Correlation between catalyst particle and single-walled carbon nanotube diameters

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Abstract

Single-walled carbon nanotubes (CNTs) were synthesised at different conditions by a novel aerosol method based on the introduction of pre-formed iron catalyst particles into conditions leading to CNT formation. The results of statistical measurements of individual CNT dimensions based on high-resolution TEM images showed the effects of the residence time and temperature in the reactor. The ratio between catalyst particle and CNT diameters was close to 1.6 and independent of the experimental conditions, thus revealing an astonishing “universality” in the growth process. A proposed geometric model of heptagon defect formation, which initiates and maintains the CNT growth, allowed us to theoretically explain the phenomenon.

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1. Introduction

Carbon nanotubes (CNTs) are of great interest since they exhibit unique and useful characteristics such as chemical and physical properties related to toughness, electrical and thermal conductivities, and magnetism (e.g., [1,2]). The properties of CNTs depend strongly on their chiralities (e.g., [3]). In turn, the chirality is determined by the CNT diameter and the orientation of the rolled graphene sheet with respect to the CNT axis. Accordingly, control of the CNT diameter is an important step towards the chirality control. During the catalytic CNT synthesis processes, one of the ways to define the size of the CNTs is to control the size of catalyst particles. It has been reported in the literature that there is a strong correlation between the sizes of catalyst particles and produced CNTs, e.g., [2,4–6]. However, the statistical validity of the experimental results is uncertain. Also, there is a lack of the understanding of the mechanism of the catalyst particle in determining the CNT dimensions.

Only a few papers have been devoted to statistical measurements of CNT dimensions and particularly to establishing the ratio between the diameters of catalyst particles and resulting carbon nanotubes. Almost all available data have been reported for the CNTs produced by the CVD method, where the presence of the substrate can significantly alter the mechanism of the CNT formation. The seminal paper by Dai et al. [7]...
confirmed their earlier observations made for multi-walled CNTs that the catalyst particle diameter should strongly correlate with the CNT diameter and suggested a new yarmulke mechanism for the single-walled CNT growth. On the basis of AFM measurements, Kobayashi et al. [8] reported the average sizes of catalyst particles and the corresponding diameters of CNTs of 1.7 ± 0.6 and 1.0 ± 0.4 nm, respectively, i.e., with the ratio of 1.7. The results presented by Cheung et al. [9] on the diameter ratio for single-walled and thin multi-walled CNTs with 2 or 3 layers showed that the ratio slightly varied in the range from 1.08 to 1.23. Zhang et al. [10] found that the diameter ratio between catalyst particles and bamboo-shaped CNTs was 1.25. Kukovitsky et al. [11] found that the ratio between sizes of nickel catalyst particles and CNTs produced on amorphous carbon film varied and depended on temperature and catalyst particle size. Even this short review devoted to only the CVD method shows that there is a large discrepancy in the results obtained for the ratio between the sizes of catalyst particles and produced CNTs. This most likely can be explained by different products (only [7] and [8] reported the growth of single-walled CNTs), low statistical samples in the presented data, and by the influence of a substrate.

Statistical studies of dimensions of CNT grown under “substrate free” conditions are absent in literature. Investigations of single-walled CNT formation in the HiPco process carried out by Nikolaev et al. [12] reported the sizes of catalyst particles and CNTs to be 5–10 nm and 0.7–1.4 nm, respectively, i.e., with a large (more than 3) ratio between diameters. According to their conjectures, catalyst iron particles continue to grow due to Fe(CO)5 decomposition even after nucleation of CNTs. As they suggested, at the time of CNT nucleation the diameter of a catalyst particle and a CNT should strongly coincide to provide conditions for the yarmulke mechanism. Recent molecular dynamic simulations carried out by Ding, Rosén, and Bolton [13] have supported this idea. However, computational results reported by Maruyama et al. [14] showed that the formation mechanism differs considerably from the yarmulke mechanism. Depending on the catalyst particle size and temperature, the formation of various nanotube cap structures was demonstrated [15], however, with the cap diameter typically smaller than the nickel particle size [14]. Thus, in order to better understand the role of catalyst particles during CNT nucleation and growth additional investigations, where the influence of a substrate and further particle growth after CNT nucleation are excluded, are needed.

The present paper investigates the effect of the catalyst particle size and the experimental conditions on the dimensions (diameter and length) of the CNTs formed in a gaseous phase (without any influence of the substrate on the processes of CNT nucleation and growth). The CNTs were synthesized by a novel aerosol method [16] based on the introduction of pre-formed iron catalyst particles into the conditions where the CNT formation can occur, thus excluding the possibility of further catalyst particle growth after CNT nucleation. The paper reveals and attempts to explain the universality in the ratio between catalyst particle and CNT diameters. It is shown that the geometry of CNT growth is determined by the overall geometry of the carbon network covering catalyst particle during CNT nucleation.

2. Experimental

2.1. Experimental setup

The experimental studies of CNT growth were carried out in a laminar flow aerosol reactor described elsewhere [16]. Briefly, the device consists of a hot wire generator (HWG) and a heated vertical tubular reactor (90 cm in length). The reactor was operated at ambient pressure. A ceramic tube, with an internal diameter of 22 mm inserted inside a furnace (Entech, Sweden) has been used as the reactor. Inside the reactor a ceramic tube with external and internal diameters of 13 and 9 mm, respectively, and with a length of 25 cm was inserted in order to maintain inert conditions for the catalyst particle formation in the HWG. The HWG, which is a resistively heated thin iron wire (0.25 mm in diameter), was placed inside the internal tube. The metal particles produced in the internal HWG tube were carried into the reactor in nitrogen/hydrogen mixture (with mole component ratio of 93.0/7.0) at the flow rate of 400 cm3/min. In the reactor, the flow with the metal particles was mixed with outer CO flow (typically 400 cm3/min). Thus, the partial vapour pressure of the carbon source (CO) was maintained at about 50.7 kPa. Downstream of the reactor a porous tube dilutor (12 L/min) was used to prevent the product deposition on the reactor walls via thermophoresis and diffusion. The product was collected from the gas phase by an electrostatic precipitator (Combination electrostatic precipitator, InTox Products, Albuquerque, NM, USA) on a carbon coated copper grid (SPI Lacey Carbon Grid, Agar Scientific Ltd, England). The morphology and the crystallinity of the as-received product were investigated with a field emission transmission electron microscope (Philips CM200 FEG).

2.2. Effect of experimental conditions on properties of produced CNTs

The effects of both temperature and outer CO flow rate on the properties of CNTs were studied. The investigations of the influence of the experimental conditions
on the CNT dimensions were carried out either at a fixed outer CO flow rate of 400 cm$^3$/min by varying the furnace temperature from 1000 via 1200 to 1400 °C, or by varying the outer CO flow rate from 400 via 590 to 765 cm$^3$/min at a fixed furnace temperature of 1200 °C. During all measurements, the inner H$_2$/N$_2$ flow was maintained at a constant rate of 400 cm$^3$/min.

Number distributions of CNT dimensions were measured manually on the basis of high-resolution TEM images. An example of such TEM images, which were used for the statistical measurements, is shown in Fig. 1(a). The measurements of diameters of CNTs and catalyst particles were carried separately, since as was found each catalyst particle resulted in the growth of a CNT [16]. The error of the dimension measurements is determined by the TEM scale bar calibrations and a ruler gradation (1 mm). The scale bar of the TEM was calibrated conventionally with the help of the crystalline silicon standard on the basis of its known crystallographic data, i.e., lattice parameters. The maximum absolute error that can appear from the dimension measurements is about 0.2 nm. The number of measurements for each dimension and for each case was varied from 60 to 150. Since the dimensions were better described by log-normal distributions, the geometric mean diameter was calculated as

$$\lg D_g = \frac{\sum n_i \lg D_i}{N},$$

(1)

where $n_i$ is the number of CNTs with a dimension of $D_i$, $N$ is a number of measurements. A standard geometric deviation can be found as

$$\lg \sigma = \left[ \frac{\sum n_i (\lg D_i - \lg D_g)^2}{N - 1} \right]^{1/2}.$$  

(2)

Number distributions of diameters and lengths of the produced CNTs and diameters of catalyst particles at various conditions are presented in Fig. 2. Fig. 2(a) shows the number length distributions of the CNTs. Increasing the CO flow rate from 400 to 765 cm$^3$/min (i.e., decreasing the residence time in about 1.5 times) leads to a decrease in the length of CNTs from 54 to 45 nm (with the geometric standard deviations of about 1.22) at fixed reactor temperature of 1200 °C. The clear effect of the residence time on the length of the CNTs can also be seen in Fig. 3(a), where the geometric mean values are plotted.

The furnace temperature has a stronger influence on diameters of CNT and catalyst particles than on the length of the CNTs. Fig. 2(b) shows number diameter distributions of the produced CNTs. The geometric mean diameter of CNTs varies from 0.84 to 1.27 nm (with the geometric standard deviation between 1.24 and 1.40) as the temperature is increased from 1000 to 1400 °C. The diameter distributions of catalyst particles initiating the growth of the CNTs produced at various conditions are shown in Fig. 2(c). The geometric mean diameters of the CNTs and the catalyst particles presented in Fig. 3(b) reveal a clear correlation. The ratio between the diameters of catalyst particles and CNTs is about 1.6 and does not depend on the experimental conditions, i.e., on the temperature and the residence time in the reactor. This intriguing universality will be discussed in the following section of the paper.
3. Discussion

We assume that the iron particle acts not only as the catalytic surface for the liberation of carbon, but also directs the carbon ordering which starts from the creation of an evolving carbon layer on the surface of the particle. This mechanism of CNT formation from an available carbon layer on the surface of a catalyst particle has been already predicted by molecular dynamic calculations in, e.g., [13,14,17] and investigated by an in situ TEM observation [18]. Then, we assume that this layer continuously transforms into the CNT network at the metal–CNT interface with nucleation of negative curvature defects in the form of heptagonal rings [17]. The iron particle is likely covered with a carbon layer in the steady-state process of CNT formation. We believe that this assumption can be used for further elucidation of the CNT stemming mechanism in our process.

We begin by noting that, for any, however complicated, continuous layered carbon system, the carbon sheet geometry is governed by local topological defects in the graphene sheets. These defects impose strict constraints on the overall shape of the system. A good example is the formation of carbon cones [19] in which conic angles are quantized by the number of pentagonal defects in the apex. Pentagonal and heptagonal rings are known to act as disclinations for a flat hexagonal graphene sheet. That means that, in experiments, one can observe only five distinct types of cones with $P = 1, 2, 3, 4$, and 5 pentagons in the apex (0 pentagons bring a plane as a degenerate cone and 6 pentagons produce a cylinder). The half of the angle in the apex can be calculated as [19]

$$\theta = \arcsin(1 - P/6).$$

In our case, we have a CNT (a cylinder) stemming from a spherical surface graphene sheet covering an iron particle (see Fig. 4). The carbon layer geometry requires a negative curvature in the region of the stem [17,20] in order to join the sphere and the cylinder. The negative curvature and the local hyperbolic geometry are constructed by the presence of heptagonal rings in the graphene sheet. We can calculate the angle $\beta = \pi - \theta$ between the spherical and CNT surfaces (the existence of such an angle is a large scale [asymptotic] manifestation of the local saddle point geometry) imposed by the topological defects, i.e., the heptagon rings. From Fig. 4 it is seen that a small part of a “phantom” conic surface (dashed lines) can be used as a locally tangential surface to smoothly connect the sphere and the cylinder. For the ratio between the diameter of the iron particle $2R$ and the diameter of the CNT $2r$ one gets

$$2R/2r = 1/\cos(\theta),$$

to which we compare the experimentally observed “universal” ratio of 1.6. We show rigorously that the ratio (4) is independent of the environmental conditions and is governed only by the geometry of the graphene layer. Therefore, the CNT steady-state growth process demands the constant creation and maintenance of heptagon defects in the stem [17,20]. Let us note that we do not consider here pentagon–heptagon pairs that

Fig. 2. Number distributions (normalized frequency versus size) of (a) lengths of individual CNTs, (b) diameters of individual CNTs, (c) diameters of catalyst particles embedded in CNTs at various conditions.
may appear in abundance in the fluctuating system geometry, adding to smoothing the graphene sheet. We are considering only topology relevant extra defects that determine the overall geometry.

Unlike the cones considered in [19], the apex of this asymptotic tangential cone should not end up with pentagons. Instead it is completed as a continuous transformation into a cylinder (CNT). Thus we have to introduce another type of cone when one should start not from the flat sheet but with a graphene cylinder and then introduce heptagonal disclination defects one by one, producing a conic torus with a half angle $h$, which connects smoothly to the spherical carbon shell around the iron particle where

$$h = \arcsin\left(\frac{H}{6}\right),$$

and $H$ is the number of heptagons.

The diameter ratios $2R/2r = 1/\cos(\theta) = 1/\sqrt{1 - (H/6)^2}$ calculated from (5) are 1.014, 1.061, 1.155, 1.342, and 1.809 for $H = 1, 2, 3, 4$ and 5, respectively. The case $H = 0$ is degenerate since this does not lead to the change in the graphene layer geometry (though it may be of a separate interest). The case $H = 6$ corresponds to a CNT normal to a flat surface, which is not the case for our CNTs, but can be applied to so-called Saito’s mechanism [17,21], where thin CNTs grew on large catalyst particles. For this special case, a detail explanation of heptagon inception, maintenance, and heptagon-assistant addition of hexagons was given in [17]. We believe that the same mechanism should work for $H < 6$ as well, as far as the only difference between the root growth from the flat surface [17] and the growth from the particle is the curvature of the particle surface (the coordinate frame can always be set on the particle so that the CNT is considered to be growing from the particle). One can see that both the values 1.342 and 1.809 corresponding to 4 and 5 heptagons in the stem are rather close to the experimental ratio 1.6. The angle $\beta$ between the spherical and CNT surfaces makes 138.19° for $H = 4$ or 123.56° for $H = 5$ to be distinguished from high-resolution TEM images [16] [see also Fig. 1(a)] where the angles of 140° and 123° are shown).

Yet, the diameter ratio 1.809 (5 heptagons) might be the most preferable in the steady-state growth process because it corresponds to the lowest value of the surface area of the CNT generated in the process and to the largest curvature. The attraction of heptagons to the large curvature in the stem [17] “condenses” the heptagons to the maximum possible number 5 in our case. The deviation of the theoretical ratio 1.809 from the experimental 1.6 ratio may come from the dynamical effects which make 4 heptagons also available. (Note that if the particles were less than the size of about 0.5 nm, there would not be enough space in the CNT circumference even for 5 heptagons: not only geometry and topology but also scales would start being important when sizes are comparable to interatomic distances in the carbon network). An additional reason for the deviation is that the shape of the liquid iron particle changes between spherical to mushroom-like during the CNT growth, because the 5 heptagon-induced graphene “corner” rolls over the liquid particle which sticks to the CNT graphene layer by cohesive forces to produce an
intermediate mushroom shape [18]. Indeed, looking at HR-TEM images shown in Fig. 1 one can see that the catalyst particles may be deformed. For a larger CNT in Fig. 1(b), one can calculate the ratio of $3.9/2.4 = 1.6$ for the catalyst particle hat and $3.9/1.9 = 2.1$ for a stem part of a mushroom shaped particle. A smaller CNT contains a spheroidal shape particle with the ratio of 1.6. Thus, the most likely way to explain the deviation from 1.809 is a dynamical transformation of the shape of catalyst particles during the growth of CNTs.

In order to check whether the revealed ratio universality is inherent for other CNTs produced by the aerosol synthesis with pre-formed catalyst particles, we have investigated the ratio for CNTs synthesised by the same method however with different carbon source-ethanol [22]. It was found that the product synthesised at 1200 °C consisted of CNT bundles with the individual CNT lengths of approximately 100–200 nm. Statistical measurements showed that the CNT diameter varied from 0.8 to 2.9 nm with a geometric mean diameter of 1.7 nm (geometric standard deviation of $\sigma = 1.22$), while the catalyst particle sizes were found to have the geometric mean diameter of 2.4 ($\sigma = 1.58$). Therefore, the ratio between diameters of catalyst particles and CNTs was found to be 1.4, which is very close to the found ratio range from 1.52 to 1.62, confirming the geometric nature of the CNT growth in the setups, where catalyst particles do not grow after CNT nucleation.

Another trial to check the universality of the ratio between diameters was performed also for the aerosol system, however, based on an in situ chemical production of catalyst particles. These experiments were carried out in a vertical flow reactor, where catalyst precursor (ferrocene) vapour in a CO atmosphere was introduced immediately to the high temperature zone to provide fast iron vapour nucleation and particle growth [23]. Statistical measurements of produced bundles of single-walled CNTs showed the ratio of 2.4 with geometric mean diameters of CNTs and active catalyst iron particles of 1.3 nm ($\sigma = 1.31$) and 3.1 nm ($\sigma = 1.30$), respectively. However, kinetic calculations and experimental results on the mechanism of CNT formation indicate the growth of catalyst particles even after CNT nucleation, similarly to the above-mentioned results by Nikolaev et al. [12]. Thus, replacing the pre-formed catalyst particles by the particles with uncertain growth history in the aerosol CNT synthesis resulted in the significant change of the ratio between the diameters of catalyst particles and produced CNTs.

By examining the available experimental data presented in this paper, the mechanism for the CNT formation by a method relying on the introduction of pre-formed particles can be proposed. Fig. 5 summarises the main stages resulting in the CNT formation in our experimental setup. In the scheme, only the most important and relevant processes are indicated. After formation of metallic iron particles and their introduction in the reactor, atomic carbon starts to release on the surface of a catalyst particle due to CO disproportionation and reaction between hydrogen and carbon monoxide. Also carbon dissolution into the iron to saturate particles occurs. Eventually particles become saturated by carbon and conditions for carbon arrangement into a regular graphene sheet including formation of hexagons and pentagons are established. The next stage is nucleation of negative curvature (heptagonal) defects in this regular carbon layer and the cap detachment. The further growth of CNTs occurs in a steady-state regime due to the presence of available carbon and additional carbon coming after the CO disproportionation and reaction between hydrogen and carbon monoxide on the opposite side of the catalyst particle. Both volume and surface diffusions are possible to deliver carbon atoms to the growing CNT network. The length of the CNTs is determined by the residence time (Fig. 3(a)) for a growing CNT in the temperature range, where the CO disproportionation and reaction between hydrogen and carbon monoxide can occur to maintain the CNT growth.

4. Conclusion

Single-walled carbon nanotubes having narrow size distribution were synthesised at different conditions by a novel aerosol method based on the introduction of pre-formed catalyst (iron) particles into the conditions of CNT formation. The statistical measurements of individual CNT dimensions (diameters of CNTs and catalyst particles initiating their growth and CNT lengths)
based on high-resolution TEM images were carried out. The effects of both temperature and residence time in the reactor on the dimensions of grown CNTs and catalyst particles were studied. It was found that increasing the CO flow rate from 400 to 765 cm$^3$/min (or decreasing the residence time) leads to a decrease in the length of CNTs from 54 to 45 nm (with the geometric standard deviation of approximately 1.22). The geometric mean diameter of CNTs varied from 0.84 to 1.27 nm (with the geometric standard deviation between 1.24 and 1.40) with a temperature increase in the system from 1000 to 1400 °C. The diameter of catalyst particles attached to CNTs is about 1.6 times larger than that of the produced CNTs over the full range of studied experimental conditions (temperature and residence time). The found universality can be explained as a result of a continuous junction between the spherical surface of the graphene layer on the catalyst particle and the cylindrical surface of the CNT. The mechanism of CNT formation was discussed.

On the basis of the experimental results presented in this paper, one can also conclude that at the conditions, where the catalyst particle growth after CNT nucleation is excluded and CNT nucleation and growth occur without the influence of a substrate, the diameters of catalyst particles and CNTs do not necessarily coincide as it was proposed in [12] based on a trivial geometry. Instead, it is proposed that the special carbon network geometry is involved and determines the ratio between the diameters of catalyst particles and CNTs.

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