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PREPARATION AND CHARACTERIZATION OF BAMBOO-LIKE CARBON NANOTUBES BY ETHANOL CATALYTIC COMBUSTION TECHNIQUE

PRZYGOTOWANIE I CHARAKTERYSTYKA NANORUREK WĘGLOWYCH O STRUKTURZE BAMBUSOWEJ METODĄ KATALITYCZNEGO SPALANIA ETANOLU

A simple combustion approach for synthesizing bamboo-like carbon nanotubes was proposed by using liquid ethanol flame on the substrates. Copper plate was employed as substrate, ethanol as carbon source and fuel, and iron chloride or iron nitrate solution as catalyst precursors, respectively. The as-grown black powder was characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The results show that some carbon nanotubes with good bamboo-like structure were obtained in our products, and these bamboo-like carbon nanotubes have diameters of about 10-100nm and length of up to several tens of micrometers. However, the morphology and microstructure of bamboo-like carbon nanotubes are affected by synthesis conditions, such as concentration of catalyst precursor solution, synthesis temperature, synthesis time, and flame perturbations etc.. According to observation and analysis of TEM images, we tentatively propose and discuss for the possible growth mechanism of bamboo-like carbon nanotubes. The results also show that the present method is simpler to synthesize carbon nanomaterials, such as nanotubes, carbon nanofibers, and nanoparticles etc.. In addition, this method has some advantages, such as flexible synthesis conditions, simple setup, easier to be controlled, more economic, and environment-friendly.

Keywords: bamboo-like carbon nanotubes; ethanol catalytic combustion technique; characterization

Zaproponowano prostą metodę spalania w celu przeprowadzenia syntezy nanorurek węglowych o strukturze bambusowej przy użyciu płomienia z ciekłego etanolu na podłożu. Jako podłoże zastosowano płytkę miedzianą, etanol jako paliwo wglowe oraz roztwów chlorku żelaza spełniających funkcje prekursora katalicznego. Powstały czarny proszek scharakteryzowano przy użyciu skaningowej mikroskopii elektronowej (SEM), transmisyjnej mikroskopii elektronowej (TEM) oraz spektroskopii Raman'a. Wyniki wskazują, że w naszych wyrobach udało się otrzymać nanorurki węglowe o silnej strukturze bambusowej o średnicy około 10 – 100nm i długości dochodzącej do kilkudziesięciu mikrometrów. Jednakżę na morfologię i mikrostrukturę tychże nanorurek wpłynęły warunki syntezy, takie jak, stężenie roztworu prekursora katalitycznego, temperatura syntezy, czas syntezy, niestabilność płomienia etc., Jak wykazały obserwacje i analiza obrazu TEM należałoby przyjrzeć się i przedyskutować możliwy mechanizm wzrostu nanorurek węglowych o bambusowej strukturze. Ponadto wyniki wskazują, że obecnie stosowana metoda syntetyzowania nanomateriałów węglowych takich jak nanorurki, nanowłókna węlowe i nanocząsteczki jest prostsza. Ponadto posiada zalety w postaci dobieralnych warunków syntezy, prostego oprzyrządowania, łatwego monitorowania, a także jeat mniej kosztowna i przyjazna środowisku.

1. Introduction

Since the first observation of carbon nanotubes (CNTs) in 1991[1], extensive research has been focused upon the synthesis of carbon nanotubes; there has been great interest in synthesizing carbon nanotubes due to their unique physical and mechanical properties[2,3] such as remarkable electronic structure[4], high mechanical strength, and capillary properties[5]. Many potential applications have been proposed for carbon nanotubes, including conductive and high-strength composites, energy storage and energy conversion devices, sensors, field emission displays and radiation sources, hydrogen storage media, and nanometer-sized semiconductor devices, probes, and interconnect [6].

For several decades, the different shapes and structures of carbon nanotubes have been found, such

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as single-walled carbon nanotubes[7], multi-walled carbon nanotubes[8], Y-shaped carbon nanotubes[9], multi-branched carbon nanotubes[10], and they have been successfully synthesized by various methods, such as arc-discharge[11], chemical vapor deposition (CVD)[12], solar method[13], and combustion approach[14]. However, combustion approach is a newly developed method, which utilizes the energy of flame to synthesize various carbon materials. In our previous work, combustion approach for synthesizing carbon nanotubes (CNTs) and carbon nanofibers (CNFs) were proposed by using liquid ethanol flame on the substrates, and without directly seeding catalyst into the flame. Herein, we report the new results for fabricating the novel bamboo-like carbon nanotubes.

The bamboo-like carbon nanotubes are tubes, which have compartment layers between the walls. Lee et al. [15] synthesized bamboo-like carbon nanotubes using thermal chemical vapor deposition. Su et al. [10] observed bamboo structure within Y-junction carbon nanotubes which were synthesized by catalytic chemical vapor deposition at 1000-1200°C [10]. Liu et al. [16] synthesized bamboo-like carbon nanotubes earlier by an ethanol thermal reduction process. However, these methods suffer from complex setup and rigorous synthesis conditions.

In this paper, bamboo-like carbon nanotubes were synthesized by using ethanol catalytic combustion (ECC) technique. Compared with above methods, combustion approach offers several inherent advantages [17]: (1) Ethanol flame can quite naturally provide both the high-temperature and the hydrocarbon reactant for carbon nanotubes synthesis at atmospheric pressure; (2) It can provides an economical method for large areas by larger flames or with multiple flames; (3) Allows a controllable residence time within a desired flame region, etc. So, it provides a potential way to synthesis the mass production a future broader application.

2. Experimental

In a typical experiment, 0.01 mol/L,0.1mol/L iron chloride solution and 0.1 mol/L iron nitrate solution were employed as catalyst precursor solution, respectively. The diameter of copper plate is about 1cm, was used as substrates for the growth of bamboo-like carbon nanotubes, and was ultrasonically washed in acetone for several minutes to clean the surface of plate. After drying, the catalyst precursor solution was applied to the clean surface of the copper plate. Then the copper substrate was baked at 60°C for several minutes to remove the solvent. At last, the modified surface was faced down against the flame when it was inserted into the central core of the flame for about 10 min. Then the black wool-like products were obtained on the copper substrate. The products were cooled naturally in atmosphere.

The as-grown black wool-like products were characterized by means of scanning electron microscopy (JEOL 6500F SEM), and structural analysis was carried out using transmission electron microscopy (TEM, JEM-200CX). The specimens for TEM analysis were prepared by dispersing the samples in ethanol followed by sonication for 10 min. A few drops of the suspension were dropped onto a copper microgrid covered with a holey carbon thin film. The Raman spectrum was measured with a Rainshaw optical confocal Raman spectrometer at room temperature. The 514 nm line of an Ar^+ laser was used as the excitation source.

3. Results and discussion

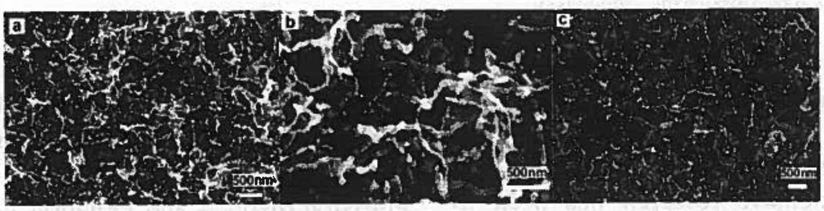

Fig. 1. SEM images of carbon nanotubes grown on copper substrate (a) with 0.01mol/L iron chloride catalyst precursor solution; (b) with 0.1 mol/L iron chloride catalyst precursor solution; (c) with 0.1 mol/L iron nitrate catalyst precursor solution

Fig.1 shows SEM images of a typical samples of carbon nanotubes grown on copper substrate with 0.01 mol/L, 0.1 mol/L iron chloride catalyst precursor solution and 0.1 mol/L iron nitrate catalyst precursor for about 10 min synthesis duration, respectively. It is very clearly shown that the large quantity of carbon nanotubes was obtained by using ethanol catalytic combustion technique. From the morphologies and appearances, these carbon nanotubes grew disorderly and randomly. The same sample has a relatively good uniformity conditions, and lengths range from hundreds of nanometers to several micrometers. From these SEM images, it also shows that different samples have different diamters. So we can conclude that the diameters of these carbon nanotubes are relative to different synthesis conditions.

Fig.2 shows the TEM images of bamboo-like carbon nanotubes grown with 0.01 mol/L, 0.1 mol/L iron chloride catalyst precursor solution and 0.1 mol/L iron nitrate catalyst precursor solution, respectively. These TEM images revealed the carbon nanotubes have a bamboo-like structure clearly, which have some compartment layers between the walls. The black arrows in Fig.2 mark the compartment layers (see arrows 1) whose curvature is always directed toward the growth direction (see arrows 2), a closed tip without any encapsulated with Fe particles (see arrows 3). However, the TEM images of carbon nanotubes grown with 0.1 mol/L iron nitrate catalyst precursor solution (Fig.2f) reveals Fe particles (see arrows 4) within the tip of carbon nanotubes, which can be due to unique synthesis conditions in our experiment. From Fig.2 a and b, it shows the diameters of bamboo-like carbon nanotubes grown with 0.01mol/L catalyst precursor solution are range from several nanometers to and 20 nm. If the concentration of catalyst precursor solution was increased more, these of bamboo-like carbon nanotubes (Fig.2c-f) grown with 0.1 mol/L catalyst precursor solution are relatively uniformly distributed in the range of 30-40nm, and they have a clear bamboo-like structure. Here, our observations are consistent with that of the SEM images of carbon nanotubes.

Comparing with different TEM images as shown in Fig.2, it is not difficult to find that the diameters of bamboo-like carbon nanotubes decrease with decreasing concentration of catalyst precursor solution. So it can conclude that the diameters of bamboo-like carbon nanotubes are affected by the concentration of catalyst precursor solution. The catalyst precursors are aggregated to form nanoparticles of different sizes from catalyst precursor solution of different concentrations because of different viscosities of precursor solutions. The precursor solution with lower concentration has lower viscosity, so it tends to form smaller catalyst precursor particles which tend to form smaller catalyst. The smaller catalysts could produce the thinner carbon nanotubes with more regular bamboo-like structure, while the catalysts with larger size tend to form irregular bamboo-like structure or solid nanowires. However, we used 1 mol/L iron chloride solution as catalyst precursor, with the other experimental conditions being identical. The results shown that there are no carbon nanotubes except for solid carbon nanowires with diameter ranging from about 50 to 150nm were found in the products from TEM. The results show the optimal concentration of catalyst precursor solution is 0.1mol/l preparation processes.

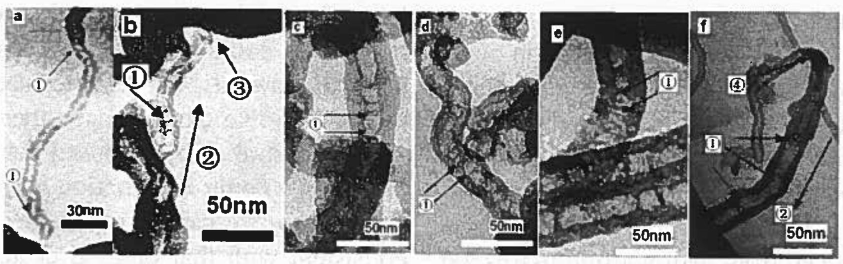

Fig. 2. TEM images of bamboo-like carbon nanotubes grown on copper substrate (a) and (b) with 0.01 mol/L iron chloride catalyst precursor solution; (c) and (d) with 0.1 mol/L iron chloride catalyst precursor solution; (e) and (f) with 0.1 mol/L iron nitrate catalyst precursor solution

In addition to, we also wanted to synthesis bamboo-like carbon nanotubes by other catalyst precursor solutions, such as cobalt nitrate, nickel nitrate etc.. However, we have not found the bamboo-like carbon nanotubes in our products, which can be due to Fe playing a key role in synthesizing bamboo-like carbon nanotubes by ethanol catalytic combustion technique.

Laser Raman spectroscopes were used to characterize the graphite structures of the combustion materials. Fig.3 shows the Raman spectrum of carbon nanotubes which was obtained with a REINSHAW optical confocal Raman microscope. The sample excitation was performed using 5mW of 514.5nm laser with 3μm spot sizes. Two samples produced exhibit mainly two Raman bands at about 1345.7cm^{-1} (in figure 3(a)), 1340cm^{-1} (in figure 3(b)), and 1593.6cm^{-1} (in figure 3(a)), 1586.5cm^{-1} (in figure 3(b)). The former corresponding to the defect-induced Raman band called the defect mode (D-band) and the latter to the Raman-allowed $E2g^2$ mode called the graphite mode (G-band). Figure 3(b) shows a strong G peak and a weak D peak, indicating relatively large size graphite clusters within the carbon nanotubes structure. While Fig. 3(a) exhibit that the intensity of G band is either approximate to that of D band, indicating relatively small size graphite clusters within the carbon nanotubes structure and their degree of graphitization is lower than that of representative sample exhibited in Fig. 3(b). Careful observation of the Fig. 3(a) and Fig. 3(b), it was found that with the increase of concentration of the precursor solution, the position of G peak shifts toward right direction. The values of 'f' (the amount of disordered carbon) are respectively calculated in the sequence of 0.01mol/l, 0.1mol/l, and as follows: 48.377%, 44.8105%. It is not hard to find that there is an optimum concentration that favors good carbon nanotubes in quality. The sample, using 0.1 mol/l iron chloride as catalyst precursor, exhibits lower value of 'f' than other samples.

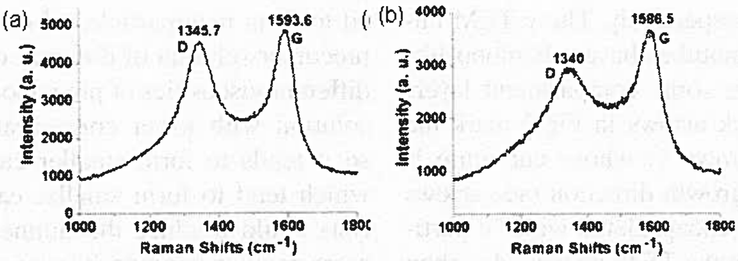

Fig. 3. (a) Raman spectrum of typical sample produced by using 0.01mol/l iron chloride as the catalyst precursor; (b) Raman spectrum of typical sample produced by using 0.1mol/l iron chloride as the catalyst precursor

However, compared with the Raman spectrum of carbon nanotubes synthesized from other methods, such as arc-discharge [11] and chemical vapor deposition [12] the present Raman spectrum reveals a large intensity of D peak. It indicates that the carbon nanotubes are synthesized by ethanol catalytic combustion (ECC) technique have a lot of disorder structure or defects. We speculate that it is possibility related to flame synthesis conditions and absolute ethanol fuel.

The catalytic growth mechanism of carbon nanotubes, up to now, the most popular mechanism of catalytic growth is as following [18, 19]: "deposition-diffusion- nucleation-growth-deactivation of catalyst". For the growth model of bamboo-like carbon nanotubes, LEE et al. [15] proposed a base growth model that carbon atoms produced from hydrocarbon-pyrolyzed were first deposited on metal particles and then formed graphitic sheets as a cap. As the cap lifts off the particle, a close tip with a hollow inside is produced. When the wall grows up towards, the next compartment layer is produced. However, LEE et al. [15] could not bring forward better explanation for compartment layer' formation. BAO et al. [20] also presented a growth model of bamboo-like carbon nanotubes, which described as follows: carbons were first deposited on metal particles, then carbons on the edge of particle tends to form wall through base growth mechanism due to the edge of particle possess strong activity, carbon atoms on the surface of particle tends to form graphitic sheets as a compartment layer due to the surface of particle possess weak activity. So the speed of wall formation is quicker than compartment layers. Following growth of wall, the compartment layers are formed. Finally the bamboo-like carbon nanotubes were synthesized. So, the growth model proposed by BAO et al. [20] the compartment layer' formation was owing to the weak activity of surface of catalyst particles, carbon atoms on the surface of particles accumulated slowly, so after a period of time it could form a thin film, following the wall grow up towards, the film formed compartment layers of bamboo-like carbon nanotubes. So, LEE et al. [15] and BAO et al. [20] proposed the growth model, which proposed a better explanation for the growth mechanism of bamboo-like carbon nanotubes. Our observations are consistent with that of LEE et al. [15] and BAO et al. [20], which are described as follows: carbon atoms were first deposited on the Fe catalyst particles (see arrows 4 in Fig.2f), because catalyst particles' edge has a stronger affinity for carbon atoms than catalyst particles' surface, which is play a key role in synthesizing bamboo-like carbon nanotubes process. Finally, bamboo-like carbon nanotubes were formed through base growth mechanism. TEM image of carbon nanotubes (Fig.4) is in concert with our depiction.

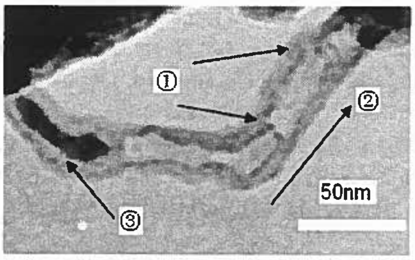

Fig. 4. TEM images of bamboo-like carbon nanotubes grown on copper substrate with 0.01 mol/L iron nitrate catalyst precursor solution. The compartment layers (see arrows 1) whose curvature is directed to the growth direction (see arrows 2), and see arrows 3 indicate Fe catalyst particles

In this paper, schematic diagrams of growth model are shown in Fig.5. The first step is carbon atoms (see arrows 1) produced from the decomposition of ethanol deposit on the catalyst metal particles (see arrows 2). Then carbon atoms diffuse through the surface and bulk of catalyst metal particles to form the graphitic sheets as a cap on the catalyst metal particles (see Fig.5a). The second and key step is the formation of hexagons may be catalytically promoted by the assistance of the catalyst metal particles [21]. While the graphitic sheets lifts off the catalyst metal particle, a closed tip with inside hollow is produced (see Fig.5b). It can be due to the strong stress function between catalyst metal particle and graphitic sheets via the high-temperature in the process of ethanol catalytic combustion. The diameters of carbon nanotubes are limited by the size of catalyst metal particles. The carbon nanotubes with a few degrees angles can be produced due to flame perturbations. If flame is steady, the carbon nanotubes with vertical direction can be synthesized. The compartment layers are grown due to the carbon atoms slowly accumulate at the inside surface of catalyst metal particle than the out surface of catalyst metal particle. At last, the compartment layers will depart from the catalyst metal particle due to the stress (see Fig.5c). While the wall grows upward, the next compartment layer is produced on the catalyst particle and will be combined with the wall [15]. A further study of the formation mechanism and mechanical property of bamboo-like carbon nanotubes is underway.

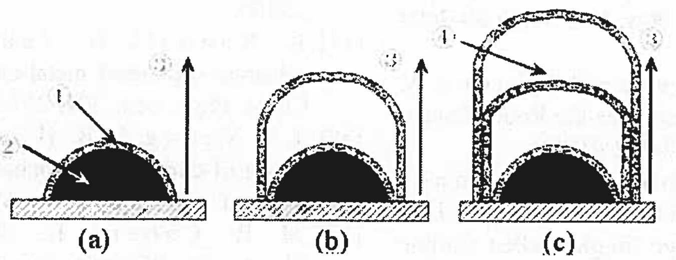

Fig. 5. Schematic diagrams of growth model. Carbon atoms (see arrows 1) were deposited on the catalyst particles (see arrows 2). The compartment layers (see arrows 4) whose curvature is directed to the growth direction (see arrows 3)

4. Conclusions

Bamboo-like carbon nanotubes have been synthesized through using ethanol catalytic combustion technique. These carbon nanotubes have a bamboo-like structure clearly. The curvature of compartment layers is directed to the growth direction, and the same base growth model can be applicable. According to TEM observations and analysis, we found that the present method induces more defects and impurities in our products. It can be due to the novel synthesis process in atmosphere, such as concentration of catalyst precursor solution, flame perturbations, pretreatment, synthesis time, and synthesis temperature etc.. On the basis of these experimental results, our group proposes a growth model for the bamboo-like carbon nanotubes. And our growth model can provide an insight into understanding the complicated growth process of carbon nanotubes. When compared with the other methods, the present approach is much simpler, more economic and easier to be controlled. Further extensive research will be carried out on the physical and mechanical properties of bamboo-like carbon nanotubes.

Acknowledgements

The authors thank Prof. X. M. Meng of Technical Institute of Physics and Chemistry of CAS for the aid in SEM analysis, Prof. X. D. Xu of Beijing University of Technology for the assistance in TEM analysis, and Prof. W. Xu, Mr. Su, Sun, and Miss Sun of Institute of Biophysics of CAS for the assistance in TEM characterization. One of Authors (X.P. Zou) thanks the partial financial support from Founding Program of Science & Technology Activity for Chinese Homecoming Fellow Abroad and Research Program of Beijing Key Laboratory for Sensor (No.KM200810772009).

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Received: 12 February 2008.