Selective production of metallic carbon nanotubes

Yasushi Matsunaga, Tadatsugu Hatori, Tomokazu Kato

Selective production of metallic carbon nanotubes

Yasushi Matsunaga, Tadatsugu Hatori† and Tomokazu Kato

Graduate School of Science & Engineering, Waseda University, Shinjuku-ku, Tokyo
169-8555, Japan

†Faculty of Science, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

Abstract. In this report, we discuss whether the optimal electric field to promote the
growth of armchair- type nanotubes (metallic character) evaluated using the previous
Hückel-Poisson method can be applied at the tip of a nanotube in a realistic system.
Setting the cross-section of a nanotube and the external field by the sheath, we estimate
an effective area at the sheath edge. Since the electric charge distribution in a nanotube
caused by the external electric field was determined in our previous study, we obtained
the electric field distribution out of a nanotube by solving the Poisson equation and
clarified the structure of the electric field lines. By determining the effective area,
we show the optimal interval of the catalyst metal, which is necessary to selectively
grow the metallic nanotubes. When nanotubes grow thickly during the initial stage of
growth, a strong electric field cannot be applied to the tips of the tubes. As a tube
grows and the tube length increases, we found that the optimal electric field decreased.
To maintain the chemical activity at the tip, the sheath electric field must be decreased.
We estimated the decreasing rate of the sheath field to the tube length.

1. Introduction

It is known that SWCNT (single-walled carbon nanotube) has the characteristics of
a metal or semiconductor according to the chiral angle[1]. However, the production
method controlling the chiral angle has not been established. The method of controlling
the chiral angle by the electric field and selectively producing an armchair type (metallic
character) was then investigated in our previous study[2]. The electronic states of
the π electrons are described by the Hückel method and their electric interactions
are self-consistently taken into account through the Poisson equation. The frontier
electron density at both ends of the nanotubes with open-ends was evaluated[3, 4, 5, 6].
The electric field intensity to promote the growth of the armchair-type nanotube was
found. The optimal intensity of a direct current electric field to efficiently make metallic
nanotubes is approximately 1V/nm[2].

In this study, we examined whether the imposition of this optimal electric field on
nanotubes through a sheath electric field is possible, and evaluated the interval required
to grow a long nanotube. To selectively produce a long nanotube by the electric field,
it is clear that the restriction arises at the interval of the tubes on a substrate. This

is because an effective electric field will not be applied at the tip of a nanotube if the interval of the nanotubes is too narrow. Using the electric charge distribution of a nanotube from our previous result, and solving the distribution of the electric field out of a nanotube, we estimated the interval of nanotubes required to actually apply the optimal electric field evaluated in our previous study.

In section 2, we present the calculation assumptions and some comments. The results are given in section 3. The interval R and the electric field lines are shown. In section 4, the relation between the electric charge induced by the external field and the tube length is shown. We discuss the dependence of the sheath electric field on the tube length with the change in the induced charge. We summarize this study in section 5.

2. Settings and calculation of electric field

We assumed a single-walled nanotube (SWNT) and a constant sheath electric field. We approximate the electric charge distribution of a nanotube by the distribution of the multi-rings. The axial electric charge distribution is given by our previous results using the Hückel-Poisson method[2]. We approximate the electric field distribution out of the nanotube formed by multi-rings with the electric charge by the Legendre function.

If a sheath electric field completely concentrates at the tip of a nanotube, the relation of the electric field and the surface area can be estimated to be $E_0 S_0 = E_1 S_1$ based on Gauss's law. Here, E_0 denotes the sheath electric field, S_0 denotes the area at the sheath edge, E_1 denotes the electric field at the tip of a nanotube, and S_1 denotes the cross section of a nanotube. However, because the charge induced in the nanotube influences the field lines and the electric field opposite to the sheath field occurs, $E_0 S_0 = E_1 S_1$ is not valid when the tube length is short as compared to the sheath length. When an electric charge distribution of a nanotube is given, we can calculate the area S_0 at a sheath edge. If S_0 is found, the interval of the metal catalyst patterned on a substrate is able to be theoretically estimated. That is, optimal numbers per unit area of nanotubes which can be effectively grown is found. Moreover, the dependence of S_0 on the nanotube length is evaluated. This is because the electric field on a tip of a tube changes with the tube length. We use the following notations and parameters as shown in table 1. Figure 1 shows the outline of the electric field lines out of a nanotube.

We set the origin of the coordinate (r, θ, ϕ) to the center of a nanotube, as shown in figure 1. From the symmetry of a tube, the electric field depends only on r and θ. We express the position of the ith-ring in the z direction as l_i. The electric potential caused by the charge in the ith-ring is approximated by the Legendre function using the following equation,

$$\phi_i = \frac{M_i}{r_i}(1 - \frac{1}{2}(\frac{a}{r_i})^2 P_2(\cos\theta_i)) + ..). \tag{1}$$

Here, we set $M_i = \frac{\lambda_i a}{2\epsilon_0}$, where M_i denotes the ith ring charge divided by $2\epsilon_0$ and λ_i denotes the ith charge per length. Also, r_i and θ_i are given by

$$r_i = \sqrt{r^2 + l_i^2 - 2rl_i\cos\theta}, \tag{2}$$

$$\sin \theta_i = \frac{r \sin \theta}{\sqrt{r^2 + l_i^2 - 2rl_i \cos \theta}}. \tag{3}$$

The total potential ϕ is summed to ϕ_i using the following equation,

$$\phi(r, \cos \theta) = \sum_{i=1}^{n} \phi_i(r_i, \cos \theta_i). \tag{4}$$

We calculate the electric field lines and examine whether the electric field lines at the sheath edge arrive at the tip of a nanotube. We define $R = L \tan \theta_0$, then R denotes the distance at the sheath edge from the nanotube axis as shown in figure 1. We examine R, by changing the tube length or the charge density in the nanotube. We set the initial condition at the sheath edge and calculate the following equation.

$$\frac{dr}{d\theta} = \frac{rE_r}{E_\theta}. \tag{5}$$

We write each component using the following equations,

$$E_r' = -\sum_i \frac{\partial \phi_i}{\partial r} = -\sum_i \left(\frac{\partial \phi_i}{\partial r_i} \frac{\partial r_i}{\partial r} + \frac{\partial \phi_i}{\partial \theta_i} \frac{\partial \theta_i}{\partial r} \right), \tag{6}$$

$$E_\theta' = -\frac{1}{r} \frac{\partial \phi}{\partial \theta} = -\frac{1}{r} \sum_i \frac{\partial \phi_i}{\partial \theta} = -\frac{1}{r} \sum_i \left(\frac{\partial \phi_i}{\partial r_i} \frac{\partial r_i}{\partial r} + \frac{\partial \phi_i}{\partial \theta_i} \frac{\partial \theta_i}{\partial \theta} \right), \tag{7}$$

$$E_r = E_r' - E_0 \cos \theta, \tag{8}$$

$$E_\theta = E_\theta' + E_0 \sin \theta. \tag{9}$$

E_0 denotes the sheath electric field. Each component is given by

$$\frac{\partial r_i}{\partial r} = \frac{r - l_i \cos \theta}{r_i}, \tag{10}$$

$$\frac{\partial r_i}{\partial \theta} = \frac{rl_i \sin \theta}{r_i}, \tag{11}$$

$$\frac{\partial \theta_i}{\partial r} = \frac{\pm l_i \sin \theta}{r_i^2}, \tag{12}$$

$$\frac{\partial \theta_i}{\partial \theta} = \frac{\pm r(r_i^2 \cos \theta - rl_i \sin \theta^2)}{r_i^2 (r \cos \theta - l_i)}. \tag{13}$$

3. Results

First, we show the result for two rings, as shown in figure 2. Then, m denotes the averaged π electron number per ring and the symbol M is defined by $\frac{me}{4\pi\epsilon_0}$. We dropped the ith suffix. The radius a is set to 1 nm and m is 2.3. The sheath electric field E_0 is set to 0.01 V/nm. The change of the distance R with the change in the length l is shown in table 2. As tube length l increases, R increases. However, R is not significantly changed.

Given the electric charge distribution as shown in figure 3, we calculated the electric field distribution for multi-rings. The 42 rings are used. In this case, when $l = 4.5$ nm, R is found to be 24 nm. We show the electric field line in figure 4. In the case of multi-rings, the curvature of the electric field line is smooth as compared with the two-ring

case. This is because the complex electric field opposite to the sheath electric field is caused by each ring charge.

4. Discussion

The area S_0 through the electric field lines at a sheath edge is also dependent on the charge induced by the external field. We set the area to $S_0(Q, l)$, where Q expresses the electric charge induced on the tube. According to Gauss's law, we assume $Q = \alpha E$, where α denotes the proportional constant related to the polarization. From the results of the Hückel-Poisson method, we found that the optimal electric field depends on the tube length as shown in table 3. These results will be discussed elsewhere. In this report, to simplify the interpretation, we assume $E^* l = \Delta\phi =$constant, where E^* denotes the optimal electric field to selectively grow the armchair type. We approximated the relation between the multi-ring charge and the two ring charge as follows.

$$Q = Q_s = \alpha E^* = c\frac{\alpha}{l}, \tag{14}$$

where c denotes the constant, Q_s denotes the induced total charge summed in the axial direction, i.e. $\int \rho dz$. In the two-ring calculation, Q is regarded as the charge me in the previous section.

Under the condition of equation (14), we changed the π electron number m corresponding to the induced charge Q and examined the dependence of the interval R on the length l. First, we set $m = 2.3$ and $l = 4.5$ nm. Changing m and l under the condition $ml =$constant, we obtain the dependence of R on l, as shown in table 4. The interval R is not strongly dependent on l and it weakly decreases. Using the conserving law $E_0 S_0 = E^* S_1$, where $S_0 = \pi R^2(l)$, we obtain $E_0(l) = cS_1/(lS_0(l))$, as shown in figure 5. From the result of figure 5, as the nanotube grows, fortunately, it is found that we should decrease E_0 in order to maintain the optimal field at the tip. By considering that R is not strongly dependent on l, E_0 is approximated by an inverse proportion to the length l.

5. Summary

The structure of the electric field line out of a nanotube was clarified. We found that the potential difference $\Delta\phi$ that gives the optimal electric field to grow the armchair-type nanotube is constant for the tube length. The minimum interval R to apply the optimal electric field at the tip was estimated. During the initial stage of the growth of the nanotube, a strong electric field is necessary. As a nanotube grows, the optimal electric field decreases. By controlling the sheath electric field versus time, it is possible to continue to apply the optimal electric field on the nanotube.

Acknowledgments

References

[1] S. Iijima, Nature **56**, 354 (1991).

[2] Y. Matsunaga, T Hatori and T. Kato, J. Appl. Phys. **95**,8149 (2004).

[3] K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, J. Chem. Phys. **22**, 1433 (1954).

[4] K. Fukui, Acc. Chem. Res. **4**, 57 (1971).

[5] Y. Kumeda, Y. Fukuhiro, T. Taketsugu, and T. Hirano: Chem. Phys. Lett. **333**, 29 (2001).

[6] Y. Kumeda, T. Taketsugu, and T. Hirano: Chem. Phys. Lett. **360**, 149 (2002).

Table 1. Parameters.

physical quantities	symbols	values
sheath length	L	1 μm
electric field at the sheath edge	E_0	0.01 V/nm
electric field at the tip of a nanotube	E_1	1 V/nm(l =4.5 nm)
tube length	l	4-500 nm
tube radius	a	0.35-1 nm

Table 2. The interval R versus the tube length l at the fixed charge, $m = 2.3$.

length l (nm)	R (nm)
4.5	19.7
9.0	25
13.5	28
45	37
90	39
450	51

Table 3. The range of the electric field in which the frontier electron density of the armchair type is greater than that of the zigzag type. By using the Hückel-Poisson method, the frontier electron densities at both ends of several types of tubes are calculated. The optimal value of the electric field is also shown at which the ratio of the frontier electron density of the armchair type to that of the zigzag type is maximized.

tube length l (nm)	electric field range (V/nm)	optimal electric field E^* (V/nm)
4.5	0.8-1.5	0.95
9.0	0.45-0.7	0.5
13.5	0.4-0.6	0.45

Table 4. The interval R versus the tube length l under the optimal condition of equation (14). We also changed the π electron number m. Although the interval R decreases, R is not significantly dependent on l.

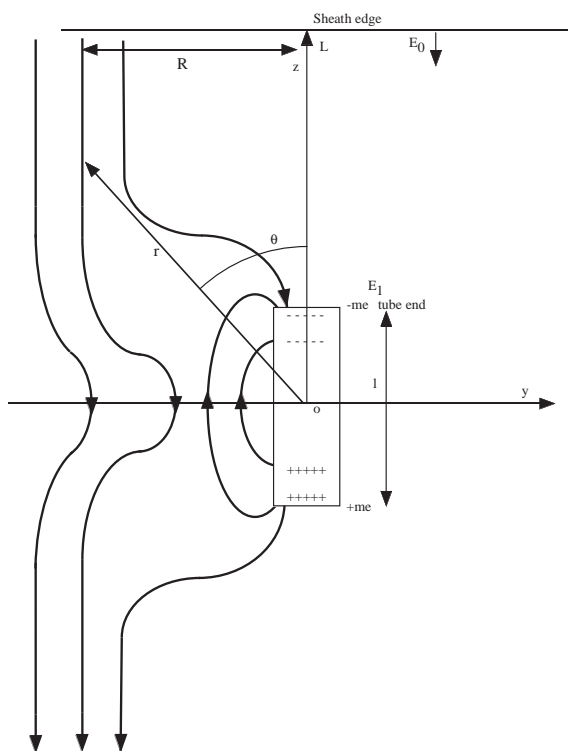| l (nm)	R (nm)
4.5	19.7
9.0	19.0
13.5	18.5
18.0	17.0
22.5	16.0
45.0	13.0

Figure 1. Outline of the electric field lines. The induced charge in the nanotube causes the reversed electric field. The zero field point exists on the y axis when the tube length is short and the external field is weak.
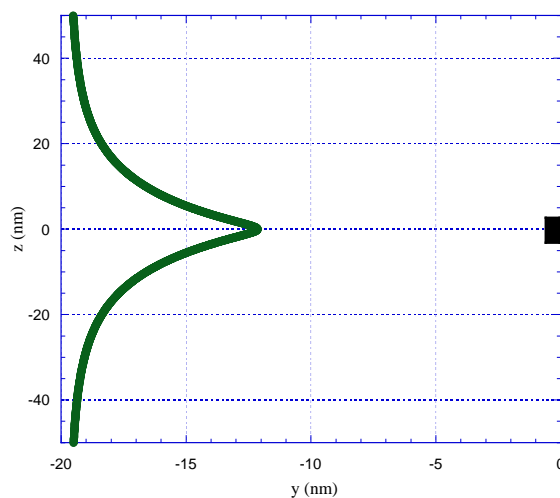

Figure 2. The electric field line for two rings. The rectangle on the right-hand side indicates the position of the nanotube.
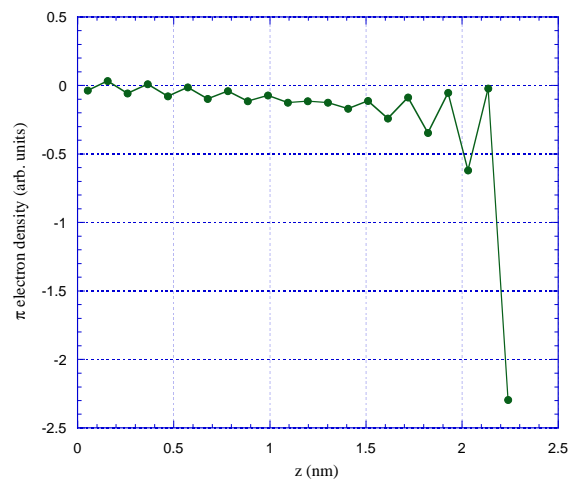
Figure 3. A typical π electron distribution in the axial position obtained using the Hückel-Poisson method.
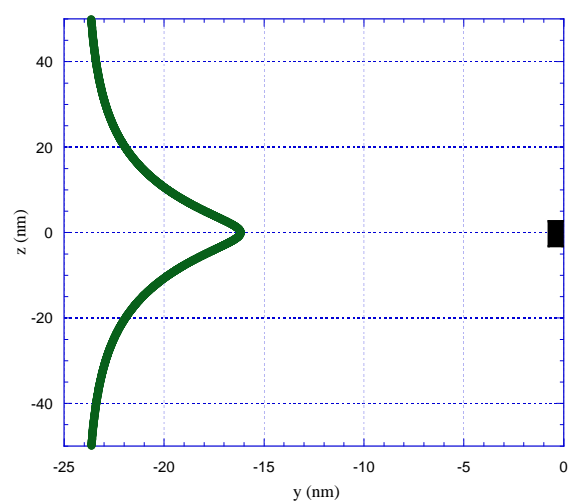

Figure 4. The electric field line for multi-rings. In correspondence with the π electron distribution of figure 3, 42 rings are used. The rectangle on the right-hand side indicates the position of the nanotube.
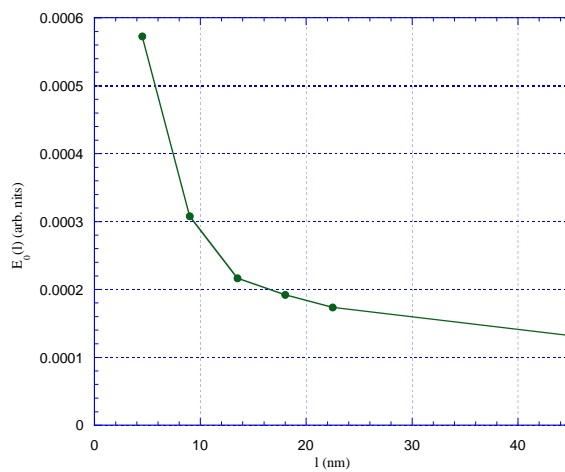
Figure 5. The sheath electric field E_0 versus the tube length l. As the nanotube grows, the optimal electric field to grow the armchair type selectively decreases. Thus, the sheath field E_0 must be decreased with the growth of the tube.