Preparation of Carbon Nanotubes by Catalytic Decomposition of Alcohol at Low Pressure.

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ABSTRACT

We report the fabrications of carbon nanotubes (CNTs) by hot filament CVD under a low precursor, using alcohol as a carbon source. The comparative studies of the properties of the nanotubes have been carried out by varying alcohol type, growth temperature and catalyst material. The obtained CNTs are characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The results show that the Fe-Co catalyst with zeolite can synthesis CNTs at a low temperature and provide small tube, compared the catalyst without zeolite. CNTs with small diameter can be obtained from methanol using a catalyst without zeolite. According to the Raman spectroscopy, the purity of the CNTs is comparable to the other previous reports.

Keywords: Carbon nanotubes (CNTs), CVD, Alcohol, Zeolite

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention because they have demonstrated the potential to make a major contribution to a variety of nanotechnological application. Significant methods for producing CNTs involve the laser vaporization, the electric arc discharge and the CVD. The CVD method, in which a hydrocarbon is pyrolyzed over a catalyst metal, has been attracting extensive attention for industrial-scale production. Among the CVD method, the hot filament CVD (HF-CVD) is a promising method to obtain CNTs (single-walled and multi-walled CNTs) at low cost.

Here, we report the fabrications of carbon nanotubes (CNTs) by hot filament CVD under a low precursor, using alcohol as a carbon source. The effect of synthesis conditions, such as the type of alcohol (ethanol and methanol), growth temperature and catalyst material (Fe-Co with/without zeolite) on the formation of CNTs is reported. The obtained CNTs are characterized by scanning electron microscopy (SEM) and Raman spectroscopy.

2. Experimental

Figure 1 presents the schematic diagram of our HF-CVD system. The growth chamber consisted of a glass chamber, a W-filament, a substrate holder, an ac power supply and a rotary pump. The catalysts used in this study were 1) Fe-Co mixed solution and 2) Fe-Co embedded in

Zeolite. $Fe(CH_3COO)_2$, and $Co(CH_3COO)_2*4H_2O$ were used as an iron and cobalt, respectively. The processes for Fe-Co mixed solution are as follows: 0.018 g of Iron acetate and 0.027 g of cobalt acetate were sonicated in 10 ml of ethanol for 30 min, giving a clear coating solution. Zeolite supported Fe-Co were prepared by mixing above solution with a 0.125 g of zeolite powder (Y-type, SiO_2/Al_2O_3 ratio 7.5), then the mixture was ultrasonically stirred for 30 min. Two types of catalyst solutions were coated on Si substrates (10x10 mm) using a spinner. Finally the samples were dried at 80 °C in air for 18-20 hours.

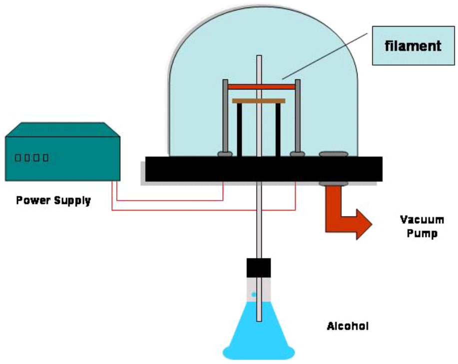


Figure 1 Schematic diagram of HF-CVD system.

The samples were then loaded into the HF-CVD reactor. After reaching base pressure (1×10^{-1} mbar), alcohol vapor (ethanol or methanol) was pulled from a beaker into the chamber. The W-filament (0.5 mm x ~ 35 mm) was electrically heated with a voltage of 5-10 V and current of 25-30 A. The temperature of filament was 1500-1800°C. The distance between filament and substrate was fixed at 3 mm. The substrate temperature (T_{sub}) could be varied by adjusting the power supply (Fig. 2). The growth time was 3-5 min. The as-grown CNT-films had a dark black color.

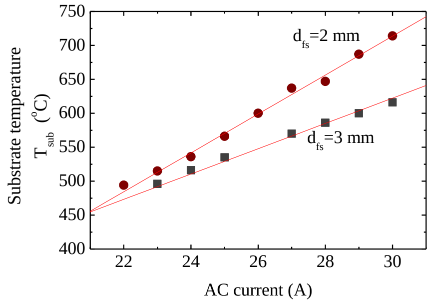


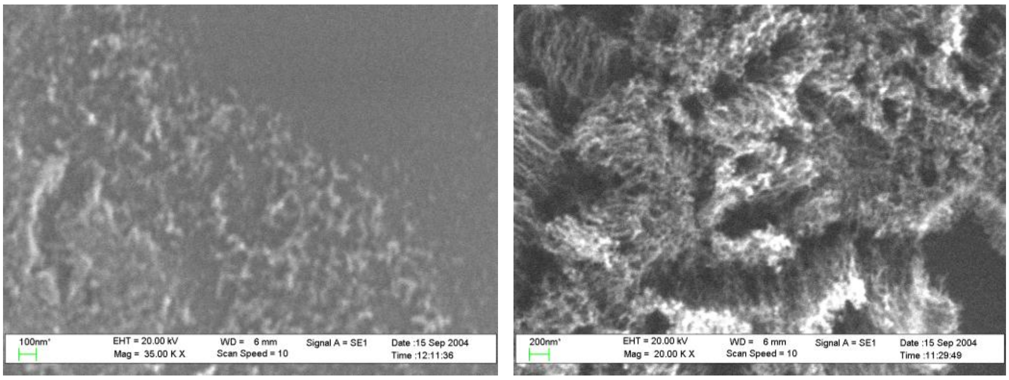
Figure 2 The substrate temperature (T_{sub}) as a function of current.

The morphologies of the CNTs were observed by scanning electron microscopy (SEM). To testify to the existence of SWCNTs, Raman scattering spectra were investigated using Nd–YAG laser with a wavelength of 1064 nm (PERKIN ELMER system 2000 NIR FT-Raman).

3. Result and discussion

From the results, the growth parameters such as substrate temperature (T_{sub}) and type of alcohol, and type of catalyst material strongly affect the formation of CNTs.

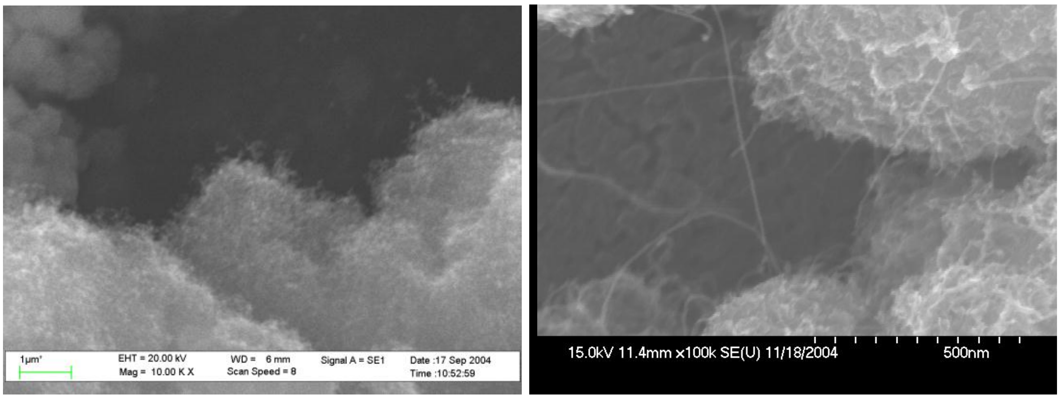
Figure 3 show the surface morphology of the CNTs obtained at different substrate temperature (T_{sub}), using ethanol alcohol as a carbon source. The coated catalyst was Fe-Co solution without zeolite. These SEM images clearly show a significant T_{sub}-dependent morphological change. For the T_{sub} below 550°C, there was almost no existence of CNTs on the sample, probably because the temperature was not sufficient for diffusion of carbon into catalysts (Fig.3 (a)). On the other hand, for the samples prepared at 650°C T_{sub}, vertically aligned and highly dense MWCNTs were obtained (Fig. 3 (b)). The tendency of growing vertically aligned MWCNTs is due to the van der Waals force between the dense tubes. The length of the tubes increased with growth time and reached ~2μm after 5 min growth.



(a) Prepared at 550°C. (b) Prepared at 650°C.

Figure 3 SEM images of CNTs on silicon substrates, obtained with ethanol and Fe-Co catalyst (without zeolite) at (a) 550°C and (b) 650°C.

When using zeolite as a support, in contrast, we found that CNTs could be deposited even at low T_{sub} of 550°C. Figure 4 (a) and (b) show a typical SEM image of samples deposited from ethanol at 550°C and 650°C, respectively. In this case, dense CNTs were grown on the zeolite surfaces. For the sample deposited at 550°C, the tubes were very short and usually surrounded with carbon nanoparticles (Fig. 4 (a)). On the other hand, the sample deposited at 650°C consisted of long tubes with less contaminates. In addition, individual grown or small-size bundle of CNTs which bridge between zeolite particles could be observed clearly by FE-SEM, as shown in Fig. 4 (b). Such phenomena were not observed in CNTs with a large diameter.



(a) at 550°C. (b) at 650°C.

Figure 4 SEM images of CNTs obtained with ethanol at (a) 550°C and (b) 650°C, using a zeolite-supported Fe-Co catalyst.

Because zeolites are porous materials with ordered crystal structures and pore arrangements, they are suitable for usage as a support material for metal catalysts to synthesis CNTs. It has been report that formed CNTs have a diameter which is closely related to the pore size of zeolite. [1] This is due to the size of the catalytic nano-particle decreases with decreasing the pore size of the zeolite. The smaller the size of the metallic particle, the smaller the diameter of the nanotubes formed. This may explain why the CNTs prepared with zeolite-supported Fe-Co (Fig. 3 (b)) had a smaller tubes than that prepared with non-zeolite-supported Fe-Co in (Fig. 4 (b)). In addition, when the size of the metals become smaller, the eutectic temperature of the metals may be reduced. Consequently, carbon atoms may be dissolved into the metal at lower temperatures. This could explain the result of a lower growth temperature for the sample prepared with zeolite-supported metals. More investigation about these relations should be conducted.

The type of alcohol was varied to investigate the yield of small-diameter CNTs. Figure 5 shows SEM image of the sample prepared by methanol at 650^{o}C using non-zeolite-supported Fe-Co catalyst. The growth condition such as growth temperature and growth pressure was the same as the sample in Fig. 3 (b), except alcohol type. It is interesting to note that the sample in Fig. 5 consisted of a lot of small-diameter CNTs. The smallest diameter was about 7 nm, estimated by FE-SEM. The difference in morphology between the sample in Fig. 3 (b) and the sample in Fig. 5 could be explained by the difference in type of alcohol. Previous literatures have reported that the optimal growth pressure depends on the kind of alcohol. The optimal pressure for ethanol was about 2 times lower than that for methanol [2]. This is explained by the different amount of the carbon supply, due to the difference in the number of carbon atoms in molecular [2-3]. Ethanol (C_2H_5OH) has 2 carbon atoms, while methanol (CH_3OH) has 1 carbon atom. It have been demonstrated that at the nanotube growth temperatures, when the carbon supply is kept low, SWCNTs rather than MWCNTs growth occurs [4-5]. Under the high carbon supply, the extreme carbons will dissolve continually into the melted catalytic and then cause the formation of

MWCNTs and/or carbon nanoparticles due to the too fast growth of the graphitic sheet. Since both samples in Fig. 3 (b) and Fig. 5 deposited under the same growth pressure, the samples prepared by ethanol may be supplied with an excess amount of carbon source. Therefore, at the same growth pressure, methanol may provide smaller tubes than ethanol. However, further investigation is required to clarify this assumption.

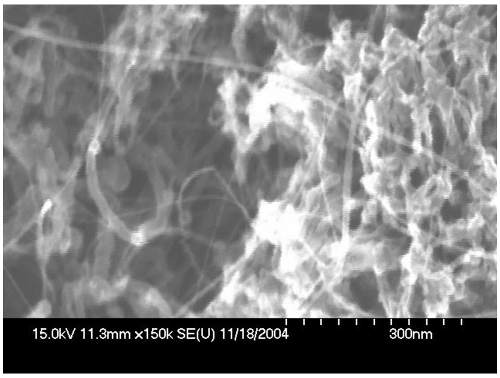


Figure 6 The result of CNTs obtained from methanol at 650°C using non-zeolite-supported Fe-Co.

Figure 7 shows a result of Raman scattering spectroscopy for the CNTs produced under the same condition of Fig. 6. Raman scattering spectroscopy is one of the most powerful tools to characterize the structure and diameter of CNTs [6].

The broad band at 1285 cm^{-1} is ascribed to as the D band due to various forms of disordered sp^2 carbon such as a-C. The intense G band at 1594 cm^{-1} is assigned to the tangential mode of the ordered carbons. Since the intensity ratio of the G-band to the D-band (I_G/I_D) was high, the purity of the sample was suggested to be high. We consider that the controllable synthesis of small diameter of CNTs may be realized by adjusting the reaction parameters. Further work to control the synthesis is in progress.

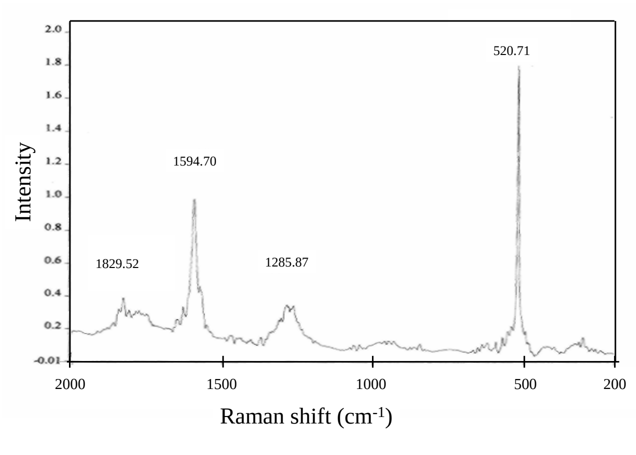


Figure 7 Raman scattering spectra for the CNTs produced under the same condition of Fig. 7.

4. Conclusion

The fabrication of carbon nanotubes (CNTs) by hot filament CVD under a low precursor was reported. Two types of alcohol, ethanol and methanol, were used as a carbon source. The results show that the Fe-Co catalyst with zeolite can synthesis CNTs at a low temperature and provide small tube, compared the catalyst without zeolite. CNTs with small diameter can be obtained from methanol using a catalyst without zeolite. According to the Raman spectroscopy, the purity of the CNTs is comparable to the other previous reports.

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