A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity

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Abstract

Single-walled carbon nanotubes (SWNT) are known to possess superior mechanical and electronic properties. However, the lack of methods for large-scale preparation limits fundamental research and application development of this unique material. Among all methods currently used for SWNT preparation, chemical vapor deposition (CVD) method represents the best hope for large-scale production. However, current CVD method has limited catalyst productivity (~40% the weight of the starting catalyst). Here we report an improved CVD method for preparation of SWNTs with high productivity using a novel aerogel supported Fe/Mo catalyst. The total amount of high-quality SWNTs produced is greater than 200% the weight of the catalysts. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Ever since its discovery by Iijima in 1991 [1], carbon nanotube has been one of the most actively studied materials in today’s research. This is not very surprising given the outstanding chemical and physical properties that this material possess and its potential applications in many different fields. For example, depending on the number of the concentric walls and the ways that a graphene sheets being rolled into a cylinder, carbon nanotubes can be either metallic or semiconductive [2]. Experiments showed that individual carbon nanotubes can behave as quantum wires [3] and can even be made into room temperature transistors [4]. In addition, these carbon nanotubes possess superior mechanical properties and chemical stability. Experimental measurements of Young’s moduli by atomic force microscope (AFM) [5] and thermal vibrations [6] afforded values of 1.3 and 1.8 Tpa, which are higher than any other known materials. Consequently, the chemical stability, superior mechanical properties, together with the ballistic transport property of metallic nanotubes and richness in electronic properties of tubes with different helicity, make carbon nanotubes ideal candidates for high strength composite materials, and for interconnections and functional devices in molecular electronics.

Although carbon nanotube materials possess many unique and technically important properties, lack of sufficient amount of materials limited the study of the fundamental properties and development of more practical applications. The discovery of a low cost, high productivity method for preparation of high-quality SWNT material will certainly solve one of the
biggest problems facing this field in the past and open new opportunities for a wide variety of applications.

Currently, carbon nanotubes are synthesized by three different techniques: (1) arc discharge between two graphite electrodes [7–11]; (2) chemical vapor deposition (CVD) through catalytic decomposition of hydrocarbon [12–21]; and (3) laser evaporation of carbon target [22–27]. Both the laser method and arc method yield high-quality SWNTs. However, both techniques suffer from the problem that it is hard to scale up the production of the nanotube materials to industrial scale. The CVD method presently presents the best hope for large scale production of nanotube materials. This method had been reported for preparation of various carbon materials such as carbon fibers and multi-walled carbon nanotubes with high yield and at large scale [12,28]. More recently, there are reports of SWNT preparation by CVD of carbon monoxide [16,17], methane [15,21] etc. Among these, methane CVD is reported to produce high-purity and high-quality SWNT materials. However, the catalyst productivity of the method is low and the best results reported so far give a total output ratio of \( \sim 40\% \) [16,21] defined as the weight gain ratio of the produced nanotubes to the starting catalyst. In this letter, we report a methane CVD method that afford high-quality SWNTs with higher output ratio ( \( > 200\% \) ) using a Fe/Mo catalyst supported on Al\(_2\)O\(_3\) aerogel, a high surface area, high porosity and ultra-low-density material made by the sol–gel synthesis and subsequent removal of the liquid solvent by supercritical drying.

2. Experimental

2.1. Materials

All materials used in the experiment are research grade materials purchased from different suppliers. Aluminum tri-sec-butoxide (ASB), Fe\(_4\)(SO\(_4\))\(_3\).4H\(_2\)O, bis(acetylacetonato)dioxomolybdenum (MoO\(_3\)(acac)\(_2\)) were purchased from Sigma/Aldrich Chemicals. Reagent grade nitric acid, ammonium hydroxide, and ethanol were purchased from VWR. High-purity methane, carbon dioxide, and hydrogen were supplied by National Welders.

2.2. Catalyst preparation

Catalysts used in the experiment were prepared using sol–gel technique [30] followed by supercritical drying. In a typical experiment, 23 g ASB was dissolved in 200 ml Ethanol in a round bottom flask under reflux condition. Then 0.1 ml concentrated HNO\(_3\) diluted with 1 ml water and 50 ml ethanol was added into the mixture. It was refluxed for 2 h or until a clear solution was formed before adding 1.38 g Fe\(_4\)(SO\(_4\))\(_3\).4H\(_2\)O and 0.38 g MoO\(_3\)(acac)\(_2\) (the amounts of Fe and Mo were chosen so that the molar ratio was Mo:Fe:Al = 0.16:1:16) into the mixture. After refluxing for two more hours, the mixture was cooled to room temperature and 5 ml concentrated NH\(_4\)OH diluted with 5 ml of water was added into the mixture under vigorous stirring. Within a few minutes, a gel was formed. It was left to age for about 10 h before the supercritical drying step was performed.

Drying of the catalysts was carried under the supercritical condition of carbon dioxide. First, the catalyst gel was sealed in a 300 ml high-pressure container, which was then cooled to 0\( ^\circ \)C and pressurized with CO\(_2\) to above 850 psi. This filled the container with liquid CO\(_2\). A solvent exchange step was followed to exchange the ethanol in the gel with liquid CO\(_2\) by slowly releasing CO\(_2\) while keeping the pressure above 850 psi for 2 to 3 h. Then, the container was pressured up to above the critical pressure (1050 psi), and warmed up to above the critical temperature of CO\(_2\) (31\( ^\circ \)C). The system was held at this condition for a short time before the pressure was slowly reduced while the temperature was kept at the same. Finally, the temperature was reduced to room temperature. The catalyst prepared this way is in the form of very fine free-flowing powder with surface areas \( \sim 600 \text{ m}^2/\text{g} \). The powder was calcined at 500\( ^\circ \)C for 30 min before used for SWNT growth.

2.3. SWNT growth

SWNT were prepared in a simple CVD setup made of a tube furnace and gas flow control units. In a typical growth experiment, \( \sim 50 \text{ mg} \) catalyst was put into alumina boat inside a quartz tube and was
heated to reaction temperature, 850°C to 1000°C, under Ar flow at a flow rate of 100 sccm. The Ar was switched to H₂ (100 sccm flow rate) for 30 min before switching to methane flow (~1000 sccm). The reaction was carried out for desired time before methane flow was turned off and Ar flow turned on and temperature reduced to room temperature. The material was then weighted and characterized.

2.4. Characterization

SWNT samples were fully characterized using TEM and SEM. TEM was performed on a Philip CM-12 operating at 100 kV. The samples for TEM were prepared by sonicating ~1 mg material in 10 ml methanol for 10 min and drying a few drop of the suspension on holy-carbon grid. SEM was performed on a Hitachi S-4700 with a beam energy of 4 kV by placing the as-grown materials on conductive carbon tape. The amount of the prepared SWNT material with respect to the catalyst was measured on a Thermal Gravimetric Analyzer (SDT 2960, TA instrument) under flowing air with a heating rate of 5°C/min.

3. Result and discussion

The key result we report in this Letter is the dramatic increase in the amount of nanotubes prepared per unit weight of catalyst using the new catalyst. As shown in Fig. 1a, the weight gain of the catalyst is measured by heating up the prepared material under flowing air in a TGA. The total weight gain of the SWNT material is calculated by the weight loss between 300°C and 700°C, where SWNT material burns in air, divided by the weight left at 700°C, which is presumably the weight of the catalyst and support materials. For a typical 60 min growth experiment at 900°C, the average weight gain using this catalyst is about 200%. The maximum weight gain we had is about 600% for a 6.5 h growth as shown in Fig. 2.

The quality of the prepared nanotube material was characterized by TEM and SEM. As shown in Fig. 3, the SEM image of the as-prepared material shows tangled web-like network of very clean fibers. The diameters of the fibers are in the range of 10–20 nanometers. TEM image of the materials shows that these fibers observed in SEM are actually bundles of SWNTs. The diameters of the tubes measured from high-resolution TEM images are between 0.9 and 2.7 nm. Both SEM and TEM images show the characteristics of high-quality SWNT materials similar to the materials prepares in laser method [22,23] and arc method [10,11]. It is worth to mention that the SEM image shown here is of as-grown materials, no purification was performed before the imaging. The fact that the image showed only nanotubes indicates that the catalyst surface is fully covered with nanotube materials. However, for samples with weight gain higher than 300%, amorphous carbon overcoat was observed. We are currently working on further improving the methods to eliminate the amorphous carbon deposit and to increase the productivity further. Nevertheless, even the current method shows catalyst productivity significantly better than the previously reported values [15,21].

The increase in the productivity of catalyst in current method can be mostly attributed to the effect of the catalyst support. Aerogels are known to have high surface area, high porosity and ultra-low-density [31]. Because of the high surface area associated with these materials, they have found increasing interest as catalysts and catalyst supports [32,33]. It has been shown that Fe₂O₃ catalyst supported on SiO₂ or Al₂O₃ aerogels exhibit catalytic activity two to three orders of magnitude higher than that of catalyst supported on conventional supports in Fischer–Tropsch synthesis [34]. Moreover, the catalyst does not deactivate with time. The authors attributed
Fig. 2. Weight gain versus reaction time plot at 900°C with methane flow at 1158 sccm.

Fig. 3. (a) SEM and (b) TEM image of SWNT sample prepared on Al₂O₃ aerogel supported Fe/Mo catalyst. Sample was prepared at 900°C under CH₄ flow. Flow rate is 1158 sccm; reaction time is 30 min; yield measured by TGA is 100.2%.

We believe these improvements to the strong interactions between the aerogel support and the catalyst as well as the high surface area of the support. We believe this is also true in our discovery. The high catalytic activity of the catalyst on this new support and the high surface area are the key factors that greatly enhanced the performance of the catalyst in preparing nanotube materials.

We have found that supercritical drying process is a crucial step in preparing high performance catalysts. It had been shown that drying of a wet gel is a very complex process [31,35]. Simply evaporating the liquid would cause the gel to shrink due to the collapse of the porous structures by the strong forces from surface tensions at the liquid/gas interfaces within the pores in the gel. This shrinkage would significantly reduce the total surface areas and pore volume of the dried material, which is normally called xerogel. In supercritical drying process, the liquid in the wet gel is put into the supercritical state and therefore there are no liquid/gas interfaces in the pores during drying. The original porous structure in the wet gels is thus reserved in the dried aerogels. We have compared the catalysts made from the same wet gel but dried differently. The aerogel supported catalyst showed a weight gain of ~200% of high purity SWNT under methane flow at 900°C for 60 min while the xerogel supported catalyst showed a weight gain of <5% under the same conditions. We have also compared the same Fe/Mo catalysts supported on Al₂O₃ aerogel and on SiO₂ aerogels prepared with a similar method, the weight gain of the catalyst on SiO₂ under the same conditions, 900°C under methane flow for 60 minutes, is also <10%. This strongly suggests that the interaction of the catalyst particles and the support materials is a key factor in the growth of SWNT materials. It is known that the surface groups on Al₂O₃ have stronger Lewis acidity than those on SiO₂, thus the interactions of the metal catalysts with Al₂O₃ are stronger than with SiO₂ [21]. The observation that SWNT growth favor strong metal-support interaction indicates that the main growth mechanism in current method is ‘base growth’ mechanism, in which the catalyst particles are attached to the support surfaces.
during the growth process. As more and more nanotubes are grown on the surface, the diffusion of the methane gas to the catalyst particles becomes more difficult. Furthermore, we have observed amorphous carbon deposition on the nanotubes at longer growth time, which further reduces the diffusion rate of methane gas to the catalyst. This would explain why the growth rate slowed down versus time as shown in Fig. 2. We believe if we can eliminate the deposit of amorphous carbon by optimizing the growth conditions, we could increase the amount of SWNTs produced per unit weight of catalyst further.

Another factor that may have contributed to increase the productivity of the catalyst is the high dispersity of the metal catalysts. Since the catalysts were prepared in a sol–gel process by dissolving Fe and Mo salts and subsequent hydrolysis at high pH under vigorous stirring, well dispersed nanoparticles composed of Fe hydroxide and Mo oxide were generated, which was then converted to metal oxides in the calcination step. We did not observe aggregates of metal particles and large metal particles, which would be inactive for nanotube growth, in our TEM images. These well-dispersed catalysts also result in a narrower size distribution of the prepared nanotube materials compared with previous CVD experiments [15,17]. More works is currently underway on controlling the diameter of the nanotubes using current method of catalyst preparation.

Purification of the material prepared in our current CVD method was also studied. Because of the highly amorphous nature of the aerogel support prepared in the current method, it is possible to remove the catalyst support by refluxing the materials in either strong acid or strong base. TGA results have shown that, reflux the material in 3 M HNO₃ for 4 h followed by filtration eliminates all the support materials (Fig. 1b), leaving nanotube materials with high purity.

In summary, we have discovered a new form of catalyst that can be used to prepare high-quality SWNT with high catalyst productivity using chemical vapor deposition method. The amount of nanotubes prepared per unit weight of catalyst was improved by at least a factor of 5 compared with a similar catalyst supported on Al₂O₃ powder. This discovery provided a way to prepare high-quality SWNT materials in large scale with low cost. The results also suggested that the growth mechanism of the SWNT in current method is ‘base growth’ mechanism, and the possible growth-limiting factor is the diffusion of methane gas through the nanotube networks. More works need to be done to further improve the productivity of the catalyst and to control their size distributions.

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References
