

Effect of the reaction atmosphere on the diameter of single-walled carbon nanotubes produced by chemical vapor deposition

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Abstract

The influence of the reaction atmosphere on the type of single-walled carbon nanotubes (SWNT) grown during chemical vapor deposition (CVD) was investigated. Methane decomposition was catalyzed by Fe/MgO and Fe–Mo/MgO catalysts in argon, nitrogen and their mixtures. Nitrogen influences the carbon species significantly. The aggregation of iron nanoparticles in nitrogen results in the growth of N-doped carbon nanofibers on the Fe/MgO catalyst. A limited iron nanoparticle aggregation in nitrogen occurred on a Fe–Mo/MgO catalyst, on which there was an increase in the diameter of the SWNTs as the reaction atmosphere was more enriched in nitrogen, which was characterized by Raman spectroscopy. These results provide an experimental basis for the rational selection of the reaction atmosphere, and suggest an approach to control the size of the SWNTs in a CVD method.
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Keywords: Carbon nanotubes; Chemical vapor deposition; Raman spectroscopy; Aggregation; Microstructure

1. Introduction

One of the most important issues in the research on single-walled carbon nanotubes (SWNTs) [1] is the control of their size and helicity. Most popular control methods focus on two major aspects: the preparation of catalysts with a size as small and uniform as possible [2], and control of the operating conditions, for instance, temperature [3] and partial pressure. However, the choice of the gas atmosphere of the catalyst has been less considered, although in a process for producing carbon nanotubes (CNTs), the selection of the ambient gas was significant for the quality and yield [4,5] of the product. The type of diluting gas is

also important for the flexibility and cost of the commercial production of CNTs. In the technologies of CNT preparation, inert gases, such as nitrogen and hydrogen are used to adjust the partial pressure of the carbon sources and control the decomposition rate.

The influence of the atmosphere on the SWNT growth was first investigated in the laser ablation method [6]. However, the most promising method to obtain CNTs efficiently and at low cost is by chemical vapor deposition (CVD) in nitrogen, which has been validated in the production of multi-walled CNTs (MWNTs) in many reports including our previous work [7]. When a more active nitrogen source (usually ammonia) is used, the formation of MWNTs is enhanced [8] and there is a tendency towards bamboo-like [9] and nitrogen-doped [10,11] CNTs. An analysis of this process indicated that nitrogen plays a role in the diffusion of carbon and etching of the catalytic sites [12]. Although many interesting phenomena have been

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discovered about nitrogen and its effects on CNT growth, there has been few reports [13] on the nitrogen-containing atmosphere in SWNT synthesis by CVD. It is worthwhile to systematically investigate whether SWNTs can be synthesized in a nitrogen gas by CVD and the kinds of requirement needed. The purpose of the present work is to examine the effects of nitrogen gas on SWNT growth on Fe/MgO catalysts by methane decomposition and the principles behind the role of nitrogen on SWNT growth. In this paper, we compare the morphology and microstructure of the carbon deposits obtained in nitrogen and in a typical inert argon gas. A relationship between the microstructure of the carbon deposits and the ambient gas is established, and based on this, a mechanism is proposed to explain the effect of the reaction atmosphere on the SWNT microstructure. This provides helpful insight into the SWNT growth mechanism during CVD and is useful for controlling SWNT production.

2. Experimental

Two kinds of catalysts, Fe/MgO [14] and Fe–Mo/MgO, were prepared and used to synthesize the SWNTs. The procedure for the Fe/MgO catalyst preparation and the production and purification of the SWNTs have been reported elsewhere [15]. In brief, magnesium oxide powder (BET surface area 27.4 m²/g) was suspended in distilled water to form a uniform suspension by strong stirring at 80 °C. Subsequently, a solution of iron nitrate (Fe(NO₃)₃·9H₂O) was added dropwise into the suspension slowly with stirring. The weight ratio of the salt in the solution to the magnesium oxide was 1:10. After drying the suspension at room temperature or 60 °C and grinding the solid, the catalyst for SWNT production was obtained. The Fe–Mo/MgO catalyst was prepared by a similar method, except that instead of the iron nitrate solution, a mixed solution of Fe(NO₃)₃ and (NH₄)₆Mo₇O₂₄ with a molar ratio of 1:3.5 (Fe to Mo) was used. The SWNTs were produced in a quartz fluidized bed reactor 50 mm in diameter. The reactant gas was composed of the diluting gas, hydrogen and methane in a composition of 10:1:1. This was introduced into the reactor at 900 °C for 30 min. Argon gas (99.999%) and 99.999% nitrogen gas or their mixture were used as the reaction atmospheres. The products were characterized by scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (the beam size used was about 40 μm in diameter from due consideration of the sample uniformity). These techniques gave the identi-

fication of the species of the product listed in Table 1. The samples from methane decomposition on Fe/MgO in argon and nitrogen, and on Fe–Mo/MgO in argon and nitrogen gases are denoted, respectively, as Samples 1, 2, 3 and 4 in the following text.

3. Results and discussion

The SEM and TEM images of the purified products from methane decomposition on the Fe/MgO catalyst are shown in Fig. 1. When the reaction was conducted in an Ar atmosphere, high-purity SWNTs can be synthesized, which are in the form of an entangled network. A detailed HRTEM observation indicated that the resultant product was mainly composed of SWNT bundles with some double-walled carbon nanotubes (DWNTs), as shown in Fig. 1(c). The Raman spectrum of sample 1 (Fig. 2) shows strong radial breathing modes (RBM) around 190 cm⁻¹. A nitrogen adsorption method indicated that the pores are distributed around 1.17 nm [16], which corresponds well with the calculated value from the formula for the Raman signals for free-standing SWNTs $\omega_{\text{RBM}} = 223.8/d_t$ [3]. The ratio of the intensities of the D-band and G-band (I_{D} and I_{G} , respectively) in the Raman spectrum of sample 1 is about 0.1, which indicates a well-crystallized microstructure. However, a drastic change occurred in the nature of the product when Ar was replaced by N₂. As shown in Fig. 1(b), sample 2 is composed of thick carbon nanofibers (CNFs) whose diameters are about 100 nm that are not SWNTs. A strong D line increased the ratio $I_{\text{D}}/I_{\text{G}}$ to 0.86, and the RBM peaks had completely disappeared, which indicated that there were no SWNTs and the microstructure of the sample was defective. An XPS analysis was carried out to identify the chemical state of this sample and 1% nitrogen was detected. The two peaks, shown in Fig. 1(d), centered at binding energies of 399 eV and 402 eV, implies a doped or absorbed nitrogen element [11]. Since the CNF diameters were about 100 nm and Fe particles tend to be encapsulated in them, the detected nitrogen must be from the surface of the CNFs and not the catalysts. Although trace N₂ may be adsorbed on the surface of the CNFs, the multiple N chemical states indicate that at least part of the nitrogen is in a solid. Thus, it can be concluded that nitrogen-doped carbon fibers were synthesized on the Fe/MgO catalyst in a nitrogen atmosphere.

The above results demonstrate that the nitrogen gas is reactive in the decomposition of methane, and it influences the morphology of the product significantly. This is quite different from the results obtained using the laser ablation

Table 1
Products from methane decomposition in different atmospheres

Sample	Catalyst	Atmosphere	RBM	$I_{\text{D}}/I_{\text{G}}$	Products
1	Fe/MgO	Ar	Yes	0.10	SWNTs
2	Fe/MgO	N ₂	No	0.86	MWNTs + CNFs
3	Fe–Mo/MgO	Ar	Yes	0.13	SWNTs
4	Fe–Mo/MgO	N ₂	Yes	0.36	SWNTs + MWNTs

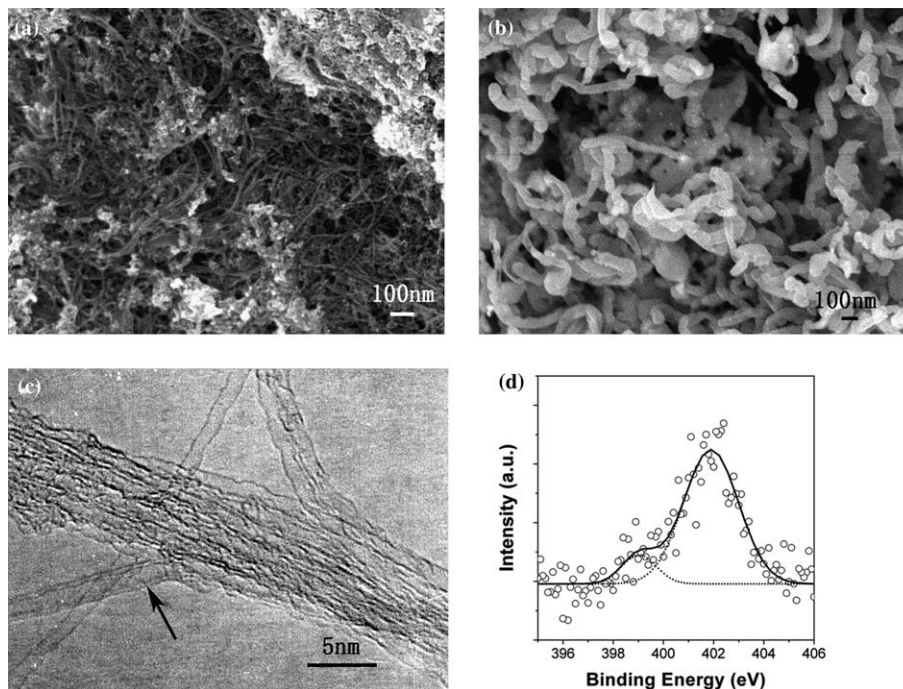


Fig. 1. Morphology of the products by methane decomposition on Fe/MgO in Ar and N₂: (a) SEM image of the product grown in Ar, and (c) HRTEM image of a SWNT bundle with a DWNT in it. (b) SEM image of the product grown in N₂. (d) XPS of the sample in N₂, indicating doped nitrogen element.

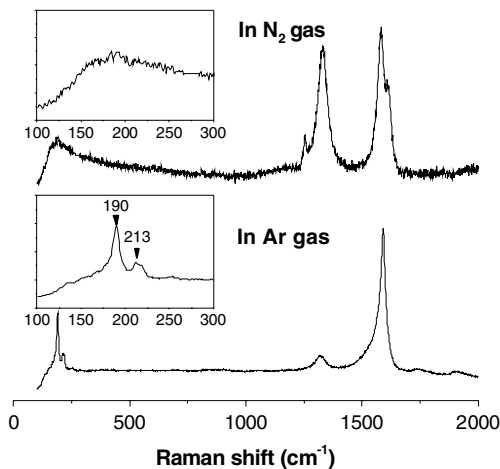


Fig. 2. Raman spectra (excited at 633 nm) of the products by methane decomposition on a Fe/MgO catalyst in N₂ and Ar.

method [4–6] or a previous thermal CVD [13] study. However, it should be noted that all the reports about the inertness of N₂ were based on bimetallic catalysts, such as Ni/Co [4–6] and Fe/Mo [13], or operation under a low pressure [4–6]. It has been shown that the atmosphere gases influence the growth of the SWNTs by gas kinetics in laser ablation [5]. Here, we will explore if the reactivity of N₂ in the methane decomposition depends on the composition of the catalysts.

Generally, iron is considered the major active component and molybdenum is the co-catalyst in alloys of Fe-containing catalysts. Good SWNTs in bundles can be

synthesized on the Fe–Mo/MgO catalyst in Ar, as shown in Fig. 3(a). After switching the atmosphere gas from Ar to N₂, SWNTs still grew. However, the growth of MWNTs or bamboo-like carbon nanofibers also began (Fig. 3(b)). These results demonstrated that the reactivity of nitrogen to grow CNFs can be effectively controlled by the addition of Mo into the catalysts, even though the selectivity to SWNTs is reduced to some extent.

In order to characterize the structural difference of samples 3 and 4 in detail, their Raman spectra were compared with each other. Due to the resonance Raman effect, the RBM of the SWNT sample strongly depends on the exciting wavelength of the laser used in Raman measurements. To show the structures of the SWNT samples as accurately as possible, three wavelengths at 514 nm, 633 nm and 785 nm were used to record the Raman scattering spectra to cover a wide range of the SWNT diameter distribution. As shown in Fig. 4, at all the wavelengths, the RBM peaks were present in both Raman spectra of samples 3 and 4, which indicated the existence of SWNT growth in Ar and N₂, although the intensity of the RBM peaks (normalized to the corresponding G peak) excited at 514 nm are relatively weaker. At 514 nm and 785 nm excitations, the distributions of the RBM are almost the same. However, it can be seen that the reaction atmosphere resulted in a clear difference in the RBM excited by the 633 nm laser: the major peak shifted from 220 cm⁻¹ to 190 cm⁻¹ on changing the reaction atmosphere from Ar to N₂, which corresponds to an increase in the SWNT diameter from 1.04 nm to 1.17 nm. Thus, although the RBMs were the same with the 514 nm and 785 nm excitations, the shift with the

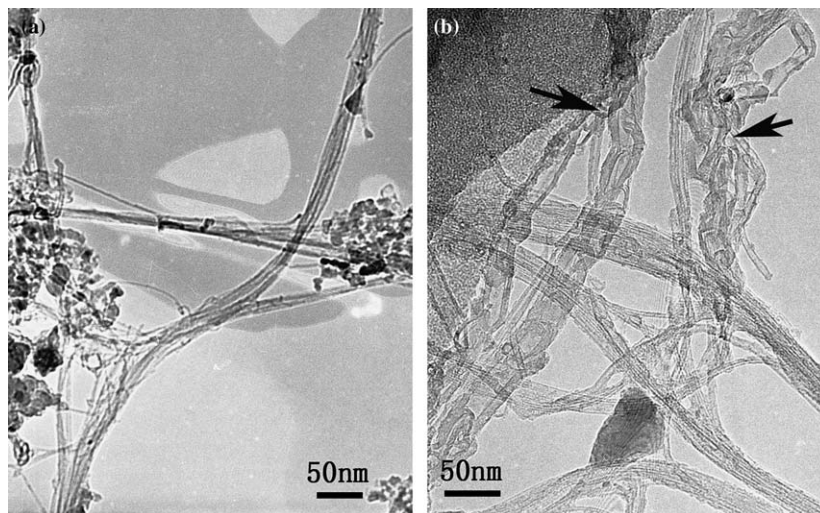


Fig. 3. TEM images of the products from methane decomposition on a Fe–Mo/MgO catalyst in Ar (a) and in N₂ (b).

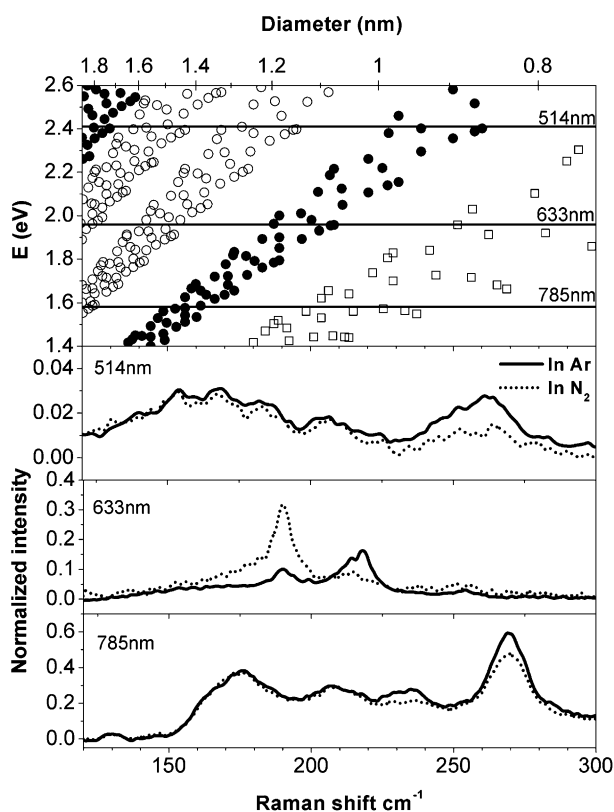


Fig. 4. RBMs, excited with 514 nm, 633 nm and 785 nm lasers, of the products by methane decomposition on a Fe–Mo/MgO catalyst in N₂ and Ar. The intensities of the Raman spectra were normalized to the corresponding G peaks. The Kataura [17] plot is attached to the top of figure, in which the solid circles represent metallic SWNTs. Hollow circles are from Maruyama [19] and squares are from Weisman [18]. The diameter was calculated by $\omega_{\text{RBM}} = 223.8/d_t$ [3].

633 nm excitation also indicated an increase in the diameter of sample 4 compared with sample 3. Furthermore, it can be suggested from the Kataura plot [17–19] at the top of Fig. 4 that metallic and semiconducting SWNTs co-exist

in samples 3 and 4. However, such a shift indicates a relatively preferred growth of metallic SWNTs in nitrogen.

To track the influence of nitrogen on the structures of the SWNT products on the Fe–Mo/MgO catalyst, the growth of CNTs on Fe–Mo/MgO in mixed atmospheres with different N₂ to Ar ratios was studied. There was a clear trend of diameter increase as shown in Fig. 5. In the sample from pure Ar, the RBM distributed around four obvious peaks, centered at 190 cm⁻¹, 214 cm⁻¹, 219 cm⁻¹ and 255 cm⁻¹, corresponding to SWNT diameters of 1.17 nm, 1.05 nm, 1.02 nm and 0.88 nm. Among the modes that can be excited by the 633 nm laser, the 1.05 nm and 1.02 nm SWNTs were dominant because they were the strongest peaks. With an increase in the fraction of N₂ to 20%, a new peak centered at 154 cm⁻¹ emerged, which indicated some larger SWNTs around 1.5 nm, from the reciprocal relationship between frequency and diameter. With further increased N₂ fractions, peaks centered at 154 cm⁻¹ and 190 cm⁻¹, due to thicker SWNTs, were more intense. Finally, in the spectrum of sample 4, although there were peaks still located at 190 cm⁻¹, 215 cm⁻¹ and 255 cm⁻¹, the 255 cm⁻¹ peak was almost submerged, and the intensity of the 190 cm⁻¹ peak was the strongest among the three. It is evident that the atmosphere of the SWNT growth changed their diameter distribution. When SWNTs grow in N₂ gas, their diameter distribution shift to larger diameters. Additionally, while the large SWNTs grew, the D line also got obviously more intense with an increasing N₂ fraction. As shown in Fig. 5(b), the $I_{\text{D}}/I_{\text{G}}$ ratio gradually increased from 0.13 to 0.36 with the increase in N₂ concentration, which was caused by impurities like MWNTs mentioned above. Thus, in general, it can also be concluded that the nanotubes tend to become thicker with increasing N₂ present on the Fe–Mo/MgO catalyst, although the presence of Mo can effectively prevent the growth of undesired CNFs. Moreover, the fact that larger and more metallic SWNTs tend to grow preferentially in

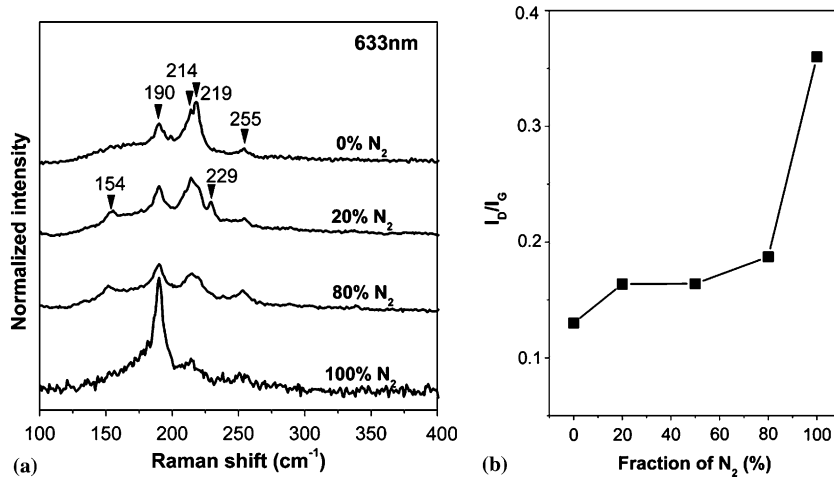


Fig. 5. Raman spectra of the samples grown in a mixed reaction atmospheres: (a) and (b) show the dependences of RBM and I_D/I_G on the N₂ fraction.

N₂ gives potentially a relatively simple approach for the controlled growth of SWNTs in the CVD method.

All the above results demonstrated that nitrogen is not inert in CNT growth by the CVD method, and its activity mainly depends on the catalyst composition. In order to understand these results, the interaction of nitrogen with the supported metal particles that serve for nanotube growth was explored. It is well-known that a complex phase equilibrium forms between iron and nitrogen, which is widely used to improve the performance of steel through nitriding [20]. Although the reaction temperature of the SWNT growth is far lower than the melting point of bulk iron, liquid iron particles are quite likely to form and act as the active sites due to their nanometer sizes, which have been shown in various systems including Fe-CH₄ [21,22]. When the Fe nanoparticles are exposed to nitrogen gas at an elevated temperature, nanoparticles with a high surface activity may lower the energy barrier of the nitriding process. Furthermore, the formation of the Fe-N-C ternary

system during CH₄ decomposition in N₂ may decrease the melting point, thus resulting in the aggregation of the metal particles, which also results in the doping of nitrogen into the deposited CNFs. As a result, the fine iron particles that promote the growth of thin CNTs disappear and the activity toward SWNTs is lost. The HRTEM image in Fig. 6 is evidence of the aggregation of the active particles in nitrogen. Large iron particles with diameters of tens of nanometer were abundantly found in sample 2, which indicated the aggregation of the small particles. It is obvious that the carbon deposit prefers to form carbon fibers or MWNTs rather than SWNTs on this catalyst due to the role of the metal particle size in determining the CNT diameter [23]. It can be derived from the above analysis that it is necessary to prevent the aggregation of Fe particles when synthesizing SWNTs in nitrogen. A second metal component that can form an alloy or composite with the major active metal is often added into SWNT catalysts in order to separate and stabilize the nanoparticles [13,14,24]. Some successful

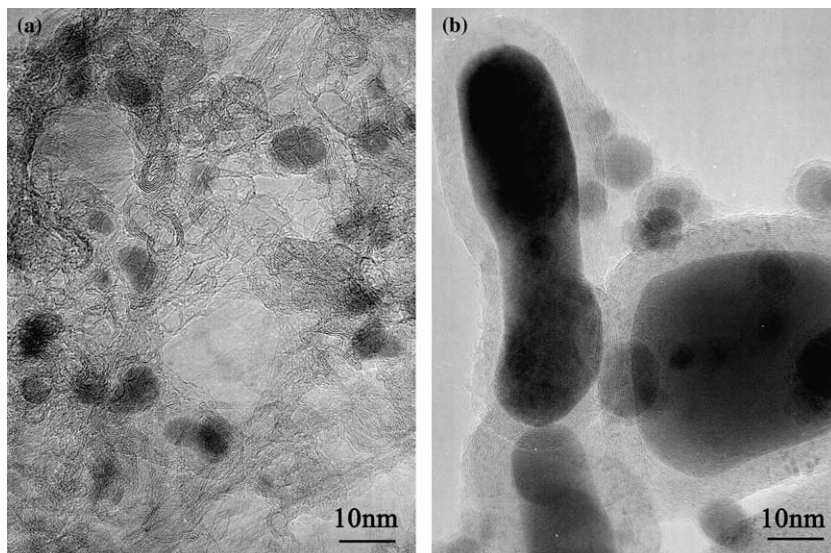


Fig. 6. Aggregation of metal nanoparticles on Fe/MgO in Ar (a) and N₂ (b) atmospheres.

catalyst systems containing Mo, such as Co–Mo [25,26] and Fe–Mo [13,14], have been widely reported. However, the selectivity of the bimetallic catalysts is often dependant on the composition of the catalysts [13,24]. When the composition of catalyst does not form a complete eutectic alloy and some free metal particles exist, aggregation is unavoidable [24]. In experiment 4, the change in the distribution of the SWNT diameter clearly indicated the aggregation of the Fe particles in a nitrogen environment. However, the aggregation was limited because of the presence of the co-catalyst Mo. Due to the limited aggregation, there were no large particles that can promote MWNT growth. Thus, Mo can be used as an effective dispersant of the active metal when present at an optimum composition in the catalysts investigated. Thus, by considering the gas in the surrounding atmosphere as a reactant, a potential approach to control CNT diameters can be established. Just by switching the ambient gas between inert Ar and N₂, SWNTs with different diameter distributions can be synthesized with the same catalyst and condition. This is more convenient than the conventional methods of controlling the catalyst composition and conditions.

4. Conclusions

A preliminary study on the influence of the reaction atmosphere on the CVD process for SWNT growth was performed. By comparing the different carbon deposits from methane decomposition in argon and nitrogen, the reactivity of nitrogen on the catalysts was determined. In argon, SWNTs can be synthesized on the Fe/MgO and Fe–Mo/MgO catalysts. On the Fe/MgO catalyst, the presence of nitrogen will result in the growth of N-doped CNFs. The characterization of the metal particle morphology allows the conclusion that the growth of the CNFs is due to the aggregation of iron nanoparticles in nitrogen. By adding molybdenum into the catalyst, the aggregation can be effectively limited, and SWNTs can be grown on the Fe–Mo/MgO catalyst in nitrogen. However, the limited aggregation of the catalyst nanoparticles still caused a change in the nanotube diameters towards large SWNTs. This finding gives a potential and convenient method to control the size and structure of SWNTs.

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