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Structural deformation of single-walled carbon nanotubes and fullerene encapsulation due to magnetized-plasma ion irradiation

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Positive and negative bias-voltages are applied to single-walled carbon nanotubes (SWNTs) in magnetized alkali–metal and alkali–fullerene plasmas. When accelerated ions are irradiated to the SWNTs through plasma sheaths, drastic structural deformations such as deflection and tube cutting of the SWNTs are observed to take place. Furthermore, this phenomenon is found to be accompanied by the fullerene encapsulation inside the SWNTs in the case of the positive-bias application in the alkali–fullerene plasma, giving the possibility that various kinds of atoms and molecules can effectively be intercalated by our plasma method. [DOI: 10.1063/1.1427744]

Because of their unique properties and substantial potentials for the application in various fields, carbon nanotubes[1] have attracted much interest and been actively studied. In particular, research, which is related to the development of functional materials such as single-walled carbon nanotubes (SWNTs) encapsulating various elements[2–6] or molecules,[7,8] has very rapidly progressed in recent years. However, prevailing methods pertaining to these hybrid-structured SWNTs production have been based on thermal vapor-phase reactions. Namely, most of the experiments have been performed at relatively high temperatures ($\gtrsim$400 °C). Moreover, a lot of time including pretreatment such as the oxidation process is essentially required. Therefore, one can feel the necessity of any other convenient and more controllable method, where various kinds of atoms, molecules, or their combinations such as alkali–halogen, alkali–fullerene, etc. can be selectively encapsulated inside SWNTs.

Actually, we have produced several endohedral metallofullerenes[9] using plasmas that consist of positive alkali–metal ions, negative fullerene ions, and residual electrons.[10] As a development of this work our concern is here focused on the formation of functional SWNTs such as N–P doped nanotubes, which are expected to show nonlinear electronic properties according to the recent theoretical simulation.[11] In this letter, we report results of bias-voltage application to SWNTs immersed in magnetized plasmas, which contain oppositely charged ions of different species, demonstrating an effectiveness of our method of the plasma-ion irradiation to SWNTs for the purpose mentioned above.

SWNTs used in this study were synthesized by an electric arc discharge method. The raw material was purified by the HIDE method[12] and dispersed by brief sonication in ethanol. Then, specimens were prepared by deposition and drying of dispersed SWNT droplets on stainless steel substrates ($15\,\mathrm{mm}\times 15\,\mathrm{mm}$) by a pipette. The substrate is immersed in a magnetized plasma column ($B=0.3$ T) as shown in Fig. 1(a). The low-temperature plasma is produced by surface contact ionization of alkali metals (Li, Na, or K) on a hot 2.0 cm diam tungsten plate under the background pressure of $(1-3)\times 10^{-6}$ 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^-, or K^+-e^-) are measured to be $(1-5)\times 10^9\ \mathrm{cm}^{-3}$ and about 0.2 eV ($\gtrsim$positive-ion temperature) by a Langmuir probe, respectively. When the temperature of an

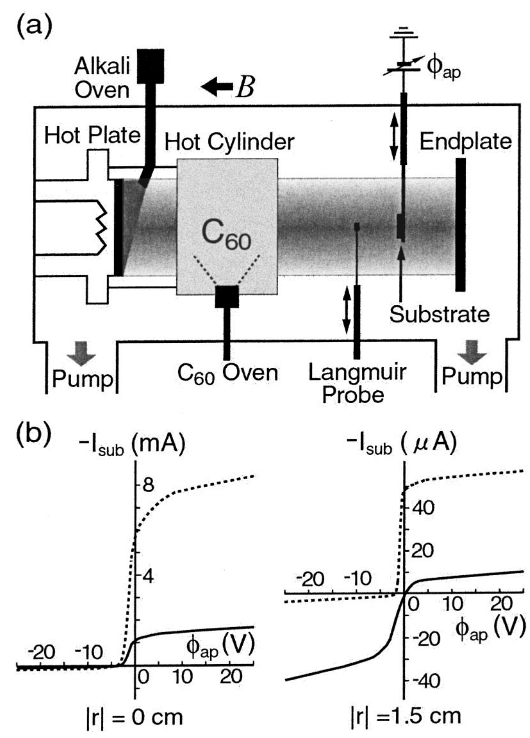

FIG. 1. (a) Schematic diagram of the experimental unit. (b) Typical substrate current–voltage characteristics obtained in the plasma core region ($|r|=0$ cm) and its periphery region ($|r|=1.5$ cm). Dotted and solid lines correspond to the cases of the alkali–metal and alkali–fullerene plasmas, respectively.

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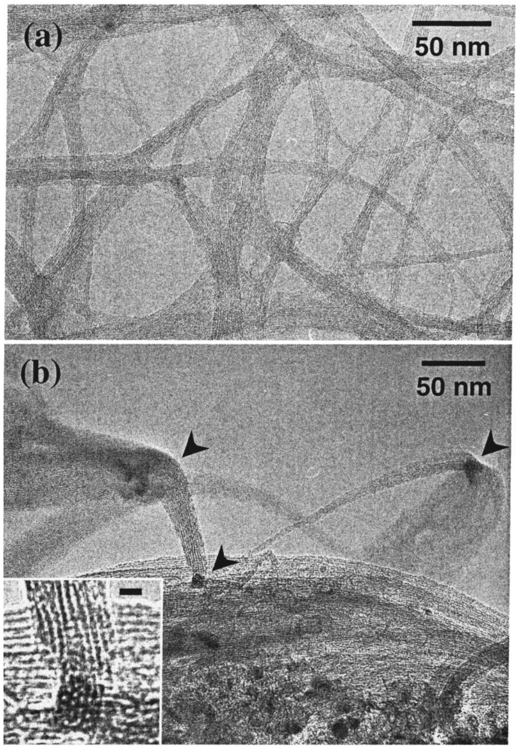

FIG. 2. Typical TEM images showing the morphology difference between before and after plasma irradiation. (a) Purified SWNTs and SWNTs irradiated by plasma electrons ($\phi_{ap}=50$ V). (b) SWNTs irradiated by ions in the alkali–metal plasma ($\phi_{ap}=-300$ V). Arrows indicate extremely deformed structures such as deflection and tube cutting. The inset in (b) gives a magnified image of tube cut region (scale bar is 5 nm).

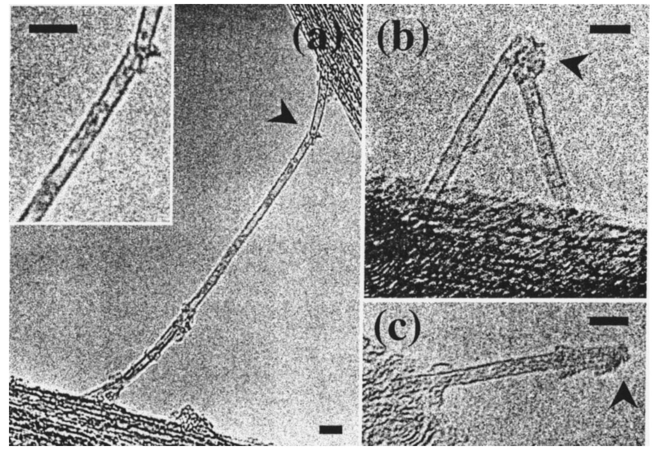

FIG. 3. TEM images obtained from the samples treated with the (a) $\phi_{ap}=10$, (b) $\phi_{ap}=20$ V in Li–C_{60} plasma, and (c) $\phi_{ap}=20$ V in Na–C_{60} plasma. Scale bar is 4 nm.

oven filled with C_{60} particles is raised 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} (≈2.65 eV). Finally, an alkali–fullerene plasma ($Li^+-C_{60}^-$, $Na^+-C_{60}^-$, or $K^+-C_{60}^-$) is generated downstream from the hot cylinder region.[10]

Figure 1(b) shows 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 the case of the alkali–fullerene plasma the negative-saturation current of the characteristic apparently decreases around the plasma core region ($|r|=0$ cm), but the positive-saturation current highly increases in the periphery region ($|r|=1.5$ cm) in comparison with the case of the alkali–metal plasma. This result indicates that the alkali–fullerene plasma is radially diffused due to large Larmor radii of C_{60}^- ions, being almost electron free in the periphery region. Thus, positively and negatively charged particles are substantially accelerated by sheaths in front of the substrate for $\phi_{ap}<0$ and $\phi_{ap}>0$, respectively, flowing into the SWNT bundles. Such a plasma irradiation is performed for 1 h. After the treatment, the SWNTs are characterized by field emission gun transmission electron microscopy (TEM) at 200 kV (Hitachi HF-2000) and energy dispersive x-ray spectrometry.

Although it has been reported that the ultrasonic treatment for SWNTs purification[13] and electron beam damage during TEM observation[14] induce a considerable amount of structural defects on the nanotubes, any deformation is confirmed not to be found in our purified original sample, as shown in Fig. 2(a). The purified SWNTs are uniformly distributed in the form of bundles. When the positive bias ($\phi_{ap}>0$) is applied to the substrate covered with the dispersed SWNT bundles in the alkali–metal plasma, no appreciable change is observed in the TEM image. This means that the electron irradiation to the SWNT bundle has no effect on its morphology. When the deeply negative bias ($\phi_{ap}<0$) is applied to the substrate, on the other hand, the extremely deformed SWNTs are clearly observed in the TEM image, as presented in Fig. 2(b). On that point, it is plausible that the perspective of the image during observation could underline the curvature of SWNT bundles. In order to clarify this ambiguity, we have repeatedly analyzed a variety of specimens and surely obtained the essential images showing SWNTs highly curved and deformed due to the plasma-ion irradiation. Moreover, this change of the nanotube morphology [the degree of deflection or tube cutting denoted by arrows in Fig. 2(b)] is enhanced with an increase in the acceleration energy of positive alkali–metal ions ($-500\ \mathrm{V}<\phi_{ap}<0$). Roughly speaking, the threshold values for the SWNTs structure deformation appear to be on the order of 10 and −100 V for the cases of the positive- and negative-bias applications, respectively. However, their details are under investigation and the quantitative results will be published elsewhere. The inset in Fig. 2(b) exhibits a magnified image of a typical triangular closed-packed structure presumably caused by tube cutting. Generally speaking, such a cross-sectional image can also be taken when an electron beam of the TEM is aligned with the bundle axis. In our case, however, the structure of the cross-sectioned image is much more clearcut and discontinuous. In particular, some of the tubes within the same bundle are clearly shown to be terminated, forming open-ended structures. In general, structural deformations of SWNTs have been thought to be undesirable because they may change their intrinsic properties. However, some recent results relating to structure manipulation are reported[15–17] because controllable structure modification may be useful in certain applications such as hydrogen storage, lithium ion battery, and hybrid structured SWNTs formation.

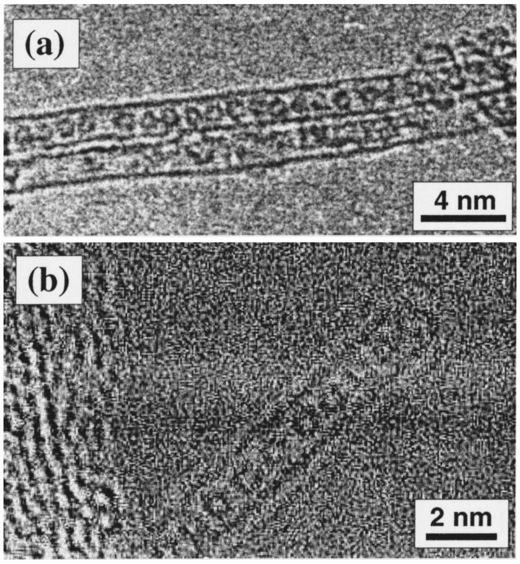

FIG. 4. TEM images obtained from the samples treated with: (a) $\phi_{ap} = 5$ V in Na–C_{60} plasma and (b) $\phi_{ap} = 20$ V in Li–C_{60} plasma. Fullerenes are well encapsulated inside the SWNTs.

Since the strong electric field parallel to the magnetic-field lines is formed in the plasma–sheath region just in front of the biased substrate, SWNT bundles would be oriented elastically in the direction of the electric field due to the concentration of induced charges at the apex of the SWNT bundles. Recently, using such an electrostatic deflection phenomenon Poncharal *et al.* demonstrated the physical and mechanical properties of individual tubes.[18] Furthermore, in our plasma system numerous charged ions with accelerated velocities simultaneously bombard the aligned SWNT bundles from the side direction because of their large Larmor radii compared with the bundle diameters, possibly resulting in the irreversible deformation as described in Fig. 2(b).

According to the above-mentioned scenario the positive-bias application in the alkali–fullerene plasma is conjectured to further enhance the structure deformation of the SWNTs because the momentum transfer from ions to SWNT bundles is proportional to the root of ion mass for a fixed ϕ_{ap}. This prediction is clearly demonstrated in Fig. 3, where a kink (a), sharp break (b), and perfect split (c) of SWNTs are observed under the condition of the positive-bias application in the alkali–fullerene plasmas. The absolute value of ϕ_{ap} for the SWNT deformation in the case of the alkali–fullerene plasma is much smaller ($\phi_{ap} \sim 10$ V, Fig. 3) than that in the alkali–metal plasma [$\phi_{ap} < -100$ V, Fig. 2(b)]. Considering the diameter difference between the fullerene C_{60} (~ 0.71 nm) and six-membered ring (~ 0.25 nm) of the carbon nanotube, C_{60}^- ions can be inserted inside the SWNT from its cut region when an open end is not plugged but persists during the plasma-ion irradiation. Figure 4 presents typical TEM images of the isolated SWNTs encapsulating a self-assembled or set of fullerene molecules. Thus, the encapsulation result in our experiment is considered to originate from the accelerated C_{60}^- impact on the SWNT bundles because such a TEM image is never observed in the case of the alkali–metal plasma, where it is impossible to directly observe alkali–metal atoms inside the SWNTs by the present TEM method. We think these modified SWNT structures may contribute to yield an enhanced encapsulation of intercalants inside the SWNTs. More work not only to search for optimal intercalation conditions but also to precisely analyze our products is under investigation.

In summary, structural deformations such as deflection, tube cutting, and tip termination of the SWNTs are clearly observed when ions are irradiated to SWNTs bundles by means of bias-voltage application in magnetized alkali–metal and alkali–fullerene plasmas. Since C_{60} encapsulated SWNTs are also found to be effectively synthesized in the case of the positive bias application in the alkali–fullerene plasma, our unique approach could have a great potential and high feasibility for the realization of new functional carbon nanotubes.

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