Controllable Fullerene-Encapsulation Inside Various Kinds of Carbon Nanotubes Using Different-Polarity Ion Plasmas

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As a new form of carbon allotropes, fullerenes and carbon nanotubes have considerably attracted the interest of scientists for a past decade. Among other researches, carbon nanotube-based hybrid materials, especially fullerene encapsulated single-walled carbon nanotubes (C_{60}@SWNTs) so called 'peapods', have been actively investigated and the understanding of their physics and chemistry has rapidly progressed, enlarging their applications. Although the yield for C_{60} peapods synthesis by the prevailing thermal diffusion method is very high, this method is less appropriate for the development of more complicated structures within SWNTs such as junction-structure through one treatment. Moreover, the encapsulation mechanism has not fully been understood in spite of its great importance for the shake of wide application to any other similar materials. For this reason, we have carried out an interdisciplinary experimental approach using different-polarity ion plasmas, which contain alkali positive , fullerene negative ions, and a small fraction of residual electrons [1]. Actually, we have reported the successful formation of fullerene peapods by ion irradiation method [2,3]. On the basis of this previous work, we here report the details of fullerene peapods formation inside SWNTs and compare them with the results in the case of other carbon nanotubes, which are double- (DWNTs) [4] and multi-walled carbon nanotubes (MWNTs) [5].

Experiments of fullerene ion irradiation to nanotubes are performed by applying positive biases φ_{ap} to a substrate, which is covered with the nanotubes and immersed in a plasma column. SWNTs and DWNTs are prepared by electric-arc method. On the other hand, sparse and well-aligned MWNTs are produced by radio frequency plasma enhanced chemical vapor deposition [5]. The sample estimation and analysis are mainly performed using field emission-transmission electron microscopy (FE-TEM) and Raman scattering spectroscopy.

Figure 1 shows various C_{60} peapods, which is obtained from samples of φ_{ap} = 20 V in the Cs^+ - C_{60}^- plasma. Completely filled nanotubes are presented in Fig. 1(a). In Fig. 1(b), although the lower tube seems to be empty and maintains a perfect tube structure, the upper tube incorporates a fullerene chain through its open end (black arrow). Figure 1(c), which presents frequently observed features in the case of SWNTs, gives evidence that the fullerenes are well intercalated using our plasma irradiation method. The production rate of peapods in the case of Li^+ - C_{60}^- plasma ($5 \times 10^8\,cm^{-3} < n_e < 5 \times 10^9\,cm^{-3}$, n_e: plasma density) is placed between 20-25 %. On the other hand, the encapsulation yield is raised up to 60-70 % in the case of Cs^+ - C_{60}^- plasma ($n_e > 10^{10}\,cm^{-3}$). Namely, the encapsulation rate linearly increases with an increase in the plasma density used. This is reasonable that higher plasma density means more increased irradiation ion-flux, which may be crucial in the enhancement of the encapsulation rate.

After the C_{60} negative ion irradiation by the positive bias application to SWNTs, the structural modification is found to be enhanced. Then, we evaluate the ratio of Raman peak intensities, I_D/I_G, as a quantitative measure of structural deformation as presented in Fig. 2. At first, when we check the relationship between the values of I_D/I_G and applied substrate bias voltage, it is found that the value of I_D/I_G increases with increasing the applied bias voltage value. In other words, the degree of nanostructure disorder increases due to increased ion irradiation energy. Secondly, we have to investigate a dependence of the I_D/I_G value on the plasma density what we used at the same substrate bias voltage. The values of I_D/I_G for the C_{60} irradiation with φ_{ap} = 10 V or 20 V in the Li^+ - C_{60}^- plasma are lower than in the case of Cs^+ - C_{60}^- plasma. Namely, the amount of structural modification increases with the enhanced C_{60} negative ion flux toward SWNTs. Finally, from the relationship between plasma density, C_{60} encapsulation yield, and I_D/I_G value, we can conjecture that the fullerene encapsulation phenomenon is closely related with the structural deformation of SWNTs. The results for the fullerene encapsulation inside DWNTs and MWNTs will be compared in detail at the meeting.

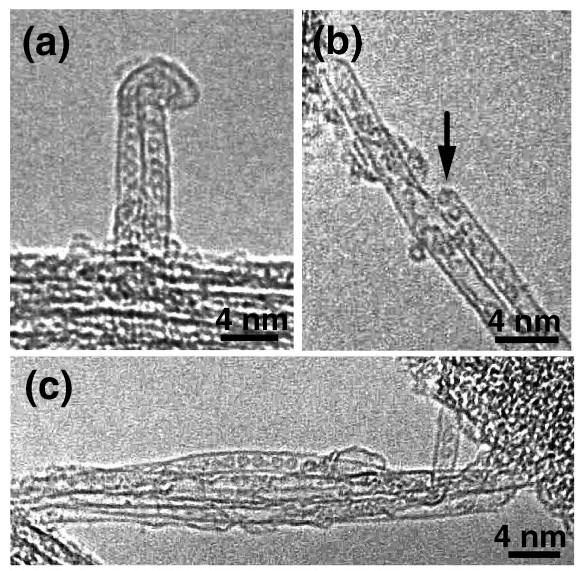

Figure 1. Various peapods obtained from the samples treated with the φ_{ap} = 20 V in Cs^+ - C_{60}^- plasma. (a) Completely filled nanotubes, (b) Peapods and open end (black arrow), and (c) Typical features of peapods.

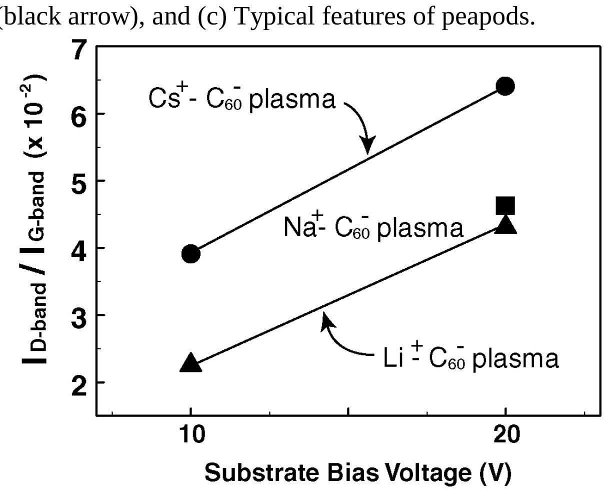

Figure 2. Variations of I_D/I_G for substrate bias voltages.

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