In situ growth of CNTs on carbon fiber by chemical vapor deposition

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Abstract. Carbon nanotubes (CNTs), as a kind of one-dimensional nanomaterial with special structure, have excellent properties in various aspects. Grafting CNTs onto carbon fiber (CF) surface to improve the mechanical properties of carbon fiber reinforced composites has been the focus at home and abroad. In this paper, chemical vapor deposition (CVD) was used to in situ grow CNTs on CF surface with carbon monoxide (CO) as carbon source and ferric nitrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O) as catalyst. The effect of different process conditions on the growth of CNTs were explored and the mechanism was briefly described. It is found that the oxidation treatment of CF could introduce a large number of reactive groups on the surface of CF, which was conducive to uniform dispersion of the catalyst. The morphology of CNTs were characterized by scanning electron microscopy (SEM). The results showed that the optimum growth concentration of catalyst precursor was 0.05 mol/L.

1. Introduction
Carbon nanotubes (CNTs) can be used as secondary reinforcements to improve the electrical and thermal conductivity and mechanical properties of carbon fiber reinforced composites (CFRCs) due to their excellent mechanical and electrical properties [1-4]. The introduction of CNTs to the CF surface increases the surface roughness of the fiber, and also improves its wettability with the resin [5]. Grafting CNTs onto CF surface to prepare CFRCs, the interface combination between the fiber and resin has been well resolved [6,7]. At present, there are various methods for grafting CNTs on the surface of CF, including chemical vapor deposition (CVD) [8,9], chemical grafting [10,11], electrophoretic deposition [12,13] and solution impregnation [14]. Among these methods, CVD can produce the high-yield and high-purity CNTs on CF, which is the most commonly used method for preparing CNTs/CF reinforcements. Sharma \textit{et al} [15] systematically studied the influence of the types and concentrations of catalysts on the microstructure of CNTs, and provided the basis for the controlled growth of CNTs on CF surface.

In this paper, CNTs were successfully grown on the surface of CF by CVD. The surface of CF was treated by nitric acid and the catalyst was loaded by solution impregnation method. The structure and morphology of CNTs/CF reinforcements prepared were analyzed by scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM). The main research includes: (1) To analyze the surface microstructure and surface oxygen-containing functional groups of CF after pretreatment. (2) To explore the optimal catalyst concentration for the growth of CNTs.
2. Experimental details
Polyacrylonitrile (PAN)-based CF used in this study was supplied by Toray Corporation, Japan. Before the experiment, CF needed to be treated to remove the epoxy resin on its surface. Appropriate amount of CF was immersed in acetone solution for 24 h, and then washed repeatedly with deionized water and dried in an oven. After acetone-treatment, the desized CF were oxidized by HNO$_3$ at 60°C for 40 min in a water bath. The catalyst used in this experiment was Fe and the catalyst precursor solution was obtained by dissolving Fe(NO$_3$)$_3$·9H$_2$O in ethanol and sonicated in an ultrasonic cleaner for 10 min to achieve uniform dispersion of ferric nitrate in ethanol solution. The CF was immersed in the catalyst solution for 1 h, and then taken out and naturally dried.

The CNTs/CF reinforcements were prepared in a horizontal tube furnace under atmospheric pressure, using carbon monoxide (CO) as carbon source and a mixture of H$_2$/Ar as carrier gas. CF coated with catalyst was put on a quartz boat and placed in the center of the tube furnace. After the furnace was installed, the tube was purged using a vacuum pump and flowing Ar. This was repeated three times, and then, the temperature was raised to 450°C at a heating rate of 10°C/min. Ar was closed and H$_2$ was introduced, the flow rate was controlled at 100 sccm for 1 h in order to reduce the catalyst to nanoparticles. After that H$_2$ was closed and Ar was introduced, when the temperature was raised to 700°C, a mixture of CO/H$_2$/Ar was injected for the growth of CNTs with a feeding rate at 100/100/200 sccm. After CNTs growth for 1 h, the reactor was turned off, allowing the system to fall to room temperature naturally under the flowing Ar. The CVD schematic diagram is shown in figure 1.

![CVD schematic diagram](image)

Figure 1. Schematic diagram of the CVD reactor.

The surface morphology of the samples was observed by SEM (FEI Nova Nano SEM 450, USA) at an operating voltage of 15 kV, all samples were fixed on the holder with conductive paste and coated by Au. Further detailed structure of CNTs were examined using HRTEM (JEOL, JEM-2100) operated at 200 kV. X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, VG, UK) was performed to study the surface chemical composition and the energy state of the pretreatment CFs using a monochromatic Al $K_{α_1}$ source (1486.6 eV) at a base pressure of 2×10$^{-9}$ mbar with the system of universal charge compensation.

3. Results and discussion
3.1. Characterization of the pretreated CFs
To form and uniformly disperse catalyst nanoparticles on the surface of CF, the CF should be pre-treated with acetone and nitric acid before being impregnated in catalyst solution. The epoxy glue on the surface of CF was removed after being soaked in acetone. The oxidation treatment increased the surface roughness and the chemically active functional groups on fiber surface, which was conducive to the adsorption of the catalyst.

The surface of the CF before and after pretreatment was observed and analyzed by SEM. The results are shown in figure 2. There were some sizing agent particles on the surface of untreated CF, and the grooves were obvious parallel to the fiber, which were produced during the production process. The sizing agent on the surface of desized CF was significantly reduced, but the small gullies and grooves were still shallow. After the oxidation, the sizing agent particles disappeared, the gullies on
the surface of CF became deeper, and the roughness became significantly larger, which was favorable for subsequent uniform loading of the catalyst particles.

![Figure 2. SEM images of CFs: (a) Untreated CF, (b) Desized CF and (c) Oxidized CF.](image)

In order to explore the changes of the elemental content on the surface of CF before and after the treatment, XPS was used to characterize it. The relative contents of the elements on the surface of CF are shown in Table 1. It can be seen from the table that untreated CF contained four elements of C, O, N and Si, the content of which was 76.78%, 15.38%, 3.89% and 3.54%, respectively. After treated with acetone, the relative percentage of carbon increased significantly, the relative percentage of oxygen decreased, indicating that the functional groups on the surface of CF and the surface activity decreased. However, the relative percentage of carbon after oxidation did not change much compared with untreated CF, but the relative percentage of oxygen increased significantly, indicating that the CF was sharply activated after oxidized.

| Types       | Surface elements abundance (%) |
|-------------|--------------------------------|
|             | C    | O    | N    | Si   |
| Untreated CF| 76.78| 15.38| 3.89 | 3.54 |
| Desized CF  | 90.56| 4.79 | 1.45 | 2.89 |
| Oxidized CF | 74.33| 21.85| 1.24 | 2.53 |

To clarify the types of oxygen-containing functional groups, C1s spectra of the CF before and after modification were peak-fitted are shown in figure 3. After treatment with acetone, the relative percentage of C-C peak increased, C-O peak decreased and C=O peak changed little. The results showed that the polar functional groups on the surface of CF reduced, that is, the surface activity of carbon fiber decreased. After oxidized, the relative percentage of C-C peak decreased, C-O and C=O peak increased, which further confirmed that the content of oxygen-containing functional groups on the surface of CF could be significantly increased after acid treatment.
Figure 3. The XPS scan spectra of C1s: (a) Untreated CF, (b) Desized CF and (c) Oxidized CF.

3.2. Characterization of CF surface after catalyst loading
CF impregnated with catalyst solution at room temperature and the catalyst reducted by H₂ were observed. The results are shown in figure 4. The surface of CF impregnated with solution was coated with a thin layer of the catalyst, which uniformly covered the CF, just like a layer of bark wrapped on CF surface. After reducted by H₂, the thin layer of the catalyst gradually split and divided into small segments, which continued to decrease in size and gradually evolved into nanoparticles. Under the action of H₂, the force between the particles became weak, finally, the uniform distribution of catalyst nanoparticles was formed on the surface of CF, which provided the basis for the uniform growth of CNTs.

In order to clarify the sizes of the catalyst nanoparticles, 50 nanoparticles were randomly measured using ImageJ software in figure 4(b). A statistical histogram distribution of catalyst nanoparticles is shown in figure 5. It can be seen from the histogram that the diameters of most particles were distributed between 10-30 nm.

Figure 4. Morphology analysis of catalysts on CF: (a) After impregnation and (b) Reducted by H₂.

Figure 5. The histogram of catalyst nanoparticles diameter distribution.
3.3. Effect of different fiber treatment methods on the growth of CNTs

In order to investigate the effect of different treatment methods on the growth of CNTs, the untreated CF, desized CF and oxidized CF were used to grow CNTs under the temperature of 700°C. As can be seen from the figure 6, the untreated CF agglomerated a large amount of bulk materials on its surface. The EDS spectrum analysis showed that the surface contained three elements of C, O and Fe. The appearance of Fe was due to the impregnation of CF in catalyst solution before the CNTs growth. Therefore, it can be inferred that since the surface of the untreated CF was too smooth, the catalyst particles agglomerated and could not be uniformly distributed, the amorphous carbon or impurity carbon was formed during the growth process.

![Figure 6. SEM images of the CNTs grown on different CFs: (a) Untreated CF, (b) Desized CF and (c) Oxidized CF.](image)

The desized CF was slightly different from the untreated CF. It can be seen from the figure 6(b) that a small amount of catalyst particles was scattered on the surface of the CF. This was because the surface roughness was still small and the surface activity was relatively low. The catalyst particles were not well adsorbed and uniformly distributed. Although very small amounts of CNTs appeared on the surface after growth, the results were not satisfactory. Interestingly, a layer of fluffy CNTs appeared on the surface of the oxidized CF. It can be found that the lengths and shapes of the CNTs were different from figure 6(c). Some of them were bent but there still existed a small amount of CNTs were erected and inserted like a needle on the surface of CF. TEM images of the CNT are shown in figure 7. It was obvious that the CNTs grown on CF were multi-walled carbon nanotube. The inner diameter of the CNT was about 17 nm, which was consistent with the diameter of the catalyst nanoparticles. So it can be obtained from the above analysis that before the growth of CNTs, the surface treatment of the CF was required. The roughness and surface activity of carbon fiber have an important influence on the growth of CNTs.

![Figure 7. TEM images of the CNT grown on CF.](image)

3.4. Effect of different catalyst concentrations on the growth of CNTs

The morphology of CNTs grown under different catalyst concentrations is shown in figure 8. As can be seen from figure 8(a), when the catalyst concentration was 0.01 mol/L, there was no formation of CNTs on the fiber surface. When the concentration was 0.03 mol/L, a small amount of CNTs with irregular morphology and distribution can be grown on the surface of the fiber. At this time, the CNTs
were combined with the inactivated catalyst particles and the impurity carbon. When the concentration continued to increase to 0.05 mol/L, the CNTs were uniformly distributed and arranged neatly on the surface of the fiber, which achieved the best state in terms of morphology and distribution. When the concentration reached 0.07 mol/L, the length of CNTs increased significantly, many of them entangled with each other. The impurity particles began to increase, the length and diameter distribution of the tube were relatively dispersed. Compared with the four images, it can be found that with the increase of the catalyst concentration, the CNTs synthesized on the fiber surface had a best growth state within a certain range. Above this range, the uniformity of CNTs distribution became worse, the impurity particles gradually increased with the increase of catalyst concentration.

![Figure 8. SEM images of the CNTs grown on CF at different catalyst concentrations (a) 0.01mol/L, (b) 0.03mol/L, (c) 0.05mol/L and (d) 0.07mol/L.](image)

It can be concluded from the above analysis that the catalyst concentration has a significant influence on the morphology of CNTs. On the one hand, when the catalyst concentration is too low, it is difficult for the catalyst to completely cover the surface of the fiber, it is easy for catalyst to diffuse into the interior of the fiber to lose activity [16]. On the other hand, when the catalyst concentration is too high, agglomeration of the catalyst is liable to occur, resulting in generation of various impurity carbon.

4. Conclusions
In this study, CNTs were successfully grown on the surface of CF with Fe catalyst. The oxidation treatment of CF improved the surface roughness, and the functional group content was beneficial for the growth of CNTs. The effect of catalyst concentrations on the growth of CNTs were also explored. These results also provided a guidance for the preparation of high-performance CF/epoxy resin composites.

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