

DNA Negative Ion Irradiation toward Carbon Nanotubes in Micro Electrolyte Plasmas

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The inside modification of carbon nanotubes using DNA negative ion irradiation in electrolyte plasmas is demonstrated. In this method, a direct current electric field is applied to an electrolyte plasma containing DNA negative ions in order to irradiate DNA ions to carbon nanotubes. In addition a radio frequency electric field is superimposed to the plasma for the purpose of changing the conformation of DNA ion molecules from random-coil shape to stretched-shape. Based on analyses using transmission electron microscopy and Raman scattering spectra, DNA is found to be encapsulated in carbon nanotubes.

Key words: electrolyte plasma, carbon nanotubes, DNA, ion irradiation, transmission electron microscopy

1. INTRODUCTION

Since single-walled carbon nanotubes (SWNTs) show various characteristics, they are one of the most interesting materials for future applications. Especially, SWNT based electronic devices have potential to surpass the silicon based electronics. However, the SWNT-based FET shows only p type characteristics in general [1]. Therefore the physical and/or chemical modification of SWNTs, which can modify the electronic properties of SWNTs, is required.

The modifications of SWNTs are roughly divided into two approaches. One is outside modification [2,3]. The other is the inside modification using other functional materials [4,5]. The outside modification, i.e., intercalation of other materials between SWNT bundle, can change electronic properties of SWNTs, which does not require so complicated procedure in general. However, intercalation is inevitably beset with problems for future applications, for example, air-stability of the intercalated SWNTs is one of the most fatal issues for the realization of SWNT based electronics because the intercalated materials are exposed to the air. On the contrary, the inside modification (encapsulation of other atom and/or molecules) has different advantage, for example, functional-material encapsulated SWNTs are expected to ensure this air-stability, because the functional materials are inserted inside SWNTs and are isolated from the air.

Although the alkali metal [5], C₆₀ [6], and simple organic molecules [7] have been used as encapsulated functional materials so far, few papers which relate to the insertion of complicated molecule such as DNA into SWNTs are reported. DNA is an interesting material not only in biology but also in electronics because of their unique properties. DNA consists of four

kinds of bases, each of which has a different electronic property [8], and the base sequence has come to be easily controlled in recent years. Therefore, the control of the electronic properties in nanometer scale is possible by selecting the base sequence. In addition, the structural sensitivity of DNA molecules would be protected by the surrounding graphite wall of SWNTs.

DNA is a typical polyelectrolyte, thus they exist as negative ions in solution phase due to their phosphoric acid part. Therefore we can regard DNA solution as an electrolyte plasma. The motion of ions in the plasma can be controlled by plasma technology such as substrate bias method [4]. Since the method is useful to form encapsulated SWNTs, we adopt it in a DNA electrolyte plasma. In this method, the selective ion irradiation can be performed by changing polarity and strength of the bias.

Since the encapsulated materials can modify the electronic characteristics of SWNTs, electrically modified SWNTs can be applied to many fields. In this paper, we have demonstrated the formation of DNA encapsulated SWNTs using the substrate bias method in the electrolyte plasma. They have possibilities to be applied to electronic devices by changing base sequence in the near future.

2. EXPERIMENT

Figure 1 presents a schematic of an experimental apparatus of the DNA negative ion irradiation in the electrolyte plasma (DNA solution) in order to encapsulate DNA molecules into SWNTs [9]. In this method, ion bombardment energy is not high enough to cause structural change of SWNTs. Therefore, SWNTs are treated by heat in order to open their tips. The open-ended SWNTs (o-SWNTs) are coated onto aluminum electrodes (anode and cathode) which

are submerged in the electrolyte plasma. The distance of the two electrodes is 1 mm and the volume of the electrolyte plasma is 5 cm³. When a direct current (DC) bias voltage (V_{DC}) is applied to the anode electrode, DNA is considered to be irradiated to it because of negative charge of DNA molecules. However, DNA molecules make up the random-coiled conformation in solution by the Brownian motion, it is difficult to encapsulate DNA molecules directly into SWNTs. When a radio frequency (RF) electric field is externally applied to DNA, on the other hand, dominant dipole moment is induced along a DNA axis because of their high anisotropy, resulting in stretching DNA molecules parallel to the external electric field due to the interaction between the external field and the induced dipole [10]. In addition, this kind of ponderomotive force [11] generated by the RF electric field is supposed to work on moving the stretched and orientated DNA molecules to both the anode and the cathode. Thus, we superimpose the radio frequency voltage (V_{RF}) upon V_{DC} in order to stretch DNA molecules and irradiate them to the electrodes, as given in Fig. 1. Furthermore, in the case that the DC and/or RF electric fields are applied, SWNTs are considered to stand on the electrodes along the electric fields and the orientation of the SWNTs is expected to be perpendicular to the electrodes [10,12].

After the irradiation of the DNA ions to the anode electrode, they are adsorbed onto the aluminum-electrode surface and the adsorption is maintained semipermanently [10]. Furthermore, the aggregation of DNA is initiated at the surface by the existence of aluminum ions coming from the V_{DC} - and/or V_{RF} - applied electrodes. Therefore, the amount of the irradiated DNA molecules to the anode-electrode surface can be estimated by measuring the concentration (c) of the DNA solution after applying V_{DC} and/or V_{RF} . In this paper, single-stranded DNA is used which consist of 15 adenines. The length of this DNA is about 5 nm.

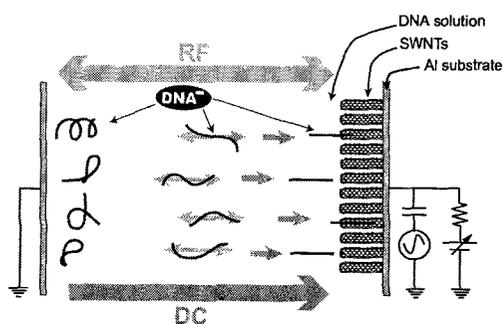


Fig. 1. Schematic of an experimental apparatus for the formation of DNA encapsulated SWNTs, where both the DC and RF electric fields can independently be applied to the electrolyte plasma (DNA solution).

3. RESULTS AND DISCUSSION

Figure 2 presents UV absorption spectra of the DNA solution, where we can find a specific absorption peak around 260 nm originating from the DNA molecules. In this experiment, only DC electric field is applied. As increasing of irradiation time (t), the absorbance is found to decrease. This phenomenon is one of the evidence of the ion irradiation. Then the concentration of the solution (c) is obtained using the normalization that the value of unity in absorbance corresponds to about $c = 35 \mu\text{g/ml}$. The time evolution of the concentration of the DNA solution with V_{DC} as a parameter is plotted in Fig. 3. It is found the concentration decreases with the irradiation time and an increase in V_{DC} . The results indicate that the DNA irradiation can be controlled by changing the strength of DC electric field and irradiation time. In the case of $V_{DC} = 10 \text{ V}$, almost all of the DNA molecules appear to be irradiated to the anode after 10 min. Based on these results, the irradiation of DNA to the o-SWNTs is performed within 10 minutes for $V_{DC} = 10 \text{ V}$.

Figure 4 shows spectra of Raman scattering

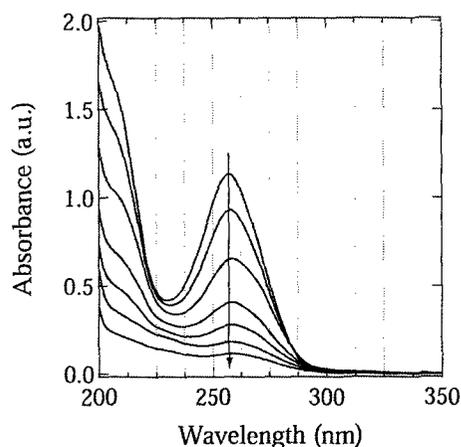


Fig. 2. Time evolution of UV absorption spectra of DNA solution. $t = 0$ -10 min. (top to bottom), $V_{DC} = 10 \text{ V}$, $V_{RF} = 10 \text{ V}$.

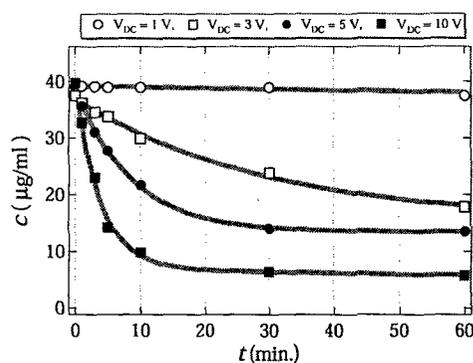


Fig. 3. Time evolution of the concentration of DNA solution with V_{DC} as a parameter.

spectroscopy in the range of the radial breathing mode (RBM) of SWNTs, which are measured by using different laser excitation energies (a) 2.54 eV and (b) 2.41 eV. The Raman spectra of SWNTs after the DNA irradiation are obtained under the dried condition after the removal of DNA attached on the surface of SWNTs by washing with water. The shape and the peak intensity of the spectra are found to be different between the cases with and without applying electric fields (indicated by dashed lines in Fig. 4), especially in the case of the excitation energy of 2.54 eV. The changes of the peak intensity in the range of the RBM are considered to be the one of the phenomena associated with interaction between DNA and carbon nanotubes. Although the effect of interaction may be very small, the signal of RBM is considered to be very sensitive

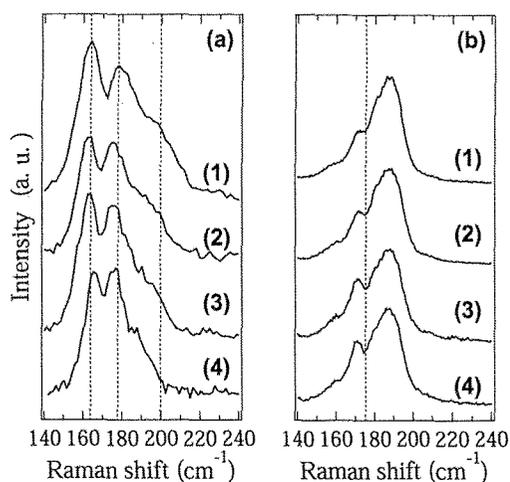


Fig. 4. Raman spectra of SWNTs after DNA negative ion irradiation. Excitation energies of laser are (a) 2.54 eV and (b) 2.41 eV, respectively. (1) w/o electric field, (2) $V_{RF} = 150$ V, (3) $V_{DC} = 10$ V, (4) $V_{DC} = 10$ V, $V_{RF} = 150$ V.

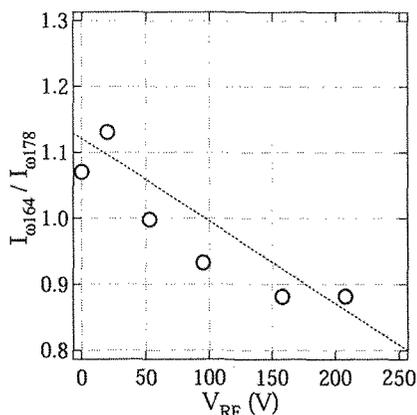


Fig. 5. The peak intensity ratio of 164 to 178 cm^{-1} in Raman spectra of SWNTs after DNA negative ion irradiation as a function of V_{RF} for $V_{DC} = 10$ V. Laser excitation energy is 2.54 eV.

to the condition of the SWNT inner region. As a result, even a slight effect of the interaction has the possibility of changing RBM, giving indirect evidence of the encapsulation of other materials inside SWNTs.

When only the DC electric field is applied, the spectra shapes become sharp (Fig. 4 (3)) and the intensity ratio of two peaks is changed compared with the case that no electric field is applied (Fig. 4 (1)). Since the DC electric field is predicted to induce the driving force enhancing the insertion of the DNA molecules as described above, such features in the Raman spectra are due to the effect of the DNA irradiation triggered by the DC field application. According to observations by transmission electron microscopy (TEM), however, the yield of DNA encapsulated SWNTs seems to be not so high under this condition.

On the other hand, an appreciable difference is recognized between the cases with and without RF electric field applied SWNTs (Fig. 4 (2)). In this situation, a part of DNA can be stretched by the RF field and inserted into SWNTs even in the absence of strong external driven force such as a DC electric field, because the length of DNA is about 5 nm and its diameter is comparatively similar to the diameter of SWNTs (1.2-1.7 nm). It is plausible that DNA can be inserted to some extent into o-SWNTs without the positive DNA irradiation, which is not inconsistent with a simulation study reported by Gao *et al.* [13]. Based on the Raman analyses, however, the yield is estimated to be quite low when only the RF electric field is applied in the absence of the DC electric field.

Furthermore in the case that both V_{DC} and V_{RF} are applied simultaneously, in other words, stretched DNA is irradiated (Fig. 4 (4)), the spectrum shape becomes sharper, for example, a hump around 200 cm^{-1} in Fig. 4 (a) disappears. In addition, we can perceive some changes in the peak intensities around 175 cm^{-1} in Fig. 4 (b) and at 164, 178 cm^{-1} in Fig. 4 (a). These results imply that the encapsulation yield of DNA into open-ended SWNTs is considerably enhanced when both the DC and RF electric fields are superimposed.

Based on the results in Fig. 4, the rate of encapsulation of DNA into SWNTs is considered to be estimated with a decrease in the peak intensity at 164 cm^{-1} compared with the peak intensity at 178 cm^{-1} . The ratio of peak intensity at 164 cm^{-1} to that at 178 cm^{-1} in the Raman spectrum is plotted as a function of V_{RF} for $V_{DC} = 10$ V in Fig. 5, where laser excitation energy is 2.54 eV. The ratio decreases with an increase in the applied RF electric field. This indicates that the stretching effect is increased. Thus, when the irradiation of DNA is performed by the DC electric field, the encapsulation ratio resultantly depends on the conformation of DNA. Therefore, effective stretch of DNA leads to the improvement of the yield of DNA encapsulated SWNTs under the constant value of V_{DC} .

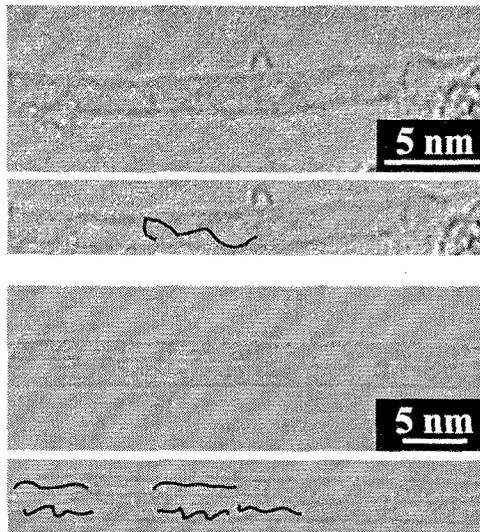


Fig. 6. HR-TEM images of SWNTs after DNA irradiation. The black lines in images indicate encapsulated materials.

The intensive observation of SWNTs undergoing the DNA irradiation is performed using HR-TEM, where the acceleration voltage is 200 kV. Figure 6 presents TEM images of SWNTs after the DNA irradiation under the condition of $V_{DC} = 10$ V and $V_{RF} = 20$ V. The 1-dimensional materials appear to be encapsulated in SWNTs, where the black lines in the images indicate the encapsulated materials. The length of the encapsulated material is about 5 nm which corresponds to that of DNA used. It is difficult to control the number of encapsulated DNA at present. Sometimes the plural number of DNA can be inserted (see bottom image). We believe that an optimized condition such as orientation of DNA and SWNTs allows high yield insertion and we can control the process in the near future using highly oriented SWNTs [14].

Since the DNA irradiation method described here utilizes the negatively charged part of DNA molecules, i.e., phosphoric acid group in the DNA molecules and the stretch of DNA molecules is caused by the interaction of the permittivity of DNA with applied external electric fields, the effectiveness of irradiation and stretch is independent of the base sequence. Therefore this formation method of DNA encapsulated SWNTs can be applied to not only specific base sequence of DNA consisting of, for example, only adenines, but also any base sequence.

4. SUMMARY

In conclusion, the DNA encapsulated SWNTs are created by applying DC and RF electric fields to the DNA solution. Based on the Raman spectroscopy and HR-TEM analyses, the

encapsulation of DNA into o-SWNTs is enhanced when both the DC and RF electric fields are simultaneously superimposed. These results lead to a claim that a process of superimposing RF electric field upon DC electric field plays a decisive role in the DNA encapsulated SWNT formation in this solution-phase procedure. The single-stranded DNA encapsulated SWNTs could have a possibility of novel electrical-modification of SWNTs.

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References

- [1] J. W. G. Wildoer, L. C. Venenma, A. G. Rinzler, R. E. Smalley, and C. Dekker, *Nature*, **391**, 59 (1998).
- [2] R. S. Lee, H. J. Kim, J. E. Fischer, A. Thess, R. E. Smalley, *Nature*, **388**, 255 (1997).
- [3] K. A. Williams, P. T. M. Veenhuizen, B. G. de la Torre, R. Eritja, C. Dekker, *Nature*, **420**, 761 (2002).
- [4] R. Hatakeyama, T. Hirata, G. -H. Jeong, *Plasma Source Sci. Technol.*, **13**, 108 (2004).
- [5] G. -H. Jeong, A. A. Frajman, R. Hatakeyama, T. Hirata, T. Yaguchi, K. Tohji, H. Mizuseki, Y. Kawazoe, *Phys. Rev. B*, **68**, 075410 (2003).
- [6] G. -H. Jeong, T. Hirata, R. Hatakeyama, K. Tohji, K. Motomiya, *Carbon*, **40**, 2247 (2002).
- [7] T. Takenobu, T. Takano, M. Shiraishi, Y. Murakami, M. Ata, H. Kataura, Y. Achiba, Y. Iwasa, *Nature Materials*, **2**, 683 (2003).
- [8] K. -H. Yoo, D. H. Ha, J. -O. Lee, J. W. Park, J. Kim, J. J. Kim, H. -Y. Lee, T. Kawai, H. -Y. Choi, *Phys. Rev. Lett.*, **87**, 198102 (2001).
- [9] T. Okada, T. Kaneko, R. Hatakeyama, and K. Tohji, *Chem. Phys. Lett.*, **417**, 289 (2005).
- [10] M. Washizu, O. Kurosawa, *IEEE Trans. Ind. Appl.*, **26**, 1165 (1990).
- [11] R. Krupke, F. Hennrich, H. B. Weber, M. M. Kappes, H. v. Lohneysen, *Nano Lett.*, **3**, 1019 (2003).
- [12] S. Suzuki, T. Yamanashi, S. Tazawa, O. Kurosawa, M. Washizu, *IEEE Trans. Ind. Appl.*, **34**, 75 (1998).
- [13] H. Gao, Y. Kong, D. Cui, C. S. Ozkan, *Nano Lett.*, **3**, 471 (2003).
- [14] T. Kato, G.-H. Jeong, T. Hirata, R. Hatakeyama, and K. Tohji, *Jpn. J. Appl. Phys.*, **43**, L1278 (2004).

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