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Investigation of Fullerenes and Carbon Nanotubes Based on Plasma Science

プラズマ科学視点のフラーレン・ナノチューブ研究

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A special remark is focused from the viewpoint of plasma science on challenging researches of fullerenes and carbon nanotubes among a variety of carbon allotropes. Their inner nano-spaces are controlled via plasma-ion acceleration/deceleration processes in the gaseous and solution states, creating novel atom/molecule encapsulated fullerenes and carbon nanotubes. For further advance of the nanoscopic plasma process individually and vertically aligned single-walled carbon nanotubes are synthesized by plasma chemical vapor deposition.

1. Introduction

Since carbon allotropes take on a diversity of structures and properties, carbon-based materials have attracted much interest of not only general materials but also plasma scientists from the viewpoint of basic science and practical materials development. The carbon chemical bond is characterized by s and p hybridized orbital: carbyne with sp hybridized orbital, graphite with sp^2 hybridized orbital, and diamond with sp^3 hybridized orbital are one-, two-, and three-dimensionally stretched, respectively. Diamond of transparency and insulator is known to be the most hardest material, while graphite of black and conductor is one of the most softest crystals. On the other hand, recently discovered fullerenes with soccerball-like structure and carbon nanotubes with cylindrical structure, which are zero- and one-dimensionally stretched, respectively, are expected to be candidates for key materials on bottom-up nanotechnology under the situation that top-down nanotechnology prevailing mainly in Si semiconductor industries approaches an inevitable limit of processing in nano scale.

2. Relation between Plasma and Nanocarbon

Plasma scientists have paid attention the fullerene and carbon nanotube in view of their formation and synthesis directly connected with self-organization process, because they were discovered using laser vaporization and arc discharge methods, where the plasma generation intrinsically took place. In this sense, thermal plasma decomposition/deposition and plasma-enhanced chemical vapor deposition (plasma CVD) have been regarded as playing some pioneering roles in the production of new kinds of nanocarbons. When we recall plasma technology on etching and surface modification of materials in semiconductor processes, on the other hand, external structure control of nanocarbons such as fullerene and carbon nanotube is hoped to be realized using extended plasma technology.

Based on the background described above, we here discuss efficient creation and structural control of novel nanocarbons using nanoscopic plasma processes. Our discussion is divided into two categories. One is concerned with inner nano-space control and surface modification of fullerenes and carbon nanotubes using fully-ionized and gas-discharge plasmas, and electrolyte plasmas in the solution state. The other is concerned with growth control of pristine carbon nanotubes by plasma CVD method.

3. Creation of Novel Structured Fullerenes

The encapsulation of atoms inside hollow cages of fullerenes is one of the fascinating tasks since their discovery. It is urgently required to develop a new method allowing the production of atom encapsulated fullerenes in large quantities. Concerning endohedral metallofullerenes, we have found that using alkali-fullerene plasmas, which consist of positive alkali-metal ions (A^+) and negative fullerene ions (C_{60}^-), is very effective and the formation rate of alkali-metal encapsulated fullerenes $A@C_{60}$ is inversely proportional to the diameter of the alkali-metal ions. This means that coulomb interactions, originating from the acceleration and deceleration of A^+ and C_{60}^- ions, have a significant effect on the atom encapsulation in C_{60} cages .

We also challenge to develop a novel method for the efficient production of $N@C_{60}$, potential applications of which have been proposed, using plasma confinement and heating technology .

4. Nano-Space Control of Carbon Nanotubes

Plasma-ion irradiation method has been adopted in order to control the inner nano-space of single-(SWNTs), double-(DWNTs), and multi-walled (MWNTs) carbon nanotubes and resultantly develop novel functional carbon-based nano-materials. When positive or negative bias-voltages are applied to a substrate covered with nanotubes and immersed in the different-polarity ion plasmas, accelerated C_{60}^- or A^+ ions are irradiated to those carbon nanotubes through collisionless plasma sheaths in front of the substrate.

It is found that drastic structural modifications such as severe bending of carbon nanotube bundles or tube tip termination take place after the plasma ion irradiation. In the case of alkali-metal irradiation, the Cs encapsulation inside the SWNTs (Cs@SWNTs) is directly observed for the first time and the configuration of which is demonstrated to comprise three varieties. In the case of C_{60}^- irradiation, on the other hand, the SWNTs and DWNTs encapsulating fullerene molecules are clearly observed. Both the degree of the structural modification and the fullerene filling efficiency are found to become enhanced in the order MWNTs, DWNTs, SWNTs, and be directly proportional to the ion irradiation energy and plasma density used. Finally, when the bias-voltage with polarity change is sequentially applied to the SWNTs, the SWNT encapsulating a junction of Cs atoms on one side and C_{60} molecules on the other is for the first time observed. It is noteworthy to emphasize our results open a new possibility for the novel structured material synthesis using plasma technology.

According to measurements of electronic transport properties using FET configurations, Cs@SWNTs exhibit n-type transport behavior, while C_{60}@SWNTs give rise to a p-type semiconductive property.

The above-mentioned plasma-ion irradiation method is applied to electrolyte micro-plasmas in solutions in order to form DNA encapsulated SWNTs (DNA@SWNTs) available for novel electronic devices. Since DNA is ball-shaped and negatively charged in the solution, AC and DC electric fields are effective for stretching due to ponderomotive force and transporting/accelerating towards a substrate covered with open-ended SWNTs in the electrolyte micro-plasma. Thus, negative DNA ions are inserted into SWNTs, forming DNA@SWNTs for the first time.

5. Growth Control of Single-Walled Nanotubes

In order to accurately and efficiently perform inner nano-space control of carbon nantoubes, pristine/empty SWNTs have to be individually and vertically aligned. Plasma CVD method has a variety of advantages in the production, but yields only MWNTs. We attempt to produce SWNTs using Plasma CVD by devising size and distribution of catalysts, and plasma-ion influx towards a growth substrate in a reactive plasma. Actually, the SWNT formation is for the first time realized using plasma CVD. Furthermore, owing to the benefits of plasma CVD, low temperature synthesis and the individual SWNT alignment control are also achieved.

6. Summary

The nanoscopic plasma processes based on substrate bias method in the gaseous and solution states yield inner nano-space control of nanocarbons and creation of novel structured fullerenes and carbon nanotubes encapsulating atoms or molecules including DNA. Single-walled nanotubes synthesized by plasma CVD could advance such a plasma-nanotechnological research.

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