One-dimensional Metallic Peanut-shaped Nanocarbon with Positive and Negative Gaussian Curvatures: Toward a New Science of Quantum Electronic Systems on Riemannian Surface

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When a C$_{60}$ film is irradiated with a 3 kV electron-beam (EB) gun in vacuum (base pressure: $10^{-7}$ Pa), we have found that EB-irradiation of a C$_{60}$ film gives rise to formation of a peanut-shaped C$_{60}$ polymer with metallic electron-transport properties in air at room temperature. The peanut-shaped polymer has both positive and negative Gaussian curvatures ($K$), which can be classified into a new $\pi$-electron conjugated carbon allotrope that is different from graphite ($K=0$), fullerenes ($K>0$), nanotubes ($K=0$ at body, $K>0$ at cap edge), and hypothetical Mackay crystal ($K<0$). In the present review article, we will introduce our recent results of the electron-transport, electronic, and optical properties of the nanocarbon, and describe theoretical analysis of its novel electronic properties on the basis of quantum mechanics on Riemannian surfaces. To our best knowledge, the peanut-shaped C$_{60}$ polymer is only an existed material with a negative Gaussian curvature, whose electronic and optical properties are known experimentally. Thus we believe that the present system will open a new science “quantum science of condensed matters in Riemannian space”.

KEYWORDS: peanut-shaped nanocarbon, Gaussian curvature, Tomonaga-Luttinger liquids, Peierls instability, quantum mechanics on Riemannian surface

1. Introduction

Since the first report on C$_{60}$ photo-polymerization$^{1}$, there have been many reports on C$_{60}$ polymers obtained by various kinds of methods, as shown in Table 1$. We have hitherto produced them from photo and electron-beam (EB) irradiation of pristine C$_{60}$ films, and investigated their structural and electric properties. As shown in Fig. 1, photo-polymerization provides two-dimensional (2D) semiconducting dumbbell-shaped C$_{60}$ polymers (left) with a resistivity of $10^3 \Omega$cm$^{3-9}$, whereas EB-polymerization does metallic peanut-shaped C$_{60}$ polymers with that of $1-10 \Omega$cm$^{10-18}$. These resistivity values were obtained using four-probe measurements at room temperature under atmospheric conditions. Both of which indicates a resistivity much smaller than that of solid C$_{60}^{10,20}$. As shown in Fig. 1 (left), the two-dimensional (2D) C$_{60}$ polymer has a $[2+2]$ four-membered cross-linkage (dumbbell-shape) between adjacent C$_{60}$ molecules by dissociation of C=C double bonds of each C$_{60}$. In this case, the whole system is not regarded as a $\pi$-electron conjugated system, thus exhibiting semiconducting. On the other hand, as sown in Fig. 1 (right), the peanut-shaped polymer has a coalesced structure via the general Stone-Wales rearrangement$^{21,22}$ between adjacent C$_{60}$ molecules. The EB-polymer can be regarded as a $\pi$-electron conjugated system, thus exhibiting metallic characters. Furthermore, when we focus on the EB-polymer from a topological aspect, this peanut-shaped structure has both positive and negative Gaussian curvatures$^{23}$, which is different from well-known $\pi$-electron conjugated carbon allotropes (see Table 2).

In the present review article, we will introduce our recent results of electron-transport$^{24}$, optical$^{25}$, and electronic$^{26,27}$ properties of the peanut-shaped C$_{60}$ polymer. Thereafter, we will briefly introduce our theoretical analysis of the effects of Gaussian
curvatures on the electronic properties of the polymer, using the quantum mechanics on Riemannian surface\textsuperscript{28, 29}. Finally, we will describe the perspective of the peanut-shaped C\textsubscript{60} polymer.

### 2. Electron-transport properties

To investigate the electron-transport properties of the peanut-shaped C\textsubscript{60} polymer, we performed four-probe measurements in vacuum\textsuperscript{24}. After 12-h EB irradiation (applied voltage : 3 kV, an incident current : 0.3–0.5 mA, spot diameter : 2 mm, sweep conditions : 10 kHz along the x-direction and 1 kHz along the y-direction) of a C\textsubscript{60} film (100 nm thick) deposited on a CsI substrate by sublimation of C\textsubscript{60} powder (99.98\% pure) at 673 K in a ultra-high vacuum (UHV) chamber (base pressure : 2 × 10\textsuperscript{−7} Pa) equipped with \textit{in situ} infrared spectroscopy\textsuperscript{30} for confirming the formation of the peanut-shaped C\textsubscript{60} polymer completely, the film was taken out of the chamber and moved into the other vacuum chamber (base pressure : 4 × 10\textsuperscript{−4} Pa). Prior to depositing a C\textsubscript{60} film on the CsI, the powder was preheated at 473 K until residual organic solvents were completely removed from the powder. Gold (Au) contacts were deposited on the peanut-shaped C\textsubscript{60} polymer through a metal mask and the film resistance was recorded as a function of the substrate temperature in the range of 9–400 K.

Figure 2 shows the Arrhenius plot of the resistance of the polymer as a function of a substrate temperature. It is found that the electron-transport

<table>
<thead>
<tr>
<th>Method</th>
<th>Reactant</th>
<th>Cross-linkage</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-irradiation</td>
<td>C\textsubscript{60} film</td>
<td>dumbbell</td>
<td>1D</td>
</tr>
<tr>
<td></td>
<td></td>
<td>single-bond</td>
<td>2D hexagonal</td>
</tr>
<tr>
<td>High-temperature and High-pressure</td>
<td>Solid C\textsubscript{60}</td>
<td>dumbbell</td>
<td>1D orthorhombic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>single-bond</td>
<td>2D tetragonal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2D hexagonal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3D tetragonal/hexagonal</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>AC\textsubscript{60} \textsuperscript{*}</td>
<td>dumbbell</td>
<td>1D orthorhombic</td>
</tr>
<tr>
<td></td>
<td>Na\textsubscript{2}RbC\textsubscript{60}</td>
<td>single-bond</td>
<td>1D orthorhombic</td>
</tr>
<tr>
<td></td>
<td>Na\textsubscript{2}C\textsubscript{60}</td>
<td>single-bond</td>
<td>2D tetragonal</td>
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<td>C\textsubscript{60} powder</td>
<td>dumbbell</td>
<td>dimer</td>
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<td></td>
<td>KCN</td>
<td></td>
<td>trimer</td>
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<td>dimer</td>
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<tr>
<td></td>
<td>C\textsubscript{60} film</td>
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<td>1D</td>
</tr>
<tr>
<td></td>
<td></td>
<td>dissociation</td>
<td>3D amorphous</td>
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</table>

* A denotes alkali metals.

### Table 1. Summary of fullerene polymers formed by various kinds of methods.

### Table 2. Classification of $\pi$-electron conjugated carbon allotropes by using Gaussian curvature.

<table>
<thead>
<tr>
<th>$\pi$-electron system</th>
<th>Gaussian curvature</th>
<th>N-membered ring</th>
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<tbody>
<tr>
<td>graphite</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>fullerenes</td>
<td>+</td>
<td>5, 6</td>
</tr>
<tr>
<td>nanotubes</td>
<td>0(body), + (cap)</td>
<td>5, 6</td>
</tr>
<tr>
<td>Mackay crystal\textsuperscript{*} (hypothetical)</td>
<td>-</td>
<td>6, 8</td>
</tr>
<tr>
<td>peanut-shaped polymers</td>
<td>+, −</td>
<td>5 − 8</td>
</tr>
</tbody>
</table>

* see Fig. 9 (taken from Ref. 41)
mechanism is changed at around 90 K. For the substrate temperature above 90 K, the electron-transport properties are behaved on the basis of thermally excited mechanism and the activation energy for electron-transport was obtained to be 0.06 eV, which is comparable to that of 0.10 eV for carbon nanotubes (CNTs). Because the present peanut-shaped C\textsubscript{60} polymer can be formed only by EB irradiation of a C\textsubscript{60} film which can be deposited on any substrate by a dry (evaporation) or wet (spin coat) process, this polymer may be superior to CNTs when applied to practical electronic device fabrications. On the other hand, for a temperature below 90 K, although the electron-transport mechanism is considered to be changed to a variable range hopping mechanism, more measurement points are further needed to clarify the hopping mechanism such as the Anderson localized one.

3. Optical properties

We next examined the dynamics of photo-excited carriers of the polymer, using two-color pump-probe femtosecond (fs) spectroscopy (a temporal resolution of 200 fs) in which a coaxial configuration between pump (1.07 eV) and probe (1.55 eV) laser beams\textsuperscript{25,31}. C\textsubscript{60} films (200 nm thick) were formed on a CsI substrate in the UHV chamber and EB-irradiated in situ in a similar manner described in the previous section. We also prepared a pristine sample without EB irradiation as a reference. The films thus formed were mounted on the cold finger of an optical cryostat, and their lifetime of photo-excited carriers in the films was recorded as a function of the substrate temperature (20–300 K).

Although the details of the results and discussion are described in the other review article (by Prof. Toda) appeared in this special issue, we briefly introduce our results of the peanut-shaped C\textsubscript{60} film. The temperature dependence of the photo-excited carriers lifetime for the peanut-shaped polymer indicated the energy gap formation at below 50 K in a similar manner to the Peierls instability for quasi-one-dimensional (1D) metallic materials such as K\textsubscript{0.3}Mo\textsubscript{32}, thus suggesting that the polymer is a 1D metal.

Interestingly, in typical quasi-1D compounds exhibiting the Peierls transition, the decay time diverges near the transition temperature at which efficient phonon transitions (both emissions and re-absorptions) greatly make the relaxation time longer at the beginning of the gap formation. However, there is no clear divergence at around 60 K, and instead both the decay time and amplitude increase monotonically with decreasing a temperature down to 20 K. We consider that the different behavior of the decay time is presumably due to a topological effect driven from the positive and negative Gaussian curvatures at present, but it is further necessary to study the present research subject.

4. Electronic properties

To clarify the origins of the metallic current-voltage (I-V) characteristics of the peanut-shaped C\textsubscript{60} polymer, we have examined its valence electronic structure around the Fermi level (E\textsubscript{F}), using in situ high-resolution ultraviolet photoelectron spectroscopy (UPS). Prior to its deposition, a 100 mg of C\textsubscript{60} powder (99.98\% pure) introduced into a Knudsen cell (K-cell) was heated at 473 K for removal of residual organic solvents from the powder in a preparation chamber (base pressure : 1 × 10\textsuperscript{−7} Pa). Thereafter, a C\textsubscript{60} film (20–30 nm thick) was formed on a copper (Cu) substrate by sublimation of the pretreated C\textsubscript{60} powder in the K-cell at 673 K for 3 min in the preparation chamber. Subsequently, the pristine C\textsubscript{60} film was transferred to an analysis chamber (base pressure : 1 × 10\textsuperscript{−8} Pa) and measured in situ by UPS with an energy resolution of 0.01–0.02 eV and with a monochromatic He I\textalpha\textsubscript{1} (21.218 eV) or He I\textalpha\textsubscript{2} (40.806 eV) emission line. Although we used the He I\textalpha\textsubscript{1} in the previous work\textsuperscript{26}, we here employed the He I\textalpha\textsubscript{2} emission line in order to examine the \pi-electron
behaviour near the $E_F$ for the outermost layers of the EB-irradiated film\textsuperscript{27}. After the measurements, the film was returned to the preparation chamber and irradiated with 3 kV EB for 0.5, 1.5, 2.5, 5.0, and 12 h. We confirmed by \textit{in situ} infrared spectroscopy that 12 h of EB-irradiation was sufficient to allow the C$_{60}$ molecules to be completely coalesced, thus forming a peanut-shaped C$_{60}$ polymer all over the film. Every after each EB-irradiation time, the film was transferred to the analysis chamber for \textit{in situ} UPS measurements. The zero value in binding energy for the present measurements was determined from the $E_F$ ( = 0 eV) of a Au film, which was deposited on the same Cu substrate as for the pristine and EB-irradiated C$_{60}$ films, by fitting its UPS spectra with a Fermi distribution function in a given temperature range. In the present substrate temperature, the $E_F$ of a semiconductor is located in the middle between the valence and conduction bands by thermal broadening, and is almost the same position as that of a metal with thermal broadening at the temperature.

\textbf{Figure 3} shows the UPS spectra of the EB-irradiated C$_{60}$ films for several irradiation times (350 K), along with the pristine C$_{60}$ film measured at 300 K: 0 h (red), 0.5 h (orange), 1.5 h (green), 2.5 h (sky blue), and 5.0 h (blue). For the pristine C$_{60}$ film (red line), some intensive narrow bands such as HOMO and HOMO-1 were observed, because of the weak interaction between adjacent C$_{60}$ molecules. On the other hand, as EB-irradiation time increases, each band becomes broadened in accordance with the disappearance of molecular character caused by EB-induced polymerization between adjacent C$_{60}$ molecules, and the valence electronic states spread monotonically toward the $E_F$ with increasing the EB-irradiation time. After 5 h of EB-irradiation, the electronic states reach to the $E_F$, as shown by the blue line.

To understand this behavior near the $E_F$ in details, we next measured the EB-irradiation time-dependence of UPS spectra of the film in the binding energy of 3 eV below the $E_F$. \textbf{Figure 4} shows the EB time-dependence of UPS spectra of the C$_{60}$ film in the binding energy region, where insets shows the symmetrised spectra in the vicinity of the $E_F$: 0 h (red), 0.5 h (orange), 2.5 h (sky blue), and 5.0 h (blue) in order to remove the effect of thermal broadening from those spectra. Because the S/N ratio of the spectrum of 1.5 h-irradiated C$_{60}$ film (the green line shown in Fig. 4) was poor in comparison with that of the others, it was omitted in this figure. As shown in Fig. 4, the electronic states in the binding energy range of 0–2 eV are gradually increased in response to the broadening of the HOMO band located at around 2.4 eV, as the EB-irradiation time increases. This indicates that EB-irradiation time reduced the energy gap, which is related to the electron-transport properties, of a C$_{60}$ film continuously. This finding implies that the electronic properties of a C$_{60}$ film can be controlled from an insulator to a metal via a semiconductor continuously only within a EB-irradiated area, which is interesting when the EB-irradiated C$_{60}$ polymer is applied to the fabrication of electronic devices.

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(color online). EB-time evolution of valence photo-electron spectra of a C$_{60}$ film in a wide binding energy region. All spectra were obtained at 350 K except that of pristine C$_{60}$ film at 300 K (taken from Ref. 27).}
\end{figure*}

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{(color online). EB-time evolution of valence photo-electron spectra of a C$_{60}$ film in the binding energy of 3 eV below the Fermi level. Inset shows the symmetrized spectra in the vicinity of the Fermi level in order to remove the effect of thermal broadening from the spectra (taken from Ref. 27).}
\end{figure*}
Why do the electronic properties of the C$_{60}$ film change continuously from insulating to metallic via semiconducting as EB irradiation time increases? One of the reasons is attributed to the change in polymerization degree upon EB irradiation. We performed the first-principle calculations of the energy gap for the dimer (C$_{60}$-C$_{60}$), trimer (C$_{60}$-C$_{60}$-C$_{60}$), and its 1D infinite system (-C$_{60}$-) with a given cross-linked structure between adjacent C$_{60}$ molecules, and obtained them to be 0.33, 0.11, and 0.02 eV, respectively, along with that of 1.67 eV for C$_{60}$ which is in an excellent agreement with experimental results of 1.6–1.8 eV. Otherwise, the other reason is attributed to that the general Stone-Wales rearrangement between adjacent C$_{60}$ molecules proceeds as EB irradiation time increases.

We next discuss the UPS results obtained after 12-h EB irradiation. Figure 5 shows UPS spectra of pristine C$_{60}$ (blue line) and peanut-shaped C$_{60}$ polymer (red line) films obtained at a substrate temperature of 300 K and 350 K, respectively, where the inset shows the UPS spectrum of the peanut-shaped C$_{60}$ polymer near the $E_F$. For the peanut-shaped C$_{60}$ polymer, each band is broadened in response to the disappearance of molecular character caused by EB-induced polymerization between adjacent C$_{60}$ molecules, and the valence electronic states spread toward the $E_F$. In order to clarify the behavior of the electronic structure of the peanut-shaped C$_{60}$ polymer in the vicinity of the $E_F$, we measured more precise UPS spectra of the pristine C$_{60}$ and peanut-shaped polymer films in the binding energy of 0–3.0 eV, as shown in the inset of Fig. 5. It was found that the photoelectron spectrum of the peanut-shaped polymer shows clearly the density of states greater than those of the pristine C$_{60}$ film near the $E_F$, and comes across the $E_F$ edge. These findings suggest that the peanut-shaped C$_{60}$ polymer has a metallic electronic structure. However, because the results shown in the inset of Fig. 5 were measured at 350 K, the effect of a thermal broadening on the spectra should be taken into account. Thus the peanut-shaped polymer can be understood to be a metal or...
semimetal, otherwise a narrow-gap semiconductor.

Then we next examined the temperature dependence (T-dependence) of the UPS spectra in the vicinity of the $E_F$ for the peanut-shaped C_{60} polymer, because the thermal broadening effects reduce with decreasing temperature. For example, Figure 6 shows the plot of the Fermi distribution function near the $E_F$ in the range of 30–350 K (350 K : red, 200 K : orange, 150 K : green, 100 K : sky blue, and 50 K : blue). At 350 K, where there is a large thermal broadening in the distribution function in a similar manner to the spectrum shown in the inset of Fig. 5. As temperature is going down from 350 K to 50 K, thermal broadening becomes smaller and the Fermi step at the $E_F$ appears clearly at 50 K, as shown in Fig. 6. We examined the T-dependence of UPS spectra near the $E_F$ for the peanut-shaped C_{60} polymer. Figure 7 shows the UPS spectra measured at 50 K (blue, top), 100 K (sky blue, second top), 150 K (green, middle), 200 K (orange, second bottom), and 350 K (red, bottom). It is found that the spectrum comes across the $E_F$ even at 50 K, thus indicating that the peanut-shaped polymer is metal. Interestingly, the spectral function does not show a Fermi step clearly even at 50 K unlike the other 1D materials shown in Fig. 6. Two or three dimensional metal such as TaSe_{2} and Rhodium always exhibit a Fermi step, but quasi-1D metal such as K_{0.3}Mo_{3} and (TaSe_{4})I does not show such the step^{34}. Accordingly, the results of Fig. 7 suggest that the peanut-shaped C_{60} polymer is a 1D or quasi-1D metal, which is consistent with the results of its photo-excited carrier dynamics described in the previous section (see the details in the review article by Prof. Toda in the present special issue).

If the peanut-shaped polymer is 1D metal, its electrons should behave based on Tomonaga-Luttinger liquids (TLL) in which the density of states (DOS) shows a power-law dependence of the binding energy and of temperature (the value of exponent $\alpha$ is less than unity)^{35}. For example, for metallic single-wall carbon nanotubes (SWCNT), a TLL behavior was observed ($\alpha = 0.5$)^{36}. In a similar manner to that for SWCNT, we examined the T-dependence of UPS spectra near the $E_F$ in the range of 30–350 K, using a monochromatic He II $\alpha$ emission line. We also observed a TLL behavior for both binding energy and temperature and obtained $\alpha$ to be ca. 0.6^{20}, thus demonstrating that the peanut-shaped C_{60} polymer is 1D metal as well as SWCNTs. Here we have a next question: what is the difference in the exponent ($\alpha$) value between SWCNT and the peanut-shaped polymer? Does the difference show a physically meaningful?

5. The effect of Riemannian surface on TLL exponent

To explain the difference in the TLL exponent value between them, we have focused our attention on the difference in their topology based on Gaussian curvature, as shown in Table 2. At the first step, we regarded the electron motion on the 1D peanut-shaped C_{60} polymer as free electrons moving on a quantum hollow cylinder with periodic radius modulation (see Fig. 8) resulting in 1D curved surface with positive and negative Gaussian curvatures aligned alternatively and periodically. On such the curved surface, Schrodinger equation dealing with electron motion cannot be written in Euclidean space but in Riemannian space^{24}. As a consequence, the single-particle DOS, $n(\omega)$, near the $E_F$ should exhibit a power-law singularity as follows,

$$n(\omega) \propto |\hbar\omega - E_F|^\alpha, \quad \alpha = \frac{K + K^{-1}}{2} - 1 \quad (1)$$

Where, $K(>0)$ is a parameter to express the strength of electron-electron interactions, and can be written as

$$K = \lim_{q \to 0} \sqrt{\frac{2\pi \hbar v_F + g_4(q) - g_4(q)}{2\pi \hbar v_F + g_4(q) + g_4(q)}} \quad (2)$$

Where, $v_F$ denotes the Fermi velocity, and $g_4(q) = V(q, m) + g_4(q)$, where $V(q, m) - V(2k_F, m)$ show $q$-dependent coupling constants. $V(q, m)$ is the Fourier transform of the screened interaction. The details of the present results and discussion were described in the other review article (by Prof. Shima) in the present special issue. It is revealed that the difference in TLL exponent $\alpha$ value between SWCNT and 1D peanut-shaped polymer is caused by a curvature-induced effective potential that works for electrons conducting along the curved surface. As far as we know, this is the first finding regarding the effect of the Riemannian curvature.
nian surface on the electronic properties of condensed matters.

6. Summary and perspectives

We reviewed our recent works on the electron-transport, optical, and electronic properties of the peanut-shaped C_{60} polymer formed by EB irradiation of C_{60} films. This polymer was found to be a 1D metal and can be regarded as a new allotrope of \( \pi \)-electron conjugated carbon materials when they are classified using Gaussian curvature. Indeed, the 1D metallic polymer exhibits a different behavior of optical and electronic properties from well-known 1D metal materials: no divergence in the decay time upon an energy gap formation associated with the Peierls transition, and the TLL exponent value larger than that of 1D metal SWCNT with zero Gaussian curvature. In particular, the difference in TLL exponent is caused by the Gaussian curvature that drives effective potentials acting on electrons motion on the Riemannian surface.

There have been some reports on carbon materials with a negative Gaussian curvature experimentally\(^{37-39} \). However, they were just observed using transmission electron microscope and not shown to have any electronic properties until now. To our best knowledge, the 1D metallic peanut-shaped C_{60} polymer is the first existed material with well-known physical properties that are affected significantly by Gaussian curvature in the Schrodinger equation on Riemannian surface.

Finally, all works introduced here have been made in collaboration with Prof. Y. Ochiai (Chiba University), Prof. T. Ito (Nagoya University), Prof. S. Kimura (Institute for Molecular Science), Prof. Y. Toda and Prof. H. Shima (Hokkaido University), and Prof. H. Yoshioka (Nara Women’s University).

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19) C. Wen, J. Li, K. Kitazawa, T. Aida, I. Honma, H.
23) The definition of “Gaussian curvature” is described in the review article (by H. Shima et al.) in this special issue.