Synthesis of Iron-Fullerene Complexes by Scattering of C₆₀ Ions on Ferrocenyl-Undecanethiol SAM Surfaces

Kenji Motohashi
Department of Biomedical Engineering, Faculty of Science and Engineering, and Bio-Nano Electronics Research Centre, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

Tomoki Tachikawa
Graduate School of Interdisciplinary New Science, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

Takashi Uchida
Graduate School of Interdisciplinary New Science, and Bio-Nano Electronics Research Centre, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

Kensei Kawamura
Department of Biomedical Engineering, Faculty of Science and Engineering, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

(Received 22 December 2017; Accepted 13 March 2018; Published 3 May 2018)

In this study, we performed a mass-spectrometric study of cluster ions scattered on glass surfaces covered with ferrocene molecules under the incidence of 4.8 keV-C₆₀⁺ (q = 1 and 2) ions. A couple of optical flats covered with 11-ferrocenyl-1-undecanethiol self-assembled monolayer surfaces (Fc-thiol-SAMs) faced each other with a shape called a tapered planar channel (TPC) and C₆₀ ions entered the wider opening gap. The mass and charge of each ion exiting from the narrower gap of the TPC were successfully analyzed using time-of-flight mass spectrometry combined with the parallel plate charge separation method. When the TPC was tilted by 2° with respect to the C₆₀ ion beam axis, the mass distribution peak shifted to ~730 u. Furthermore, we conducted an elemental analysis of the scattered particles deposited on a Si substrate by inductively coupled plasma mass spectrometry. A significant increase in the amount of iron atoms was confirmed for the deposited substrate, as compared with non-deposited substrates. [DOI: 10.1380/ejssnt.2018.127]

Keywords: Fullerenes; Low energy ion scattering; Molecule-solid scattering and diffraction-inelastic; Clusters

I. INTRODUCTION

Nano-carbon clusters containing metal atoms are very useful for industrial applications owing to their unique mechanical, optical, electrical, and catalytic properties. Functionalized or endohedral fullerenes containing metal atoms have especially attracted great attention because of their diverse applications. In the last decade, synthesis of many endohedral metallofullerenes (EMFs) [1] that encapsulate Li [2], La [3-5], Sc [6, 7], Gd [8, 9], Yb [10, 11], Ba [12], and Sm [13] have been reported. It is expected that EMFs encapsulating Gd atom(s) or Gd@C₈₂ [8, 9] can be used as contrast agents in magnetic resonance imaging (MRI) owing to the increased stability of the Gd (III) ion, minimal toxic effects, high solubility in water, and high proton relaxivity [14]. Metal-fullerene complexes, which include Os [15, 16], Zn [17], and Co [18] are also important in fullerene chemistry because of their potential applications in biological, magnetic, electronic, catalytic, and optical devices. One of the authors involved in the present study succeeded in synthesizing an Fe–C₆₀ complex by low energy Fe⁺ ion irradiation on C₆₀ thin films [19, 20]. Fe–C₆₀ complex, along with EMF Fe@C₆₀, may be useful for application as a contrast agent in the MRI because the Fe atom is a low-cost and safe alternative to Gd. Therefore, we have focused our efforts toward the development of a novel synthesis method for Fe–C₆₀ and Fe@C₆₀ complexes. In the present study, we

FIG. 1. Schematic illustration of the tapered planar channel (TPC).
demonstrated the synthesis of an iron-fullerene complex by scattering of C_{60} ions on ferrocene (Fe)-terminated undecanethiol self-assembled monolayer surfaces (Fe-thiol-SAMs).

II. EXPERIMENTAL

A schematic illustration of the tapered planar channel (TPC) used in this study is shown in Fig. 1. The TPC consists of a pair of BK7 glass optical flats (Sigma Koki OFB-20803-10), an aluminum plate possessing an entrance hole with a diameter of 1.5 mm, and an enclosure with a 10 mm-diameter exit hole. The enclosure is not included in the figure to avoid complexity. The 11-ferrocenyl-1-undecanethiol [HS-(CH$_2$)$_{11}$Fe(C$_5$H$_3$)$_2$] self-assembled monolayer surfaces (Fe-thiol-SAMs) (Prochimia Surfaces) were adsorbed on the surfaces of the two optical flats that were covered with Au (100 nm)/Ti (10 nm) thin films. The Fe-thiol-SAMs were formed by soaking the optical flats covered with Au/Ti thin films in 1 mM (= 1 mol/m$^3$) solution of ethanol at room temperature for approximately 27 h. These two Fe-thiol-SAM surfaces were arranged by sandwiching four ball bearings in such a way that they face each other with a tapered shape. The diameters of two ball bearings were 0.8 mm and that of the other two being 2.0 mm. Thus, the gap of the TPC at the entrance (G$_1$) is 2.0 mm, whereas the gap at the exit (G$_2$) is 0.8 mm. The taper angle with respect to the ion beam axis was $\sim$2.0°. The TPC can be tilted around the rotational axis, which passes through the entrance hole. The tilt angle $\theta$ was defined with the positive direction corresponding to clockwise rotation, as shown in Fig. 1.

Figure 2 shows a schematic illustration of the experimental setup using time-of-flight mass spectrometry (TOF-MS) combined with the parallel plate charge separation method. Ion beams [4.8 keV-C$_{60}$$^{q+}$ ($q = 1$ and 2)] were extracted from the Bio-Nano ECRIS beam line [21] at the Bio-Nano Electronics Research Centre in Toyo University. The ion beam entered the entrance hole with a diameter of 1.5 mm after being chopped by a rectangular pulse voltage ($V_c = 20$ V, $T_{on} = 0.3 \mu$s, and $T_{off} = 19.7 \mu$s) applied to the parallel plate PP$_1$, as shown in Fig. 2. The ions or atoms scattered at the Fe-thiol-SAMs adsorbed on the inner walls of the TPC can exit from the large hole with the diameter of 10 mm. After exiting from the hole, the particles entered another parallel plate (PP$_2$) applying a uniform electric field of $E = 112$ V/cm. The trajectory of each particle was separated with its mass and charge state by the electric field in the PP$_2$. Therefore, the mass $m'$ and the charge state $q'$ of the scattered particle can be analyzed by measuring the displacement $Y$ and the time-of-flight $T$ at the detector in the following equation,

$$
\frac{m'}{q'} \approx \frac{eEL_5}{Y} \left( \frac{L_5}{2} + L_6 \right) \left( \frac{T - L_3 + L_5}{L_3 + L_4 + L_5 + L_6} \right)^2,
$$

where $v_0 = \sqrt{2eV_0/m}$ and $m$ are the initial velocity and the mass, respectively, of C$_{60}^{2+}$ extracted from the Bio-Nano ECRIS with the extraction-bias voltage $V_0 = 2.40$ kV and $e$ is the elementary electric charge. The lengths $L_1$, $L_2$, $L_3$, $L_4$, $L_5$, and $L_6$ are 3.0, 14.4, 2.0, 9.1, 5.0, and 12.0 cm, respectively. The detector of the scattered particle was a two-dimensional position-sensitive detector with microchannel plates (2D-MCP-PSD) [22]. After the TOF-MS combined with the parallel plate charge separation method mentioned above, we performed inductively coupled plasma mass spectrometry (ICP-MS) for the scattered particles deposited on Si(100) substrates. The substrate was set 20 mm behind the exit of the TPC. The fluence of the C$_{60}^+$ ion beam entering the TPC was approximately 1.4 x 10$^{14}$ cm$^{-2}$. Both the TOF-MS experiments and the deposition for ICP-MS were performed in a vacuum chamber evacuated to $< 2 \times 10^{-6}$ Pa by a turbo molecular pump and a scroll pump. The ICP-MS was
conducted using an iCAP-Q (Thermo Fisher Scientific). The deposited and non-deposited substrates placed in the vacuum chamber and another non-used substrate kept in air were independently digested in a strong acid solution using a microwave digestion system (ETHOS EASY, Milestone General). The substrates and a mixture of 11.25 mL of HNO$_3$ and 3.75 mL of HCl were placed in a gas-tight high pressure vessel and were processed at 230°C for 20 min. The sample diluted with pure water to 5% acid solution was set in the iCAP-Q.

III. RESULTS AND DISCUSSION

Figure 3(a) shows the XY-position distributions of the number of scattered particles detected with the MCP-PSD when tilt angle $\theta = 0^\circ$ and the electric field of the parallel plate $E = 0$ V/cm, as the C$_{60}^{2+}$ (4.8 keV) ion beam entered the TPC. This XY distribution is almost the same as the cross-sectional image of the incident C$_{60}^{2+}$ ion beam scraped off the TPC. Figure 3(b) shows the Y distribution of Fig. 3(a) integrated along the Y axis. This graph nearly coincides with the density distribution of the incident C$_{60}^{2+}$ ion beam, i.e., the charge state $q' = q = 2$, along the Y axis. Figures 4(a) and 4(b) show the XY and Y distributions, respectively, of the number of scattered particles when $\theta = 0^\circ$ and $E = 112$ V/cm. Charge states $q' = 2$ and $q' = 1$ of the scattered particles were clearly separated by applying the electric field to parallel plate PP$_2$. Note that there were almost no neutrals because almost no particles were found around $Y = 0$. The fraction of the number of scattered particles with $q' = 0$ was less than 4%, whereas the fractions with $q' = 2$ and 1 were 90% and 6%, respectively. This result suggests that the majority of ions were transmitted to the TPC without charge exchange collisions [23] with the inner walls at zero tilt angle. Figures 5(a) and 5(b) show the XY and Y distributions, respectively, of the number of scattered particles when $\theta = 2^\circ$ and $E = 112$ V/cm. It is clear that when the TPC was tilted by 2° with respect to the ion beam, the charge states of the scattered particle were separated to $q' = 2$, 1, and 0. The populations of charge states $q' = 2$, 1, and 0 were 87%, 6%, and 7%, respectively. For $\theta = 2^\circ$, almost all C$_{60}^{2+}$ ions entering the TPC will geometrically collide with the left-side planar surface because they face each other at 4° due to summed angle of the taper and the tilt angles. However, even in this situation, the small number of particles with charge states of $q' = 1$ and 0 suggests that the charge exchange collisions between C$_{60}^{2+}$ ions and the Fc-thiol SAM surfaces only played a minor role in the scattering processes. It is important to note that the peak position of $Y = 15.5$ mm for the ions with $q' = 2$ scattered at $\theta = 2^\circ$, as shown in Fig. 5(b), shifted slightly downward, as compared with the peak of $Y = 16.5$ mm for the ions with $q' = 2$ scattered at $\theta = 0^\circ$, as shown in Fig. 4(b). This result suggests that ions with $q' = 2$ scattered at $\theta = 2^\circ$ became heavier than those scattered at $\theta = 0^\circ$, which implies that some fullerenes captured atoms or molecules from the Fc-thiol-SAMs on the left-side planar surface of the TPC.

Figure 6 shows the time-of-flight (TOF) spectra of scattered particles including $q' = 2$, 1, and 0 for (a) $\theta = 0^\circ$ and $E = 0$ V/cm, (b) $\theta = 0^\circ$ and $E = 112$ V/cm, and (c) $\theta = 2^\circ$ and $E = 112$ V/cm, when the C$_{60}^{2+}$ ion beam entered the TPC. The rise time at approximately 12.2 $\mu$s.
observed in Fig. 6(b, c) was delayed as compared with the rise time at approximately 12.0 µs observed in Fig. 6(a). The tail behind 12.6 µs observed in Fig. 6(b, c) was not found in Fig. 6(a). These results suggest that the number of molecules slower than the initial C_{60}^{2+} ions increased. Furthermore, the small rise-time delay of Fig. 6(c) compared with Fig. 6(b) also implies that slow molecules exited from the tilted TPC.

Figure 7 shows the mass distributions of scattered particles exiting from the TPC at θ = 0° (black) and 2° (red), according to Eq. (1) with q′ = 2. A more massive distribution for θ = 2° than for θ = 0° is clearly demonstrated. The peak at approximately 700 u for θ = 0° shifted to ~730 u for θ = 2°. The widths of both distributions were almost the same (FWHM ~85 u), where each distribution includes an uncertainty of ~17 u (20%), which is due to the sum of the relative errors of the position Y (10%) and time width T_{ON} (10%). This is evidence of the formation of heavier clusters than C_{60} fullerenes (mass: 720 u) by scattering of C_{60}^{2+} ions on the Fe-thiol-SAM surface. The heavy clusters may include Fe-C_{60} complexes because the full width of the mass distribution of θ = 2° ranges from 645 u to 815 u, which covers the mass of FeC_{60} (776 u). It is important to note that the collision between fullerene ion and Fe-thiol-SAM surface may occur even at θ = 0° because the gap at the exit of the TPC is narrower than the beam diameter. Hence, the particles scattered at the glancing angle (or tapered angle of 2°) may include not only heavier ions due to the gain of atoms but also lighter ions resulting from the loss of carbon atoms. Therefore, it seems reasonable to assume that the peak position (~700 u) of the distribution was the result of the balance between the gain and loss of atoms. This would explain why the peak in θ = 0° was observed at 700 u instead of 720 u. The same reasoning can be applied for the case of θ = 2°, even though it differs from the case of θ = 0° since almost all fullerene ions were scattered on the unilateral surface of the TPC at an angle of 4°. The peak was then observed at m′ ≈ 730 u instead of 776 u.

We carried out ICP-MS of the scattered particles deposited on a Si(100) substrate to verify the formation of Fe-C_{60} complexes. We used C_{60}^{+} ions instead of C_{60}^{2+} to increase the total fluence in this experiment. Figure 8 shows the signal intensities of the Fe atoms from the deposited and non-deposited substrates set in the vacuum chamber, as well as another non-deposited substrate kept in air. We clearly observed a significant increase in the Fe signal intensity in the deposited substrate compared with the other two non-deposited substrates. It should be mentioned that the substrates might be easily contaminated by iron due to the use of stainless steel apparatuses including a vacuum vessel, vacuum pumps, tweezers, and fixing tools, among others, and from dust particles in the air. Nevertheless, the Fe signal corresponding to the deposited substrate was more intense than that of non-deposited substrates. Therefore, we conclude that Fe-C_{60} complexes were successfully synthesized and extracted using this method.

**IV. CONCLUSION**

In this study, we performed a mass-spectrometric study of cluster ions scattered on optical flats covered with ferrocene-terminated alkanethiol self-assembled monolayer surfaces under the incidence of 4.8 keV-C_{60}^{q+} (q = 1 and 2) ions. The mass and charge state of each ion scattered on the surfaces were successfully analyzed using TOF mass spectrometry combined with the parallel plate charge separation method. By tilting the surfaces with respect to the C_{60}-ion-beam axis, the mass distribution peak shifted from ~700 u to ~730 u. Furthermore, we performed elemental analysis of the scattered particles deposited on Si substrates using inductively coupled plasma mass spectrometry. A significant increase in the amount of iron atoms was confirmed as compared with the non-deposited substrates.

**ACKNOWLEDGMENTS**

This work was supported by JSPS KAKENHI (Grant Number JP26400419 and JP17K05602). The authors would like to thank Mr. M. Osumi and Mr. A. Uruma for their help in taking the experimental data.

---


