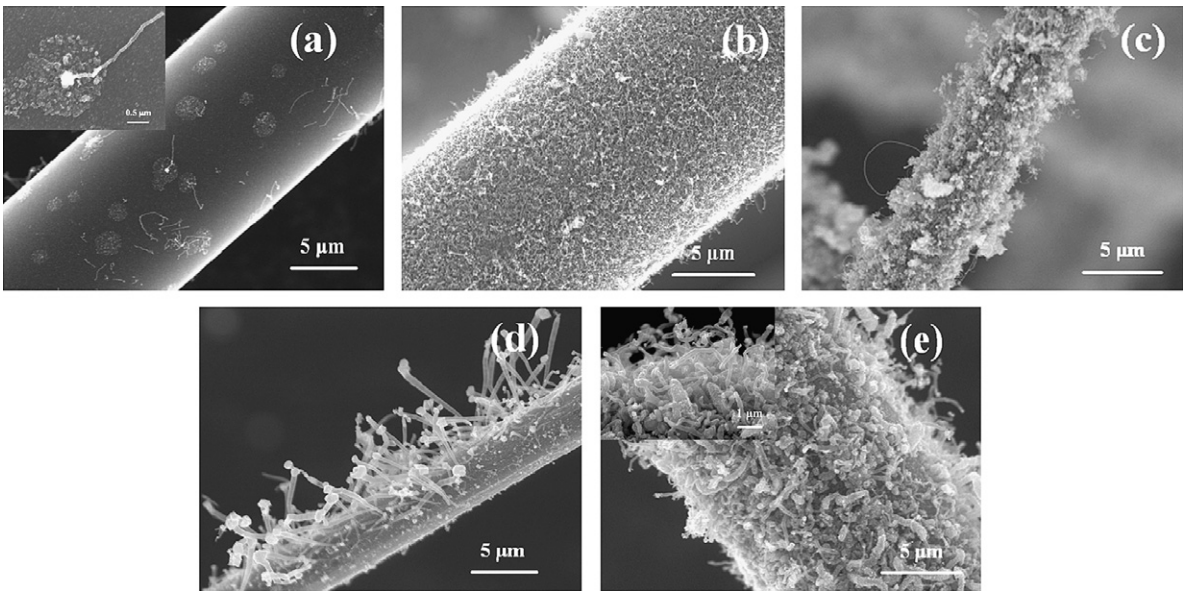

Fig. 2 – The low-resolution SEM images of carbon particles (a), high-density CNTs (b), CNTs with carbon particles (c), carbon submicrotubes (d), and a mixture of carbon nanomaterials (e) grown on carbon microfiber substrate with different pretreatment conditions.

tical to the surface of the carbon microfiber, and the length of the carbon submicrotubes ranges from 5 to 10 μm. After the carbon microfibers are immersed in the solution of $Fe(NO_3)_3$/ferrocene/acetone, a mixture of carbon nanomaterials are grown on the surface of the carbon microfibers. In Fig. 2e, it can be seen that the surface of the carbon microfiber is covered entirely by the product. The sizes of the product are not uniform, and the surface morphology of them is also different. One part is smooth and the other part is rough shown in the inset of Fig. 2e.

The high-resolution SEM images of the obtained products on carbon microfibers with immersion treatment are shown in Fig. 3. As seen in Fig. 3a, the high-density CNTs are not grown vertically on the surface of the carbon microfiber, but rather interlace one another. The diameters of the CNTs range from 20 to 50 nm. In Fig. 3b, it can be noted that the CNTs with carbon particles are very long on the surface of the carbon microfiber. They are not linked with the surface of the carbon microfiber, only the roots are linked with the carbon particles and these CNTs are enlaced one another. As shown in Fig. 3c, the diameter of the carbon submicrotube is about 400 nm. The wall of the carbon submicrotube is very thin and the outer wall is also very rough. In the inset of Fig. 3c, it can be seen that the carbon submicrotubes have

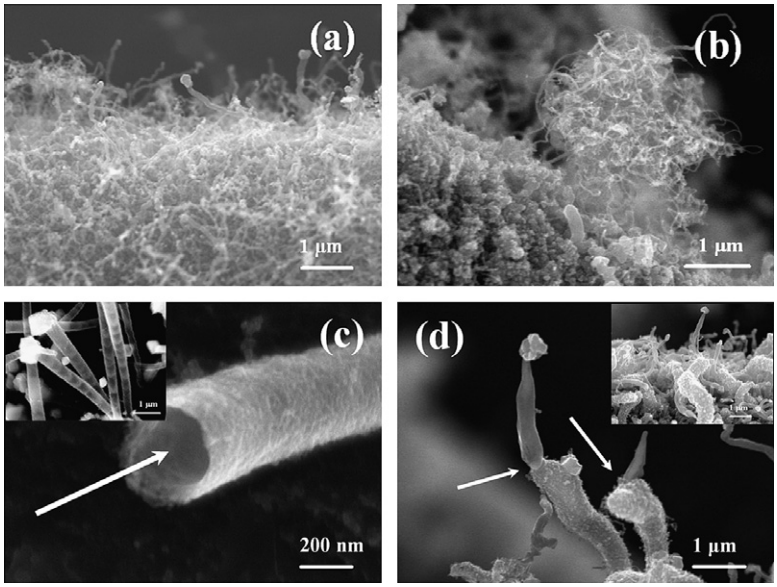

Fig. 3 – The high-resolution SEM images of high-density CNTs (a), CNTs with carbon particles (b), carbon submicrotubes (c), and a mixture of carbon nanomaterials (d) grown on carbon microfiber substrate with different pretreatment conditions.

clear bamboo-like structure. Fig. 3d shows the SEM image of a mixture of carbon nanomaterials. It can be noted that the surface of the below part of the product is covered by carbon nanoparticles and the surface of the above part is smooth. The diameters of the rough part and the smooth part of the product are about 600 nm and 300 nm, respectively. Moreover, a distinct boundary can be observed between the two parts shown in Fig. 3d by arrows. Furthermore, the growth of the mixture of carbon nanomaterials on the carbon microfibers is disordered, as seen in the inset of Fig. 3d.

Raman spectrum is a powerful tool for the microstructural analysis of carbon nanomaterials. Generally, for the Raman spectrum of CNTs, two strong peaks are present at about 1352 cm^{-1} and 1582 cm^{-1}, which are commonly known as the first-order D band and G band. The D band at about 1352 cm^{-1} is associated with the presence of other carbonaceous impurities and defects in the hexagonal graphitic layers [18]. The G band at about 1582 cm^{-1} corresponds to an E_{2g} mode of graphite, which is due to the sp^2-bonded carbon atoms in a two-dimensional hexagonal graphitic layer [19]. To further characterize the crystal quality and graphitization degree of the obtained products, the Raman spectra of carbon particles, high-density CNTs, CNTs with carbon particles, carbon submicrotubes and a mixture of carbon nanomaterials grown on carbon microfibers are shown in Fig. 4. The first-order D band and G band appear in the Raman spectra of every sample, and the secondary order mode of the D band can also be observed at about 2705 cm^{-1}. The ratio of the intensity of the D and G peaks is known to be correlated with the quality of graphitic structure. The I_D/I_G ratio is smaller, the graphitization degree of the product is higher. The I_D/I_G ratios of Samples A, B, C, D and E are estimated to be about 0.885, 0.650, 0.770, 1.218 and 0.874, respectively. For Sample D, the high ratio of the I_D/I_G indicates that the defects of graphitic structure are present in the carbon submicrotubes. However, the low ratio of the I_D/I_G of Sample B indicates that the high-density CNTs grown on the carbon microfiber have higher graphitization degree, compared with other carbon nanomaterials grown on carbon microfibers.

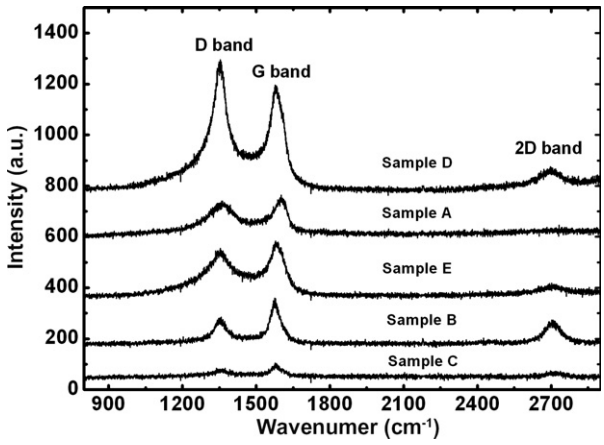

Fig. 4 – The Raman spectra of carbon particles (Sample A), high-density CNTs (Sample B), CNTs with carbon particles (Sample C), carbon submicrotubes (Sample D) and a mixture of carbon nanomaterials (Sample E) on carbon microfiber substrate.

Further, the microstructure of CNTs and carbon submicrotubes were also analyzed. Fig. 5 shows the HRTEM images and selected area electron diffraction (SAED) patterns of CNT and carbon submicrotube. As seen in Fig. 5a, the diameter of the CNT is about 23 nm and the thickness of the wall is about 7.5 nm. In the inset of Fig. 5a, the diffraction pattern of (002), (100) and (110) planes of CNTs can be observed. As shown in Fig. 5b, the graphitic defects are present on the surface of the carbon submicrotube, which is in accordance with the strong D peak in the Raman spectrum of the carbon submicrotube. In the inset of Fig. 5b, the diffraction patterns of (002), (102), (110) planes of carbon submicrotubes are also observed.

To further understand the effect of carbon microfiber pretreatment on the growth of carbon nanomaterials, the surface change of carbon microfibers from the pretreatment was analyzed. Fig. 6 shows the SEM images of carbon microfibers before and after the boiling in the solution of H_2SO_4/HNO_3. As seen in Fig. 6a, the surface of the sulcate carbon microfiber is smooth. In the inset of Fig. 6a, it can be noted that the grooves on the surface of the carbon microfiber are shallow. However, after the carbon microfibers are boiled in the solution of H_2SO_4/HNO_3, the grooves on the surface of the carbon microfiber get deep, and some parts of the surface are destroyed shown in Fig. 6b. The inset of Fig. 6b clearly shows the destroyed surface of the carbon microfiber. It is known that some defects or non-graphite phase (i.e., amorphous carbon)

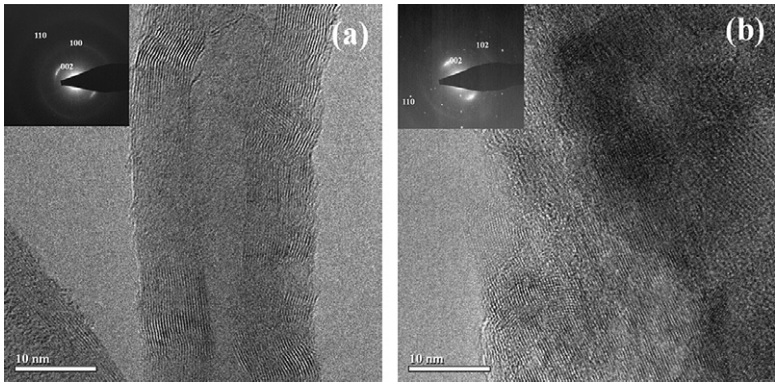

Fig. 5 – The HRTEM images and SAED patterns of CNT (a) and carbon submicrotube (b).

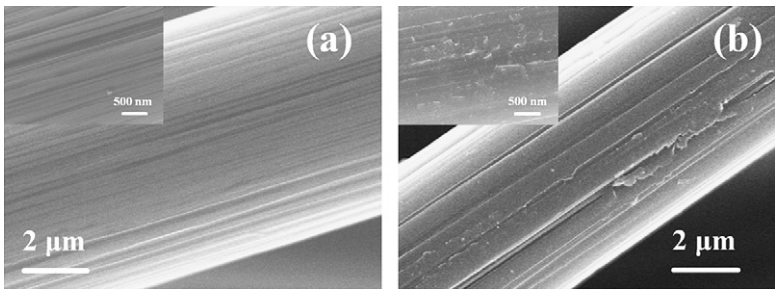

Fig. 6 – The SEM images of carbon microfibers before (a) and after (b) the boiling in the solution of H_2SO_4/HNO_3.

are present on the surface of carbon microfibers. We considered that the acid treatment removed the non-graphite phase on the surface of carbon microfibers, and destroyed the structure of carbon microfibers at the location of the graphitic defects. The surface of carbon microfibers was activated by the acid treatment and was favorable for the adsorption of ferric particles and the growth of carbon nanomaterials.

Fig. 7 shows the SEM images of carbon microfibers immersed in the different solutions. As seen in Fig. 7a, many $Fe(NO_3)_3$ nanoparticles are adsorbed on the surface of the carbon microfiber. In the inset of Fig. 7a, it can be observed that the sizes of the particles range from about 30 to 100 nm, and the distribution of the particles is uniform. In Fig. 7b, it can be noted that the deposits ($Fe(NO_3)_3$ and $Fe(OH)_3$) with small sizes on the surface of the carbon microfiber form smooth thin film. As shown in Fig. 7c, some ferrocene particles or clusters are adsorbed on the surface of the carbon microfiber. The particles or clusters are large and are distributed randomly on the surface. In Fig. 7d, the surface of the carbon microfiber is covered by a smooth thin film and some particles (ferrocene, $Fe(NO_3)_3$ and $Fe(OH)_3$) with different sizes are adsorbed on the surface of the film. In comparison with the different carbon nanomaterials grown on carbon microfibers with different pretreatment, it can be concluded that the content and size of ferric particles adsorbed on the carbon microfibers is correlated with the density of carbon nano- and submicro-tubes. However, the smooth film adsorbed on the surface of carbon microfibers is unfavorable for the formation of tubular structure, but is responsible for the growth of carbon particles.

The morphology and microstructure of the obtained products were hardly affected by the tiny change of other experimental parameters, such as the temperature (973 K, 1073 K) and the gas flow rate (40:200 sccm) and so on. Furthermore, the experiments without floating catalysts had also been performed by only the pretreatment of carbon microfibers. However, the results were similar to that of the experiment with only floating catalyst. In comparison with the experiments by only floating catalysts, only the pretreatment of carbon microfibers and floating catalysts with the pretreatment of carbon microfibers, it can be concluded that both floating catalysts and the pretreatment of carbon microfibers play roles on the growth of carbon nanomaterials. However, the real catalyst precursor for the growth of carbon nanomaterials is

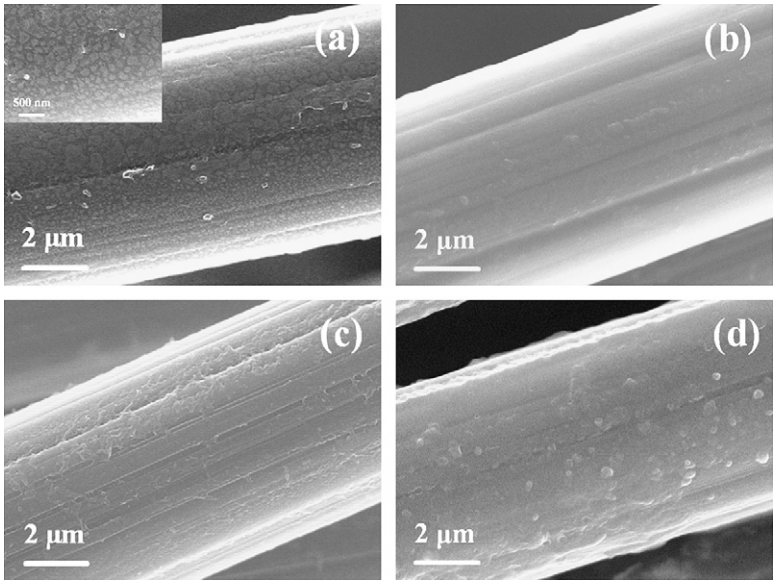

Fig. 7 – The SEM images of carbon microfibers immersed in the solutions of $Fe(NO_3)_3$/xylene (a), $Fe(NO_3)_3$/acetone (b), ferrocene/acetone (c) and $Fe(NO_3)_3$/ferrocene/acetone (d).

mainly the ferrocene at the front of the reactor. The Fe component on the surface of carbon microfibers has different effect on the growth of different products. Because of the growth of the carbon nanomaterials on carbon microfibers without hydrogen, the $Fe(NO_3)_3$ or $Fe(OH)_3$ did not play the role of catalyst. The pretreatment activated the surface of carbon microfibers and decreased the diffusion of the floating catalysts into the carbon microfibers when the carbon nanomaterials were grown. When the high-density CNTs and CNTs with carbon particles were grown on the carbon microfibers, the real catalyst was the ferrocene at the front of the reactor. The $Fe(NO_3)_3$ or $Fe(OH)_3$ on the surface of carbon microfibers provided the growth sites of CNTs and carbon particles, and provided the interface transition between carbon microfibers and carbon nanomaterials. When the carbon submicrotubes and a mixture of carbon nanomaterials were grown, partly, the ferrocene particles deposited on the surface of carbon microfibers played the role of catalyst on the growth of submicro-products owing to the large size of the ferrocene particles deposited on the substrate. But the main catalyst was still the ferrocene at the front of the reactor because the quantity of the ferrocene particles deposited on the surface of carbon microfibers was too little.

4. Conclusion

In summary, using floating catalyst method, carbon particles, a high-density CNTs, CNTs with carbon particles, carbon submicrotubes and a mixture of carbon nanomaterials were synthesized on carbon microfibers with different pretreatment of the carbon microfiber substrate. The results indicate that the pretreatment of carbon microfiber substrate greatly affected the morphology and microstructure of the obtained products. Both the ferrocene at the front of the reactor and the Fe component on the substrates are responsible for the growth of the carbon nanomaterials. The carbon microfibers/CNTs should be good cold cathode materials owing to the well electronic conductivity and chemical stability of the carbon microfibers and the exceptional electron emission ability of the CNTs. A new kind of composite materials can be produced when the hollow carbon submicrotubes are filled with other nanomaterials. Moreover, these carbon nanomaterials grown on carbon microfibers can used to fabricate electrodes to be used in electrochemical applications like fuel cells and sensors and so on. Therefore, the carbon microfibers-based composite materials will exhibit potential applications in many fields.

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