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Possible role of charge transport in enhanced carbon nanotube growth

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ABSTRACT We consider the role of electric fields during metal-catalysed thermal chemical vapour deposition growth of carbon nanotubes and show that enhanced growth occurs from a negatively biased electrode. An electric field, applied externally to the growing tubes and/or generated as a result of electron emission or self-biasing, may strongly affect the carbon supply through the catalyst nanoparticle, enhancing the growth rate. Different aspects of the growth process are analysed: the nature of the nanoparticle catalysis, carbon dissolution kinetics, electron emission from the nanotube tips, charge transport in the nanotube–catalytic nanoparticle system and carbon drift and diffusion through the catalyst under the action of the electric field. A fundamental tenet for modelling of charge-transport dynamics during the nanotube growth process is proposed.

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1 Introduction

Like many great discoveries, carbon nanotubes (CNTs) were initially observed too early to be fully appreciated by the scientific community [1, 2]. However, already the authors of [1] found that, to grow ‘worm-like’ structures, three types of catalysts were suitable, namely iron, cobalt and nickel. Being rediscovered in 1991 [3], CNTs caused a sensation and are still gaining popularity due to their unusual properties and wide variety of available and potential applications.

Debate on the mechanisms of CNT nucleation and growth is still proceeding. Detailed reviews of the proposed mechanisms are widely available in the literature (see e.g. [4–6]). A number of open questions remain, such as the detailed mechanism for high growth rates on the order of 100 nm/s for plasma chemical vapour deposition

(CVD) growth of multiwalled nanotubes [7–9] up to as high as 11 $\mu\text{m/s}$ observed in thermal CVD growth of exceptionally long single-walled nanotubes [10], corresponding to approximately the same amount of carbon deposition as in the plasma experiments. In this paper we draw attention to an effect which can play a key role in CNT growth, namely enhancement of the carbon supply through the catalyst particle to the nanotube edge by charge-carrier transport. We omit considerations of the CNT nucleation stage, accepting the thermodynamic analysis given comprehensively in [4], and focus on the CNT growth mechanism. As a basis, we are guided by the most credible and accepted viewpoint that carbon dissolves in the metal catalyst particle, diffuses through it and is incorporated in the edge of the growing nanotube anchored to the catalyst particle [4, 7, 11].

2 Carbon nanotube growth in the presence of an electric field

Many studies have been reported in recent years concerning the growth of carbon nanotubes in the presence of electric fields. The original arc discharge production method involved a DC discharge with the nanotube material being deposited at the cathode [3]. However, in the present study we will concentrate on metal-catalysed growth of carbon nanotubes in chemical vapour deposition processes (thermal and plasma-enhanced), although our ideas may also be relevant for the high temperature production conditions prevalent in arc discharge and laser vaporisation processes.

The most common occurrence of electric fields in nanotube growth is during plasma-enhanced chemical vapour deposition (PECVD). See [6] for a review of PECVD methods. These methods are used to grow vertically aligned individual nanofibres, where the catalyst particle is typically situated at the tip, or films of aligned multiwalled carbon nanotubes where the catalyst typically remains at the base [8]. Some interesting observations have been made concerning the influence of substrate bias (either via an applied DC bias or through self-biasing) [7, 12–15]; however, a comprehensive review of this goes beyond the scope of the present paper. It appears that quite different growth mechanisms are operating and which one dominates will depend on the details of the plasma environment and catalyst preparation. One can state with confidence that the alignment of

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both the nanotubes and the nanofibres produced by PECVD is due to the presence of an electric field and that the alignment increases with the magnitude of the electric field (until, for high biases, sputtering begins to dominate over growth [16]). Furthermore, the growth of vertically aligned carbon nanofibres requires the presence of energetic positive ions, directed towards the substrate (or nanofibre tip), and hydrogen atoms.

Ono et al. [17] demonstrated that individual carbon nanotubes could be grown from catalyst particles deposited on Si tips only when a negative bias was applied to the tip. A positive bias inhibited the growth. Sarangi and Karimi [18] observed that the diameter and length of nanotubes grown on metal wires were increased when applying a plasma with a negatively biased substrate. On the other hand, Avigal and Kalish [19] claimed better alignment for a positively biased substrate in tip-growth experiments where a small electric field ($0.05 \text{ V}/\mu\text{m}$) was applied during growth in a cold-wall reactor; however, they made no statement concerning the efficiency of the tip growth for the two bias conditions. Finally, in flame synthesis experiments, thick layers of aligned carbon nanotubes could be found to grow in the presence of an electric field (negatively biased substrate) [20].

All the experimental situations discussed above are complex and, although the presence of an electric field can obviously play an important role in influencing the growth, it is extremely difficult to determine the main influences in the complicated plasma or flame environments. In recent years, external electric fields have also been applied during thermal CVD growth of single-walled nanotubes. The main reason for these studies has been to develop ways of producing aligned single-walled nanotubes on a silicon chip [21–23].

We have been interested in developing this method to control the alignment and positioning of nanotubes with the aim of developing techniques for growing single-nanotube devices on chips [24]. While carrying out these studies we observed an asymmetry in the growth when the nanotubes were growing from the electrodes supplying the aligning field. We found a significant enhancement of growth of single-walled carbon nanotubes from nega-

tively biased electrodes. We attribute this as being due to the effect of field emission from the growing nanotubes. We speculate that this may be related to the role of charge transport through the catalyst particle and provide arguments for this hypothesis. Our model can also explain many of the electric field-related phenomena reported in the literature and discussed briefly above.

3 Experimental details

An example of a growth experiment is shown in Fig. 1 where the electrodes, supplying an electric field during nanotube growth, are separated by $14 \mu\text{m}$. The electrodes are made of Mo, deposited using e-gun evaporation. The lower electrode had a $+20 \text{ V}$ potential applied during growth while the top electrode was grounded and the doped Si substrate, underlying a 400-nm thermally grown SiO_2 layer, was floated. The catalyst used to promote the growth consists of a multilayered film of 10-nm Al_2O_3 , 1-nm Fe and 0.2-nm Mo [25], which is patterned at the edges of the electrodes close to the gaps (visible as the lighter triangular patches in Fig. 1). The substrate is placed on a home-made holder and contact pads are connected via Ta clamps and electrical feedthroughs to a voltage supply. The furnace, enclosing a quartz tube containing the sample, is heated in a flow of 300 sccm H_2 and 500 sccm Ar at atmospheric pressure. When the temperature

has reached 900°C , Ar is switched to 500 sccm methane, which is the carbon precursor for the CNT growth. We have shown that under these gas-flow conditions there is no gas-flow-induced alignment of the nanotubes. The sample is exposed to the growth conditions for a few minutes (typically 3–5 min) before the voltage is applied over the electrode gaps. The growth is then performed for 20 min after which time the methane flow is switched back to Ar and the furnace is switched off. Extensive Raman, atomic force microscopy and scanning electron microscopy (SEM) studies have shown that the nanotubes grown in this way are single-walled nanotubes with the catalyst particle remaining at the base.

Two interesting observations can be made from Fig. 1. Firstly, the nanotubes growing from the upper electrode are significantly longer than those growing from the lower, positively biased electrode. Secondly, the nanotubes growing from the upper electrode are surrounded by a darkened area in the electron-microscope picture. We have recently shown that this effect is due to a local surface melting and trench formation in the SiO_2 induced by the exceptionally high temperatures reached as a consequence of electron field emission [26].

An analysis of 70 individual nanotubes growing from both electrodes of similar geometry on a single chip is shown in Fig. 2. The electric field at the shortest distance between the elec-

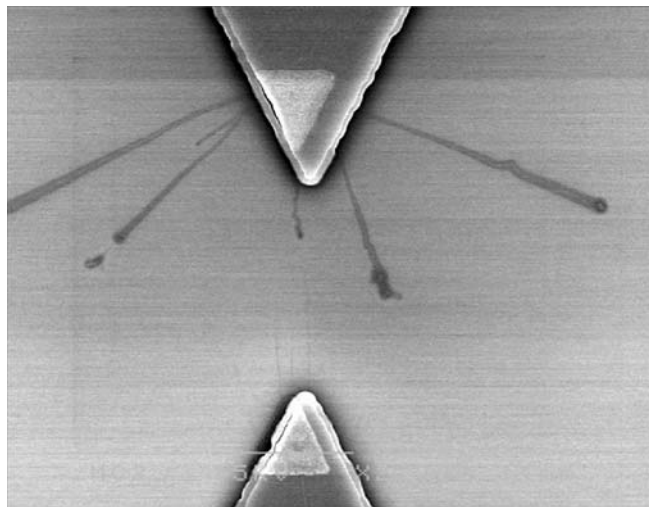


FIGURE 1 SEM picture of single-walled nanotubes growing from biased electrodes under conditions where the nanotubes grow close to the surface (electrodes switched on after growth has started). Upper electrode grounded, lower electrode $+20 \text{ V}$. The shortest distance between the electrodes is $20 \mu\text{m}$

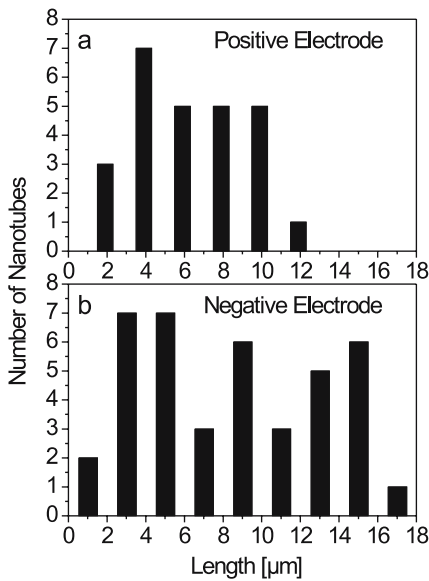


FIGURE 2 Length distributions of single-walled nanotubes growing from electrodes in a geometry identical to that of Fig. 1. (a) Positively biased electrode, (b) negatively biased (grounded) electrode. A total of 70 nanotubes were analysed from different samples and electrode pairs. The average length from the negatively biased (grounded) electrode is $8.4 \pm 4.6 \mu\text{m}$ and from the positively biased electrode is $5.2 \pm 3 \mu\text{m}$. The errors represent the standard deviation

trodes used in the study varies from 0.8 to $1.4 \text{ V}/\mu\text{m}$. There is a clear tendency for the nanotubes growing from the positively biased electrode to be shorter than those growing from the grounded electrode. There are also significantly more nanotubes growing from the grounded electrode (41 from the grounded electrode and 29 from the positive electrode). The average length and standard deviation are $5.2 \pm 3 \mu\text{m}$ and $8.4 \pm 4.6 \mu\text{m}$ for growth from the positively biased and grounded electrodes, respectively. A similar effect is seen from the electron-microscope picture in Fig. 3a. In this case the applied field was also around $1 \text{ V}/\mu\text{m}$ (the field decreases by a factor of 1.2 on going from the left to the right-hand side of the picture). The upper electrode is grounded and the lower electrode is biased at +20 V. Again, the nanotubes growing from the upper electrode are significantly longer than those from the lower electrode. Figure 3b shows a side view of the same sample. Here, it is possible to see undulations caused in the oxide surface by the strong heating [26].

The more efficient growth of longer nanotubes from the negatively biased electrode does not depend on the trench

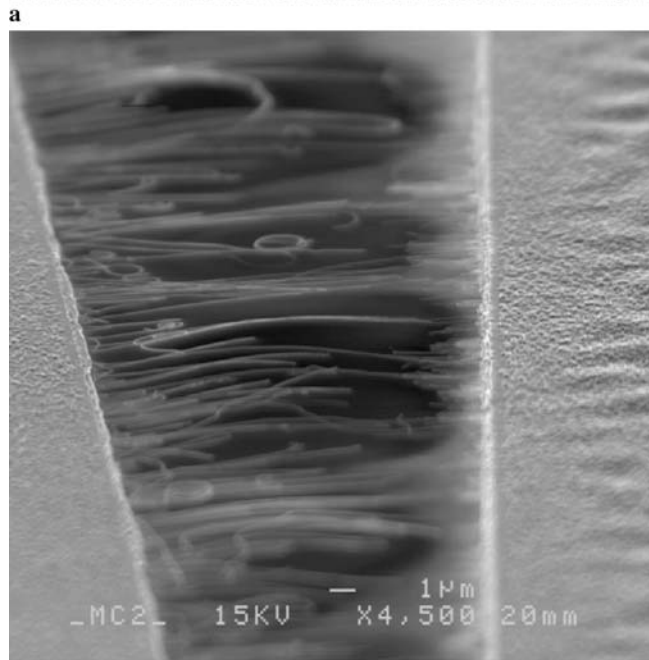
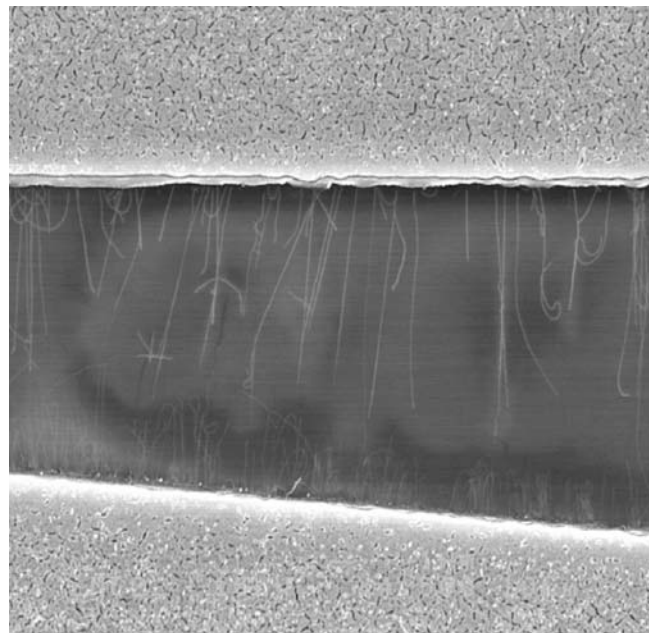


FIGURE 3 (a) SEM picture of single-walled nanotubes grown from biased electrodes. The applied field was around $1 \text{ V}/\mu\text{m}$ (note that the distance between the electrodes increases slightly on moving from left to right). Upper electrode grounded, lower electrode +20 V; (b) the same sample but observed from the side. The strong local heating due to electron emission from the nanotubes growing from the grounded electrode was sufficient to melt the underlying oxide layer [25]

formation and high local temperatures, nor does it depend on which electrode is grounded. The samples shown in Figs. 1 and 3 have been grown in such a way that the nanotubes grow close to the oxide surface (the aligning field was switched on after the nanotubes started to grow) [26]. If the aligning field is present from the start of growth, then the nanotubes tend to first grow

upwards [23] and are sufficiently far away from the substrate during growth that there is much less local heating of the substrate and no deformations are observed. Under these conditions we still observe the asymmetry in nanotube growth. This is illustrated in Fig. 4 where the upper electrode is grounded and the lower electrode is at a potential of -20 V (the substrate is floated,

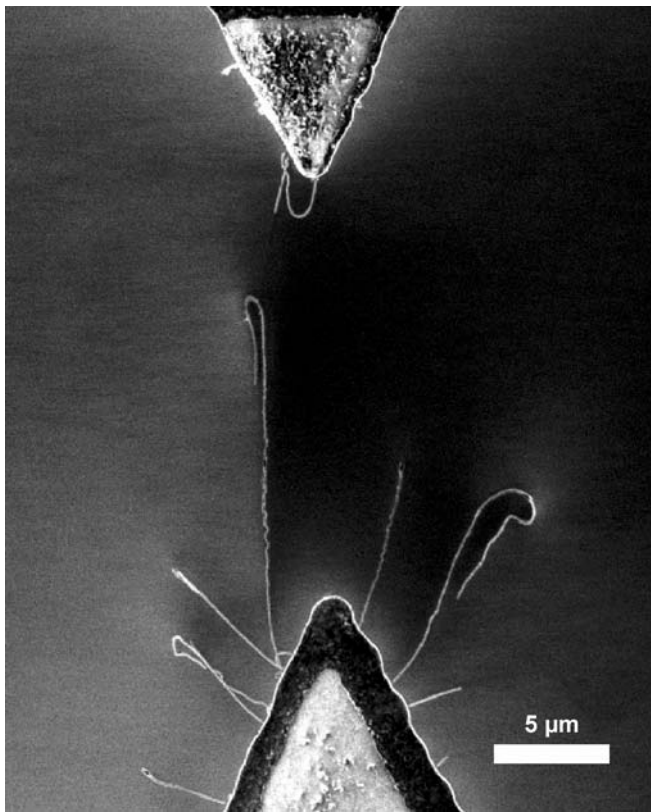


FIGURE 4 SEM picture of single-walled nanotubes grown from biased electrodes under conditions where the nanotubes grow relatively far from the surface (electric field present from start of growth process). Upper electrode grounded, lower electrode -20 V, substrate floating. The shortest distance between the electrodes is $24\ \mu\text{m}$

as before). In this example, the shortest distance between the electrodes is $24\ \mu\text{m}$. Out of 45 nanotubes analysed in this sample, 34 grew from the negatively biased electrode.

It is clear from our present experiments and from previously published results [26] that the growth from a negatively biased electrode in thermal CVD can lead to high temperatures of the growing nanotube due to the occurrence of field emission. It is therefore possible that an increased temperature at the catalyst could help to remove deposited amorphous carbon and thus reduce catalyst poisoning, allowing the growth of longer nanotubes. However, in this situation the electrode acts as a heat sink, so that the temperature at the base of the nanotube is not expected to be significantly higher than that of the furnace, but there will be a strong temperature gradient along the growing nanotube [26, 27]. We therefore do not think that enhanced temperature at the catalyst particle can explain our results. Instead, we consider the role of ion drift through the catalyst particle as being

the main source of the enhanced growth from the negatively biased electrode.

4 Charge-assisted nanotube growth

4.1 Indications of the role of charge transport

The discussion of experimental results in Sect. 3 indicates that any model of nanotube growth in the presence of an electric field should take charge transport into consideration. We base our present model on a model developed to describe laser-induced charging of different types of materials [28, 29]. An additional justification for the model is the recent discovery of charging effects in chemical reactions catalysed by small metal clusters [30]. There are several facts which indicate the importance of charge-carrier transport during CNT growth: the increased length of single-walled nanotubes growing from the negatively biased electrode in thermal CVD (Figs. 1–4); strong alignment of nanotubes and nanofibres in PECVD [6, 7, 12–16]; field-

enhanced growth of multiwalled nanotubes in PECVD from a negatively biased substrate [17, 18]; dense growth of aligned multiwalled nanotubes in flame synthesis from a negatively biased substrate [20] and high growth rate experiments, e.g. $> 100\ \text{nm/s}$ rates for growth of multiwalled nanotube films in PECVD [7–9] that are difficult to explain by carbon diffusion in the catalyst particle alone [9, 31].

Additional evidence for charge-transport effects is found in non-CVD growth experiments. Srivastava et al. have studied the effect of the applied electric field on the alignment, length and diameter of nanotubes produced by arc discharge [32]. An optimum electric field, on the order of $0.2\ \text{V}/\mu\text{m}$, was found to correspond to the situation with the best alignment as well as the longest and highest-diameter nanotubes. For higher applied fields the nanotubes become overheated and lose their alignment (presumably also eroding).

We take as well established that nanotube growth proceeds predominantly via carbon diffusion through the catalyst particle and that diffusion is the mechanism limiting or favouring the growth rate [4]. Modelling [33, 34] has shown only minor temperature gradients in the catalyst particle, so the diffusion is governed by the concentration gradients of carbon dissolved in the nanoparticle. However, as far as we are aware, the importance of carbon-ion drift has not been taken into consideration in any growth models so far. To probe whether carbon-ion drift can significantly influence the dynamics of the carbon supply for CNT growth, we will first consider the details of the processes of carbon dissolution and transport in the catalyst particles.

(1) For the following discussion we will assume that the small nanoparticles used to catalyse growth of single-walled nanotubes at high temperatures are in the liquid state [35]. Then the diffusion law should be written in the form

$$D = D_1 T / \mu, \quad (1)$$

i.e. the diffusion coefficient D is determined by the viscosity μ of the liquid solution at temperature T . The viscosity of liquid Fe–C alloys depends on both the carbon content and the temperature.

For the diffusion of carbon in bulk liquid iron $D_1 = 2.5 \times 10^{-14}$ [36].

The assumption of a liquid catalyst particle appears essential to explain the high growth rates that have been observed experimentally (e.g. [7–10]). Jost et al. [37] studied the formation of single-walled nanotubes grown from NiCo particles in thermal CVD and showed that the diffusion of carbon through the catalyst particle followed a $T^{2.4}$ behaviour. Microgravity experiments in space have shown that diffusion through liquid metal particles follows a T^2 law [38]. We suggest that an enhanced supply of carbon to the growing nanotubes can be achieved by charge-carrier transport. This could explain many of the observations of increased growth from biased substrates and is discussed in detail below.

(2) Another important question concerns the dissolution kinetics of carbon in liquid catalyst nanoparticles. It is known that halide atoms dissolved in liquid metals bind an additional electron more tightly than in free space as a result of screening by conduction electrons [39]. The authors of [39] have predicted that oxygen atoms having a rather high electron affinity (~ 1.46 eV [40]) can also exist independently in liquid metals without the formation of oxide molecules and that negative ions (O^{2-}) should be electronically stable. It can be speculated that, by the same reason, carbon atoms with an electron affinity not much less than that of oxygen (1.263 eV [40]) are also able to form negative ions when dissolved in iron or other metal particles. It is quite possible that, in view of recent findings [30], the presence of carbon anions could be responsible for the high chemical activity of carbon in liquid iron [41]. If carbon can exist in liquid catalyst particles in the form of free negative ions, then the transport of carbon in the catalyst nanoparticles will indeed be strongly influenced by the electric field. It should also be mentioned that carbon atoms have no tendency to aggregate in liquid metals [42], a point in support of a charged state. A recent report of electrochemical production of carbon nanomaterials [43] suggests that carbon anions, produced with the help of metal grains in a high electric field, are responsible for the growth.

(3) A third important issue in CNT growth is the possibility of charge carrier transport generation in the ‘growing nanotube–catalyst nanoparticle’ system. CNTs are excellent field emitters and under the conditions present during field-enhanced growth there can be a significant field-emission current. This is our explanation for the extreme local heating of the substrate found when growing single-walled nanotubes from a negatively biased electrode (Figs. 1 and 3) [26]. This leads to charge-carrier transport and to charging of the CNT–catalyst system.

In the absence of an electric field, thermionic field emission can occur, as described by the Richardson–Dushman equation. The typical temperatures of CNT growth are not sufficient to induce pure thermionic electron emission from nanotubes, with a work function of approximately 5 eV. However, the reaction $CNT + C$ is exothermic and should result in an energy release of several eV in every act of C addition to the CNT. Hence, the nanotubes during the growth process may be considerably hotter than the surrounding atmosphere, which may result in appreciable electron emission even in the absence of an external field. In addition, collisions of hot atoms, ions and electrons can lead to collisional CNT ionisation.

Following the above discussion, it can be expected that electron emission from the CNTs during the growth process, especially in the presence of an electric field, can be very effective. The growing nanotubes will be positively charged as a result of electron emission, and electrons (as well as negative ions, C^{m-}) will drift from the catalyst nanoparticle to the nanotube in order to neutralise the excess positive charge (a situation similar to that considered in [28, 29] for fs-laser-irradiated targets). The ‘looping’ of the nanotubes, clearly observed in Fig. 4 and in many of our growth experiments, may be due to a positive charging at the nanotube tip due to strong field emission leading to electrostatic deflection by the positively charged electrode. This is under further investigation.

It should be mentioned that there are some additional effects of charge-carrier transport that can play a role during CNT growth accompanied by

electron emission from the growing CNTs. As assumed above, negative carbon ions can drift within the catalyst to the anchored end of the nanotube together with electrons. The electron current can induce convection of the liquid metal as well as carrying a component of liquid alloy as a result of collisions [44]. Convection in liquid catalyst nanoparticles due to the Bénard–Marangoni instability, implying the presence of a solid nanoparticle core, has been considered in [31]. However, it seems that convection can also occur in a completely melted catalyst under conditions of high electron current. Finally, during laser vaporisation growth of CNTs, electron emission combined with the effects of buffer gas can remove excitation of the CNTs obtained due to release of the condensation energy, thus leading to positive charging of the CNT–catalyst particle system.

Thus, a general conclusion can be made that, under many conditions of CNT growth, charge-carrier transport in the ‘CNT–catalyst nanoparticle’ system can take place as a result of field or thermionic emission, or a combined emission process.

4.2 Model for charge-induced CNT growth in the presence of an electric field

We consider a nanotube growing via the base-growth mechanism in the presence of an electric field (either thermal CVD with an aligning field or in PECVD). The system is illustrated in Fig. 5, where we assume that the nanotube is oriented along the applied electric field. Under the action of the electric field, the hot nanotube is emitting electrons during growth. The electrons drift along the nanotube towards its upper part under the external electric field superimposed with the self-consistent field. As the electron mobility in the CNT is higher than that in the nanoparticle, positive charge is accumulated at the CNT–nanotube contact. As a result, electrons and negative carbon ions drift through the nanoparticle towards the nanotube base, where carbon precipitates. Hereafter, we base our arguments on a drift–diffusion approach developed for describing laser-induced charging of different materials by ultra-

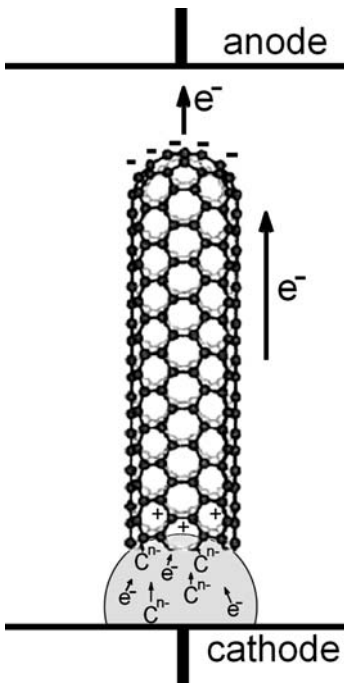


FIGURE 5 Model for electric field enhanced nanotube growth for nanotubes grown by the base-growth method. Field- and temperature-induced electron emission from the nanotube tip generates an electric current along the CNT to compensate for the electron deficiency, causing positive charging at the nanotube base. As a result, electrons and negative carbon ions drift toward the tube through the catalyst nanoparticle, enhancing the growth process

short IR laser pulses [28, 29, 45]. The model implies the possibility of spatial charge separation and generation of local electric fields. Also, the external electric field should be taken into account. The following factors therefore have to be considered for the model construction: (a) a nanotube can emit electrons during growth; (b) under the action of the electric field, the electrons drift along the tube to its emitting tip; (c) because of the difference in electron mobility, there should be strong charge and electric field gradients at the CNT–catalyst nanoparticle contact region; (d) charge transport in the catalyst nanoparticle consists of drift and diffusion of the electrons and negative carbon ions; (e) the kinetics of carbon dissolution on the surface of the catalyst nanoparticles should be considered.

Under the above assumptions, the governing equations for modelling should be as follows [28, 29]:

The continuity equations for the charge carriers:

$$\frac{\partial n_x}{\partial t} + \frac{1}{q_x} \frac{\partial J_x}{\partial x} = 0, \quad (2)$$

where n_x denotes the carrier densities with subscripts $x = e$ and C^{m-} representing electrons and carbon anions, respectively; J_x is the electric current density and q_x is the carrier charge (e for electrons and me for carbon anions).

The equations of motion describing charge-carrier transport with the electric current density J_x include both drift and diffusion terms, which can be written in a general form as

$$J_x = |q_x| n_x \mu_x E - q_x D_x \nabla n_x. \quad (3)$$

Here μ_x is the carrier mobility, D_x is the diffusion coefficient for the component x and E is the electric field. Notice the difference between the viscosity μ in (1) and the mobility μ_x , which is distinguished by the subscript.

The Poisson equation to calculate the electric field distribution in the CNT–nanoparticle system perturbed as a result of the breaking of quasi-neutrality due to electron emission from the CNT is

$$\frac{\partial E}{\partial x} = \frac{e}{\varepsilon_0} (n_i - n_e) \quad (4)$$

and for the catalyst nanoparticle

$$\frac{\partial E}{\partial x} = \frac{1}{\varepsilon_0} \left(\nu e n_i - \sum_m q_{C^{m-}} n_{C^{m-}} - e n_e \right), \quad (5)$$

where ν is equal to the number of valence electrons and i refers to positive ions. The dielectric permittivity in (4) and (5) is taken to be $\varepsilon = 1$ because of the small size of the catalyst nanoparticles. The boundary conditions for the electric field at the top of the CNT can be determined using Gauss' law, taking into account the applied electric field and the field enhancement factor [46].

The number of continuity equations to describe the catalyst nanoparticle (2) depends on the charge state of carbon that is an unexplored subject. However, as the starting point, it is reasonable to assume that all the ions are in the same charge state and to consider the two extreme cases with $m = 1$ and 4. As a boundary condition at the top of the CNT, an electron-emission term has to be introduced in the form of the thermal-field emission equation [47].

The equations of motion have the forms

$$J_e = |e| n_e \mu_e E - e D_e \nabla n_e, \quad (6)$$

$$J_{C^{m-}} = m |e| n_{C^{m-}} \mu_{C^{m-}} E - m e D_{C^{m-}} \nabla n_{C^{m-}}, \quad (7)$$

for electrons and negative carbon ions, respectively. Note that for negative particles drift is aligned with diffusion. Equation (7) is applied only to the nanoparticle, and (6) works throughout the CNT–nanoparticle system. The diffusion coefficient for the electrons is given by the Einstein relation as $D_e = kT\mu_e/e$, where T is the temperature and k is the Boltzmann constant. For carbon atoms and ions, a diffusion coefficient of the form given in (1) should be applied. The carbon-ion mobility can be expressed as $\mu_{C^{m-}} = m e D_{C^{m-}}/kT$ [44]. The electron mobility in the liquid catalyst can be evaluated using the data on resistance. For liquid iron, as an example, the specific resistance ρ is $130\text{--}140 \times 10^{-6} \Omega \text{ cm}$ at a temperature slightly above that of the thermodynamic melting point [40]. The electron mobility is evaluated as $\mu_e = (\rho e n_e)^{-1} \sim 3 \times 10^{-5} \text{ m}^2/(\text{V s})$ ($\nu = 2$ for Fe). The electron mobility in nanotubes has been reported to be extraordinarily high, $> 10 \text{ m}^2/(\text{V s})$ at room temperature [48]. Such a strong difference between the electron mobilities in the CNT and in the nanoparticle should cause a positive charge to be accumulated at the CNT–nanoparticle contact region (Fig. 5). As a result, the negative carbon ions will efficiently drift through the nanoparticle to the nanotube under the action of the electric field calculated self-consistently by (4) and (5).

5 Discussion

With our present knowledge, a quantitative calculation would be too speculative since too many parameters are unknown. However, the model can guide research strategies, which could be of importance for developing a more quantitative theory as well as for providing a better understanding of CNT growth mechanisms and developing better means of controlling the growth and increasing the growth efficiency. Here, based on our proposed mechanism of charge-induced CNT growth, we discuss some important issues aimed at better understanding the growth process.

Let us evaluate the electric field under which the carbon-ion drift dominates over diffusion. From (7) we have

$$men_{C^{m-}} - \mu_{C^{m-}} |E| \geq meD_{C^{m-}} \nabla n_{C^{m-}} \quad (8)$$

or

$$men_{C^{m-}} |E| / kT \geq \nabla n_{C^{m-}}. \quad (9)$$

This gives a rough condition

$$|E| = \frac{\Delta n_{C^{m-}} kT}{\Delta x men_{C^{m-}}}. \quad (10)$$

Assuming $\Delta n_{C^{m-}} \sim n_{C^{m-}}$ in a distance corresponding to the nanoparticle size (giving an upper estimate), we obtain $|E| = kT / (\Delta x me)$. For $\Delta x \sim 2$ nm, $T \sim 1173$ K, and $m = 1-4$, this gives $E \sim (1-4) \times 10^7$ V/m. This is approximately one order of magnitude higher than the electric fields that are typically used for directed growth of single-walled nanotubes [21] and is higher than the field strength used to grow the nanotubes illustrated in Figs. 1–3. Note, however, that the internal field strength is not necessarily the same as the externally applied field. Although electron emission is determined by the external electric field, the internal field generated in the CNT–nanoparticle system can differ substantially from the applied one. For field-emission currents on the order of μ A, the estimated internal field in the nanotube is only on the order of 0.1 V/ μ m; however, the internal field of the catalyst nanoparticle can be higher than this. As a rough estimate we consider the specific resistivity of cast iron near the melting point ($200 \mu\Omega$ cm), giving a voltage drop across the nanoparticle on the order of millivolts for μ A currents. This gives an internal electric field in the nanoparticle on the order of V/ μ m, similar to the applied external field. It should be admitted that this value is very approximate and expected to be an underestimate. The resistance has been estimated by the maximum value of the particle cross section. A more precise value of the electric field and its distribution inside the CNT–nanoparticle system can be obtained via the solution of the Poisson equation in the framework of the model proposed by us in this paper. However, to apply this model more data are needed and one of the aims of our paper is to draw attention to what kind of

parameters are necessary for modelling in order to obtain a better understanding of the processes taking place in CNTs during their growth.

Two further comments concerning the above estimation should be made. First of all, the assumption $\Delta n_{C^{m-}} \sim n_{C^{m-}}$ gives an upper estimation of the electric field required for ion drift to dominate over diffusion, i.e. it is likely that ion drift can play an important role at lower field strengths. Furthermore, as both drift and diffusion of negative carbon atoms are directed to the nanotube base, drift addition to diffusion may become important at considerably smaller fields. A second comment concerns the possible dependence of the drift–diffusion ratio on the nanoparticle size (10). This can lead to a catalyst-size-dependent contribution to CNT growth under otherwise similar electric field conditions.

Brief mention should be made of liquid metal behaviour under high electric fields such as used in nanotube growth experiments. Many studies are devoted to charge transport in liquid metals [44]. The applied electric field strongly influences the distribution of the concentrations of the liquid alloy components. The metal ions drift as they are subjected to the field action:

$$\mathbf{F} = q\mathbf{E} = z^* |e| \mathbf{E}. \quad (11)$$

In the case of metals the value of the effective valence z^* is usually negative, as the dominant mechanism includes momentum exchange with electrons [44]. Generally, the effective valence is not connected to the usual chemical valence and varies in the literature in the range from 0 to 564 [44]. At high electric fields, intensive charge-carrier transport causes convective flows as was already mentioned in Sect. 4.1 and predicted in [31]. Under such circumstances, the ion-diffusion coefficient should be changed to the effective coefficient $D_{\text{eff}} > D_x$ for all components of the liquid nanoparticle. This leads to further complication of the proposed model. However, if turbulent diffusion is developed in the catalyst nanoparticles as a charge-transport process under the action of the electric field, this should intensify the nanotube growth process to a considerable extent.

The model presented in Sect. 4.2 can be applied for any method of CNT growth. Even if electron emission is weak, a redistribution of the charge within the CNT–nanoparticle system can be modelled in the framework of (2)–(7). For CNT growth in an arc discharge, along with the electron and ion currents collected by the tube as a capacitor, one should consider the emissive properties of the tube. For laser-stimulated CNT growth [49], along with the occurrence of thermal-field emission, photoemission has to be taken into account under the action of laser radiation.

It should also be mentioned that the difference in the growth rates of individual CNTs in an external field, observed by Bonard et al. [50], can be explained in the context of our model. Nanotubes of different radius and length have different field enhancement factors and, thus, different emission currents. In the framework of the self-consistent equations (2)–(7), the carbon supply through the nanoparticle depends on the emission current, thus governing the growth process.

6 Conclusions

We have addressed some of the issues listed in [6] as topical in order to achieve large-scale CNT production. We directed attention to some interesting observations made by us and by other groups concerning the growth of carbon nanotubes in the presence of an electric field and considered the species and mechanisms that may be responsible for the growth. The kinetics of carbon dissolution in liquid metals has been discussed under the assumption that carbon ions gain a negative charge. The carbon supply to the growing tube through the catalyst has been considered on the basis of the drift–diffusion approach, and it has been shown that ion drift can dominate over diffusion under the action of electric fields that are estimated to be less than an order of magnitude higher in strength than external fields typically applied for aligned CNT growth. We therefore suggest that the observed growth enhancement could be greater if external fields higher than the typical V/ μ m can be applied. An electric field is seen to be important, not only for aligning carbon nanotubes dur-

ing growth, but it can also be a major parameter affecting the overall growth process and leading to the exceptionally high growth rates that have been observed by some groups. However, a number of issues still remain to be clarified and we hope that this work will stimulate more research in this area.

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