In-situ continuous growth of carbon nanotubes on the surface of carbon fibres

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Abstract. An efficient method for growing carbon nanotubes (CNTs) on the surface of continuously moving carbon fibres has been developed by a unique open-ended chemical vapor deposition (CVD) furnace. Scanning electron microscopy (SEM) is used to observe the morphological characteristics of CNTs grown on carbon fibre surfaces, and high-resolution transmission electron microscopy (HRTEM) is used to study the microstructure of CNTs. The results show that the CNTs achieve uniform and orderly growth. In the process of CNTs growth, the cross-linking of adjacent graphite crystallites is formed and the damage of the catalyst nanoparticles to the fibres is repaired, so the tensile strength is increased compared to the carbon fibres undergoing reduction. CNTs-grown carbon fibres can be used to fabricate the flexible supercapacitor electrodes to improve electrochemical capacitance and promote electrochemical stability.

1. Introduction

As portable and wearable devices have become the mainstream of modern electronic products, the flexible energy storage devices have attracted more and more attention from researchers [1-4]. Due to its fast charge/discharge rates, superb cyclic lifetimes, low maintenance cost, and operational safety, supercapacitor is widely studied as a promising candidate for energy storage [5,6]. In order to obtain high performance flexible supercapacitors, the design and manufacture of advanced flexible electrodes with a combination of high electrochemical capacitance and excellent electrochemical stability is critical. With the advantages of high specific surface area, excellent electrochemical stability, good electrical conductivity and design flexibility, graphite carbon material [7-10], including carbon fibers, carbon nanotubes (CNTs) and graphene, have been widely used in the manufacture of flexible supercapacitor electrodes.

Carbon fiber has unique advantages as electrode materials, such as good corrosion resistance, excellent design flexibility, ultra-light quality and so on. In addition, CNT is one of the most commonly used electrode materials in supercapacitors, with extremely high specific surface area and electrical conductivity. At present, more researchers have fabricated the flexible CNTs/carbon fibers hybrid electrodes by utilizing the synergistic effect of carbon fibers and CNTs to attain better electrochemical properties. So far, several methods have been reported for grafting or attaching CNTs to the surface of carbon fibers: (i) in-situ growth of CNTs using chemical vapor deposition (CVD) [11-13], (ii) chemical grafting of activated carbon fibers and functionalized CNTs [14], (iii)
electrophoretic deposition of CNTs [15,16]. Among various technologies for the synthesis of CNTs, CVD is the most versatile and promising technology in mass production, so, the growth of CNTs has been extensively explored [17-19]. However, CNTs grown on the carbon fiber surface are only at small-scale, making it difficult to carry out on large-scale continuous production, which limits its application in supercapacitors. Therefore, it is very necessary to fabricate CNTs/carbon fibers materials through continuous production technology to expand the application fields of flexible electrodes in supercapacitors.

In this paper, the carbon fibers were impregnated with catalyst precursor after the electrochemical oxidation treatment. The successful synthesis of CNTs was then achieved by cracking acetylene (C₂H₂) on the surface of catalyst nanoparticles supported by carbon fibers. More importantly, the continuous growth of CNTs on moving carbon fiber surfaces has met the requirements of large-scale production, promoting the application of CNTs/carbon fibers flexible electrodes in supercapacitors. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) were used to observe the surface morphology of carbon fibers and the microstructure of CNTs. In brief, the morphology and properties of CNTs-grown carbon fibers were systematically studied.

2. Materials and methods
The experiment described in this paper was carried out using polyacrylonitrile (PAN) based carbon fibers provided by Toray Inc. After removing the sizing agents at 450°C in an inert gas atmosphere for 90 mins, the continuous process involved in growing CNTs on carbon fiber surfaces is shown in figure 1. The carbon fibers were first electrochemically oxidized with current intensity of 0.4 A to promote uniform coating of the catalyst precursor. The modified fibers were then transferred to deionized water to remove residual electrolyte and subsequently dried in air at 90°C. After this, the carbon fibers were immersed into catalyst precursor (CO(NO₃)_2) with a concentration of 0.05 mol L⁻¹ for 10 minutes to obtain a uniform catalyst coating. After being dried at 80°C, the carbon fibers with catalyst film were finally pulled through the horizontal tube furnace by an electrical motor system for continuous growth of CNTs and gathered by a winding machine. The carbon fibers speed was 3 cm min⁻¹ throughout the process and provided N₂ atmosphere. Hydrogen (H₂) was introduced into the furnace zone at 450°C to convert the catalyst precursor layer into metal nanoparticles. Subsequently, a mixed gas of H₂ and C₂H₂ was introduced in a furnace zone at different temperatures for 10 minutes to synthesize CNTs and the throughput rate of the continuous system in this experiment was 3 cm min⁻¹.

![Figure 1](image_url)

Figure 1. Schematic chart for continuous growth process of CNTs.
The morphological characteristics of carbon fiber surfaces were inspected by SEM (Hitachi, SU-70, Japan) operated at 15 kV. The microstructure of grown CNTs were observed using HRTEM (JEOL, JEM-2100, Japan) operated at 200 kV. The Raman microscope (Renishaw, inVia, UK) was used to measure the Raman spectra to determine the order of CNTs. The laser wavelength used in the Raman test was 633 nm. The mechanical properties of the carbon fibers after growth of CNTs was characterized by XQ-1C Fiber Tensile Tester. Measurement procedures and methods were in accordance with ASTM D3822-07 specification and the numerical values were calculated according to the following equation:

$$\sigma = \frac{4F}{\pi d^2}$$

where \(\sigma\) represented the tensile strength (Pa), \(F\) represented the maximum breaking load (N), \(d\) represented the effective diameter (m).

3. Results and discussion
In order to reveal the universality of the problem, a total of three sets of experiments were conducted. Figure 2 shows the typical SEM images of CNTs grown on carbon fiber surface at different temperatures. As can be seen from figure 2, the CNTs are uniformly distributed on the surface of carbon fibers. The excellent results of CNTs indicated that the catalyst precursor was uniformly distributed on the surface of carbon fibers after electrochemical oxidation, thus forming uniform nanoparticles after the reduction process. In addition, the growth of CNTs is enhanced as the temperature increased. When the growth temperature is 650°C, the dense CNTs layer uniformly covers the carbon fiber surface. As can be seen from the enlarged view (figure 2(d)), CNTs is relatively short. When the temperature is raised to 750°C, as shown in figure 2(f), CNTs are entangled with each other and the length is increased significantly, forming a fluffy structure on the surface of fibers.

![Figure 2. SEM images of CNTs grown on carbon fiber surface at different temperatures, (a) 650°C, (b) 700°C, (c) 750°C; (d), (e) and (f) were enlarged views of (a), (b) and (c), respectively.](image)

Currently, the generally accepted growth model for CVD method was “decomposition-diffusion-deposition” [19-22]. First, the carbon source (C\(_2\)H\(_2\)) was cracked on the surface of catalyst nanoparticles to form pyrolytic carbon atoms. Then, pyrolytic carbon atoms were bound to the active sites in catalyst nanoparticles. The pyrolytic carbon atoms diffused in the catalyst nanoparticles and eventually deposited on the other side to form CNTs. As the temperature increases, the pyrolysis
carbon atoms become more active and accelerate their diffusion inside the catalyst nanoparticles. Therefore, CNTs grow faster, forming a three-dimensional network on carbon fiber surfaces.

Figure 3 shows the Raman spectra of CNTs-grown carbon fibers at different temperatures. Because Raman spectroscopy is very accurate for the orderly characterization of carbon materials, it can be used to characterize the microstructure of materials. D band and G band are characteristic peaks of disordered and ordered carbon, respectively, usually located at \(~1300\text{ cm}^{-1}\) and \(~1600\text{ cm}^{-1}\). And the order of carbon materials can be determined by the relative intensity values \((R=I_D/I_G)\) \([23,24]\). As can be seen from figure 3, different experimental samples exhibit two obvious characteristic peaks in the Raman spectrum, namely D band and G band. At the same time, it is found that the R value gradually decreases as the growth temperature of CNTs increases. It indicates that high temperature promotes the orderly growth of CNTs.

![Raman spectra of CNTs-grown carbon fibers at different temperatures.](image)

**Figure 3.** Raman spectra of CNTs-grown carbon fibers at different temperatures.

![Changes in tensile strength of carbon fibers after growing CNTs at different temperatures.](image)

**Figure 4.** The changes in tensile strength of carbon fibers after growing CNTs at different temperatures.
Tensile strength test was carried out on carbon fibers which has undergone catalytic reduction and grown CNTs at different temperatures, and compared with the carbon fibers before the experiment (marked as “As-received”). For the convenience of observation, the tensile strength is presented as a histogram (figure 4), and the specific experimental data are shown in table 1.

### Table 1. The variation in carbon fiber parameters of different samples.

| Samples  | Maximum breaking load (cN) | Effective diameter (μm) | Tensile strength (GPa) | Standard deviations |
|----------|-----------------------------|-------------------------|------------------------|---------------------|
| As-received | 17.32                        | 7                        | 4.50                   | 0.11                |
| Reduction | 15.43                        | 7                        | 4.01                   | 0.38                |
| 650°C     | 17.16                        | 7                        | 4.46                   | 0.15                |
| 700°C     | 15.86                        | 7                        | 4.12                   | 0.21                |
| 750°C     | 16.28                        | 7                        | 4.23                   | 0.18                |

From figure 4, it can be seen that the tensile strength of carbon fibers decreases significantly after reduction, which indicates that catalyst nanoparticles damage carbon fibers and destroy the continuous structure of the surface, resulting in a reduction in mechanical properties. However, the tensile strength after catalytic growth of CNTs at different temperatures is increased compared to the carbon fibers undergoing reduction. It indicates that the defects are repaired during the growth of CNTs. Kim et al [25,26] showed that not only CNTs were formed after the decomposition of the carbon source, but the gap between the catalyst and the carbon fiber was filled in the CVD process, thus improving the tensile strength. It is found that the tensile strength after CNTs growth at 650°C is higher than that at other temperatures because the etching by catalyst nanoparticles is intensified as the temperature increased. However, the repair of defects is enhanced due to the bulk growth of CNTs at 750°C, so the tensile strength is higher compared with that at 700°C. In order to exert the excellent performance of CNTs in supercapacitors, and taking into account the surface morphology and properties of carbon fibers, CNTs-grown carbon fibers obtained at 750°C are the most promising electrode material.

**Figure 5.** HRTEM micrographs of CNTs.

HRTEM was applied to further characterize the microstructure of CNTs. Figure 5 shows the micrographs of CNTs, where figure 5(b) is a locally enlarged image. The morphology of CNTs with hollow structure is composed of a layer-by-layer graphite structure, and the pitch of the fine graphite layer is about 0.347 nm. And it can be observed from figure 5(b) that the direction of graphite layer on the wall of CNT is consistent with its axis, demonstrating the great crystallization properties. In addition, the diameter of CNTs is approximately 20-30 nm according to the enlarged image.
4. Conclusions
In summary, a novel technique for large-scale continuous growth of CNTs on moving carbon fibers by catalytic CVD scheme has been demonstrated. Single fiber tests of different samples in the experiment show that the reduction of catalyst nanoparticles severely damages the carbon fiber and destroys the continuous structure of the surface. However, as the growth of CNTs, the tensile strength is improved. In addition, it is found that high temperature promotes the orderly growth of CNTs. The research has shown that it will be a promising online manufacturing technology for CNTs-grown carbon fibers, and it is reasonable to believe that it also provides basic theoretical support to fabricate new nanocomposites with better comprehensive electrochemical properties.

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