

Effect of electron irradiation on fullerene derivatives

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1. Introduction

Fullerenes (C_{60}) have recently attracted many interest in the field of organic solar cells [1], organic thin film transistors [2] due to its good electron accepting property. However, its solubility seems to be poor in most organic solvents, limiting the feasibility of solution-based fabrication process. To increase the solubility, many derivatives of fullerenes are synthesized and evaluated in such application fields. In this study, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) [3], a most widely used fullerene is irradiated by an electron beam, and its change in molecular structure is evaluated.

2. Methods and Results

In this section, sample preparation methods and conditions of electron irradiation will be described. Electron-irradiated PCBM was characterized by 1H -NMR, FT-IR, and Raman spectroscopy.

2.1 Experimental

Chlorobenzene solution of PCBM was prepared and spread on a substrate for electron irradiation. After electron irradiation, samples were collected as powders for characterization. To investigate the change in the molecular structures of PCBM due to electron irradiation, attenuated total reflection Fourier transform infrared (ATR-FTIR) and high resolution dispersive Raman spectra were measured with the spectrometers (IFS66V/S & HYPERION 3000 and LabRAM HR UV/Vis/NIR, respectively). The irradiation of an electron beam on PCBM films were carried out at room temperature and in vacuum lower than 2×10^{-5} Torr. An electron beam was generated from a thermionic electron gun with electron energy at 50keV and current density of the electron beam was $1.6 \mu A cm^{-2}$. The total electron fluence was varied by adjusting the irradiation time. The samples were irradiated by 1 h, 2 h, and 4 h, which corresponds to total electron fluence of $3.6 \times 10^{16} cm^{-2}$, $7.2 \times 10^{16} cm^{-2}$, and $1.44 \times 10^{17} cm^{-2}$.

2.2 FT-IR spectroscopy

The molecular bond in PCBM decompose as electron irradiation increases. By comparing the change in

relative intensities of each vibration bands, the butyric acid methyl ester side chain was most vulnerable to electron irradiation, followed by the C_{60} cage. However, all the vibration bands still exist, not disappear, indicated that molecules of non-modified PCBM and modified PCBM due to electron irradiation co-exist.

2.3 Raman spectroscopy

The Raman spectra shows typical vibration modes of the C_{60} cage which is the core of PCBM. After electron irradiation, the intensity of $A_g(2)$ mode rapidly decreases, indicating the deformation of C_{60} cage. It is known that knock-on collision of C atom by energetic electrons in fullerenes are possible, which agree with our irradiation condition. The slope of the background at $1.44 \times 10^{17} cm^{-2}$ electron fluence indicates the photoluminescence produced by the fragments of fullerene deformation [4].

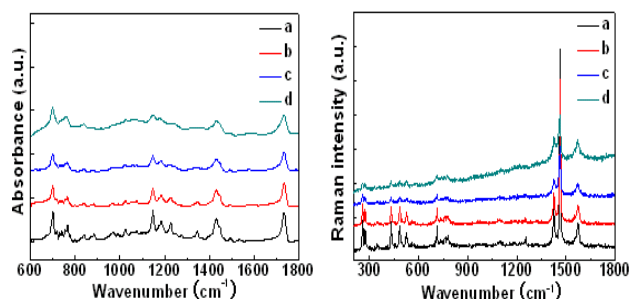


Fig. 1. FT-IR (left) and Raman (right) spectra of PCBM irradiated at electron fluence of (a) non-irradiated (b) $3.6 \times 10^{16} cm^{-2}$ (c) $7.2 \times 10^{16} cm^{-2}$ (d) $1.44 \times 10^{17} cm^{-2}$

2.4 1H -NMR

1H -NMR of electron-irradiated PCBM reveals the formation of methoxy-substituted phenyl ring of PCBM. Also, the formation of methoxy-substituted naphthalene was observed by such mechanism [5]. The aliphatic chain of butyric acid methyl ester was fused on the phenyl ring to form a naphthalene, and a methoxy radical was substituted.

3. Conclusions

PCBM, a fullerene derivative was irradiated by an electron beam, and the change in molecular structure was characterized by ¹H-NMR, FT-IR, and Raman spectroscopy. The molecular bonds of PCBM were gradually decomposed by electron irradiation, creating methoxy-substituted phenyl and naphthalene of PCBM.

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