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Creation of 1-D Novel Structure inside Single-Walled Carbon Nanotubes Using Plasma Ion Irradiation Method

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Abstract—**In order to explore novel functional nanomaterials, we have developed a new synthesis method of SWNTs encapsulating foreign elements by the bias-voltage application to SWNTs in plasmas, which contain oppositely-charged ions of different species. In contrast to pristine samples, a remarkable change of the nanotube structure is observed after the plasma-ion irradiation. The Cs encapsulation inside SWNTs is for the first time realized and the encapsulated Cs configuration is confirmed to comprise three varieties. C_{60} encapsulated SWNTs are also found to be effectively synthesized in the case of the positive bias application in the alkali-fullerene plasma. The yield on peapod formation is directly proportional to the plasma density used. In the end, it is noteworthy that our unique experimental approach is a good candidate for the creation of novel-functional nanomaterials.**

Keywords—Single-walled carbon nanotubes (SWNTs); plasma ion irrradiation; 1-D encapsulation; novel-structured SWNTs

I. INTRODUCTION

Single-walled carbon nanotubes (SWNTs) [1], which are formed by rolled graphene sheets, are a subject of intensive investigation as a novel type of nano-structured materials due to their profound condensed physics originated from the 1-dimensional structural uniqueness, and potential applications to many fields. Especially, it is very attractive that intrinsic electronic and mechanical properties of carbon nanotubes can be controlled by introduction of various foreign atoms, molecules, and their derivatives [2-4]. For example, the recent report has presented the possibility of nano-scale electronic device for the case of intercalation of a (alkali metal / halogen element) junction inside the SWNTs [5]. In order to realize 1-dimensional novel structure mentioned above, we attempt to perform an original approach of ion irradiation using different-polarity ion plasmas [6], where various kinds of atoms, molecules or their combinations can be selectively encapsulated within carbon nanotubes. Here, we present the validity of our plasma method and report the successful formation of the SWNTs encapsulating alkali metals as well as fullerene molecules. Furthermore, we demonstrate the evident effect of alternative Cs/C_{60} ions irradiation on SWNTs, which for the first time realizes the encapsulation of a Cs/C_{60} junction inside the SWNT.

II. EXPERIMENTAL DETAILS

SWNTs prepared by an arc discharge method were used in this study. The SWNTs purified by HIDE method [7] was dispersed by brief sonication in ethanol. Then, droplets of this suspension were dripped and dried on stainless steel substrates (15 mm × 15 mm). The substrate is immersed in a magnetized plasma column (B = 0.2 T) as shown in Fig. 1. The low-temperature plasma is produced by surface contact ionization of alkali metals (Li, Na, K or Cs) on a hot tungsten plate (2.0 cm diameter) under the background pressure of $(1 \sim 3) \times 10^{-6}$ Torr and flows toward an endplate situated at a distance of 60 cm from the hot plate. The density and electron temperature of this alkali-metal plasma ($Li^+ - e^-$, $Na^+ - e^-$, $K^+ - e^-$ or $Cs^+ - e^-$) are measured to be $1 \times 10^9 \sim 10^{10}$ cm^{-3} and about 0.2 eV ($\geq$ positive-ion temperature) by a Langmuir probe, respectively. When the temperature of an oven filled with C_{60} powder (MTR Ltd., high purity of 99.5+%) is raised up to 400 °C, which is installed inside a side hole of a hot (~ 450 °C) copper cylinder (6.0 cm diameter, 20 cm length) situated near the tungsten plate, attachment of electrons to sublimed C_{60} molecules ($C_{60} + e^- \rightarrow C_{60}^-$) takes place in the alkali-metal plasma due to relatively high electron affinity of C_{60} ($\approx$ 2.65 eV). Finally, an alkali-fullerene plasma ($Li^+ - C_{60}^-$, $Na^+ - C_{60}^-$, $K^+ - C_{60}^-$ or $Cs^+ - C_{60}^-$)

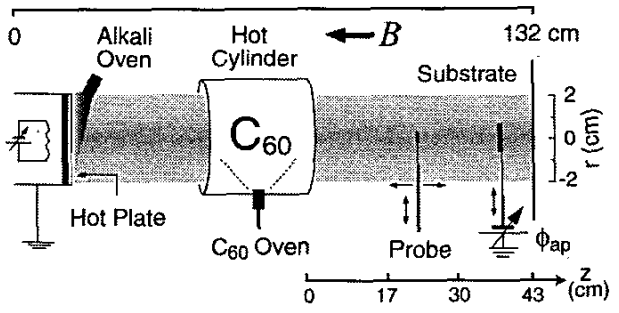

Figure 1. Schematic illustration of experimental setup.

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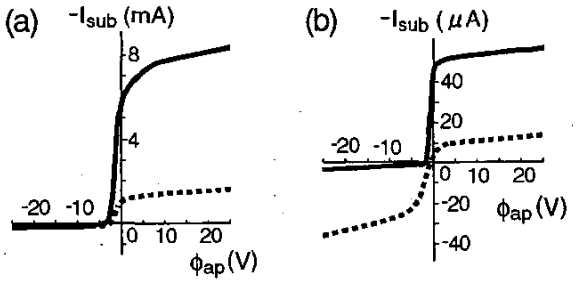

Figure 2. Typical substrate current-voltage characteristics obtained in the (a) plasma core region ($|r| = 0$ cm) and (b) its periphery region ($|r| = 1.5$ cm). Black lines correspond to the case of alkali-metal plasma and dotted lines correspond to the case of alkali-fullerene plasma.

with a very small fraction of the electron density is generated downstream from the hot cylinder region. Fig. 2 presents typical current (I_{sub}) - voltage characteristics of the substrate, to which DC bias voltages (φ_{ap}) are applied with respect to the grounded hot plate. In comparison with the case of the alkali-metal plasma (black lines), the negative-saturation current of the characteristic apparently decreases around the plasma core region (Fig. 2(a), $|r| = 0$ cm), but the positive-saturation current highly increases in the periphery region (Fig. 2(b), $|r| = 1.5$ cm) in the case of the alkali-fullerene plasma (Dotted lines). This result indicates that the alkali-fullerene plasma is radially diffused in the axial magnetic field due to large Larmor radii, r_L (= $mv_\perp / eB$; m : ion mass, $v_\perp$: ion velocity perpendicular to B, e : electron charge and B : magnetic field), of C_{60} negative ions ($r_L = 4.65$ mm) with the mass much larger than that of alkali-metal positive ions ($r_L = 0.85$, 1.54, 2.01, and 3.71 mm for Li, Na, K, and Cs, respectively), being almost electron-free in the periphery region. Thus, positively-charged and negatively-charged particles are substantially accelerated by sheaths in front of the substrate for $\varphi_{ap} < 0$ and $\varphi_{ap} > 0$, respectively, flowing into the SWNT bundles. All plasma-ion irradiation experiments are performed for 1 hour. Field emission gun transmission electron microscopy (FE-TEM, Hitachi HF-2000) operated at 200 kV and having a point-to-point resolution of 0.23 nm is used for the structural characterization of SWNTs. Energy dispersive X-ray spectrometry (EDS, Noran Instruments) is also utilized for the chemical element detection. Purified and ion irradiated SWNTs are also characterized by Raman scattering spectroscopy (Jovin Yvon T-64000) using Ar ion laser at a wavelength of 488 nm. In case of the Cs irradiation, Z-contrast technique by scanning TEM (STEM, Hitachi HD-2000), which is capable of chemical elements mapping under the nanometer-scale, is adopted for the purpose of Cs confirmation.

III. RESULTS AND DISCUSSION

A. Alkali metal encapsulation inside SWNTs

When the positive bias ($\varphi_{ap} > 0$) is applied to the substrate covered with the dispersed SWNT bundles in the alkali-metal plasma, no appreciable structural change is observed in the FE-TEM image. This means that the plasma-electron irradiation to the SWNT bundles is of no effect on its morphology. On the other hand, when the deeply negative bias ($\varphi_{ap} < 0$) is applied to

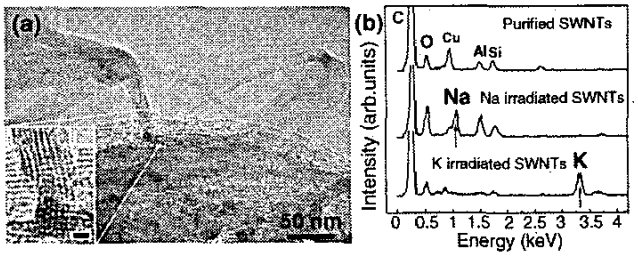

Figure 3. (a) Representative FE-TEM image showing the structural deformed SWNTs irradiated by φ_{ap} = - 300 V in Na - C_{60} plasma. Inset in (a) shows a magnified image of tube cut region and scale bar is 4 nm. (b) Comparison of EDS spectra recorded from the purified- (upper), Na^+ irradiated- (middle) and K^+ irradiated- (lower) SWNTs.

the substrate, the extremely deformed SWNTs are clearly observed. Fig. 3(a) taken from the specimen irradiated with the application of - 300 V in the Na-fullerene plasma shows heavily deflected SWNT bundles. Especially, the inset, magnified cross-sectioned area designated by white dotted lines, well presents an open end due to cutting of the tube bundle. Each small circle in the bundle corresponds to the cross-section of an individual tube with a diameter ~ 1.4 nm. The similar features such as tube deflection or tube cutting are evidently different from the original morphology observed. Moreover, this change of the nanotube structure is enhanced with an increase in the acceleration energy of positive alkali-metal ions (- 300 V < φ_{ap} < 0).

According to EDS results as shown in Fig. 3(b), alkali metals are confirmed to be well doped in the SWNT bundles in both the sodium (middle) and potassium (lower) plasmas, where a result of the sample before the plasma ion irradiation (upper) is also compared. At this stage, however, it is impossible to determine whether the alkali elements are encapsulated inside the SWNTs or not. Therefore, Cs is selected as dopant because of its large diameter (~ 0.33 nm) and heavier weight as compared to other alkali metals. The latter is advantageous to make the dopants easier to be detected by STEM technique, while the former is beneficial for doping only through the open end (not via the tube wall) and for the stability of a junction configuration.

Although many attempts have so far been challenged to identify encapsulated materials inside the SWNTs, successful results reported are few. Z-contrast technique by STEM is very useful for characterizing chemical elements spatial distribution at the atomic scale. Fan *et al.* have recently reported that iodine atoms intercalated by capillary wetting method inside SWNTs are encapsulated in the form of helical chains [8]. It is generally known that large contrast differences in Z-contrast image are originated from the intensity differences of high-angle scattered electrons, which are proportional to the square of atomic number (for instance, C = 6 and Cs = 55 in our case).

Fig. 4 clearly reveals the difference between the outside adsorption and the inside encapsulation of Cs. Fig. 4(a) shows the thin bundle composed of 2-3 individual nanotubes, which illuminate very brightly due to Cs presence in Fig. 4(b), bridging 2 thick bundles. Arrows in Figs. 4(c) and 4(d) designate the junction point between hollow (left-side) and Cs filled (right-side) regions of the SWNT. These figures imply a

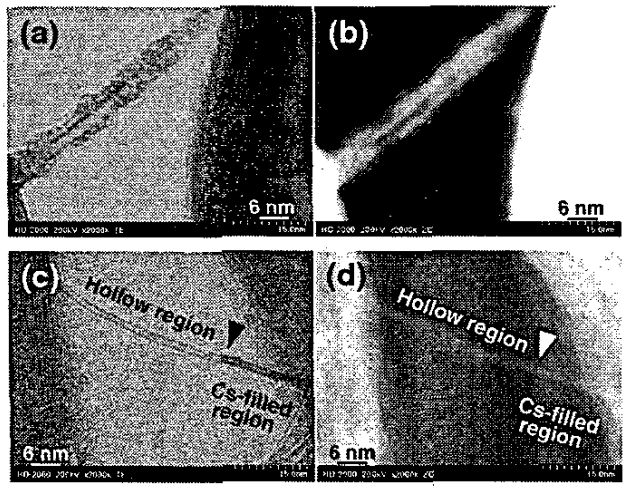

Figure 4. (a) Bright-field STEM image of Cs adsorbed SWNTs. (b) Z-contrast image corresponding to (a). (c) Bright-field STEM image of Cs filling inside individual nanotube. (d) Z-contrast image corresponding to (c).

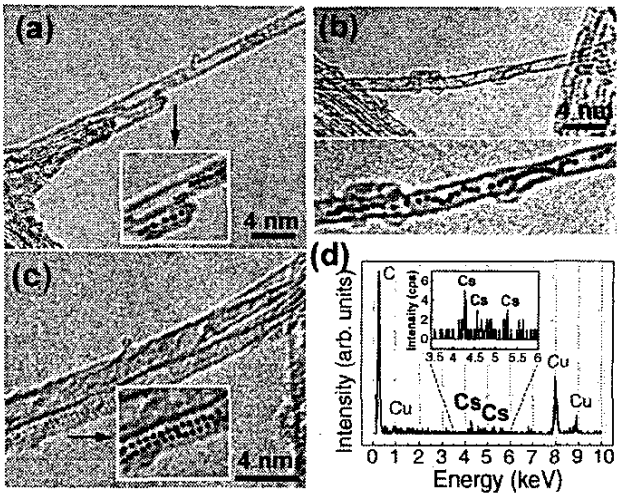

Figure 5. High resolved FE-TEM images and EDS spectrum obtained from the samples treated with the φ_{ap} = -100 V in the Cs plasma. (a) Linear configuration of intercalated Cs. Inset underlines the intercalated Cs by dotting with black circle. (b) Helical shape of encapsulated Cs inside the individual nanotube bridging two bundles. Upper image is original and bottom is marked image by dotting Cs trace. (c) Lower tube is partially intercalated and presumably crystallized. Inset emphasizes the crystallization of Cs. (d) EDS result recorded from very thin bundles, each of which is composed of 4-5 individual tubes, reveals the Cs existence.

very important fact that Cs ions can not enter the nanotube presumably through the side-wall defect, although side-wall diffusion is predicted both experimentally and theoretically in the case of Li which has small diameter compared with that of Cs or the hexagonal ring of the tube. If the side-wall defects such as a '5-7 defect' which would be produced by the bombardment of numerous Cs ions act as a window for intercalation, we cannot explain how this local filling takes place. In other words, if Cs is only attached to the exterior of individual nanotube, it is very hard to consider why Cs does not distribute uniformly over the entire tube. From these reasons, we finally conclude that the Cs intercalation takes place via opened ends which are considered to be caused by momentum transfer from impact Cs ions to SWNTs.

Fig. 5 gives high resolved FE-TEM images and EDS spectrum obtained from the samples treated with φ_{ap} = - 100 V in the Cs plasma. The linear and spiral configurations of intercalated Cs are clearly shown in Figs. 5(a) and 5(b), respectively. The inset in Fig. 5(a) stresses the intercalated Cs by dotting with black circles and the bottom image in Fig. 5(b) is also marked by dotting for a spiral chain of intercalated Cs inside the individual nanotube bridging two nanotube bundles. A helix configuration of intercalants inside the SWNTs is recently predicted in the case of iodine intercalation by capillary filling method [8]. In Fig. 5(c), on the other hand, we can find 2 or 3 individual nanotubes combined each other by Van der Waals attraction. Although the upper tube looks vacant, the lower tube is observed to be partially intercalated and, presumably, crystallized. The inset especially reveals the regularly located 2 rows of Cs. As for the Cs intercalation inside the (10, 10) nanotube, the Cs crystallization is basically possible according to their diameter comparison. The diameter of the (10, 10) tube is generally known to be about 13.6 Å and π electron-cloud thickness is considered to be 1.7 Å. Therefore, the inner space of the (10, 10) tube is approximately 10.2 Å as a diameter [9]. Judging from this structural comparison, there remains still room of 3.52 Å between 2 rows of Cs having the 3.34 Å diameter. Strictly speaking, the accurate encapsulation site of Cs has to be determined on the basis of the comprehensive understanding of the detail of interaction energy between the tube wall and intercalant, which is governed by the competition between Van der Waals and coulomb forces. Concerning this point about Cs encapsulation, some results will be published in elsewhere [10]. In any case, the result well indicates the existence of Cs in the irradiated SWNTs, as shown in Fig. 5(d). Here, in order to obtain an accurate compositional information from a localized and isolated SWNT bundle composed of 4 ~ 5 individual tubes, the electron beam size is compressed (~ 5 nm diameter) in the EDS analysis, which inevitably yields a relatively weak intensity of the Cs spectrum-peak.

B. Fullerene encapsulation inside SWNTs

When the alkali-fullerene plasma instead of the alkali-metal plasma is used, on the other hand, more drastic changes of the SWNTs are observed as demonstrated in FE-TEM images of Figs. 6(a) and 6(c), which are obtained from the samples treated in the range of the positive-bias application (φ_{ap} = 5 ~ 20 V) in the alkali-fullerene plasma. From these images, we can clearly find the isolated SWNTs containing a self-assembled or set of fullerene molecules as well as modified morphology. The production rate of this material is about 60 ~ 70 % in the case of plasma density 10^{10} cm^{-3} as shown in Fig. 6(b). The encapsulation yield is estimated on the basis of the length of encapsulated parts to the total length of clearly visible nanotubes in the high resolved image taken by FE-TEM. The encapsulation yield is found to obviously increase with increasing the plasma density because higher plasma density means increased irradiation ion-flux, which may be crucial in the enhancement of the encapsulation rate.

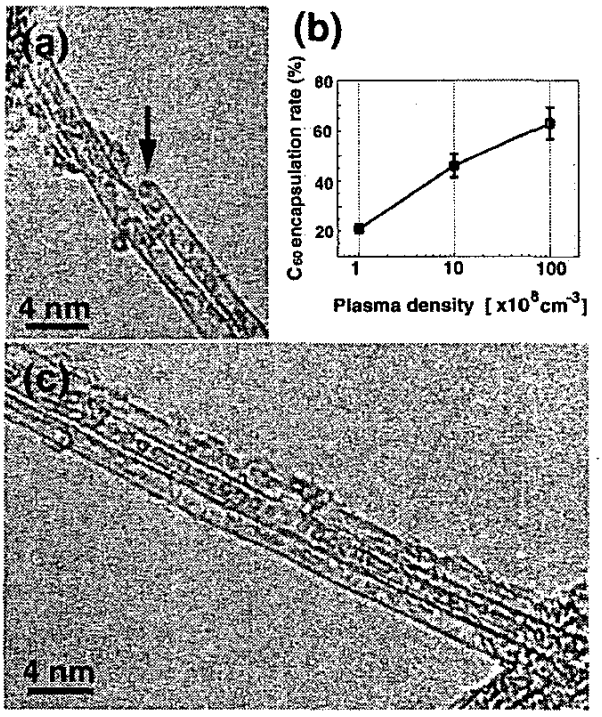

Figure 6. (a) High resolved FE-TEM image showing the fullerenes are incorporated through its open end (black arrow). (b) The quantitative relationship between alkali-fullerene plasma density and C_{60} encapsulation yield. (c) Completely filled nanotubes by close-packed fullerenes.

Fig. 6(a) gives a direct evidence that the fullerenes are well intercalated, presumably through the open end of the SWNT as indicated by a black arrow. These features are evidently due to the accelerated C_{60}^- impact toward the SWNT bundles because such a FE-TEM image is never observed for the positive-bias application in the alkali-metal plasma. We confidently anticipate that these modified SWNT structures contribute to yielding an enhanced encapsulation of various intercalants inside the SWNTs. Because the C_{60} molecules having the diameter of 0.7 nm are separated from the SWNT walls by a van der Waals distance of ~ 0.35 nm, the geometry of spheroidal C_{60} molecules are known to be the most suitable structure for encapsulation into general (10,10) SWNTs having the diameter of ~ 1.4 nm [9]. Fig. 6 (c), which presents frequently observed features in this study, gives a decisive evidence that the fullerenes are well encapsulated in the case of plasma ion irradiation method.

C. SWNTs encapsulating Cs/C_{60} junction structure

We have finally performed an experiment of bias application with instantaneous polarity change between positive and negative values in the Cs-fullerene plasma (φ_{ap} = 20 V/ 30 min. and φ_{ap} = -100 V/ 30 min.), which allows the alternative irradiation of both C_{60}^- ions and Cs^+ ions to the same sample, respectively. As a result of elaborate FE-TEM and EDS analyses, the SWNT actually encapsulates a junction of electron-donor Cs atoms on one side and electron-acceptor C_{60} molecules on the other (not shown here). At present, we do not yet know whether this junction system really reveals the electronic non-linear property as theoretically predicted in the similar system [5], and it is needed to establish an optimal synthesis condition. However, it is eminently worthy to note that our results show a high feasibility of the creation of this novel-functional nano-material in near future.

IV. CONCLUSIONS

We have demonstrated a new synthesis method of SWNTs encapsulating foreign atoms by the bias-voltage application to SWNTs in plasmas, which contain oppositely-charged ions of different species. In contrast to purified samples, a remarkable change of the nanotube structure is observed after the plasma-ion irradiation. The Cs encapsulation are for the first time realized by ion irradiation to SWNTs and the encapsulated Cs configuration is confirmed to comprise three varieties by FE-TEM and STEM observation. C_{60} encapsulated SWNTs are also found to be effectively synthesized in the case of the positive bias application in the alkali-fullerene plasma. Furthermore, it is noteworthy that we have directly verified the existence of 'Cs/C_{60}' junction structure encapsulated SWNTs, which are synthesized successfully by means of the bias application with prompt polarity change in the Cs^+ - C_{60}^- plasma.

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