Simulation for growth of multi-walled carbon nanotubes in electric field

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Abstract

An electric field was introduced for producing multi-walled carbon nanotubes (MWCNTs) in flames and it was found that a low biased voltage was enough to synthesize well-aligned MWCNTs. Finite element method was adopted to simulate the growth of MWCNTs in electric field and calculate the electrostatic forces acting upon MWCNT itself and the catalyst particle at the MWCNT tip. The numerical results revealed that: (1) the electrostatic repulsive force induced by the similar charges of neighboring MWCNTs is strong and favorable to overcome van der Waals force, which consequently is a main factor to align MWCNTs; (2) the electrostatic attractive force along the field direction acting on the catalyst particle at MWCNT tip is much larger than that on the tube, which plays a key role for vertical growth of MWCNTs; (3) the value of the electrostatic attractive force acting on the nanotube and catalyst particle is related to height, density and diameter of MWCNTs.

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1. Introduction

Well-aligned carbon nanotubes (CNTs) exhibit excellent field emission properties and expect promising applications in flat panel displays [1]. Up to now, many methods have been developed for growing well-aligned CNTs based on variant alignment mechanisms such as “overcrowding growth” [2,3], “template hindrance growth” [4,5] and “electric field induced growth” [6–16]. Comparing to other methods, electric field induced growth has been considered to be a more effective and controllable method for producing well-aligned single-walled carbon nanotubes (SWCNTs) [6] and multi-walled carbon nanotubes (MWCNTs) [7–13].

Generally, CNTs growth controlled by electromagnetic field was more frequently discussed in processes, such as chemical vapor deposition (CVD) [6,7], plasma enhanced chemical vapor deposition (PECVD) [8–10] and arc discharge [11]. However, generally, the electric field introduced by high bias voltage (several hundreds volts) was not purposely designed for growing well-aligned MWCNTs, but for generating glow discharge or arc discharge [8–11]. It is supposed that a vertically aligned orientation was achieved in PECVD by the alignment force on MWCNTs induced by plasma sheath electric fields [12,13]. In the case of PECVD, the potential does not vary linearly as a function of distance from the electrodes, which fell mainly in the cathode region known as cathode sheath [10]. The sheath electric field near the substrate surface was much stronger than any other regions between two electrodes, which depended on many parameters such as ion current density, sheath width and ion’s charge and mass according to the Child law. That is to say, the local electric field is more likely influenced by the density and energy of ion current striking upon the MWCNTs. Different ionic species were considered by Blazek et al. [12] and Wei...
et al. [13] to perform numerical calculations of the electrostatic force on the tip of the MWCNT, which came out totally different magnitudes of local electric field and electrostatic force.

For the above reasons, a relatively simple and calm reaction environment is necessary to simulate the growth mechanism of well-aligned MWCNTs induced by an electric field. Flaming process fits these requirements with advantages, such as simple experiment set-up, convenience of applying electric field, negligible influence of flame on electric field. Recently, Merchan-Merchan et al. [14] and Xu et al. [15] showed that MWCNTs grown in flames tended to be vertically aligned on catalytic probes which was operated at floating potential mode (300 mV) or applied low voltage bias (2 V). In our previous work [16], it has been proved that the electric field generated by 25 V DC power supply not only induced growth of well-aligned MWCNTs in a good morphology on large area, but also improved MWCNT diameter uniformity and crystallinity of graphite sheets.

Recently, finite element method (FEM) has been widely and also successfully used for evaluating nanomaterials properties, such as modeling MWCNT structure and deformation [17], simulating SWCNT electrical and thermal transport [18], and studying the modulus of nanotube-reinforced polymers [19]. In the present work, based upon the previous experimental results [16], a FEM is used to model the MWCNTs growth in the electric field. In this model, the electrostatic forces acted upon the MWCNT and the catalyst particle on the MWCNT tip were investigated by treating them as two isolated but electrically conductive objects. The repulsive forces between MWCNTs were computed and analyzed for the first time, and the attractive forces along the electric field direction, which is consistent with the reports by Merchan-Merchan et al. [14] and Xu et al. [15]. We have demonstrated that the electrostatic force acting on the catalyst particles at the tips of the MWCNTs played a key role during MWCNT growth. Preliminary calculation has revealed that the electrostatic force acting upon the catalyst particles was much larger than that upon the MWCNTs, even more than 500 times at the first stage of MWCNT growth [16].

However, the knowledge concerning the growth mechanism induced by electric field is still not completely known, i.e. why does such a small bias voltage induce dramatic alignment of MWCNTs? What other factors help the alignment of MWCNTs besides the electrostatic attractive force? How do various parameters influence the electrostatic force? In the following section, model calculation is carried out to answer these questions.

### 3. Basic equations and models

Generally, in order to estimate the apex field-enhancement associated with a pointed protrusion on a flat planar surface, there are three physical models: ‘hemisphere on a plane’, ‘floating sphere at emitter-plane potential’ and ‘hemisphere on a post’. Thereinto, the ‘hemisphere on a post’ model is geometrically more realistic than the other two models [20]. In the present work, a ‘hemisphere on a post’ model was used for simulating MWCNT growth with a catalyst particle on the tip, as shown in Fig. 2. The MWCNTs and catalyst particles were defined as two contacted objects with different materials.

Actually, the local electric field changes with the well-aligned MWCNT length variation during growing. However, the MWCNT growth was simplified to be an electrostatic field problem. And a FEM program Maxwell (Maxwell 2D, Ansoft Corp.), which was widely used in engineering electromagnetic field research, was used to calculate the electric field and electrostatic forces acting upon the MWCNTs.

The basic equations used for the present electrostatic field simulation were Poisson equation and Laplace equation. The boundary value of the electrostatic field could be obtained by solving Poisson equation or Laplace equation while satisfying the given boundary conditions. The basic equation solved by Maxwell 2D electrostatic field solver was given by

$$\nabla \cdot (\varepsilon \nabla \phi) = -\rho$$  \hspace{1cm} (1)

where $\varepsilon$ is the dielectric constant, $\rho$ is the charging density and $\phi$ is scalar electric potential.

According to fundamental electromagnetics theory, the electric force of a charged conductor in an electric field can be determined by Coulomb’s law or integrating the electrostatic pressure over the conductor surface [19]. However, the charge distribution over a conductor generally is difficult to be calculation, especially for a complicated geometry. Therefore, a more convenient and applicable ‘virtual work principle’ has been used to calculate the
electric force. That is, the forces on a conductor within a system can be obtained by assuming a differential displacement of the body and computing the resulting change in the electrostatic energy of the system. The basic processes are (1) the conductors are connected with the power supply and maintain a constant voltage; (2) the electric field will be changed when the conductor has a displacement which leads to a charge/discharge phenomena between the conductor and power supply; (3) according to ‘principle of work and power’, the field energy variation is equal to the work done by external force, then, the corresponding electric force is obtained.

In the present work, the electric forces acting upon a MWCNT and catalyst particle were calculated based on the ‘virtual work principle’ by using FEM. Firstly, a unit area \( \Delta S \) was selected from the catalyst particle with a displacement \( d \) along the normal direction. Then, the electrostatic energy reduction in the system was equal to the product of energy density and unit volume \( \Delta S d l \):

\[
-dw = \frac{1}{2} E^2 \Delta S d l
\]

where \( E \) is the local electric field on the surface of catalyst particle.

Secondly, according to the “principle of work and power”, there was a relationship:

\[
-dw = \Delta F \cdot d l / n
\]

where \( n \) is unit vector along the normal direction of the particle surface.

![Fig. 1. Top view of well-aligned MWCNTs grown in electric field from ethanol flame with different biased voltages: (a) 25 V; (b) 550 V.](image-url)
The voltage of the catalyst particle maintained constant because it was connected with the power supply through MWCNT. Combining Eqs. (2) and (3), the electric force $D_F_n$ along the normal direction was given by

$$D_F_n = \frac{1}{\varepsilon_0} \frac{d\omega}{dt}$$

where $\varepsilon_0$ is the vacuum permittivity ($8.8542 \times 10^{-12}$ F/m).

Lastly, the electric force acted upon per unit area of the catalyst particle was

$$f = \frac{1}{2} \varepsilon_0 E^2 n$$

The net force in the normal $y$-direction on the catalyst particle could be determined by integrating the unit force $f$ over the hemisphere surface:

$$F_y = \int_0^{\pi/2} \int_0^d f_y = \int_0^{\pi/2} \frac{1}{2} \varepsilon_0 E^2 \cdot 2\pi r \sin \theta \cos \theta \cdot r \, d\theta = \frac{1}{2} \varepsilon_0 E^2 \pi r^2$$

$$F_x = \int_0^{\pi/2} \int_0^d f_x = \int_0^{\pi/2} \frac{1}{2} \varepsilon_0 E^2 \cdot 2\pi r \sin^2 \theta \cdot r \, d\theta = \frac{\pi}{8} \varepsilon_0 E^2 \pi r^2$$

In order to further simplify the calculation, the following hypotheses were proposed: (1) comparing with MWCNTs, the size of two electrodes was infinite large; (2) the macroscopic electric field between two electrodes was uniformly distributed and the MWCNT influence was negligible.

The boundary conditions of the model were (1) supposing conductive connection of the catalyst particles and MWCNTs with the anode, the potentials on the particle surface and MWCNTs kept in constant; (2) in order to effectively isolate the charge and voltage sources outside the model, a balloon boundary was adopted to simulate infinite solving space, and a “charge” mode was selected to match the charge in infinite far area and solving space.

4. Numerical simulations and discussion

4.1. The FEM simulation

The FEM mesh consisted of more than 10,000 triangle elements. The fine elements were assigned to the crucial regions of MWCNTs and catalyst particles, while coarser mesh was used in the other regions. Ten passes were carried out for the calculation and the target error was specified to be 1%. Generally, the energy error reached a much smaller value than the target error after 3–5 passes. Table 1 shows the convergence data at each iteration step of one sample project. The precision of the calculation was fully satisfactory for the present purposes.

4.2. Electrostatic force for a single MWCNT

For simplifying the presentation, we first consider a single MWCNT, on which the electrostatic force is only along $y$-direction. Fig. 3 shows the electrostatic forces along $y$-direction acting on a catalyst particle and MWCNT with...
diameter \( D = 20 \) nm. Obviously, the electrostatic force \( F_y \) on the particle increased linearly with the MWCNT length increasing, and however, the force on the MWCNT decreases rapidly, as shown in the inset of Fig. 3. The magnitude of the electrostatic force on the particle was about 6–9 orders larger than that on the MWCNT. For example, for an MWCNT with length of 1000 nm, the electrostatic force acting upon the particle was \( 8.38 \times 10^{-12} \) N and that upon the MWCNT was \( 1.26 \times 10^{-19} \) N.

Generally, it has been recognized that the field enhancement factor increases with the increasing length of MWCNT [12,13]. In the present case, the calculation showed that the field enhancement factor was resulted from the reinforcement of local electric field around the particle at the tip of MWCNT in contrast with a macroscopic electric field \( \sim 6.5 \times 10^2 \) V m\(^{-1}\) [16]. This was because that along with the MWCNT growth, the local electric field enhanced and charge density increased which then led to a strong ‘point effect’, which was embodied by the reinforcement of local electric field and continuously increased the charge density, and resulting in the large electrostatic force on the catalyst particle. Meanwhile, the charge density on the MWCNT surface decreased rapidly until it reached a quite small value and kept nearly constant.

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**Fig. 3.** The electrostatic attractive forces acting on single MWCNT and catalyst particle along \( y \)-direction (MWCNT diameter \( D = 20 \) nm).

**Fig. 4.** The electrostatic attractive force \( F_y \) and repulsive force \( F_x \) on two MWCNTs and catalyst particles (MWCNT diameter \( D = 20 \) nm, intertube distance \( d = 80 \) nm).
4.3. Electrostatic force for double MWCNTs

In the case of two MWCNTs, in addition to the above attractive force $F_y$, a repulsive force $F_x$ between two MWCNTs due to the similar charges on MWCNTs and particles should be taken into account \([14,16]\). Fig. 4 illustrates profiles of the electrostatic forces (including electrostatic attractive force $F_y$ and repulsive force $F_x$) acting on the catalyst particle and MWCNT with diameter $D = 20$ nm and intertube distance $d = 80$ nm. Results revealed that: (1) the relationship between electrostatic forces and MWCNT length of two MWCNTs was similar to that of single MWCNT, and the force acting on particle was also larger than that on the MWCNT, i.e. for MWCNTs with length of 1000 nm, value $F_y$ on particle was $3.97 \times 10^{-12}$ N and $F_y$ on MWCNT was $2.7 \times 10^{-15}$ N; (2) the repulsive force $F_x$ between particles was larger than that between MWCNTs, i.e. for MWCNTs with length of 1000 nm, value $F_x$ on particle was $2.39 \times 10^{-12}$ N and $F_x$ on MWCNT was $2.32 \times 10^{-13}$ N; (3) the magnitude of repulsive force $F_x$ between MWCNTs was about 1–2 orders larger than that of the attractive force $F_y$ on MWCNT. This was because according to Coulomb’s law, the electrostatic force between two point charges has inversely proportional relationship with the square of the distance. Therefore, when two MWCNTs grew within a comparatively small distance, the repulsive interaction ($F_x$) on MWCNTs was expected to be stronger than the electrostatic attractive force $F_y$ on the MWCNTs.

Similar to above single MWCNT case, the force $F_y$ on the catalyst particle was always larger than that on the MWCNT due to the field enhancement effect. However, the extra strong repulsive forces $F_x$ between two particles and MWCNTs ensure their separation and alignment \([14]\). We believed that the repulsive forces $F_x$ provided a possibility for avoiding entanglement of MWCNTs by overcoming van der Waals force and thermal vibration and then improved the growth of well-aligned MWCNTs, especially in the case of low voltage biased between the substrate and the electrode \([14,15]\). Many theoretical models...
have been developed to deal with the van der Waals interaction between MWCNTs [21–23]. The most widely used approach of the long-range dispersion interaction is described by a carbon–carbon Lennard-Jones potential $V_{cc}$ given by

$$V_{cc} = C_6/d^6 + C_{12}/d^{12},$$

where $d$ is the carbon–carbon distance, $C_6 = 20 \text{ eV Å}^6$ and $C_{12} = 2.48 \times 10^4 \text{ eV Å}^{12}$ are constants fitted to reproduce the structural properties of graphite. Roughly, it was found that the approximation of the van der Waals forces was smaller than the electrostatic repulsive force $F_x$ between two MWCNTs with diameter $D = 20 \text{ nm}$ and intertube distance $d = 80 \text{ nm}$. On the other hand, another factor that may influence the alignment of CNT by thermal vibration is also demonstrated to be negligible small by Zhang [6].

4.4. Electrostatic force for multi-MWCNTs

When a large amount of MWCNTs were considered, the ‘screen effect’ among MWCNT array could not be neglected. Fig. 5 shows the distribution of local electric field around the MWCNTs with variant amounts. It was found that: (1) a single MWCNT exhibited the largest field enhancement factor due to its sharp field distribution; (2) in case of double MWCNTs, a field screen area started to be formed between MWCNTs, as shown in blue color. (3) when the amount of MWCNTs increased to 100, a strong

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1 For interpretation of colour in Figs. 2–15, the reader is referred to the web version of this article.
‘screen effect’ was expected which then greatly weakened the local electric field around MWCNTs and the catalyst particles.

Fig. 6 illustrates the variation of electrostatic force $F_y$ on the catalyst particle versus the amount of MWCNTs. Obviously, the electrostatic force $F_y$ declined sharply with increase of MWCNTs amount due to the strong ‘screen effect’. While the MWCNTs amount exceeds 10, $F_y$ nearly kept in constant to be $2.08 \times 10^{-13}$ N for MWCNTs with length $L = 500$ nm and $2.06 \times 10^{-13}$ N for MWCNTs with length $L = 1000$ nm.

Fig. 7 gives the relationship between electrostatic force $F_y$ on MWCNT and the amount of MWCNTs. Different from the above profile for particle, there was a peak value for the electrostatic force $F_y$ ($F_{y\text{-peak}} = 1.95 \times 10^{-13}$ N for MWCNTs with length $L = 500$ nm and $F_{y\text{-peak}} = 8.31 \times 10^{-14}$ N for MWCNTs with length $L = 1000$ nm) on MWCNT at the amount around 8, and then the force $F_y$ decreased to a constant value about $2.09 \times 10^{-14}$ N when the amount exceeded 50. These results implied that the local electric field around the catalyst particles decreases faster than that around MWCNTs with MWCNT amount increased. When MWCNT amount increased to the range between 7 and 9, the local electric field around the catalyst particles decreased to a constant value. Correspondingly, the charge density on the catalyst particle reduced to the lowest level and that on MWCNT increased to the maximum value. Further increase of MWCNT amount would lead to enhance ‘screen effect’ and weaken the local electric field around MWCNTs, which resulted in decrease of charge density. Therefore, the electrostatic force $F_y$ on MWCNT was reduced continuously until it was nearly constant.

4.5. Electrostatic force during MWCNTs growth

From our previous research, the growth of well-aligned MWCNTs was primarily determined by the electrostatic force $F_y$ acting upon the catalyst particles because it was much larger than that acting upon MWCNTs [16]. Therefore, it was necessary to simulate the MWCNTs growing process in the electric field.

According to the above discussion, the electric field and electrostatic forces became stable and closed to the practical conditions when MWCNT amount was 100. Therefore,

![Fig. 9. The distribution of local electric field around MWCNTs with increasing MWCNT length (MWCNT diameter $D = 20$ nm, intertube distance $d = 80$ nm, length $L = 20$ nm, 50 nm, 100 nm, 500 nm, 1000 nm).](image9.png)

![Fig. 10. Plot of the electrostatic attractive force $F_y$ on catalyst particle as a function of intertube distance (MWCNT diameter $D = 20$ nm), evaluated for 36 different MWCNT lengths.](image10.png)
the following simulations for electrostatic force $F_y$ acting upon the catalyst particle versus MWCNT length and intertube distance were carried out in a model with 100 MWCNTs, and the ‘screen effect’ between MWCNTs was considered, which was different from the above single and double MWCNTs cases shown in Figs. 3 and 4.

Fig. 8 illustrates the relationship between the electrostatic force $F_y$ acting on catalyst particle and MWCNT length. The results showed that: (1) when the MWCNT length was less than the intertube distance, the electrostatic force $F_y$ increased rapidly with the length increasing; (2) when the MWCNT length reached and surpassed the intertube distance, the electrostatic force $F_y$ increased slowly and closed to a constant value, which is similar to the theoretic calculation in Ref. [12]. This could be explained by the local electric field distribution around MWCNTs with increasing MWCNT length, as shown in Fig. 9. That is, at the beginning of MWCNTs growth ($L < d$), the ‘screen effect’ among MWCNTs was weak and the ‘point effect’ was strong which resulted in an enhancement of the local electrical field. With MWCNT length increasing, however, when MWCNTs grew longer than the intertube distance, the field enhancement factor around MWCNT tips decreased sharply [24] and the ‘screen effect’ among MWCNTs greatly increased which then resulted in a confinement of the strong local electric field around MWCNT tips. Therefore, the influence of MWCNT length on the local electric field became smaller and the force $F_y$ increased slowly with the MWCNT length increasing [16].

In addition, Fig. 10 shows another relationship between the electrostatic force $F_y$ acting on catalyst particle and the intertube distance. It was obtained that: (1) the force $F_y$ increased with the intertube distance; (2) for MWCNT array with smaller length, the force $F_y$ increased in a slower rate than that for the longer MWCNTs; (3) for MWCNT length $L > 70$ nm, the force $F_y$ became a linear relationship with the intertube distance despite variant MWCNT lengths. This relationship is totally different from the calculation in Ref. [12], which is believed to be the result of different distribution of macroscopic electric field, that is, the potential vary linear as a function of the distance from the electrodes in our case but it does not in Ref. [12].

As discussed above, the influence of intertube distance on the force $F_y$ could also be explained using the distri-
tion of local electric field, as shown in Fig. 11, i.e. the ’screen effect’ became weaker for MWCNT array with large intertube distance.

4.6. Electrostatic force for MWCNTs with variant diameters

Generally, it is difficult to grow MWCNTs with a uniform diameter no matter what kind of synthesis method is adopted, however, which has great influence on MWCNT physical and chemical properties [25]. In this section, the simulation was focused upon the relationship between electrostatic force and MWCNT diameter during growing.

Fig. 12 shows the plot of the electrostatic attractive force $F_y$ on catalyst particle versus MWCNT length (intertube distance $d = 80$ nm), evaluated for six different MWCNT diameters. Obviously, the electrostatic attractive force $F_y$ on catalyst particle with different MWCNT diameters exhibit the similar trend as shown in Fig. 8.

Fig. 13 shows the relationship between the electrostatic repulsive force $F_x$ on catalyst particle and MWCNT and the MWCNT length and diameters. It was obtained that: (1) the repulsive forces $F_x$ on MWCNT and catalyst particle are very strong with an order of magnitude of $1.0 \times 10^{-12}$ N and both increased linearly with MWCNT length increasing; (2) for the MWCNT with the same diameter, the repulsive force $F_x$ on MWCNT is larger than that...
on catalyst particle; (3) the repulsive force $F_x$ on MWCNT with larger diameter is smaller and than that with smaller diameter, however, the repulsive force $F_x$ on catalyst particle has the opposite tendency. To sum up, we found that the electrostatic repulsive force $F_x$ acted on MWCNT and catalyst particle by the surrounding MWCNTs with the same polarity was very strong, even stronger than the attractive force along the electric field direction. This electrostatic repulsive force may be another important factor to align the MWCNTs when very low biased voltage is applied.

Fig. 14 shows that the attractive force $F_y$ on the catalyst particle expressed almost a linear variation with MWCNT diameter. In fact, the local electric field strongly depended upon the MWCNT geometry, especially, the diameter of catalyst particles, when the intertube distance and MWCNT length kept constant. Then, as the diameter increased, the area with strong local electric field became larger, as shown in Fig. 15. Therefore, if the electrostatic attractive and repulsive force acted on per unit area was the same, the whole force acted upon the catalyst particle with larger surface would be enhanced. As a result, electrostatic attractive and repulsive force acted on MWCNT would be reduced correspondingly.

5. Conclusions

The FEM provides an effective method to simulate the growth process and electrostatic forces of well-aligned MWCNTs in electric field. The calculation of the electrostatic forces acting on the nanotube and catalyst particle with variant parameters such as MWCNT length, density and diameter provides a guide for growing well-aligned MWCNTs in electric field and also a possibility for further fabricating field emission device and other applications based on well-aligned MWCNTs.

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