Effect of hydrocarbons precursors on the formation of carbon nanotubes in chemical vapor deposition

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Abstract

High-temperature decomposition of hydrocarbons may lead to the formation of carbon deposits. However in our present studies, we found that the morphology of carbon deposits over MgO supported Fe catalyst during chemical vapor deposition (CVD) process was closely related to the thermodynamic properties and chemical structures of hydrocarbon precursors. Six kinds of hydrocarbons (methane, hexane, cyclohexane, benzene, naphthalene and anthracene) were used as carbon precursors in this study. Methane which has a pretty simple composition and is more chemically stable was favorable for the formation of high-purity single walled carbon nanotubes (SWNTs). For high-molecular weight hydrocarbons, it was found that the chemical structures rather than thermodynamic properties of carbon precursors would play an important role in nanotube formation. Specifically, the CVD processes of aromatic molecules such as benzene, naphthalene and anthracene inclined to the growth of SWNTs. While the cases of aliphatic and cyclic hydrocarbon molecules seemed a little more complicated. Based on different pyrolytic behaviors of carbon precursors and formation mechanism of SWNTs and multi-walled carbon nanotubes (MWNTs), a possible explanation of the difference in CVD products was also proposed.
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1. Introduction

Since the discovery by Iijima [1], carbon nanotubes have drawn much attention and interest due to their myriad properties and potential applications [2–4]. Carbon nanotubes can be classified into single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), which may exhibit unique properties due to their different atomic structures [5]. It is therefore of great significance to comprehensive understanding of the growth mechanism and hence better control of the structure properties of the products. Till now, carbon nanotubes can be synthesized with arc-discharge, laser ablation, catalytic chemical vapor decomposition (CVD), flame synthesis, solar energy route, etc. [6–10]. Arc-discharge and laser ablation methods may yield high-quality product. It is however difficult to scale up the production. In contrast, the CVD method has become more popular and considered at the moment the

best approach for low-cost and large-scale synthesis of high-quality nanotube materials [11,12].

As the growth mechanism of carbon nanotube in CVD process generally involves the dissociation of carbon precursors into carbon atoms, dissolution and saturation of these atoms in the catalyst metal particles and further precipitation into tubular carbon deposits, it is obvious that the types of carbon precursors, furnace temperature, types and particle size of catalysts, and types of support materials may greatly affect the growth process of carbon nanotubes. Among these growth conditions, carbon precursors would undoubtedly play a key role to affect the structure properties of carbon deposits. Several hydrocarbons have been used as precursors for the CVD growth of carbon nanotubes. For example, Dai and coworkers [11] reported the synthesis of high-quality SWNTs with methane and alumina supported Fe catalyst at 900 °C. Besides, benzene has been applied to large-scale production of SWNTs with a floating catalyst method [13]. On the other hand, Benito et al. also reported the growth of MWNTs and carbon fibers from benzene CVD [14]. However, there is little systematic study on the effect of carbon precursors using

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a given set of reaction parameters (catalyst, reaction time, growth mode, etc.) up to now. Investigating the CVD product of different carbon precursors within the same reaction system is thus crucial towards understanding how nanotube formation is influenced by the features of carbon precursors.

In the present study, we addressed this issue by selecting six hydrocarbons, including methane which was relatively chemically stable at high temperature and easily decomposable than high-molecular weight hydrocarbons such as saturated aliphatic hexane, unsaturated cyclohexane, and aromatic benzene, naphthalene and anthracene as carbon precursors for the catalytic decomposition studies with fixed-bed growth mode. It was found that in comparison with their pyrolytic behaviors, the chemical structures of carbon precursors played a much more important role in nanotube formation. Methane and aromatic molecules were found to favor the growth of SWNTs. Although aliphatic hydrocarbons of high-molecular weight such as hexane and cyclohexane which were more chemically unstable than methane showed similar thermodynamic parameters, the morphology of as-prepared carbon deposits was more complicated. Cyclohexane was capable of the formation of both SWNTs and MWNTs, depending on the ambience. Nevertheless, carbon flakes were mainly formed when hexane was input. The difference in the nanotube formation is tried to understand by combining their different pyrolytic behaviors and growth mechanisms for single-walled and multi-walled nanotubes.

2. Experimental

Carbon nanotubes were synthesized by chemical vapor deposition of hydrocarbons over MgO supported Fe catalyst, which was prepared by chemical impregnation method [15]. Briefly, 1 g alkaline magnesium carbonate was immersed in 10 ml $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solutions (10 mg/ml), followed by sonication and drying to yield a yellowish powder. The obtained catalyst was then inserted into a tube furnace and heated to desired temperature (500–850 °C) in Ar atmosphere at a flow rate of 300 sccm. Carbon sources were fed in by passing 100 sccm Ar through liquid hydrocarbons (hexane, cyclohexane and benzene) or by heating solid hydrocarbons (naphthalene and anthracene) in an evaporator set at ~150 °C. The reaction time was 30 min, after which the system was cooled down to room temperature. The as-prepared carbon soot was sonicated in 37% HCl and successively in water to remove the catalyst.

Micro-Raman experiments were carried out with Renishaw system 1000 in ambient atmosphere and at room temperature. Raman spectra were recorded using 50 mW He–Ne laser (632.8 nm) and CCD detector. The final spectra presented were obtained by averaging at least 15 spectra recorded at different points over entire sample surface.

Thermogravimetric analysis (TGA) was conducted on a Universal V25H TA instrument. For a typical experiment, ~5 mg purified sample was put in an alumina crucible and heated in airflow, at a rate of 10 °C/min to 800 °C.

Scanning electron microscopy (SEM) was conducted on a JEOL JBM-6301F instrument operating at 25 kV. For SEM characterization, the purified samples were dispersed in 1,2-dichlorobenzene to form a brownish solution. A few drops of this solution was then dripped on Si wafer and left dry. Transmission electron microscopy (TEM) was performed on a Hitachi 810 instrument operating at 200 kV. The samples for TEM characterization were dispersed in deionized water and dripped on copper grid.

3. Results and discussion

Gaseous hydrocarbons, such as CH_4, C_2H_4 and C_2H_2, have been widely used for the formation of carbon nanotube deposits. The growth condition for SWNTs is a bit more rigorous than that for MWNTs, which needs a higher temperature and is more dependent on the preparation of catalysts. Moreover, methane is more preferred for the growth of high-purity SWNTs rather than any other gaseous hydrocarbons, as it is comparatively chemically stable at high-temperature and has the simplest structure. The benefits from the combination of these two features are supposed to result in the formation of uniform fragments for the further growth of single walled carbon nanotubes. However, the achievement for methane CVD growth of single-walled carbon nanotube deposits would largely depend on the features of catalysts as well. In our previous study, we found that MgO supported Fe catalyst was highly effective for the high-purity formation of SWNTs [15]. Due to the strong interaction between Fe species and MgO support, the catalyst particles may remain well-dispersed status at an elevated temperature, thus keeping their activity and avoiding amorphous carbon deposition. Fig. 1 showed typical Raman and SEM characterization results of SWNT products obtained by methane CVD over MgO supported Fe catalysts at an optimized temperature (750–900 °C) and after removal of MgO and Fe impurities with HCl. In Raman spectra, the radial breath mode (RBM) within the band 100–300 cm^{-1} is characteristic of SWNTs [16]. Other signals such as D- and G-bands centered at 1350 and 1590 cm^{-1} can serve as rough evaluation of the purity of tube products [16,17]. Raman analysis revealed that SWNTs grown on this kind of catalysts showed stronger intensity of RBM peaks and lower intensity of the D-line. High I_G/I_D ratio
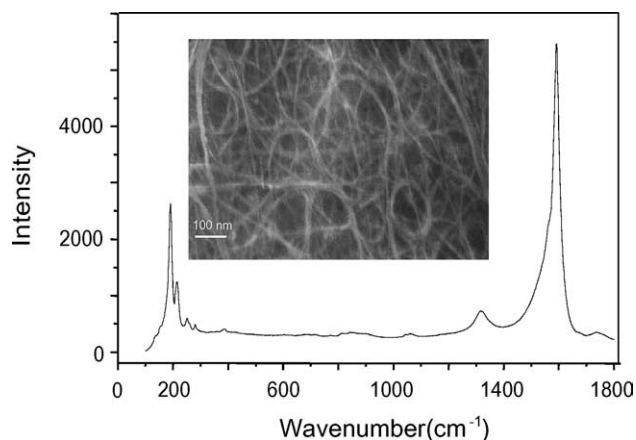
Fig. 1. Raman spectrum and SEM image of SWNTs prepared with methane as carbon source.

(∼15) indicated that the prepared SWNT material was of good purity and quality. SEM image (inset of Fig. 1) showed that abundant SWNTs were formed in bundles and highly entangled.

Besides gaseous hydrocarbons, some liquid hydrocarbons such as hexane, benzene, toluene and xylene, etc. have been also effectively used for the growth of SWNTs and MWNTs with floating CVD methods [18–20], in which ferrocene is sublimated or injected as catalysts. The MgO–Fe catalyst has been proved to be a good catalyst for the CVD growth of SWNT by methane, does it also work well for some liquid hydrocarbons? According to the widely accepted growth mechanism of carbon nanotube in CVD process, hydrocarbon precursors are supposed to thermally decompose and dissociate into carbon atoms first, then dissolve in catalytic metal particles until saturation and lastly precipitate into tubular carbon deposits. So in this sense, the intention for us to choose liquid hydrocarbons is to see if these carbon sources may promote the formation of tube deposits since they are much more easily decomposed than methane at high temperatures. In our experiment, hexane, cyclohexane and benzene were tentatively selected for the study, as they typically represent different kinds of hydrocarbons (i.e. aliphatic, cyclic and aromatic) and contain the same number of carbon atoms in each molecule. Making a comparison between them will be helpful for us to understand the effect of the features of chemicals on the formation of tube deposits over MgO–Fe catalysts.

Fig. 2 showed the Raman spectra and SEM images of carbon deposits prepared with different carbon sources. For the sample prepared with benzene, the Raman spectrum was typical of SWNTs, as indicated by strong RBM peaks and weak D-band (Fig. 2a). According to Bandow's equation [17], the nanotubes had a wide diameter distribution ranging from 0.9 to 1.5 nm. The intensity ratio between G- and D-modes was 13.5,

comparable to that of high-quality SWNTs prepared by methane CVD [21]. In SEM image (Fig. 2b), rope-like bundles, tens of nanometers in diameter, could be observed. High-resolution TEM (Fig. 3) showed that these bundles consisted of SWNTs with typical diameter of ∼1 nm. The nanotubes had clear and integrated sidewalls, indicating very little amorphous carbon or defects. Combining Raman, SEM and TEM, it can be concluded that high-quality SWNTs were formed when benzene was used as carbon source.

When cyclohexane was introduced as carbon precursors, the deposit gave a quite different Raman spectrum (Fig. 2a), as no RBM peaks but strong D-band was observed. Thick tubes (20–40 nm in diameter) could be seen in SEM image, suggesting the formation of MWNTs (Fig. 2c). As for hexane, Raman spectrum indicated no SWNTs in the sample (Fig. 2a), and SEM revealed that most deposits consisted of flake-like impurities (Fig. 2d).

Thermogravimetric analysis (TGA) can be used to study the thermal stability of carbon deposits and to distinguish the forms of carbon species according to their different combustion temperatures. Fig. 4 showed the TGA curves of carbon deposits prepared with different six-carbon sources. For the sample prepared with benzene, the derivative of weight loss gave a peak at 598 °C, which could be attributed to the combustion of SWNTs [22]. As there was only one peak in the weight loss curve, the purity of the sample was high, which was correspondent with Raman and SEM results. For cyclohexane as carbon source, the weight loss peak was centered at 618 °C. Combined with Raman and SEM results, it could be ascribed to the combustion of MWNTs, which agreed well with previous work [23]. The fact that MWNTs showed higher thermal stability than SWNTs might be due to the strong interaction between graphene layers in MWNTs, which stabilized their structures and made them more inert. With respect to hexane as carbon source, a board peak centered at 638 °C could be attributed to the combustion of flake-shaped graphite. This sample showed even higher stability than MWNTs, since graphite sheets were generally better crystallized than tubular structures.

Table 1 showed the thermodynamic parameters of the thermally decomposed reactions of some concerned hydrocarbons in this study [24]. First, it could be found that the Gibbs free energies of hexane, cyclohexane and benzene were pretty lower than that of methane at 800 °C, which meant at a same temperature these three liquid hydrocarbons are more seriously decomposed than methane and they would have lower decomposition temperature. However, lower decomposition temperature did not give rise to the lower formation temperature of tube products. Methane and benzene were both available for the formation of SWNTs, the lowest temperature in terms of methane was around 650 °C in our
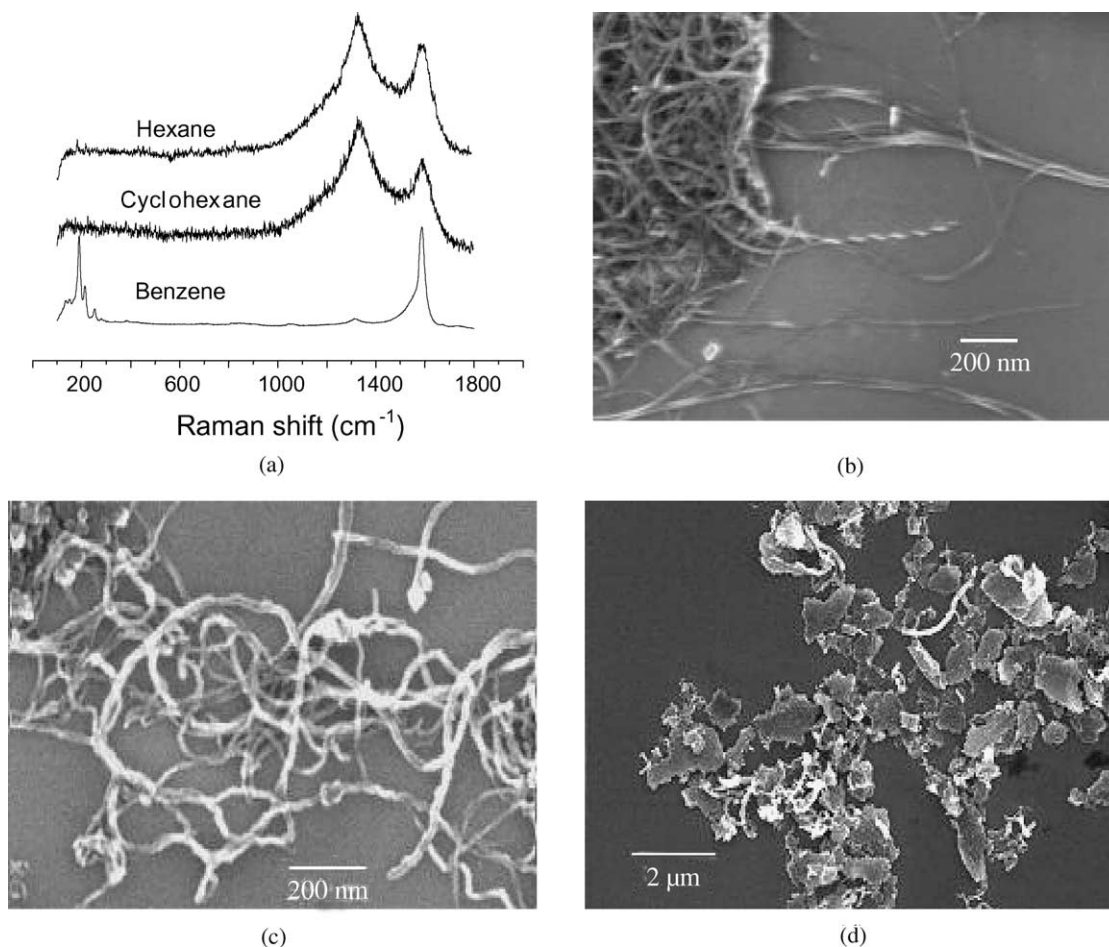
Fig. 2. Raman spectra (a) and SEM images (b–d) of as-prepared carbon deposits with benzene (b), cyclohexane (c) and hexane (d) as carbon sources.
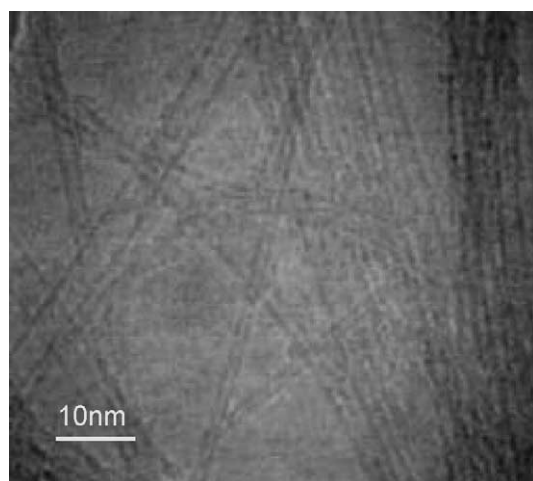

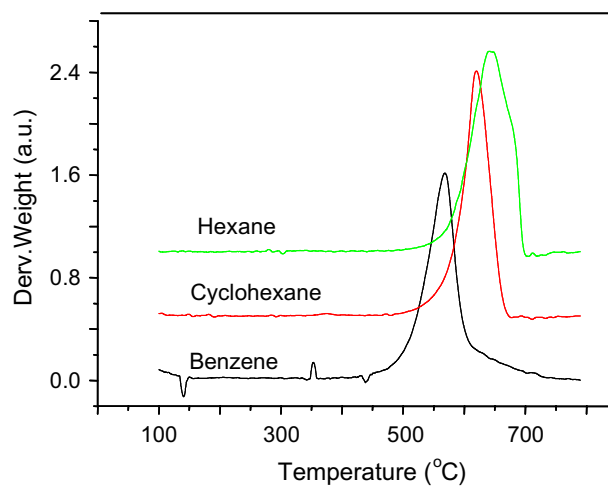Fig. 3. HRTEM image of the SWNTs prepared with benzene as carbon source.

Fig. 4. Thermogravimetric analysis of carbon deposits with different carbon sources.

system, while in the case of benzene, it should be kept high up to 800 °C although benzene can be decomposed at lower temperature. With respect to hexane and cyclohexane whose reaction Gibbs free energies are even much lower than both benzene and methane, no SWNTs but other forms of carbon deposits such as

Table 1
The thermodynamic parameters of concerned hydrocarbon precursors at 800 °C

Reactions	ΔH (KJ)	ΔG (KJ)	lg k	Forms of carbon deposits
$CH_4 = C + 2H_2$	90.1	−27.2	1.322	SWNT
$C_6H_{14}(g) = 6C + 7H_2$	206.4	−480.1	23.38	Graphite flake and MWNT
$C_6H_{12}(g) = 6C + 6H_2$	155.4	−479.8	23.36	MWNT
$C_6H_6(g) = 6C + 3H_2$	−62.9	−273.7	13.30	SWNT
$C_{10}H_8(g) = 10C + 4H_2$	−127.3	−439.6	21.40	SWNT
$C_{14}H_{10}(g) = 14C + 5H_2$	−202.6	−630.7	30.70	SWNT

MWNT and graphene flakes were produced. It revealed that the formation and morphology of carbon deposits was not simply determined by the pyrolytic behaviors of hydrocarbons.

Compared to hexane and cyclohexane, benzene is a relatively more stable molecule due to its aromatic structure. Mass spectrum data and study on pyrolysis of benzene indicated that its dissociation behavior showed more uniform and simpler which mainly involved in the cleavage of small conjugated fragments from the molecule [25,26]. Due to its thermal stability [24], there was very little self-catalyzed deposition on the sidewall of primarily nucleated nanotubes, and thus MWNTs were not formed. As for cyclohexane and hexane, their decomposition reactions have quite similar ΔG and reaction rate constant. In comparison with benzene, the cleavage of cyclohexane and hexane into small fragments would be much easier. On the other hand, as both of them are aliphatic compound, their more complicated cleavage routes may lead to more kinds of fragments. This would presumably increase the possibility for other unfavorable fragments to deposit on the sidewall of primarily nucleated nanotubes, causing the formation of MWNTs rather than SWNTs.

In order to confirm that conjugated sp^2 structures favored the formation of SWNTs, we further tested polycyclic molecules, i.e. naphthalene and anthracene as carbon sources. As shown in Fig. 5, both Raman spectra and TG analysis indicated the formation of SWNTs. There are several notable features of nanotube synthesis with these precursors. First, we could observe the formation of SWNTs with polycyclic precursors when furnace temperature was raised above 700 °C. While for benzene, no deposit was found at 700 °C, and SWNTs started to grow above 800 °C. In other words, the critical temperature for SWNT formation was 100 °C lower for polycyclic molecules than for benzene. This could be reasonably understood with the data in Table 1. Naphthalene and anthracene are more unstable compared with benzene, which meant they were able to decompose at lower temperature. The efficiency for the CVD growth of SWNTs with polycyclic molecules may be due to the formation of semi-fullerene medium species [27], which probably serve as the nuclei for nanotubes and facilitate the growth. However, the SWNTs prepared with naphthalene and anthracene showed
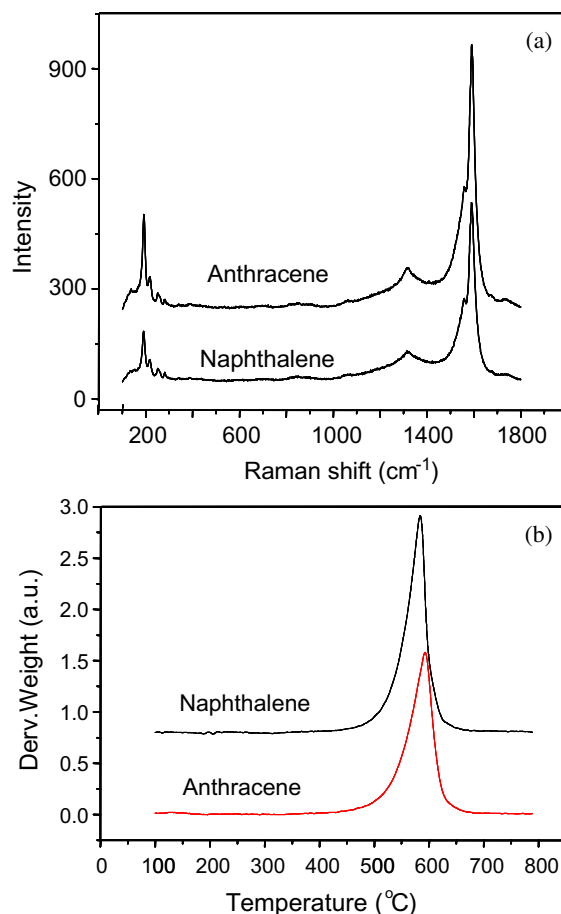

Fig. 5. Raman spectra (a) and corresponding TGA curves (b) of carbon deposits prepared with naphthalene and anthracene as carbon sources.

lower purity than those prepared with benzene, as indicated by higher D-band intensities. This might be caused by the non-catalytic pyrolysis of these relatively large molecules. Second, the Raman spectra of SWNTs materials prepared with naphthalene and anthracene are characteristic with a shoulder peak at 1559 cm^{-1}, which was previously attributed to resonant Raman scattering from metallic nanotubes [28]. It should be admitted that the relative amount of metallic nanotubes within the samples cannot be told from Raman spectra, and the mechanism for their abundance is not clear. However, this feature is favored, since it demonstrated the possibility to control the electronic structure of SWNTs,

which is crucial towards their applications as building blocks for nanoelectronic devices.

It was worth mentioning that the CVD product was also greatly influenced by injection of H_2, which may interfere the decomposition equilibriums of various carbon sources. Specifically, CVD process of cyclohexane in Ar atmosphere yielded MWNTs. While in H_2 atmosphere, some SWNTs were formed within the product according to Raman spectrum, SEM and TG analysis (Fig. 6). The characteristic RBM band of SWNTs emerged in the Raman spectrum of as-formed carbon deposit. From TGA curve, two combustion peaks appeared, one at 566 °C and the other at 617 °C, corresponding to the characteristic combustion temperature of SWNTs and MWNTs respectively. On the other hand, introduction of H_2 into benzene CVD caused severe reduction of purity of the SWNTs, as indicated by Raman spectra (data not shown). For aphilitic hydrocarbons, the role of excess H_2 may hinder their serious decomposition reactions at high-temperatures. For aromatic compounds, the possible catalytic hydrogenation reaction into aphilitic ones may disturb

the formation of SWNTs. In return, it provided further evidence to show that the chemical structures of hydrocarbons would play an important role to determine the morphology of carbon deposits.

4. Conclusion

In summary, we demonstrated the dependence of nanotube formation on the chemical structures of the hydrocarbon precursors. It was found that aromatic molecules were favored for the growth of SWNTs, while aliphatic molecules generally tended to form MWNTs or non-tubular carbon structures. It should be noted that the formation of SWNTs or MWNTs does not merely depend on carbon precursors, but also has strong correlations with other growth conditions such as catalyst, temperature and gas flow rate, etc. However, the present work shows the possibility of selective synthesis of SWNTs or MWNTs by a choice of carbon precursor. Moreover, the study may also shed light on the growth mechanism of nanotubes, which is crucial towards their controlled synthesis and future applications.

Fig. 6. Raman spectrum (a), SEM image (inset) and TGA analysis (b) of carbon deposits prepared with cyclohexane in H_2 atmosphere.

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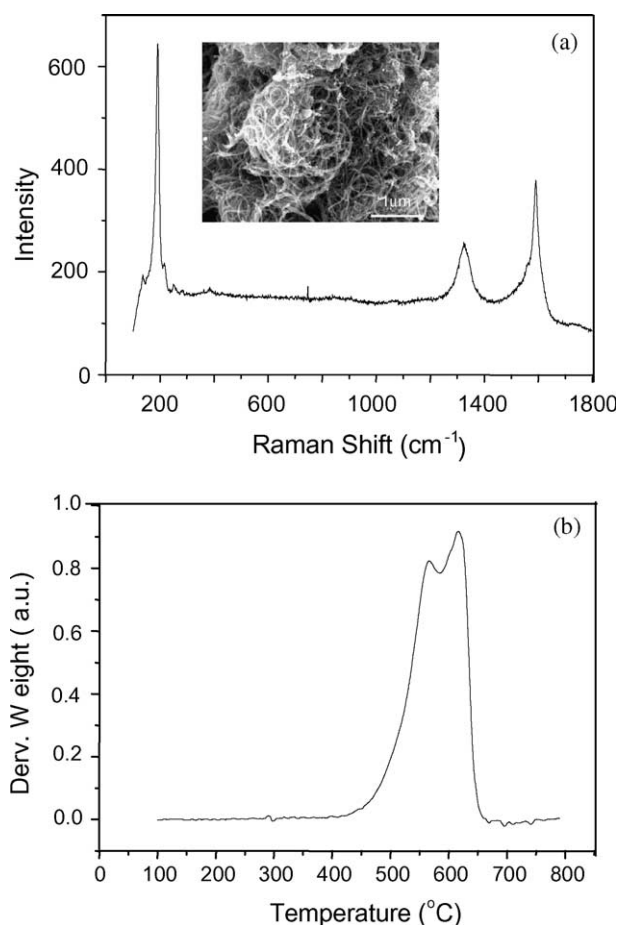
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