Optical Properties of High Purity Nitrogen Atom Endohedral Fullerene Synthesized by Controlled Plasma Ion Irradiation

プラズマイオン制御照射により合成された
高純度窒素内包フラーレンの光学的特性

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An optical investigation has been carried out on a purified nitrogen atom endohedral fullerene ($N@C_{60}$) synthesized by controlling nitrogen ion irradiation energy to the fullerene (C_{60}). We have realized the highest as-synthesized purity of 0.56 % in the world. The samples are purified up to 40 % using high performance liquid chromatography (HPLC) and characterized by a laser-desorption time-of-flight mass spectrometer (TOF-MS) and ultraviolet-visible (UV-Vis) absorption spectroscopy. In TOF-MS, the peak at the mass number 734 indicating $N@C_{60}$ is clearly observed. Furthermore, the UV/Vis absorption spectrum of high purity $N@C_{60}$ is significantly different from that of the pure C_{60}, i.e., a new peak at 345 nm appears for $N@C_{60}$.

1. Introduction

Fullerene-based materials are extremely interesting and promising for possible applications in nanotechnology. Especially, endohedral fullerenes have attracted great interest in their physical and/or chemical properties such as pseudoatom behavior, magnetism, nonlinear optical behaviors, and superconductivity [1]. For example, it has been shown that $N@C_{60}$ could have some unique advantages in isolating the atom from its environment, thereby providing a building block for the qubits of the quantum computer [2]. However, one of the problems of probing the properties of these new materials is the difficulty in producing them in large enough amounts. The production rate of $N@C_{60}$ is quite low compared with the ordinary fullerenes, which yield only limited quantities (e.g., only a few nanograms) of a pure product after laborious isolation procedures due to the extreme difficulties in producing large amount quantities and isolating pure samples. Although $N@C_{60}$ has been studied over the last decade, the purity is still extremely low at present (10^{-3}-10^{-2} %). Therefore, the high yield synthesis of $N@C_{60}$ using plasma system is required in order to progress the development of promising quantum devices.

Here, we present a simple method for the synthesis of high-yield $N@C_{60}$ by a radio-frequency (RF) plasma. Also, using multi-step high performance liquid chromatography (HPLC), $N@C_{60}$ is purified and characterized using ultraviolet-visible (UV-Vis) absorption spectroscopy and matrix-assisted time-of-flight mass spectrometer (MALDI TOF-MS) analysis.

2. Experimental results and discussion

$N@C_{60}$ can be synthesized by nitrogen ion bombardment to C_{60}. Experiments on the $N@C_{60}$ synthesis are performed under the conditions as follows: applied RF power P_{RF} = 500 W, nitrogen gas pressure P_{N2} = 25 Pa, grid bias voltage V_g = -90 V, substrate bias voltage V_{sub} = -90 V and synthesis time = 60 min. After the synthesis, the sample is dissolved in toluene and filtered through a 0.2 μm membrane before the HPLC purification process. The design and operation of the RF-plasma system is reported in detail in our previous literature. [3]

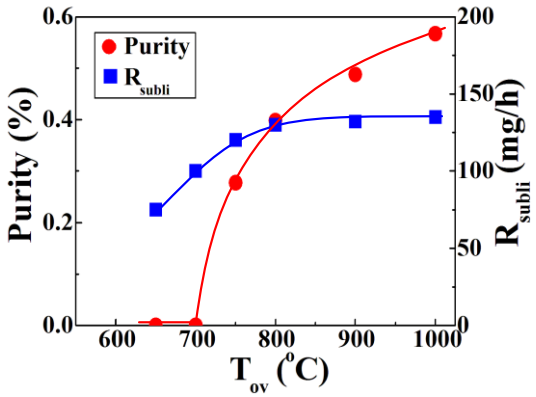

Fig. 1. Dependence of purity and C_{60} sublimation rate on T_{ov} at V_g = -90 V, V_{sub}= -90 V and P_{RF}= 500 W.

Figure 1 shows the purity and C_{60} sublimation rate (R_{subli}) as a function of oven temperature (T_{ov}). It is found that the purity increases with an increase in T_{ov} and the highest purity of 0.56% is realized although R_{subli} is almost the same from 800 to 1000 ^{o}C. The increase in the purity is considered to be caused by sublimation of C_{60} with dispersed form and expansion rate increases as T_{ov} increases.

Figure 2 shows a mass spectrum of the sample with purity of 40% after condensation and pristine C_{60}. In both cases, the mass/charge values yielding spectrum intensity peaks are observed in the range from 720 to 724 owing to the existence of carbon isotopes in C_{60}. However, in the case of $N@C_{60}$ with purity of 40%, the peak at 734 indicating $N@C_{60}$ is clearly observed.

Figure 3 shows the UV/Vis absorption spectra of different $N@C_{60}$ purity in the range of 300-600 nm. It is obviously recognized that there is a significant difference in the peak at 345 nm between the ($N@C_{60}$ with purity of 20 % and 40 %) enriched samples and $N@C_{60}$ with purity of 5 %. The peaks at 345 nm gradually increase, as purity increases. Compared to the case of the $N@C_{60}$ with purity of 5 %, the peak becomes broad in the $N@C_{60}$ with purity of 20 % and 40 %. In addition, the C_{60} absorption peak at 406 nm is greatly diminished in the $N@C_{60}$ with purity of 20 % and 40 % [4], which suggests that the absorption spectrum of $N@C_{60}$ is different as purity increases**.**

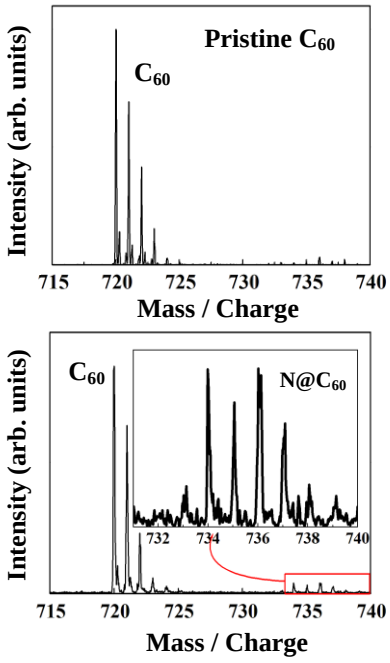

Fig. 2. Mass spectrum of solution after solvent extraction obtained by MALDI TOF-MS analysis. The purity of $N@C_{60}/(C_{60}+N@C_{60})$ in the solution is about 40%, which is enhanced by HPLC.

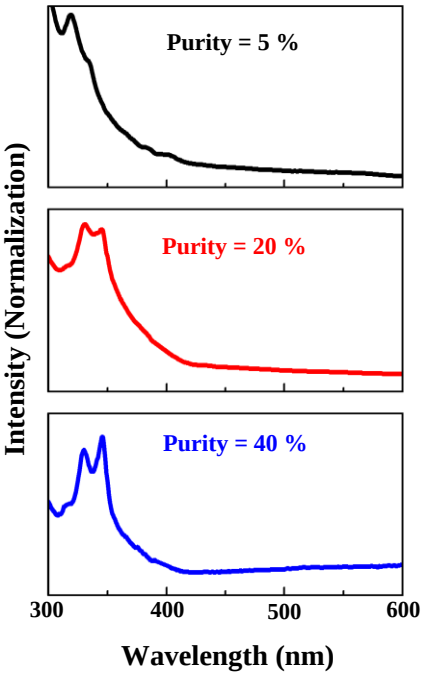

Fig. 3. The UV/Vis absorption spectra of the $N@C_{60}$ with purity of 5 %, 20 % and 40 %, respectively.

4. Summary

We have presented a simple method for the high purity $N@C_{60}$ synthesis using an RF discharge with external control of DC bias voltages. It is found that the purity increases with an increase in T_{ov} and the highest purity of 0.56% is realized. Furthermore, the $N@C_{60}$ sample enriched using HPLC sample is characterized by MALDI TOF-MS and UV/Vis absorption spectroscopy. In MALDI TOF-MS, the peak at the mass number 734 indicating $N@C_{60}$ is clearly observed. In addition, the UV region of the absorption spectrum of the high purity $N@C_{60}$ is significantly different from the low purity $N@C_{60}$ at the wavelength of 345 nm.

Acknowledgments

This work was partly carried out at the Evaluation and Analysis Center, Research Institute of Electrical Communication, Tohoku University. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sport, Science and Technology, Japan.

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