

In Situ TA-MS Study of the Six-Membered-Ring-Based Growth of Carbon Nanotubes with Benzene Precursor

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Abstract: By using the in situ thermal analysis–mass spectroscopic technique, combined with transmission electron microscopic characterization of the carbon nanotube (CNT) product, we have studied the chemical vapor deposition (CVD) growth of CNTs with Fe–Co/ γ -Al₂O₃ catalyst and benzene precursor in the range of room temperature to 700 °C. The growth process has been clearly illuminated, which starts from the reduction of catalyst around 645 °C followed by the dissociation of carbon–hydrogen bonds of benzene and the sequential growth of CNTs. A surprising fact is that no possible hydrocarbon species derived from benzene was detected, indicating that the carbon–carbon bond was not broken under our experimental conditions. All of the experimental results strongly reinforce the six-membered-ring-based growth model, and a schematic elucidation is presented accordingly. This in situ study not only reveals the unique and convincing information directly related to the growth mechanism from the involved chemistry, but also provides a powerful way to clarify the mechanism of CVD synthesis of CNTs with other precursors.

Introduction

The discovery of carbon nanotubes (CNTs)¹ has opened a new fascinating family of nanotubular structures with great scientific and technological importance.² Despite the unceasing increase of family members from the evenly banded nanotubes of layered compounds in the past 10 years^{2,3} to the faceted nanotubes of nonlayered compounds recently,^{4–6} CNTs have still been the most important due to their superior properties and significant potential applications in many fields as reflected in the frequent achievements reported.^{2,7–10} The synthesis of CNTs by arc-discharge¹ and laser ablation¹¹ involves the condensation of carbon atoms generated from evaporation of solid carbon sources, with the reaction temperatures close to the melting point of graphite. These two methods favor the production of well-graphitized CNTs but are difficult to scale-up. The chemical vapor deposition (CVD) method has been successful in making carbon fibers, filaments, and tubular

structures for many years.^{12–14} The growth process usually involves heating a catalyst to a certain temperature in flowing carbon precursors such as hydrocarbons and carbon monoxide over a period of time. In most cases, the growth temperature is typically in the range of 550–1000 °C. For the mild preparation conditions and the potential for mass production, CVD has been an important method for the synthesis of CNTs, and considerable progress has been achieved.^{2,15–18} However, although some valuable growth models have been speculated on the basis of experimental results in CVD growth of CNTs,^{2,19–21} the growth mechanism is still a long-standing issue,^{22–24} and little has been learned about the chemistry involved. Through mass spectral studies on the effluent of the methane CVD system at 900 °C for growing single-walled CNTs, it is found that methane underwent a negligible self-pyrolysis and the small concentration of benzene converted from methane on catalyst favored the growth of the product because the highly reactive benzene could

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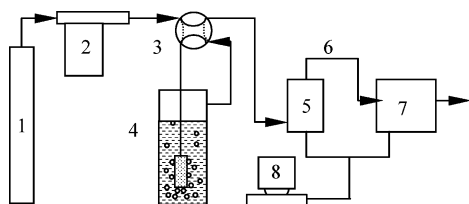


Figure 1. Schematic experimental setup for the in situ study of CVD synthesis of CNTs with benzene precursor by the TA-MS technique. (1) Nitrogen tank; (2) mass flowmeter; (3) four-way valve; (4) generator of benzene saturated vapor; (5) thermal analyzer (reactor); (6) capillary tube; (7) mass spectrometer; (8) workstation.

provide an efficient carbon-feedstock for nanotubes.²⁴ Very recently, with benzene as precursor, well-graphited and high-productive quasi-aligned CNTs have been produced in our lab, and a six-membered-ring-based (C_6 -based) growth for this synthesis is tentatively suggested.^{25,26} It would be more convincing to study the CNT formation with in situ thermal analysis coupled with mass spectroscopy (TA-MS) by learning the chemistry involved. In this paper, the dynamical process for CVD synthesis of CNTs with benzene precursor has been investigated by the in situ TA-MS technique. With this method, the information about the effluent species, the variation of weight, and thermal-flow during the whole process could be obtained on line. The C_6 -based growth mechanism is reasonably deduced.

Experimental Section

The optimized binary Fe–Co/ γ - Al_2O_3 catalyst, 1.51 mmol g^{-1} of Fe– 1.51 mmol g^{-1} of Co/ γ - Al_2O_3 , is used in this study, which is the same as we used in our previous CNT synthesis with benzene precursor.²⁶ The Fe and Co species in the catalyst came from the corresponding nitrate precursors. The catalyst experienced 3 h of annealing at $500 \text{ }^\circ\text{C}$ during its preparation; hence, Fe and Co oxides existed on the surface of the γ - Al_2O_3 support. The experimental setup and procedure is schematically illustrated in Figure 1. The CNT growth was performed in situ in a thermobalance of the thermal analyzer (STA-499C, NETZSCH) at atmospheric pressure, with 3 mg of catalyst in a corundum crucible. Benzene was introduced into the reactor by bubbling the benzene saturation vapor generator at $22 \text{ }^\circ\text{C}$ with N_2 with a flowing rate of 40 ml min^{-1} . The feed rate of benzene was estimated to be about 10.0 mg min^{-1} . The effluent was introduced into the mass analyzer (QUADSTAR-422, PFEIFFER) online through a capillary tube at $170 \text{ }^\circ\text{C}$. With introducing benzene, the reactor was heated at the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $700 \text{ }^\circ\text{C}$, and then kept there for 30 min. Thermogravimetry-differential scanning calorimetry (TG-DSC) profiles were recorded for this process; meanwhile, a mass spectral analysis in the range of 1.5–80 amu was taken every 59 s. The reactor was then cooled to ambient temperature in N_2 . A blank experiment (without catalyst) was also carried out in the same procedure for comparison. The product was characterized by transmission electron microscopy (TEM, JEOL-JEM-1005).

Results and Discussion

A typical TEM image of the product is shown in Figure 2, which consists of abundant CNTs with a diameter of around 20 nm. The catalyst particle is affixed to the tube end, which reflects the crucial function of the catalyst in this synthesis.²⁵ Figure 3 exhibits the TG-DTG(derivative thermogravimetry)–

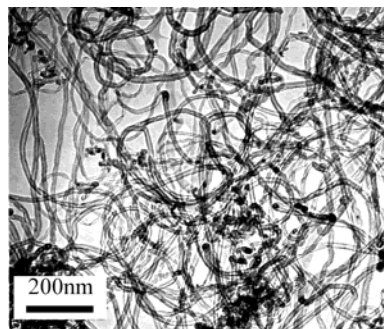


Figure 2. Typical TEM image of the CNTs synthesized in the in situ TG-MS system.

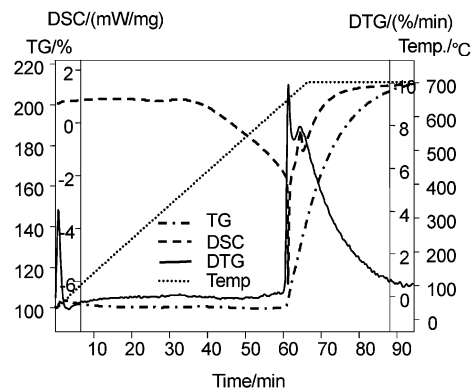


Figure 3. TG(DTG)–DSC profiles of the preparation process.

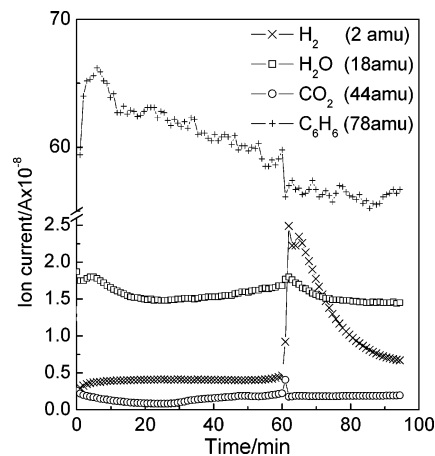


Figure 4. The change of the ion currents for certain atomic mass units during the experimental period.

DSC profiles of the preparation process, and the corresponding mass spectra are shown in Figures 4 and 5, respectively. A sharp endothermic peak appears around $645 \text{ }^\circ\text{C}$ in the DSC profile (Figure 3), which is simultaneously accompanied by the formation of H_2O (18 amu) and CO_2 (44 amu) species as revealed in the corresponding mass spectral information (Figure 4), resulting from the reduction of the oxide species of the catalyst. It is clearly seen that this reduction is followed by three events: (1) the beginning of the weight gain (Figure 3); (2) the sudden decrease of benzene species (78 amu) (Figure 4); and (3) the release of hydrogen (2 amu) (Figure 4). These phenomena arise from the growth of CNTs through the consumption of benzene. The above results also imply that the active catalytic species for the growth of CNTs is metal rather than oxide, which is strongly supported by our thermodynamic analysis on the

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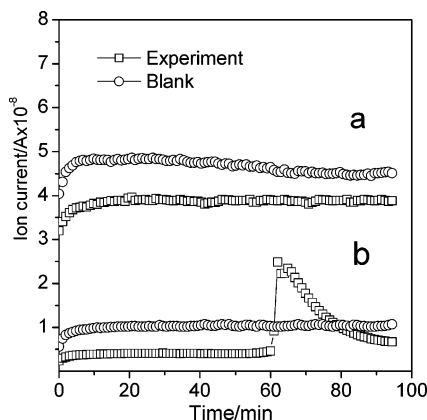


Figure 5. Typical changing behavior of the ion currents related to the atomic mass units for possible hydrocarbon species (a), and for hydrogen (b). Specifically, curve (a) corresponds to acetylene with 26 amu. The blank experimental results are also listed for comparison.

endothermal reduction process and the energy-dispersive X-ray analysis (EDX) on the catalyst particles affixed to the end of CNTs.

Obviously, the identification of the carbon species involved in the reaction of CNT growth is an important clue to elucidate the growth mechanism. Special attention has been paid to the amu of the possible hydrocarbon species from CH₄ to C₅H_x, including alkane (16, 30, 44, 58, 72 amu), olefin (28, 42, 56, 70 amu), and alkyne (26, 40, 54, 68 amu). Surprisingly, it is found that all of these species experienced a negligible variation during the whole process as typically shown in Figure 5a, which is the same tendency as in the blank experiment for comparison. Meanwhile, hydrogen was released dramatically after the programmed heating for about 1 h (around 645 °C), and then the releasing rate of hydrogen in the reaction system decreased gradually, considerably different from the case for blank experiment as shown in Figure 5b. These results indicate that, without catalyst, benzene did not dissociate in this temperature range. In contrast, with the Fe-Co/ γ -Al₂O₃ catalyst we used, the carbon-hydrogen bond did dissociate for partial benzene molecules when the system was heated over 645 °C because H₂ was released; however, the carbon-carbon bond was not broken because no possible hydrocarbon species was detected. In other words, the dehydrogenated benzene molecules were converted directly to CNTs as shown in Figure 2.

According to the above experimental results and analysis, the growth mechanism could be reasonably deduced. As benzene was introduced into the reactor, it was adsorbed on catalyst surface to form a shell of benzene before reaction. Accompanied by the reduction around 645 °C, the catalyst was activated and the C-H bond of the benzene molecules was dissociated with the release of a large amount of H₂ as detected by MS. Meanwhile, the dehydrogenated hexagonal rings of carbon (h-C₆) directly aggregated to form the graphene sheets on the catalyst surface, and CNTs were then developed through sequential incorporation of the h-C₆ into the graphene layers through surface diffusion. This process is schematically illustrated in Figure 6. According to this mechanism based on the experimental analysis of the chemical species involved in the CNT growth, many related experimental phenomena could be well understood. As it is seen, the changing tendency of the DTG profile in Figure 3 and that of the ion current of the released hydrogen in Figure 4 unbelievably resemble each other,

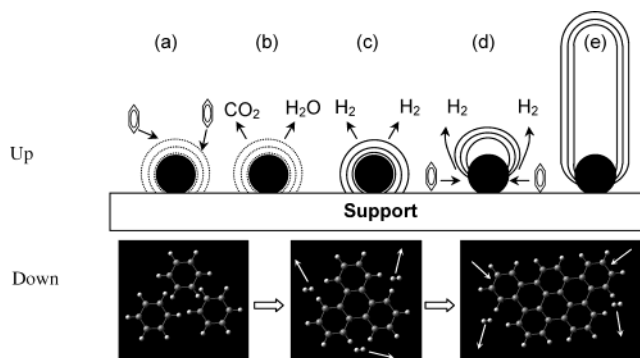


Figure 6. Up: Schematic illustration of the C₆-based growth mechanism of CNTs with benzene precursor. (a) Absorption of benzene molecules on catalyst surface; (b) reduction of catalyst; (c) dehydrogenation of benzene molecules and formation of graphenes; (d) continuous growth of CNTs; (e) final state of the product. Down: The speculative construction of graphene sheet from hexagonal carbon units, corresponding to (c)–(e) in the up illustration. Gray dot, C; white dot, H.

even in the splitting details around the peaks. This is a little surprising, but an inevitable result when the proposed growth mechanism works because the h-C₆ and the released H₂, which are the only two species from the same precursor of benzene molecules, are directly correlated. The splitting peaks may be associated with the binary components of the catalyst. The decay of the growth rate, which is very common in CVD growth of CNTs, is probably due to the rising diffusion difficulty or gradual catalyst deactivation with the growth of CNTs. Actually, although the present C₆-based growth mechanism has not been proposed previously, there do exist some supporting indications in the literature where the cyclic radicals seem to be the direct precursor for the growth of CNTs.^{24,27,28} A brief thermodynamic estimation also supports this growth model. As known, the six-membered ring framework of benzene is unusually stable. Each carbon-carbon connection is an average of 1.5 bonds, midway between a single and a double bond.²⁹ This bond energy (~478 kJ mol⁻¹) is higher than that of the C-H bond (~416 kJ mol⁻¹). In addition, even though the stability of the aromatic ring would be lost, there is a strong tendency to reconstruct the aromatic structure. Therefore, under certain conditions, for example, with suitable catalyst and temperature, the carbon-hydrogen bond could be selectively dissociated, while the carbon-carbon connection is still retained. Thus, the dehydrogenated h-C₆ species are generated, which could form the graphene sheets on the catalyst surface for sequential growth of CNTs.

Conclusions

In conclusion, the CVD growth of CNTs with benzene precursor was first studied by the in situ TA-MS technique, combined with TEM characterization of the CNT product. The involved chemistry has been inferred, and the growth process has been clearly illuminated, which starts from the reduction of catalyst followed by the dissociation of the carbon-hydrogen bonds of benzene and the sequential growth of CNTs. A surprising fact is that no possible hydrocarbon species derived from benzene was detected, indicating that the carbon-carbon bond was not broken under our experimental conditions. All of

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the experimental results strongly reinforce the C₆-based growth model, and a schematic elucidation is presented accordingly. This in situ study not only reveals the unique and convincing information directly related to the growth mechanism from the involved chemistry, but also provides a powerful way to clarify the mechanism of CVD synthesis of CNTs with other precursors.

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Supporting Information Available: Thermodynamic analysis on the reduction process corresponding to the sharp endothermal peak in the DSC profile, EDX result on the catalyst particles affixed to the end of CNTs, the comparison of changing tendency of the DTG profile and that of the ion current of the released hydrogen during the experimental period, and the changes of ion currents for possible hydrocarbon species derived from benzene (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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