Investigations of mechanism of carbon nanotube growth

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Received 14 June 2006, accepted 4 August 2006
Published online 26 September 2006

Studies on the formation of single-walled carbon nanotubes by an aerosol method based on the introduction of pre-formed catalyst particles into conditions leading to carbon nanotube synthesis are presented. Carbon monoxide and iron nanoparticles were used as carbon source and catalyst, respectively. The carbon nanotube growth was found to occur at a temperature of around 900 °C in the heating section of the reactor with a growth rate exceeding 1.1 µm/s. A detailed analysis of possible processes during carbon nanotube formation revealed heptagon transformation as a limiting stage. A mechanism for carbon nanotube formation on the basis of the geometrical consideration was proposed.

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1 Introduction

Carbon nanotubes (CNTs) have been the subject of great interest since their discovery due to their remarkable mechanical, optical, electrical and thermal properties [1]. Many applications have already been demonstrated for this extraordinary material. However, success in any applications strongly depends on the ability to synthesize CNTs with controlled dimensions, i.e. length, diameter, and chirality. The development of production methods for CNT synthesis with specific qualities requires detail understanding of the mechanisms of CNT formation.

The present paper studies the mechanism of formation of single-walled CNTs in the gas phase (i.e. without the influence of the substrate on the processes of CNT nucleation and growth). The CNTs were synthesized by an aerosol, so called HWG, method [2–4] based on the introduction of pre-formed iron catalyst particles into conditions leading to CNT formation. In our process, the possibility of further catalyst particle growth after CNT nucleation is excluded in contrast to the methods discussed in [5]. This can help to correlate the resultant CNT dimensions to those of the introduced catalyst particles. On the basis of the analysis of the systematic investigations and theoretical calculations the mechanisms for the CNT formation are proposed.

2 Experimental

2.1 Experimental setup

The experimental investigations of CNT formation were carried out in a laminar flow aerosol reactor described elsewhere [2–4]. The device consisted of a hot wire generator (HWG) and a heated vertical...
tubular reactor 44 cm in length. A stainless steel (or ceramic) tube, with 22 mm internal diameter inserted inside a furnace (Entech), has been used as the reactor. The HWG, which is a resistively heated thin iron wire (0.25 mm in diameter), was placed inside a ceramic tube (with external and internal diameters of 13 and 9 mm) inserted inside the reactor to maintain inert conditions for catalyst particle formation. The particles produced in the HWG tube were typically carried in a H$_2$/N$_2$ mixture (with mole component ratio of 7/93) at a flow rate of 400 cm$^3$/min and mixed with outer CO flow (typically $Q_{CO} = 400$ cm$^3$/min) inside the reactor. Downstream of the reactor a porous tube dilutor (12 L/min) was used to prevent the product deposition on the walls via thermophoresis and diffusion. The reactor was operated at ambient pressure. The average residence time inside the reactor was about 2–3 s.

The product was collected from the gas phase by an electrostatic precipitator (Combination electrostatic precipitator, InTox Products) on a Lacey carbon coated copper grid (Agar Scientific Ltd). In order to detect the location and temperature where CNTs start to grow in situ sampling from the centerline of the reactor was carried out. For this purpose, a stainless steel rod with an attached silica thin film coated nickel TEM grid (Structure Probe Inc) was rapidly inserted into the reactor and held in position for 1 min. The product was collected due to the thermophoretic forces between the hot ambient temperature atmosphere in the reactor and the cold sampling rod. The temperatures at the in situ sampling locations were measured by thermocouples after the collection. On-line measurements of the gaseous composition after the reactor were carried out by a Gasmet Fourier-transform infrared spectroscopy (FT-IR) gas analyser. The morphology and the crystallinity of the as-obtained product were investigated with a field emission transmission electron microscope (TEM, Philips CM200 FEG).

2.2 Experimental results

The experimental investigations were carried out at the furnace temperature of $t_{furn} = 924$ °C if not otherwise specified. Varying total hydrogen concentration in the system (0, 3.5 × 10$^{-2}$, 3.5, 50%) it was found that H$_2$ is essential for the process of CNT formation. No CNTs were produced when the reactor was operated without hydrogen (in pure N$_2$ and Ar atmospheres through the HWG). The role of hydrogen in the system was found to protect the HWG and catalyst particles from their oxidation. Furthermore, hydrogen was found in providing carbon atoms in addition to CO disproportionation reaction:

$$\text{CO} + \text{CO} \leftrightarrow \text{C} + \text{CO}_2, \quad \Delta H = -169 \text{kJ/mol}, \quad (1)$$

according to CO hydrogenation reaction:

$$\text{H}_2 + \text{CO} \leftrightarrow \text{C} + \text{H}_2\text{O}, \quad \Delta H = -136 \text{kJ/mol}. \quad (2)$$

It is worth noting that these reactions have similar thermodynamic behavior [4]. Appreciable reaction rates for reaction (1) were observed in the temperature interval from 470 to 820 °C with a maximum rate at 625 °C. Reaction (1) occurs also even at lower temperatures (down to 325 °C) and temperatures up to 900 °C however at very low rates. At temperatures lower than 325 °C the reaction is limited kinetically. At temperatures higher than 900 °C it is limited thermodynamically [4].

In order to correlate the sizes of catalyst particles and CNTs, statistical measurements on the basis of the high resolution TEM images were carried out at different temperatures, residence time in the reactor and hydrogen concentrations. Mostly, CNTs with diameters in the range from 1.2 to 1.4 nm were synthesised. It was found that the ratio between the catalyst particle size and CNT diameter is around 1.5–1.6 for all studied cases and does not depend on the experimental conditions.

In order to detect the location and thereby the temperature, where the CNT growth starts, an in situ sample collection was carried out. TEM observations revealed the presence of CNTs on the TEM grid introduced to a temperature of 908 °C and higher. At sampling temperatures of 894 °C and lower only catalyst particles (no CNTs) were found. The distance of the “growth window” between the 894 °C and 908 °C locations was 1.5 cm. This temperature range coincides with the results reported in [2], where the growth of CNTs was observed to start from the wall reactor temperature of 890 °C. In addition, the aver-
average length of CNTs collected at 908 °C was the same as collected after the reactor (about 60 nm). On the basis of the in situ sampling experiments, the CNT growth rate can also be estimated. The residence time in the “growth window” taking into account the Poiseuille velocity distribution is calculated to be 0.054 s. Then, the CNT growth rate is estimated to exceed 1.1 μm/s.

3 Discussion

In order to better understand the mechanism of CNT formation let us examine the processes that can limit the formation of the CNTs, i.e. carbon release due to chemical reactions; carbon transport through catalyst particles or on the surface of particles and CNTs; nucleation; and the growth of CNTs.

First of all, the process of carbon delivery to the catalyst particles, i.e. reactions (1) and (2), should be considered. As was described earlier, appreciable reaction rates for CO disproportionation occurred in the temperature interval from 470 to 820 °C. Taking into account that the kinetics of the CO hydrogenation reaction (2) is faster than that of CO disproportionation [6] one can conclude that the carbon delivery process should be sufficient at temperatures of around 500 °C. Thus, if the reactions were the limiting stages, the CNTs would already grow at 500 °C. Certainly, there must be some other process determining the CNT formation at low temperatures.

Let us consider the processes of carbon delivery due to volume diffusion in iron particle and surface diffusion on iron particles and CNTs. The volume diffusion of a carbon atom in α-Fe crystalline phase can be calculated as

\[ D_v = D_0 \exp (-E_{av}/k_B T) , \]

with a pre-exponential coefficient of \( D_0 = 7.9 \times 10^{-7} \) m²/s and an activation energy of \( E_{av} = 0.79 \) eV [7].

The diffusion of carbon atoms on the iron surface can be found on the basis of the following equation:

\[ D_s = a_0^2 \nu \times \exp (-E_{as}/k_B T) , \]

where the iron interatomic distance \( a_0 \approx 0.29 \) nm, the frequency of thermal vibrations \( \nu \approx 3 \times 10^{13} \) Hz and the activation energy of surface diffusion \( E_{as} = 0.35 \) eV [8]. Let us estimate the characteristic time needed for a carbon atom to migrate across a 2 nm sized iron particle via volume diffusion (\( \lambda = 2 \) nm) and surface diffusion (\( \lambda = 3.1 \) nm) with a diffusion coefficient of \( D \) as

\[ \tau = \lambda^2/(4D) . \]

Figure 1 presents the calculated characteristic times for the temperature dependent diffusivities. Both surface and volume diffusivities are quite high and so would not be expected to limit the processes of carbon delivery for CNT growth, even assuming that the iron particle is solid.

Another important carbon delivery process is carbon diffusion on the surface of CNTs. It is worth noting that calculations for diffusion on CNT surfaces with parameters reported by Louchev [8] (\( a_0 \approx 0.14 \) nm, \( E_{as} = 0.13 \) eV) show even shorter characteristic times than for the diffusion on the surface of an iron particle. As was revealed by Krasheninnikov et al. [9], carbon atom adsorption and migration strongly depend on the diameter and chirality of CNTs. We carried out calculations of the characteristic diffusion times for CNTs with various chiralities using the parameters reported in [9] (\( a_0 = 0.246 \) nm, \( \nu \approx 4 \times 10^{12} \) Hz, and \( E_{as} = 1.0 \) eV for the largest residence time) and found a significant increase in the characteristic times for surface diffusion as shown in Fig. 1. Even so, it can be concluded that the surface diffusion of carbon atoms is not a limiting stage.

Also nucleation cannot be a limiting stage. According to Maruyama et al. [10] and Ding et al. [11], calculations nucleation of CNTs occurs in a nanosecond time scale.

Based on the above consideration, we believe that the unknown limiting stage is the growth of CNTs. As was found on the basis of the statistical measurements of CNT dimensions, the ratio between the diameters of catalyst particles and CNTs does not significantly depend on the experimental conditions and is in the range between 1.5–1.6. In order to explain this phenomenon a geometric model of heptagon...
defect formation, which initiates and maintains the CNT growth, was proposed [5]. It was suggested that the growth of CNTs occurs from the ordered (containing hexagons and pentagons) carbon layer on the surface of catalyst particles. We assumed that this layer continuously transforms into the CNT network at the metal–CNT interface via nucleation of negative curvature defects in the form of heptagonal rings [5]. It was found that theoretical values for the diameter ratios between catalyst particles and CNTs are 1.34 and 1.81 for respectively 4 and 5 heptagons in the base of a CNT. According to the mechanism described in [4], the iron particle is covered with a carbon layer in the steady-state process of CNT formation. The CNT growth can be represented as a continuous carbon feed from the graphene layer (on a catalyst particle) to the cylindrical surface of a CNT via a defect junction. The junction is achieved through the creation of topological defects in the form of heptagons. Accordingly, the continuous regeneration of heptagons (following by the generation of hexagons into the growing CNT and pentagon–heptagon pairs) can be the limiting stage in the CNT growth. The characteristic time for the heptagon formation can be estimated as

\[ \tau = \nu^{-1} \times \exp \left( \frac{E_{\text{ah}}}{k_B T} \right), \tag{6} \]

where \( E_{\text{ah}} \) is an energetic barrier for the heptagon formation in the carbon network, reported to be 4.6–4.7 eV [12, 13]. For such a large energy, the characteristic time is estimated to be \( 2 \times 10^6 \) s at 900 °C. But this high energy may be significantly reduced if additional carbon atoms are present [12]. These extra carbon atoms can catalyze the bond switching in Stone–Wales (SW) defects [12] and make the so-called “handles” over hexagons to produce heptagons after relaxation [14].

Figure 2 shows the schematic of this CNT growth mechanism. The additional atoms can be attached as handles (adatoms) to an already existed heptagon (Fig. 2a) and, by creating a bridge between atoms [14], make it generate an extra hexagon into the network in the wake of the heptagon (Fig. 2b, c). This makes the heptagon shift constantly with respect to the nanotube carbon network frame thus bringing the growth dynamics into the system. An important observation is that the extra atom in a heptagon decreases the total energy by 0.5 eV per handle due to the curvature effect [14]. That means that the four or five heptagons in the stem of the growing nanotube, where curvature is large, act as generators of hexagons for the nanotube by attracting extra atoms for handles. On the other hand, the number of heptagons in the stem does not change because, as shown in [5], it is determined by the overall geometry. Also the quartet/quintet of heptagons remains grouped in the stem while each heptagon is generating hexagons in its wake. Indeed, if one heptagon advances faster relatively to the nanotube frame then the local curva-
Figure 2 (online colour at: www.pss-b.com) Schematic of CNT growth governed by insertion of two carbon atoms into a heptagon followed by its transformation into a new heptagon and an additional hexagon into the carbon network. The 5–7 pair in plate b) may annihilate with some other 5–7 defects under SW transformation and is not shown in plate c). One can notice that a) and c) differ only by a shift which corresponds to the CNT growth in vertical direction.

The rate of hexagon generation in the wake of this heptagon would slow and would return the heptagon to the group because its relative velocity decreases. We propose that it is the “heptagon flow” rate that limits the nanotube growth rate. Certainly, many hexagons can be created independently of this “heptagon route” (e.g., by adding atoms to dangling bonds) but this process is as fast as the growth of the carbon layer over the iron particle and can not be a limiting stage in the CNT growth. Rough estimation supports the heptagon route. Indeed, the characteristic velocity $V$ of a heptagon motion is

$$V = \frac{a_0}{\tau_h},$$

where the shift $a_0 = 0.246$ nm is the size of the hexagon; $\tau_h$ is a time for the process of heptagon transformation shift, which can be found according to (6). Note, that $E_{ah}$ can be estimated empirically (from the in situ sampling experiments). Taking into account (6) and (7), for $V = 1.1 \mu$m/s (calculated for the growth time of 0.054 s) at a temperature of 900 °C:

$$E_{ah} = k_B T \ln \left( a_0 \times \frac{v}{V} \right),$$

one gets 2.8 eV, that can be compared to the energies predicted in [12] to be within the range 0.7–2.3 eV. It is worth noting that the energy value would not significantly change even if the growth time is decreased 10 times. Then the calculated energy is 2.6 eV.

Comparing the temperature dependence given by (6) and (8) for the characteristic time of heptagon transformation with the characteristic times of diffusion processes discussed above (Fig. 1), it appears that (8) indeed determines the limiting process of the growth.

### 4 Conclusion

Experimental results on the formation of single-walled CNTs under different experimental conditions by an aerosol method based on the introduction of pre-formed catalyst particles into conditions leading to CNT formation were analysed. Carbon monoxide and iron nanoparticles were used as a carbon source and a catalyst. Hydrogen was found to prevent the oxidation conditions in the reactor and to provide additional carbon for the growth of CNTs. On the basis of in situ sampling it was detected that the CNTs start to grow at a temperature of around 900 °C in the heating section of the reactor at the growth rate exceeding 1.1 µm/s. A detailed analysis of possible processes during CNT formation revealed heptagon transformation as the limiting stage. The energy of this transformation was calculated to be up to 2.8 eV. A possible mechanism of CNT formation on the basis of the geometrical consideration of graphite sheet was proposed.
Acknowledgements  Financial support from the Academy of Finland and the Creative Research Initiatives Program supported by the Korean Ministry of Science and Technology are gratefully acknowledged.

References


