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Synthesis of High-Purity Few-Walled Carbon Nanotubes from Ethanol/Methanol Mixture

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Few-walled carbon nanotubes (FWNTs) can be synthesized in a simple chemical vapor deposition (CVD) system using ethanol as the carbon source. However, the raw materials always contain a significant amount of impurities due to decomposition of ethanol molecules on the catalyst support, which makes the purification difficult, resulting in a low yield of purified nanotubes. Here, we report that with use of an ethanol/methanol mixture as the carbon source, FWNTs with high purity can be prepared. Through a simple purification process, highly pure FWNTs can be obtained. A systematic study of the effect of ethanol/methanol ratio revealed the origin for the improved purity of the sample. Under the growth conditions studied, ethanol acted as the carbon source while methanol acted as "carbonaceous impurity remover" to remove the impurities deposited on the MgO support and hindered the formation of such impurities.

Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted extensive attention due to their unique electrical and mechanical properties and potential applications.[1] Most of the research has focused on two kinds of CNTs, single-walled carbon nanotubes (SWNTs)[2,3] that consist of only one layer of graphite sheet and multiwalled carbon nanotubes (MWNTs)[4] that consist of up to dozens of layers of sidewalls. Recently, a new kind of CNTs, few-walled carbon nanotubes (FWNTs), has attracted much attention due to their unique structure that can potentially solve some existing problems associated with either SWNTs or MWNTs.[5] Strictly speaking, FWNTs are a special kind of MWNTs that consist of 2−6 layers of sidewalls and have the structural perfection similar to SWNTs. They can be considered as an intermediate between SWNTs and MWNTs. An example of FWNTs are double-walled carbon nanotubes (DWNTs),[6−8] which have been studied extensively.

Due to their unique structure, FWNTs have special properties different from SWNTs and MWNTs. For example, FWNTs can retain the remarkable mechanical and electronic properties of the inner layers when the outmost layer is functionalized to improve the solubility of the materials in various solvents and improve the interaction between the nanotubes and the polymer matrix around them in high-performance composites. Compared with MWNTs, especially MWNTs made from chemical vapor deposition (CVD) methods, FWNTs generally have much better structural perfection, making them better candidates in applications like composites and field emission. FWNTs also form bundles with smaller diameter than those of SWNT bundles. In applications related to field emission, this has been proven to be advantageous in lowering the voltage threshold and improving the stability at high emission current.[5]

Among the three common methods in producing CNTs—arc discharge,[1−4,9,10] laser ablation,[11−14] and CVD[15−17]—CVD has already proven to be the best choice in producing a large amount of CNTs at relatively low cost. Various carbon sources have been used in CVD, such as hydrocarbons,[18,19] carbon monoxide,[20,21] and alcohols.[22,23] Alcohols are par-

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ticularly attractive because they are safe to handle and were observed to produce less impurity in the synthesis of SWNTs. The etching effect by oxygen-containing radicals generated during alcohol decomposition is believed to be the cause of improved purity.[24] Currently, almost all of the reported results on CNT synthesis using alcohol CVD used pure alcohol as carbon sources and CNTs were synthesized at relatively low temperature, below 900 °C.[25−27]

FWNTs can be synthesized using alcohol CVD at higher temperature (1000 °C or higher) as demonstrated recently in our group. However, carbonaceous impurities always form simultaneously with CNTs, making it difficult to purify the sample and limiting the application of the product. Although CVD method can produce a large amount of CNTs with relatively low cost, it is the purification step that is the bottleneck for obtaining a large amount of highly purified CNTs. Currently, purification is becoming the rate-limiting step for many of the bulk applications using nanotubes. It is easy to obtain milligram or even gram quantites of highly purified nanotubes using many of the published purification processes developed over the past few years.[28−33] However, the purity and yield drop dramatically when handling a large amount of samples. Impurities in raw CNT product can be divided into two groups, non-carbonaceous and carbonaceous impurities. Non-carbonaceous impurities can be easily removed by treatment with acid or base since they are mainly metal catalyst and support. However, it is much more difficult to remove carbonaceous impurities, including amorphous carbon, carbon fiber, and MWNTs (in the case of SWNT and FWNT synthesis) because they are made of carbon and their chemical properties are similar to those of CNTs. The common purification method relies on selective oxidation of carbonaceous impurities. The key to purification is to control the oxidization reaction so that only carbonaceous impurities are removed while CNTs remains unreacted. However, due to the similarity in the chemical reactivity of the impurities and the CNTs, a large portion of the CNTs are lost in purification. One way to solve this problem is to continuously improve the selectivity of the purification process and the other way is to reduce the percentage of non-tube carbonaceous species in the raw sample.

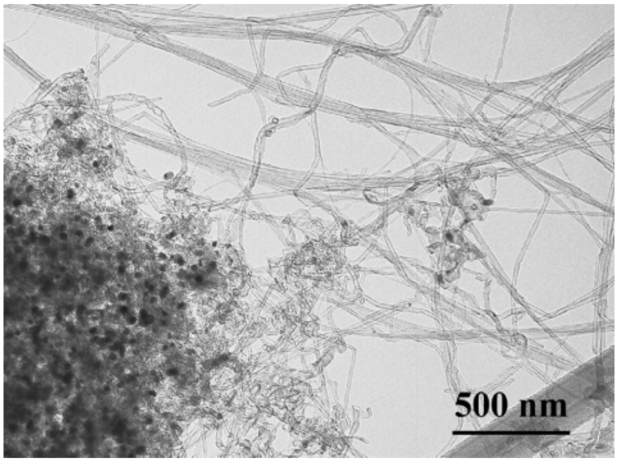

Figure 1. TEM image of raw FWNT material, which was treated by HCl to remove catalyst and support.

Here, we report a strategy to employ an alcohol mixture as the carbon source for CNT synthesis. We have identified that the majority of the impurity in our process are due to carbon deposition on the surface of the catalyst support. The use of an ethanol/methanol mixture as the carbon source increases the FWNT percentage in the raw samples by reducing the carbonaceous species deposited on the catalyst support to almost zero. A systematic study of the effect of ethanol/methanol ratio revealed the mechanism for the improved purity of the sample. Under the growth conditions studied, ethanol acted as the carbon source while methanol acted as a "carbonaceous impurity remover" to remove the impurities deposited on the MgO support of catalyst and hindered the formation of such impurities.

Experimental Section

The catalyst was prepared by a combustion method.[5] First, a clear solution was prepared by dissolving $Mg(NO_3)_2{\cdot}6H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, citric acid, and glycine in deionized (DI) water. The atomic ratio between metals is Co:Mo:Mg = 1:3:48. The solution was then heated to evaporate the solvent; after all the solvent was evaporated, the residue combusted. The catalyst was obtained by collecting the ashes and annealing them at 500 °C for 1 h. MgO blank catalyst was prepared by the same procedure with $Mg(NO_3)_2$, glycine, and citric acid.

FWNTs were synthesized in a 1-in. quartz tube heated in a tube furnace. The carbon source used for FWNTs synthesis was an ethanol/methanol mixture with different ratios and all the ratios mentioned in this paper are volume ratios. In a typical experiment, the catalyst was first heated from room temperature to 1100 °C under a 1500 sccm Ar and 500 sccm H_2 mixture. After the temperature reached 1100 °C, H_2 was turned off, Ar was increased to 2000 sccm, and the methanol/ethanol mixture was added to the system using a syringe pump at a controlled rate of 20 mL/h. After 20 min, the methanol/ethanol mixture was turned off and the system was cooled down to room temperature.

To purify the sample, the raw material was first heated under a 1:4 air/Ar mixture (350 sccm air and 1400 sccm Ar) at 575 °C for 2.5 h and then stirred in 6 M HCl to remove the Co/Mo catalyst and MgO support. The sample was rinsed with diluted KOH aqueous solution and deionized water (DI water).

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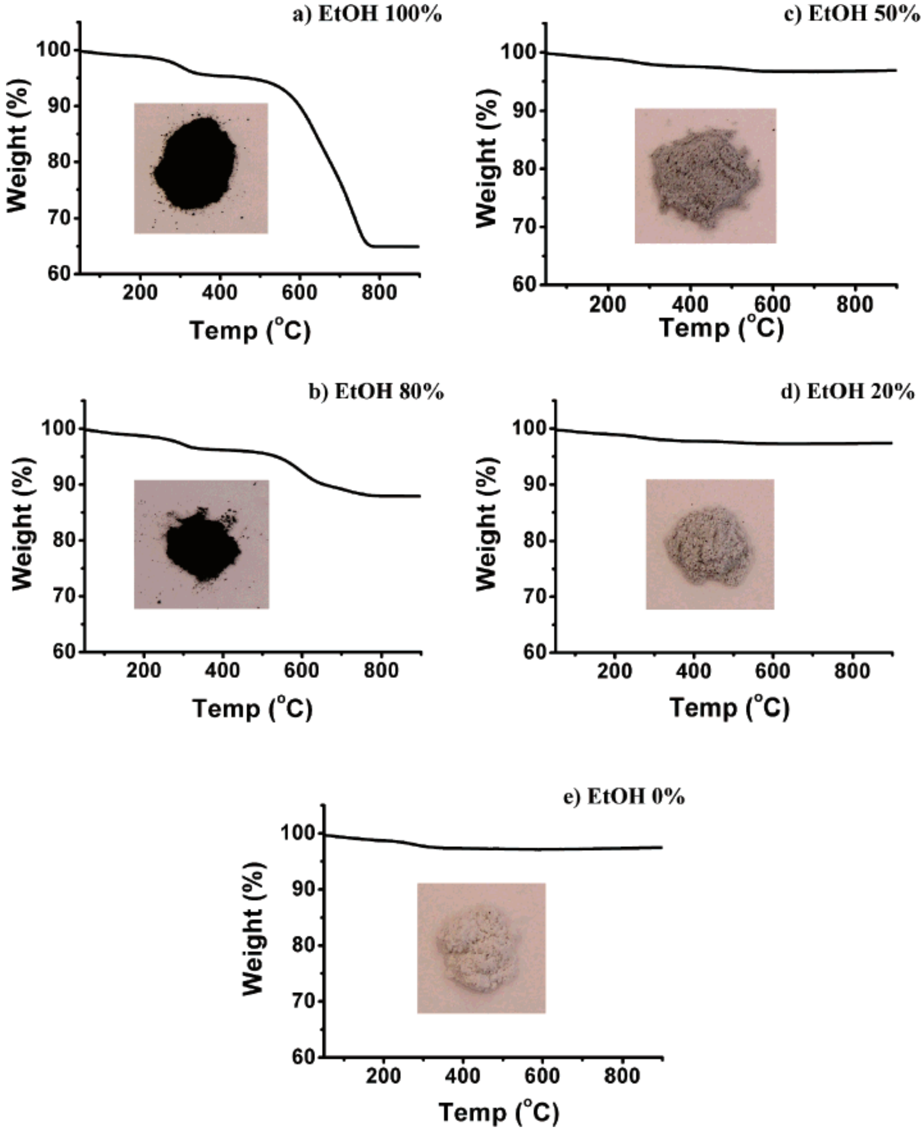

Figure 2. Photographs and TGA weight loss plots of MgO blank samples using ethanol/methanol mixture with different ethanol volume percentage.

Both the raw and purified products were characterized with thermogravimetric analyzer (TGA), transmission electron microscopy (TEM), and X-ray diffraction (XRD). All the TGA measurements were done under diluted air (20 vol % air and 80 vol % Ar). TEM samples were prepared by dispersing the FWNT samples in ethanol under assistance of sonication and drop-drying the mixture on copper grids (Ted Pella) at room temperature.

Results and Discussion

Other than FWNTs, there are always carbonaceous impurities in FWNT raw material (Figure 1 and Figure 1S in the Supporting Information). These non-CNT carbonaceous species make purification of FWNTs rather difficult and inefficient. These impurities form due to not only the inhomogeneity of catalyst particles but also deposition of carbon on MgO support. Blank control samples were prepared by treating pure MgO powder at exactly the same condition as FWNT synthesis with ethanol as carbon source. A photograph and TGA weight loss plot of this MgO blank control sample is shown in Figure 2a. The black color of the control sample suggests that there are significant amounts of carbonaceous species deposited on the MgO even without the catalyst nanoparticles under such a condition. TGA weight loss plot shows the carbon yield is ~54% and TEM image shows there (Figure 3) are no CNTs in the sample. It is important to prevent the formation of these non-CNT carbon species on MgO support to improve the FWNT purity in raw material.

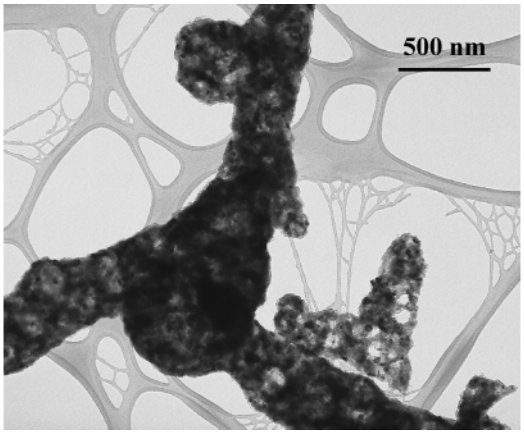

Figure 3. TEM image of MgO blank samples using ethanol as carbon source.

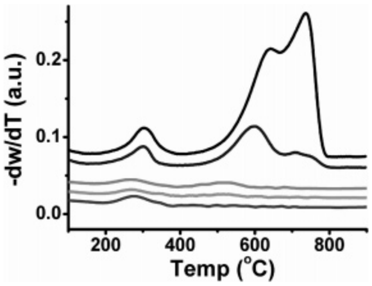

Figure 4. First-order differentiation plots of weight loss plots of MgO blank samples, from top to bottom, EtOH 100 vol %, EtOH 80 vol %, EtOH 50 vol %, EtOH 20 vol %, EtOH 0 vol %.

Table 1. Peak Positions in Figure 4 (°C)

EtOH 100%	EtOH 80%	EtOH 50%	EtOH 20%	EtOH 0%
736	708			
642	598			
		528	515	
304	301	267	268	276

To reduce the formation of these carbonaceous impurities, an ethanol/methanol mixture was explored as the carbon source for FWNT synthesis. Figure 2 shows photographs and TGA weight loss plots of a series of control samples using ethanol/methanol mixtures of different volume ratios as carbon sources on blank MgO supports. It is clear that the five samples can be divided into two groups according to their colors: samples made from 100 and 80 vol % ethanol belong to one group which are black (Figures 2a and 2b) and samples made from 50, 20, and 0 vol % ethanol belong to another group which are white or light gray (Figures 2c−2e). Carbon yields of these blank samples can be deduced from TGA weight loss plots. The two black samples show a significant amount of carbon deposited, while lighter colored samples show almost no carbonaceous species. These results suggest that addition of methanol to ethanol reduce the carbon deposit on pure MgO support notably, especially when the methanol percentage in the mixture is higher than 50 vol %.

More information is shown in Figure 4, which shows the first-order differentiation of the weight loss plots of the blank samples. First-order differentiation of the TGA weight loss plot can be used to evaluate the composition of the samples. Peaks at higher temperatures indicate the existence of carbonaceous species with higher burning temperatures and less defective graphite. The number and position of the peaks depend on TGA parameters such as heating speed, carrier gas composition, flow rate, and the amount and ratio of carbonaceous species in the sample. Burning temperatures of carbonaceous impurities are important since selective oxidation of carbonaceous impurities under diluted air is the most efficient method so far for FWNT sample purification. Higher burning temperature of the carbonaceous impurities results in less effective purification and/or very low purification yield.

Peak positions in Figure 4 are summarized in Table 1. There are up to four peaks in each of the plots. The highest is around 700 °C and only samples prepared with 100 and 80 vol % ethanol show this peak. The lowest is around 280 °C and all the samples show this peak. Samples with higher ethanol percentage (100 and 80 vol %) show a peak around 600 °C and those with low ethanol percentage (50 and 20 vol %) show a peak around 520 °C. Samples prepared with pure methanol do not show these peaks. Peak intensities of samples also vary considerably as a function of ethanol volume percentage. These results suggest that when the ethanol percentage in the mixture is no more than 50 vol %, the amount of carbonaceous species deposited on MgO support is small and easily removed. Higher purity raw FWNT material with less carbonaceous impurities thus is expected from a carbon source with low ethanol percentage. This expectation is confirmed by purification results. Samples prepared by using low ethanol percentage carbon source are almost free of impurities after purification, while considerable carbonaceous impurities can still be found in the purified samples obtained from raw samples prepared with higher ethanol percentage carbon sources (Figure 5 and Figure S2 in the Supporting Information).

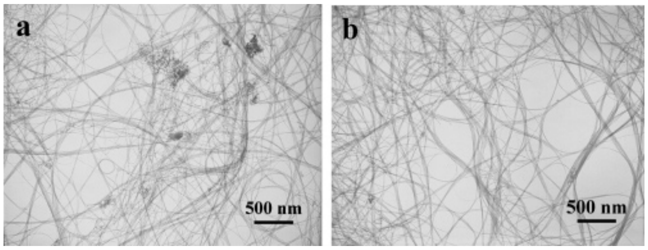

Figure 5. TEM images of purified samples from raw material using carbon source with different ethanol percentages: (a) 100 vol % ethanol and (b) 50 vol % ethanol.

Among all the reported results of CNT synthesis with alcohol as the carbon source, most used ethanol[22,25−27] as the carbon source and only a few used methanol.[23,34] Oxidative radicals formed during alcohol decomposion are considered to play an important role in the CNT growth.[22,24] The oxidative radicals have two effects on CNT material, one is etching carbonaceous impurities and the other is making carbonaceous impurities more defective so that they are easier to remove by selective oxidation. Here, methanol and ethanol, the two simplest members of alcohols, have been explored as carbon sources for FWNT synthesis. However, they acted totally differently. Under the specific growth conditions, ethanol, by itself, can act as the carbon source for FWNT growth, while methanol cannot be used as a carbon source at the same conditions. Samples made from pure methanol do not show any carbon deposition. TGA and XRD results show no carbon signal and no CNTs were found under TEM (Figure S3 in the Supporting Information).

The effect of adding methanol to ethanol is not simply to dilute ethanol in the feeding gas stream. For example, when a carbon source of ethanol only was fed with a rate of 10 mL/h, the carbon yield on pure MgO support is 38%. In contrast, a mixture of 50 vol % ethanol and 50 vol % methanol fed with 20 mL/h deposits almost no carbon on MgO support (Figure 2c). We suggest that oxidative radicals generated from methanol decomposition play an important role in the FWNT growth. The decomposition of methanol resulted in a stronger oxidative environment during FWNT

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growth. Under such conditions, carbonaceous species with less stable structure may be removed. A similar effect has also been reported by Maruyama et al.,[23,34] whose results showed that there are fewer small diameter SWNTs in samples made from methanol than those from ethanol. Under the FWNT growth conditions, an oxidative environment is strong enough to remove almost all carbon deposit on MgO support when methanol was employed as carbon source. This hypothesis is consistent with the decreased carbon yield of raw FWNT material as a function of the increased methanol percentage in the mixture. Moreover, although an oxidative environment can help to remove carbonaceous impurities during the FWNT growth, FWNTs may also be removed if the oxidizability of the environment is stronger than necessary. If 1% O_2 is added to Ar carrier gas, almost no FWNTs can be found in the sample.

Conclusion

High-purity few-walled carbon nanotubes are prepared by a chemical vapor deposition method with an ethanol/methanol mixture as the carbon source and Co/Mo/MgO as catalyst. Compared to the samples prepared from pure ethanol as the carbon source, samples from an ethanol/methanol mixture are of higher purity and can be easily purified. It is proposed that the oxidative radicals generated by methanol decomposition hindered the formation of carbonaceous impurities on MgO support. Thus, the produced raw materials contain less carbonaceous impurities and the carbonaceous impurities have more defects. Such impurities have lower burning temperatures under airflow compared to impurities prepared from pure ethanol during nanotube growth, making the purification with air oxidation more effective.

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Supporting Information Available: TEM images of raw material and purified samples; TGA weight-loss plot, XRD, and TEM image of the methanol sample. This material is available free of charge via the Internet at http://pubs.acs.org.

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