



Possible tactics to improve the growth of single-walled carbon nanotubes by chemical vapor deposition

Hao Yan, Qingwen Li, Jin Zhang*, Zhongfan Liu

Centre for Nanoscale Science and Technology (CNST), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

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Abstract

The growth time, growth mode and the method of preparing the supported catalysts play an important role in the growth of single-walled nanotubes (SWNTs). Their effects on the chemical vapor deposition (CVD) growth of SWNTs with MgO-supported catalysts were investigated in this study. It is shown that the growth rate of SWNTs was large during the initial few minutes of growth, however the quality of the tubes was low owing to the formation of many defects. Long term growth may favor the formation of tubes with high quality and high yield, but the introduction of other forms of carbon (impurities) is also unavoidable. There was a balance between the increase in yield and quality and sacrifice of the purity during growth of SWNTs. MgO-supported catalysts prepared by the co-precipitation method were found to be more effective for the synthesis of SWNTs than those prepared by the widely used impregnation method. The size and dispersion state of the catalyst were found to be crucial in enhancing the growth of SWNTs. In addition, growth on the surface of SWNTs over nanosized catalyst films was shown to be more favorable for the synthesis of tube products with higher quality, yield and purity.

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1. Introduction

Since their discovery in 1991 [1], carbon nanotubes have attracted much attention due to their unique properties [2–4]. At present they can be used as SPM tips [5], to fabricate field-emission devices [6], synthesize high-strength materials [7], etc. Single-walled nanotubes (SWNTs) are especially intriguing, as they have an atomically well-defined structure, providing an ideal model of low-dimensional nanostructures. The scaleable synthesis of SWNTs with high yield and quality is therefore of great importance for both theoretical research and practical use.

Chemical vapor deposition (CVD) appears to be a promising method to achieve this [8], as it is advantageous compared with other methods such as arc-discharge or laser-ablation with its low cost, simple apparatus and multiple adjustable parameters to control the fine structures

of the tube products. When a gaseous hydrocarbon flows over a metal catalyst at high temperature, many forms of carbon deposits can be produced, such as carbon fiber, amorphous carbon, multi-walled carbon nanotubes, single-walled carbon nanotubes, etc. [8]. The forms of carbon materials are found to be closely dependent upon the types of carbon source, the properties of the support materials and the catalytic metals. In general, the successful growth of SWNTs may be mainly attributed to the formation of well-dispersed metal nanoparticles, which can be achieved by choosing suitable support materials. During the CVD growth of SWNTs, the role of the support materials is not only to load the metal species, but importantly to prevent metal particles from aggregating into large clusters, otherwise MWNTs or other kinds of carbon materials may be formed. Therefore, many attempts have been made to prepare supported catalysts for the optimal growth of SWNTs. For instance, Liu was successful in greatly improving the yield of SWNTs by using an alumina aerogel-supported Fe/Mo catalyst [9]; Dai synthesized SWNTs by preparing silica/alumina-supported Fe, Co or

*Corresponding author. Tel.: +86-10-6275-2555; fax: +86-10-6275-7157.

E-mail address: jzhang@chem.pku.edu.cn (J. Zhang).

Ni oxide catalysts [10,11]; and, more recently, MgO has also been found to be effective for the growth of high-quality SWNTs [12–14]. In the present study, we found that the yield, purity and textural properties of as-prepared SWNTs were greatly dependent upon the size of the support materials and the method of catalyst preparation. Using nanosized MgO support materials, which have a greater surface area and thereby a high loading efficiency of metal salts, improved the yield of as-prepared SWNTs. Compared with the commonly used impregnating method, a co-precipitation method was shown to be more effective in obtaining well-dispersed metal catalysts, which can raise the carbon yield to 40% without further optimization. Furthermore, the growth of SWNTs could be greatly improved by preparing nanosized MgO-supported metal catalyst films for the surface growth process.

2. Experimental

2.1. Preparation of catalysts

Three methods were used to synthesize MgO-supported Fe catalysts. The first is the chemical impregnation method, which is the most widely used method in previous work [12,14]. Typically, 20 g $\text{Mg}(\text{OH})_2(\text{OH})_2\text{CO}_3$ was mixed with 200 ml of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution (10 mg/ml). The suspension was sonicated for 0.5 h and dried at 100 °C overnight. The so-formed yellow powder was ground thoroughly for further use. The catalyst prepared by this method was denoted as catalyst CI. The second was the co-precipitation method. 20 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.3025 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved together in 250 ml ethanol and 1:1 $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added dropwise under vigorous stirring until pH 8. The precipitate was then rinsed with ethanol and dried in air at 100 °C. The catalyst prepared by this method is denoted as catalyst CP. The third method was used for the surface growth of SWNTs, so it was fabricated using the following procedure. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and polyethylene glycol (PEG) (MW 8000) were dissolved together in ethanol at a weight ratio of 3:2:0.3. The solution was sonicated until it became clear. The resulting gel solution of metal slats was then spin-coated on a clean Si(111) surface at a spin rate of 3500 rpm. After evaporation of the ethanol solvent, the covered Si wafer was further heated at 600 °C for 1 h before being used for NT growth.

2.2. Growth of SWNTs

The reaction was carried out in a CVD system consisting of a tube furnace and a gas flow control unit. In a typical experiment, about 0.5 g catalyst (or catalyst-coated Si wafer) was put in a quartz boat and placed in the middle of the tube furnace. The temperature was raised to 850 °C

in Ar atmosphere at a flow rate of 300 ml/min before CH_4 was introduced into the system at 100 ml/min for 30 min. CH_4 was then turned off and the furnace was cooled to room temperature in an Ar flow. The impurities in the carbon deposits, mainly including support and catalyst, were removed by acid treatment with concentrated HCl, if needed.

2.3. Characterization

The Raman spectrum was recorded in ambient atmosphere at room temperature, using a 50 mW He–Ne laser with wavelength 632.8 nm and a CCD detector. Each spectrum given is an average of at least 10 spectra taken from different points of the sample. For Raman characterization, the catalyst was not removed from the post-growth material.

SEM characterization was carried out using a field-emission instrument operating at 25 kV. The samples were prepared as follows: a small amount of the sample was sonicated in a 1,1-dichlorobenzene solution for 2 h. A drop of the clear liquid was then applied onto a piece of silicon wafer and left to evaporate. TEM examination was performed at 200 kV.

Carbon yield was measured as follows: a certain amount of as-prepared carbon material (catalyst together with carbon deposit) was weighed (W_1) and then heated in air at 800 °C for 30 min. The remainder, consisting of only the catalyst support, was cooled to room temperature and weighed again (W_2). Carbon yield (%) was calculated as $(W_1 - W_2)/W_2$.

3. Results and discussion

3.1. Dependence of the yield and purity of as-grown SWNTs on growth time

The yield of carbon nanotubes has a close relationship with the injection time of the carbon source. In general, the longer the injection time the more hydrocarbon molecules pass over the catalyst, and therefore the higher the carbon yield of the deposits. The growth of nanotubes is a rapid process [1], which may terminate when catalyst particles are poisoned by impurities. Fig. 1a shows the dependence of the carbon yield on growth time when methane gas flows over catalyst CI. It can be observed that, during the initial stage of growth, the yield of carbon deposits clearly increased with time up to 30 min, with longer growth times not producing the same increase in yield. Typically, the carbon yield was around 12% with 30 min of growth time, while after 120 min, the yield only reached 23%, implying that the growth rate had slowed. Fig. 1b is the differential form of Fig. 1a, which may be used to roughly estimate the growth rate of the tube products. As shown in Fig. 1b,

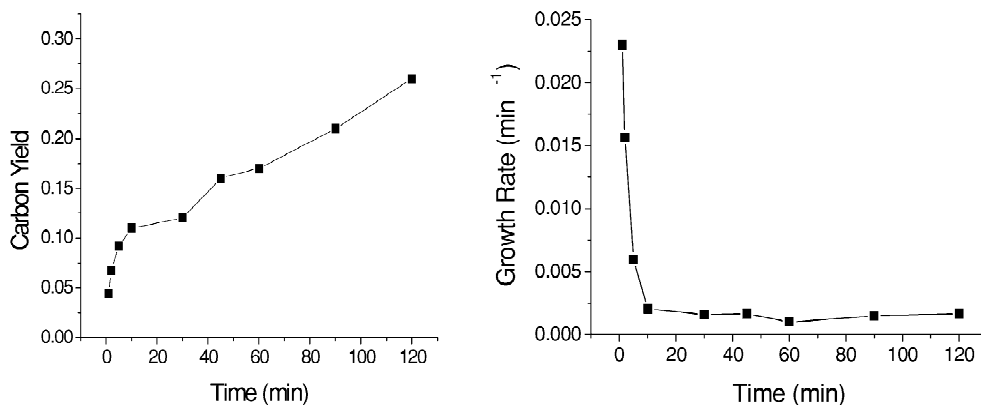


Fig. 1. Curve showing the dependence of the yield of carbon deposits on the growth time and its differential curve.

within the first 30 min, the growth rate of tubes decreased with growth time, while in the latter period, it appeared to be unchanged with time. This suggests that most of the growth had taken place in the first 30 min. The further increase in carbon yield during long growth times might be due to the deposition of amorphous carbon on the MgO support, since in our experiment we found that CH_4 could also readily deposit carbon on MgO without the presence of a catalyst.

Raman spectroscopy is a powerful technique to identify and evaluate the quality of as-prepared SWNT products. Three modes are useful in the Raman spectra of SWNT samples. RBM (radial breathing mode) frequencies centered around 200 cm^{-1} can be used to estimate the diameters of SWNTs [15]. The G-line mode located around 1580 cm^{-1} is assigned to the C–C bond motions due to the introduction of curvature into a graphite sheet, and the D-line centred around 1350 cm^{-1} is usually ascribed to the existence of disordered carbon in bulk samples [15,16]. The intensity ratio of the G- and D-lines is often regarded as an indicator of the purity of as-prepared tube samples [17]. Fig. 2 shows the Raman spectra of as-prepared SWNTs samples obtained with different growth times. The corresponding intensity ratio of the G- and D-lines was measured and plotted. Generally, large I_G/I_D corresponds to high-purity tube products. From Fig. 2, three kinds of purity distributions can clearly be distinguished. In the initial stage of growth, especially when the growth time was less than 15 min, the purity of the tube products increased with growth time. This result can be rationalized from the results of TEM characterization (Fig. 3). Within the first few minutes of growth, the as-grown SWNTs were always short and the tube walls were defective and unclear. However, when the growth time was longer than 10 min, the tubes grew more perfectly and had an average length of around several micrometers. In this case the intensity ratio, I_G/I_D , was observed to increase with growth time. However, when the

growth time was further increased, the I_G/I_D ratio decreased slightly. Combined with the results shown in Fig. 1b, this phenomenon may imply that the initial growth of SWNTs was kinetically controlled, as the catalytic sites were active and fresh for the formation of tubes. After growing for some time, the growth process might change to be thermodynamically dominated, which means that, in this period, a SWNT would modify its structure to a more perfect and stable state. In this situation, however, with the continuous injection of carbon and the probable poisoning of the catalytic particles, other forms of carbon would be deposited, reducing the final purity of the SWNT products. This becomes even worse at longer growth times. In this regard, there is a balance between the growth of SWNTs and sacrifice of the purity of the as-prepared tube products. Considering both quality and quantity, we chose 30 min as the optimum growth time, which ensures the growth of SWNTs with a relatively small amount of amorphous carbon and gives a comparatively high productivity.

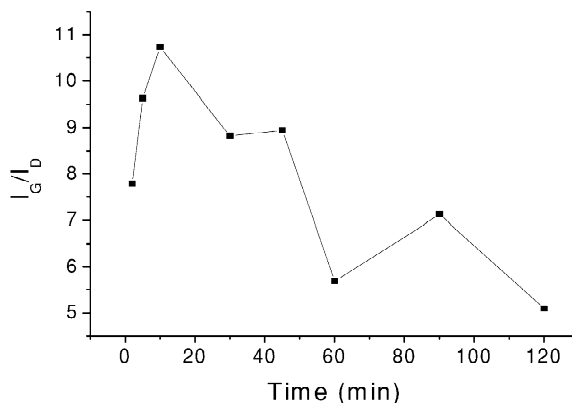


Fig. 2. Influence of growth time on the resulting intensity ratio I_G/I_D .

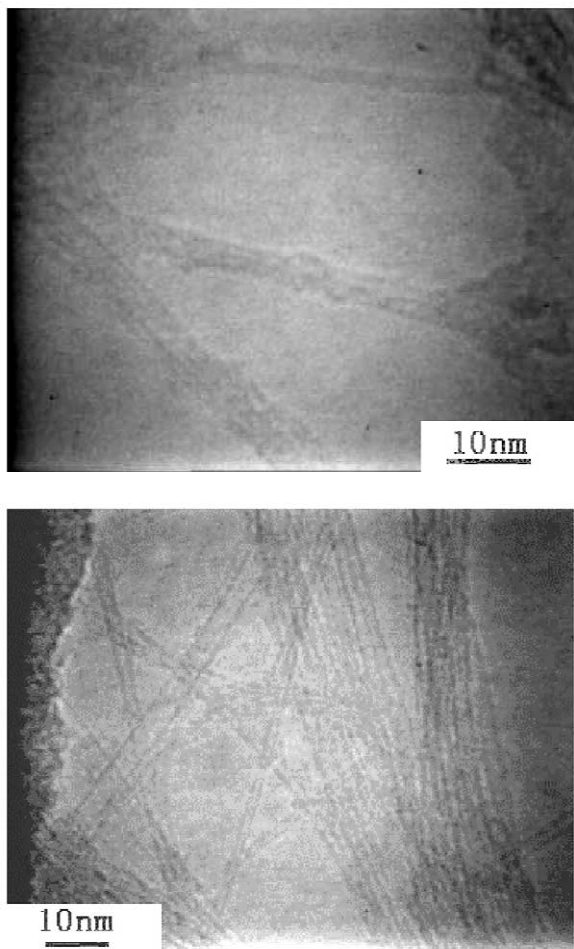


Fig. 3. HRTEM images of SWNTs with 2 min (top) and 30 min (bottom) growth times.

3.2. Dependence of the growth of SWNTs on the preparation of the catalysts

In our experiments, we found that the growth of SWNTs, especially parameters of interest such as yield and purity, not only greatly depended upon the growth time, but also had a close relationship with the preparation of the catalysts. In general, the supported catalysts used in previous work were usually prepared by an impregnation method. CVD synthesis of SWNTs using an Fe catalyst (CI) resulted in a growth yield of around 12% for a growth time of 30 min. Another method, co-precipitation, was also attempted to prepare supported catalysts. Fe salts were added during the precipitation of Mg nitrites with ammonia in ethanol solution. Methane CVD growth of SWNTs on such catalysts (CP) gave a yield of up to 40%, notably higher than when using the CI catalyst with the same Fe loading. Fig. 4 shows the Raman spectra of SWNTs grown on the CP catalysts. Compared with the Raman spectra

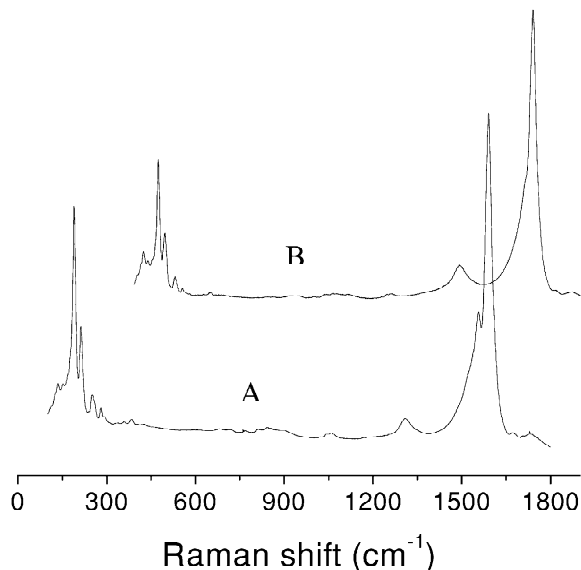


Fig. 4. Raman spectrum of SWNTs grown over a catalyst prepared by the co-precipitation method (A) and by the impregnation method (B).

obtained on the CI catalyst under similar growth conditions, a stronger intensity of the RBM peaks, a lower intensity of the D-line and, therefore, an extremely high I_G/I_D ratio (~ 40) were observed, indicating that the prepared SWNT material is of good purity and quality. Fig. 5 shows SEM images of the as-grown SWNT materials prepared using CP and CI catalysts without further purification treatment. The growth time for both was 30 min. For the CP catalyst, ultra-fine catalyst particles together with single and bundled SWNTs are observed, while for the CI catalyst, only large catalyst grains are present and no tubes are observed. This suggests that the CP catalyst is more favorable for SWNT growth.

The effectiveness of this co-precipitated catalyst may be attributed to two factors. First, compared with the chemical impregnation method, ammonia precipitation of metal salts in EtOH favors the formation of nanosized catalyst particles, so the catalyst has a greater surface area and therefore more catalytic sites. Second, co-precipitation of Mg and Fe salts would result in the formation of a Mg–Fe complex, which results in the iron species being well dispersed and having a strong interaction with the MgO support. These factors increase the catalytic activity of the catalyst and inhibit the formation of large Fe particles at elevated temperature. Thus we may conclude that the co-precipitation route is superior to the conventional chemical impregnation method for methane CVD growth of SWNTs.

It is also worth mentioning that the sizes of the individual tubes and bundles of SWNTs grown on the CP catalyst are clearly smaller than those grown on the CI catalyst. From Fig. 4, the appearance of high wavenum-

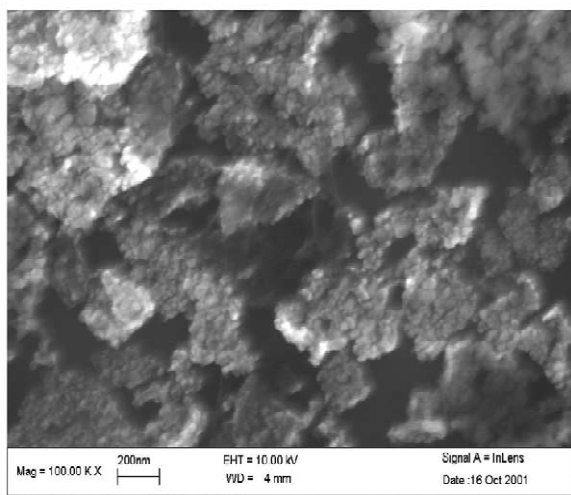
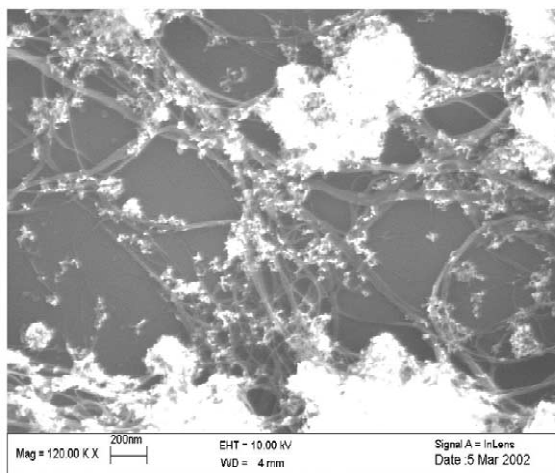


Fig. 5. SEM images of SWNTs grown on two kinds of catalysts: CP (top), CI (bottom).

bers, such as 250 and 280 cm^{-1} , can be observed in the RBM peaks. According to Bando's equation [15], $d/\text{nm} = 223.75/(\nu/\text{cm}^{-1})$, these peaks are related to smaller-diameter tubes. The structures of the fiber-like bundles and the formation of small-diameter tubes may be attributed to the formation of ultra-fine catalyst particles [18,19].

3.3. Dependence of the growth of SWNTs on their growth mode

Reduction of the particle size of the catalysts was effective in improving the growth of SWNTs. However, the coalescence of the catalysts during the bulk synthesis of SWNTs is not favorable with respect to the best utilization of each active site. We consequently attempted to fabricate a nanosized catalyst film on Si(111) for the surface growth of SWNTs. In this work, a MgO-supported

Fe catalyst film was prepared using the sol-gel method combined with a spin-coating technique, as described in Section 2.1. Fig. 6 shows SEM images of a catalyst-coated surface and the subsequent growth of SWNTs on this surface. It can be observed that the size of the prepared catalyst particles is small and uniform and of the same order as those obtained by the co-precipitation method. Methane CVD growth on this surface led to the formation of a SWNT film. This film was uniform, dense and had fewer catalyst particles associated with the SWNTs, indicating very high productivity and purity. The Raman spectrum shows that this film consists of high-quality SWNTs. This result further confirms that small, well-dispersed catalyst particles on the support material might greatly favor SWNT growth.

Besides the surface growth mode, the floating CVD technique may also be a useful approach to obtain SWNTs with special properties. It has recently been reported that 20 mm long SWNT strands may be directly grown by the ferrocene catalytic pyrolysis of *n*-hexane with an enhanced vertical floating method [20]. Vaporized ferrocene catalytic

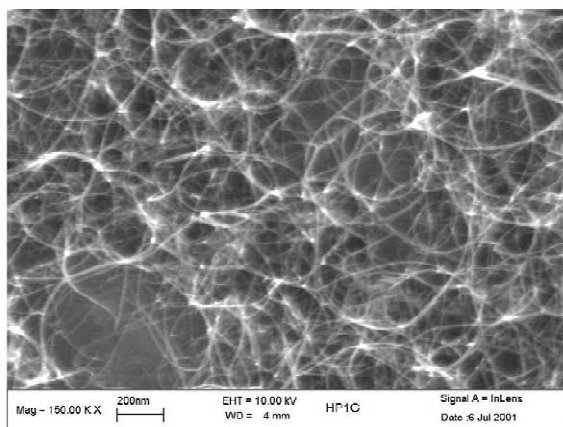
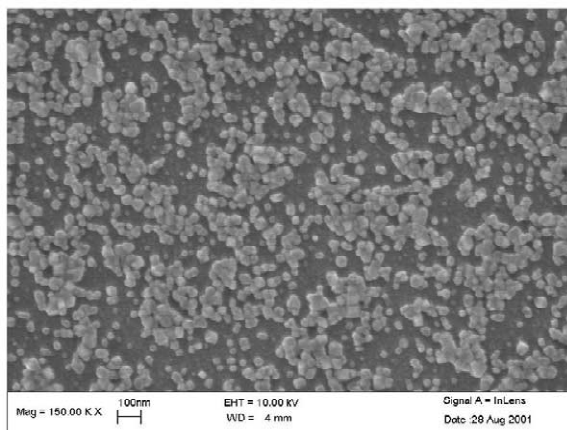


Fig. 6. SEM images of a catalyst film-coated Si surface (top) and the growth of SWNTs on this film (bottom).

particles may ensure sufficient contact with hydrocarbon molecules, while vertical floating of the catalytic particles and hexane enable the growth of SWNTs along a preferred direction and assembles them into long arrays. In summary, SWNT products of the desired quality and properties may be obtained by suitable utilization of the catalytic activities of catalyst particles, growth time and growth modes.

4. Conclusions

We carried out a series of experiments to improve the CVD synthesis of SWNTs, and found that growth time, preparation of the catalysts and growth mode greatly affect SWNT growth. The quality and purity of as-prepared SWNT products varied with growth time. There was an optimum time at which we could obtain SWNT products with acceptable quality and productivity. We further optimized the preparation of the catalyst by changing from a conventional chemical impregnation method to a novel co-precipitation method. The catalyst thus obtained was found to be highly active for SWNT growth with a carbon yield of up to 40% without further optimization. This high performance of the catalyst was attributed to reduced particle size and the excellent dispersion of Fe species over the MgO support. Finally, we prepared a catalyst-coated Si(111) surface by a sol–gel method which was found to be even more effective for SWNT growth and the SWNTs deposited on it formed a dense film.

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