

CVD synthesis and purification of single-walled carbon nanotubes on aerogel-supported catalyst

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Abstract. Single-walled carbon nanotubes (SWNTs) were synthesized by disproportionation of carbon monoxide on an aerogel-supported Fe/Mo catalyst. A simple acidic treatment followed by an oxidation process produced a high purity (> 99%) of SWNTs. The nanotubes obtained are bundled SWNTs and free of amorphous-carbon coating. Several factors that affect the yield and the quality of the SWNTs were also studied. This method shows great promise for large-scale production of SWNTs.

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Single-walled nanotubes (SWNTs) have shown many unique electrical and mechanical properties. Their potential applications include field emitters [1], gas storage and separation [2], nanopores [3], chemical sensors [4] and high-strength composites [5]. Currently there are three principal techniques to produce high-quality SWNTs: laser ablation [6], electric arc discharge [7] and chemical vapor deposition (CVD) [8–12, 17]. Both laser ablation and arc discharge methods have the problem that it is difficult to scale-up the production of SWNTs to industrial level. The CVD method is currently the best hope for large-scale production of SWNTs. Previously, the catalyst for the CVD method is made either by impregnating a catalyst precursor into a powdered catalyst support, such as silica powder and alumina powder [8–10], or by decomposing the precursor in the gas phase together with a carbon source at elevated temperature [11, 12]. Benzene [12], ethylene [17], methane [8, 9] and carbon monoxide [10, 11, 17] have been used as a feeding gas for SWNT production.

Previously, the CVD method had the disadvantages of low yield and amorphous-carbon impurities, which limited its application for large-scale production of nanotubes. Recently, we reported a CVD method using alumina aerogel as a catalyst support [9] and using Fe/Mo nanoparticles as catalysts to

promote SWNT formation using methane as the feeding gas. A much higher output ratio was achieved. In the present work, we have changed the feeding gas to CO in order to improve the quality of the SWNTs. We have found that the amount of amorphous-carbon impurities in the raw product was significantly reduced, especially when bulk amounts of catalysts were used.

1 Experimental

1.1 Catalyst preparation

All materials used in the experiment are research-grade from different suppliers. Aluminum tri-sec-butoxide (ASB) and bis(acetylacetonato) dioxomolybdenum ($\text{MoO}_2(\text{acac})_2$) were purchased from Aldrich Chemicals. $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, nitric acid and ammonium hydroxide were purchased from Fisher Scientific. Ethanol (200 proof) was from VWR. High-purity carbon monoxide, argon and nitrogen were supplied by National Welders.

Alumina-aerogel-supported Fe/Mo catalysts were prepared according to [9] with modifications. 5.2-g ASB was dissolved in 35-ml hot ethanol. When the solution became homogeneous, 60- μl HNO_3 (69%) and 0.20-ml H_2O diluted in 25-ml ethanol were added to the mixture. After it was refluxed for 2.5 h, 0.37-g $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ and 0.10-g $\text{MoO}_2(\text{acac})_2$ dispersed in 15-ml ethanol were added to the clear sol. After another 1 h, the mixture was cooled to room temperature. A mixture of 1.0-ml ammonia and 1.0-ml H_2O plus 5-ml ethanol was then added to the sol with vigorous stirring. A gel was formed within 30 s. It was left to age for about 12 h before being dried.

Drying of the gel was carried out under the supercritical condition of ethanol [13]. Firstly, the gel (50–55 ml) was put into a 100-ml high-pressure container. The system was purged with N_2 for 15 min. Then a high pressure of N_2 (200 psi) was added to the container and the system was sealed. A programmable heater brought the system to 260 °C in 2.5 h. The system was held at this temperature for 20 min.

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The vessel was then depressurized slowly while the temperature was maintained at 260 °C. Finally, the aerogel was slowly cooled to room temperature with N₂ as purging gas. The powder obtained was calcined at 500 °C in air for 1 h before being used for SWNT synthesis.

1.2 SWNT synthesis

The method of synthesis has been described before [9]. Briefly, an alumina boat was loaded with about 50-mg catalyst and was put into a quartz tube. It was heated to 860 °C under an Ar flow (200 sccm). The Ar flow was shut off and CO (1000 sccm) was introduced when the temperature reached 860 °C. After a certain reaction time (15 to 120 min), the CO flow was switched back to Ar while the system was cooled to room temperature. The yield is defined as the mass increase divided by the starting catalyst mass.

1.3 Sample characterization

A 1.0-mg sample of SWNTs was sonicated in methanol and then a drop was placed onto a holey-carbon grid for transmission electron microscope (TEM, Philips 301) observation. The content of carbon in the sample was measured by a TGA (Thermalgravimetric Analyzer) system (SDT 2960, TA instrument) under an airflow at a ramp rate of 5 °C/min.

2 Results and discussion

2.1 Feeding gas

In our previous experiments, we used methane as a carbon source [9]. A high yield of SWNTs was achieved in that study. The purity of the raw products is very good when a thin layer of catalyst was used for growth. However, when a large amount of catalyst was used, we found more amorphous carbon in the product with methane as feeding gas, making the purification of the raw materials a challenge. Using carbon monoxide, the amount of amorphous carbon is significantly reduced. We think this difference is related to the thermodynamic equilibrium properties of the two chemical reactions [15]:



For CH₄, higher temperature favors carbon formation, while for CO, higher temperature favors carbon consumption. We have also observed that the yield of nanotubes at higher temperature is lower when CO was used as feeding gas. When large amount of catalysts were used, the thermal exchange between the gas molecules and the surrounding environment is more efficient in the bulk of the catalyst compared with in the surface layer. Therefore, inside the bulk of the catalyst, the temperature of the gas molecules is higher. For methane, amorphous carbon is more likely to form, while for CO, the formation of carbon is not favorable. Experimentally, we have observed that when CO was used as feeding gas, only a thin surface layer of the catalyst (~ 1 mm in thickness) produces nanotubes; underneath, the catalyst remains unreacted.

When methane was used, more amorphous carbon was produced within the bulk of the catalyst. Although the yield of nanotubes is lower using CO as feeding gas, the overall purity of the materials is much better. In addition, the Raman spectrum also showed that the diameter distribution of the nanotubes made by the CO CVD method (1.0–1.5 nm) is narrower compared with the products made by methane CVD (0.9–2.7 nm) [9]. More work is under way to use a fluidized-bed reactor [16] to overcome the limits caused by catalyst packing.

2.2 Optimization of SWNT-synthesis conditions

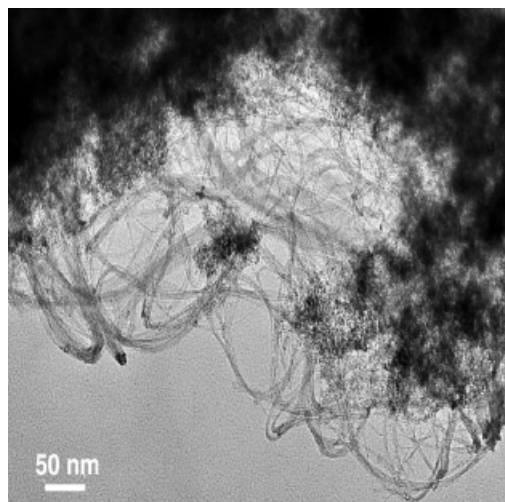
We carried out systematic studies to optimize the growth conditions for nanotubes. We have found that the optimal reaction temperature is about 860 °C. When the reaction temperature is higher than 880 °C, the yield is lower. On the other hand, when the reaction temperature is lower than 820 °C, the product contains amorphous carbon.

The flow rate of CO also affects the experiment outcome. When it is higher than 1000 sccm, the product shows the best quality. If a lower flow rate of 500 sccm is applied, a small amount of multiwalled nanotubes (MWNTs) is observed together with SWNTs. The exact cause of the formation of MWNTs is still under investigation in our group.

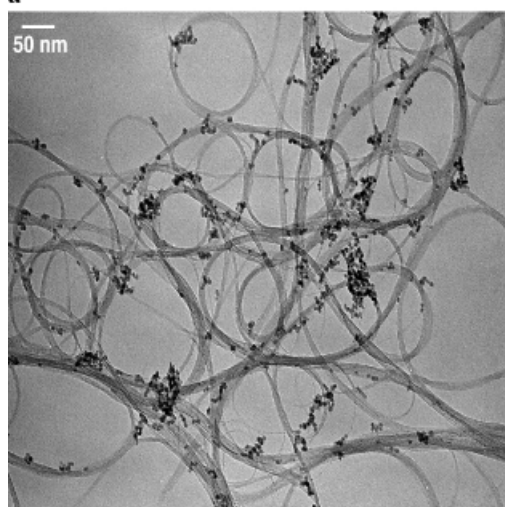
Another important factor is the surface area of the catalysts. Simply evaporating the ethanol in the wet gel would cause the gel to shrink and significantly reduce the total surface area and pore volume. The resulting material is called a xerogel. A xerogel catalyst showed a weight gain of less than 20% with 60-min reaction time, while the aerogel catalysts gave a weight gain of around 80%. Typically the surface areas measured by the BET (Brunauer–Emmett–Teller) method on our aerogel and xerogel catalyst areas are 500–600 m²/g and < 100 m²/g, respectively. Therefore the surface area of the catalyst support is an important factor that affected the SWNT yield.

2.3 Purification of SWNTs

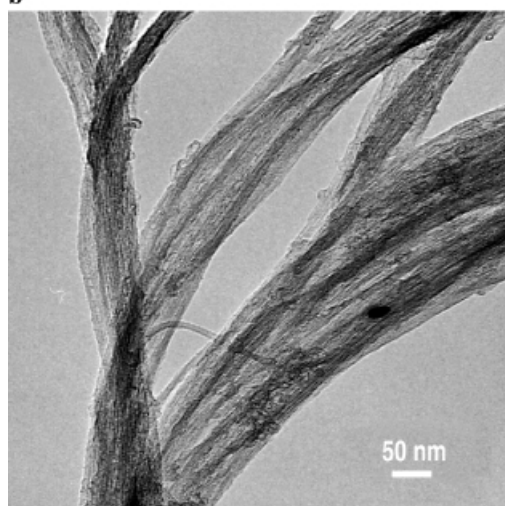
The raw product contains the aerogel support, catalyst particles and a small amount of amorphous carbon (mostly as a coating on the catalyst nanoparticles) as impurities (Fig. 1a). A purification scheme was designed to remove all of these undesired impurities. In a typical purification experiment, about 100-mg raw material was mixed with 5-ml hydrofluoric acid (52%) and 15-ml H₂O to dissolve the aerogel support. It was stirred for 18 h and then centrifuged to remove HF acid. The SWNTs obtained still contained many metal nanoparticles, presumably because the nanoparticles are coated by carbon layers. To further purify the product, a two-stage gas-phase oxidation procedure was taken [14]. First, the sample was heated in a 15% air/Ar mixture at 400 °C for 1 h. A wash in 5-ml concentrated HCl acid (37%) dissolved the metal oxides that formed during the oxidation process. In the second stage, the oxidation process was carried out at 450 °C for 1 h and then the sample was washed again in HCl acid. Such oxidation steps burned the carbon coating on the catalyst particles, making them exposed to acid attack, while leaving the nanotubes unaffected because of the higher stability of nanotubes against oxidation compared with amorphous



a



b



c

Fig. 1a–c. TEM images of **a** raw product, **b** SWNTs after the second oxidation step and **c** purified SWNTs

carbon (Fig. 1b). The final purified product consists of mainly (> 90%) SWNTs in bundle form (Fig. 1c). Thermogravimetric data shows that the purified SWNTs contain a negligible amount of metal oxide (Fig. 2).

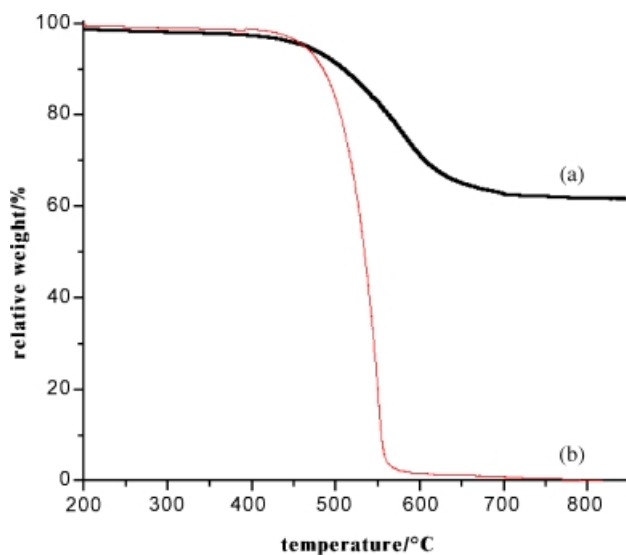


Fig. 2. TGA plots of (a) raw material (30-min runtime) and (b) purified SWNTs

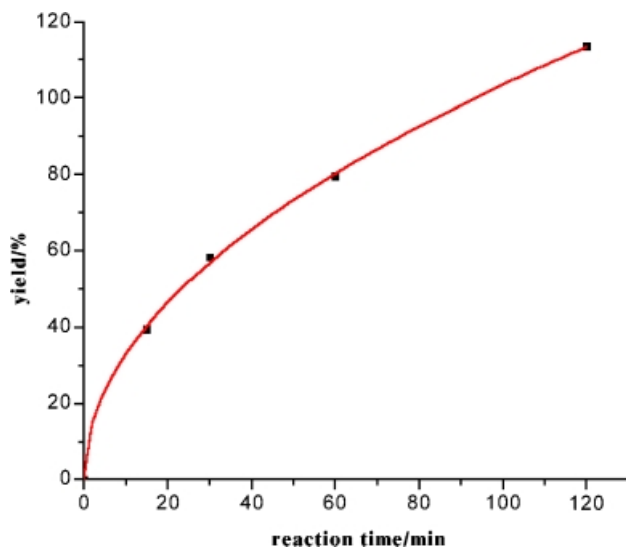


Fig. 3. Weight gain of the catalyst as a function of reaction time

2.4 Growth kinetics

The relationship between the SWNT yield and the reaction time is also studied. As shown in Fig. 3, the fit gives a time dependence of $t^{1/2}$. This is consistent with the observation of Hafner et al. [17]. Although the $t^{1/2}$ dependence remains to be proved, the trend of this curve shows that the growth rate decreases with time. One obvious reason is that the gas-diffusion rate becomes lower with more SWNTs grown on the catalyst. This also explains why catalysts with high porosity like aerogel can greatly enhance the SWNT yield.

3 Summary

We have developed a new procedure using the CVD method to produce SWNTs with high yield and quality. There are many important factors that affect the yield and quality of

SWNTs, including the surface area of the supporting material, reaction temperature and feeding gas. A two-step purification procedure involving acid washing and oxidation in diluted air produced high-purity SWNTs.

Although many experimental results have been obtained on the growth mechanism of nanotubes [18–20], there are many aspects to be considered before a comprehensive understanding could be developed. We hope the present study leads to a better interpretation of the SWNT-growth mechanism and further optimization of the synthetic process.

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