Synthesis of single-walled carbon nanotubes over Co–Mo/Al₂O₃ catalyst by the catalytic chemical vapor deposition of methane

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Received 14 December 2012
Accepted for publication 6 June 2013
Published 1 July 2013
Online at stacks.iop.org/ANSN/4/035018

Abstract
A series of alumina-supported Co–Mo samples prepared by the wet impregnation method have been used as catalysts for the synthesis of single-walled carbon nanotubes (SWNTs) by chemical vapor deposition (CVD) using CH₄ at 900 °C. The mass ratio of the bimetallic catalyst with a composition of Co:Mo:Al₂O₃ has been demonstrated to play an important role in the formation of the single-walled carbon nanotubes obtained. In addition, the selection of solvent to disperse the Co–Mo/Al₂O₃ catalysts has a significant effect on the resulting quality of the carbon nanotubes produced.

Keywords: CVD, single-walled carbon nanotube, carbon nanotubes, Co–Mo/Al₂O₃, CH₄

Classification numbers: 5.06, 5.14

1. Introduction
Carbon nanotubes (CNTs) have many potential applications in the areas of electronics, energy storage, biotechnology and medicine [1–6]. These potential applications have received broad attention due to their superior physical and chemical properties [7], such as high electron conductivity, superior surface property, excellent field emission property, metal and semiconductor properties [8, 9].

The common techniques for synthesizing CNTs can be divided into three main methods: arc discharge, laser ablation and chemical vapor deposition (CVD) [10–12]. Of those, CVD has been widely used, owing to its potential to produce a large amount of CNTs of high purity and the ability of controlling reaction conditions to produce the desired type of carbon nanostructures. It is a promising method to grow carbon nanotubes in which typically hydrocarbon gases are dissociated on catalyst at the temperature of 600–1200 °C.

In this work, the CVD method using CH₄ at the temperature of 900 °C is used to produce single-walled carbon nanotubes that are grown on alumina-supported Co–Mo catalysts.

We have known that the yield and selectivity toward single-walled carbon nanotubes (SWNTs), as well as the overall nanotube quality, depend on operating conditions (e.g. temperature, pressure, gas composition) and catalyst preparation parameters (e.g. type of metal used, total loading, addition of a second metal, type of support) [13–19].

The aims of this research are to understand exactly the role of the various chemical components presented in catalyst for producing of SWNTs, to control process conditions, to develop synthesis techniques for SWNTs on patterned catalyst that allow integration for electronic devices and to transfer the process to an industrial CVD instrument.

2. Experimental methods
2.1. Preparation of catalysts
Bimetallic Co–Mo catalysts supported on catalyst supports Al₂O₃ (Sigma-Aldrich), were prepared using...
the incipient wetness impregnation by mixing fumed alumina nanoparticles, cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich, 99.99%) and ammonium heptamolubdate tetrahydrate (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Sigma-Aldrich, 99.99%) salts in de-ionized water (DI) or methanol solvent. Aluminum oxide C (Al$_2$O$_3$) has an average primary particle size of about 13 nm and a specific surface of 100 m$^2$ g$^{-1}$. The catalytic suspension is ready to use after 120 min sonication at 90$^\circ$C. After impregnation, catalysts deposited on the Si/SiO$_2$ substrate were dried in an oven at 90$^\circ$C.

2.2. SWNTs synthesis

For the first step, the reactor was purged through flowing Ar of 500 sccm. This gas is used during the heating step. Temperature was continuously increased to 900$^\circ$C for 10 min. As soon as the temperature reached 900$^\circ$C, a flow of 400 sccm CH$_4$, 150 sccm H$_2$ was introduced into the chamber and kept for 10 min for the carbon growth. Finally, the reactor was cooled down to room temperature under flowing Ar.

2.3. SWNTs characterization

The yield of SWNTs was monitored by Raman spectroscopy, using a laser excitation of 633 nm (He–Ne laser). The collection time was 30 s and three spectra from different spots were averaged for each sample.

3. Results and discussion

The first result about synthesizing of the CNTs is to use de-ionized water (DI) or methanol for dispersing Co(NO$_3$)$_2$·6H$_2$O and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O salts and aluminum oxide C. This mixture forms the catalysts Co–Mo/Al$_2$O$_3$ prepared for producing CNTs using methane. The molar mass ratio chosen for Co:Mo:Al$_2$O$_3$ is 1 : 3 : 2. When one solvent is selected for dispersing the mixture, the ratio of the catalysts will be considered for the aim of producing the high yield of carbon nanotubes.

3.1. Using de-ionized water (DI) as solvent

Scanning electron microscope (SEM) images of a representative sample after synthesis of CNTs by CVD at 900$^\circ$C are presented in figure 1(a). The figure shows that the density of carbon nanotubes in deposited carbon is low. However, SEM images cannot determine exactly the difference of products in this experiment. For study of the carbon products, we need the Raman spectra to determine and classify the different types of carbon products. The Raman spectra of SWNT samples consist of radial breathing modes (RBMs) and G- and D-band peaks. The G-band peak relates to the graphite content in the sample, while the D-band one is associated with disorders like vacancies, grain boundaries and other defects. Thus, a ratio of these peaks indicates the purity of the sample.

Raman spectra in figure 1(b) indicate that the film of CNTs sample contains a small proportion of high-quality single-walled carbon nanotubes. This judgment is based on the presence of several RBM signals (between 100 and 300 cm$^{-1}$), a high G-band ($\sim$1590 cm$^{-1}$) and a D-band ($\sim$1350 cm$^{-1}$) having a half-intensity compared to the G-band in this sample. However, the quality of the tubes can be identified using a very low ratio between the D-band and G-band. Thus, Raman spectrum of the sample using DI water shows the high ratio of $I_D/I_G$ of D-band intensity $I_D$ over G-band one $I_G$($\sim$0.53) indicating that sidewalls of nanotubes are more defective and the graphitic impurity is large.

3.2. Using methanol as solvent

The electron microscopic observation shows that the sample using the methanol is covered by carbon nanotubes (figure 2(a)). The Raman spectra of produced carbon nanotubes show bands at $\sim$1340 and $\sim$1590 cm$^{-1}$ corresponding to D-band and G-band, respectively, and RBM peaks (figure 2(b)). A low ratio $I_D/I_G$ (0.27) obtained by using the methanol indicates that the sidewalls of nanotubes are less defective and the graphitic impurity is slighter than that obtained by using the DI water.
Figure 2. (a) SEM image of SWNT grown onto Co–Mo/Al₂O₃ catalysts and (b) Raman spectra of CNTs with catalysts having the ratio Co:Mo:Al₂O₃ = 1:3:2. Methanol is used as solvent to disperse.

Figure 3. (a) SEM image of SWNT grown onto Co–Mo/Al₂O₃ catalysts and (b) Raman spectra of CNTs with catalysts having the ratio Co:Mo:Al₂O₃ = 1:3:3. Methanol is used as solvent to disperse.

3.3. Ratio Co:Mo:Al₂O₃ of 1 : 3 : 3

When the ratio of Co:Mo:Al₂O₃ is 1 : 3 : 3, SEM and TEM observations of the sample show that carbon nanotubes are present (figures 3(a) and 4). They are SWNTs confirmed by Raman spectra (figure 3(b)): the presence of some RBM peaks is observed in the range 130–300 cm⁻¹ and the nanotube tangential graphitic G-band modes at 1560–1600 cm⁻¹ and disorder D-band modes at 1320–1380 cm⁻¹ are also found.

The Raman spectrum of the sample with a ratio Co:Mo:Al₂O₃ = 1:3:3 in this experiment reveals that the spectra shows an RBM peak in the high intensity and a very low ratio I_D/I_G (0.2) obtained. This result indicates that a significant SWNT concentration is produced and the defects of nanotubes are less important.

3.4. Ratio Co:Mo:Al₂O₃ of 1 : 3 : 4

When increasing the mass of alumina supports in the mixture Co–Mo/Al₂O₃ with the ratio Co:Mo:Al₂O₃ of 1:3:4, the carbon nanotubes are also present, but the ratio I_D/I_G (0.35) is high indicating that the defects of sidewalls of nanotubes remain considerable (figure 5). The low RBM peaks shown also in this experiment reveal that the high alumina concentration supports result in the agglomeration phenomenon that happens between them to form the large particles. Alumina supports containing the Co–Mo catalysts prevent the growth of CNTs on them.

3.5. Ratio Co:Mo:Al₂O₃ of 3 : 1 : 3

TEM observation shows that the sample using higher cobalt (II) nitrate concentration with the ratio Co:Mo:Al₂O₃ of 3:1:3 is also covered by carbon nanotubes (figure 6(a)). However, the Raman spectra of produced carbon nanotubes show very low RBM peaks and a very high ratio I_D/I_G (0.71) (figure 6(b)).

By comparison between figure 3(b) and other ones (figures 2(b) and 5(b)), it can be seen that the use of higher cobalt (II) nitrate hexahydrate content results in an decrease of the carbon nanotubes density. Here we had to consider the role of Co and Mo species. According to the experimental results of many authors, no CNT growth occurs when catalyst
contains only Mo species and alumina supports are put in the same temperature conditions of CVD process as those to produce CNTs [20–23]. In fact, these authors have been discussing the role of the molybdenum in catalysis for CNTs growth. They found that molybdenum is inactive for the formation of CNTs and deduced that the role of molybdenum

Figure 4. (a) SEM image and (b) TEM image of SWNT grown onto Co–Mo/Al₂O₃ catalysts having the ratio Co:Mo:Al₂O₃ = 1 : 3 : 3. Methanol is used as solvent to disperse.

Figure 5. (a) SEM image of SWNT grown onto Co–Mo/Al₂O₃ catalysts and (b) Raman spectra of CNTs with catalysts having the ratio Co:Mo:Al₂O₃ = 1 : 3 : 4. Methanol is used as the solvent to disperse.

Figure 6. (a) SEM image of SWNT grown onto Co–Mo/Al₂O₃ catalysts and (b) Raman spectra of CNTs with catalysts having the ratio Co:Mo:Al₂O₃ = 3 : 1 : 3. Methanol is used as the solvent to disperse.
is to promote the decomposition and the aromatization of methane at elevated temperatures.

Thus, noticing the connection between our experimental results (from figures 1 to 6), we see the contact between Mo and Co on the catalyst, where CNT growth takes place. If the roles played by Mo species from ammonium heptamolubdate tetrahydrate are suggested to promote the decomposition of methane to produce CNTs, the Co species mainly generate the catalytic activity. However, with the increase of cobalt (II) nitrate hexahydrate content compared with that of ammonium heptamolubdate tetrahydrate, CNTs density will decrease.

3.6. Calculation of the diameters distribution of obtained SWNTs

The diameter (d) is determined by measuring the RBM frequency and applying the formula: \( v_{RBM} = \frac{224}{d} \) (nm) [24–26]. From the frequency of RBM peaks obtained in figure 7, we can calculate the diameters distribution of obtained SWNTs.

In this research we chose the samples with the ratio Co:Mo:Al\(_2\)O\(_3\) of 1:3:2 and 1:3:3 for calculating the diameters since these samples gave the high yield of carbon nanotubes as explained above. The results are presented in table 1. The nanotube diameters are mainly distributed from 0.76 to 1.69 nm.

4. Conclusion

The optimum value of the ratio (Co(NO\(_3\))\(_2\)·6H\(_2\)O):(NH\(_4\))\(_2\)Mo\(_7\)O\(_{24}\)·4H\(_2\)O:Al\(_2\)O\(_3\) was found to obtain the maximal yield of carbon products by chemical vapor deposition (CVD) using CH\(_4\) at 900°C. Under the investigated conditions the best value of this ratio is 1:3:3. However, at the value 1:3:2 of this ratio the values of diameters of carbon nanotubes are smaller than those in the case of the ratio having the value 1:3:3.

The selection of the solvent of methanol to disperse the Co–Mo/Al\(_2\)O\(_3\) catalysts has a significant effect on the resulting quality of the carbon nanotubes produced.

Table 1. Diameters of SWNTs determined from the experimental Raman spectra and presented formula.

| Co:Mo:Al\(_2\)O\(_3\) | Frequency, \(v_{RBM}(\text{cm}^{-1})\) | Diameter, d (nm) |
|----------------------|--------------------------------------|------------------|
| 1:3:2                | 132                                  | 1.69             |
|                      | 149                                  | 1.50             |
|                      | 192                                  | 1.16             |
|                      | 221                                  | 1.01             |
|                      | 265                                  | 0.84             |
|                      | 270                                  | 0.82             |
|                      | 286                                  | 0.78             |
|                      | 294                                  | 0.76             |
| 1:3:3                | 137                                  | 1.63             |
|                      | 140                                  | 1.60             |
|                      | 162                                  | 1.38             |
|                      | 197                                  | 1.13             |

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