Fabrication of C_{60} LB films by horizontal lifting method

Atsushi Yamashita, Shin-ichi Morita[†], Issei Matsuoka, Yasuhiro F. Miura* and Michio Sugi

Graduate School of Engineering, Toin University of Yokohama
1614 Kurogane-cho, Aoba, Yokohama 225-8502
Fax: 81-(0)45-974-5290, *e-mail: yfmiura@cc.toin.ac.jp

The fullerene (C_{60}) film at the air/water interface has been transferred onto hydrophobic substrates by the conventional horizontal lifting method. The area per molecule at 30 mN/m is 0.076 nm^2 in case the concentration of the spreading solution is 1.0 mM, while it is 0.131 nm^2 in case the solution concentration is 0.1 mM, indicating that the C_{60} film at the air/water interface becomes 42 % thinner by diluting the solution, although both values suggest the formation of macroscopic clusters at the air/water interface. The area per molecule also increases appreciably by raising the subphase temperature from 17 °C up to 33 °C, indicating that the film thickness at the air/water interface decreases 33 % by raising the subphase temperature. Distinct absorption bands are seen at around 221 nm, 270 nm and 346 nm and the optical density indicates that the thickness of the transferred film increases 34% in case the subphase temperature is elevated from 17°C up to 33°C. The actual transfer ratio is estimated to be 1.9 times higher by raising the subphase temperature from 17 °C up to 33 °C, considering that the floating C_{60} film becomes thinner by elevating the subphase temperature. It has been demonstrated that the C_{60} films at the air/water interface can be efficiently transferred by the conventional horizontal lifting method if the spreading solution is diluted down to around 0.1 mM and the subphase temperature is elevated up to 33 °C.

Key words: Fullerene (C_{60}), Langmuir-Blodgett films, Horizontal lifting method, Transfer ratio

1. INTRODUCTION

The methodology for fabricating the Fullerene (C_{60}) thin film systems has been explored, since Hebard and co-workers reported on superconductivity in the potassium-doped C_{60} both as films and bulk samples [1]. Pioneering works adopted solution evaporation [2], thermal evaporation [3-7], self-assembled (SA) method [8], and Langmuir-Blodgett (LB) technique [9-12]. Among them, the LB technique has certain advantages over other methods because it allows us to assemble functional molecules into tailored two-dimensional molecular sheets of relatively large areas with fairly low energy cost.

Earlier works on the C_{60} LB films seem to open up the possibility for future application. For instance, Wang and co-workers reported on superconducting transition of 8.3 K in the C_{60} LB film doped by potassium [11]. Ikegami and co-workers also reported on superconducting transition of 23 K in the C_{60} LB film doped by rubidium [12] In the two systems, however, superconducting phases were detected by low magnetic field microwave absorption signal (LFS) and global superconductivity has not yet been realized, which is probably due to the granular nature of the films.

Although C_{60} is not an amphiphilic molecule typically used for forming monomolecular layer, relatively smooth layers are obtained at the air/water interface by mixing with amphiphilic matrix molecules, such as icosanoic acid or dioctadecyldimethylammonium perchlorate [10]. These matrices, however, tend to form micrometer-size domains that may limit electrical and optical functions in the ultra-thin systems. Relatively well-organized films can be also obtained by

chemical modifications such as introducing the alkyl chains together with polar groups. In those cases, however, the molecular asymmetry may alter the electronic and optical functions found in the bulk C_{60} systems.

Therefore, we have been interested in the fabrication of C_{60} LB films without using any matrices and chemical modifications and reported that a modified horizontal lifting method, which is first proposed by Ishii [13], can transfer the C_{60} layer at the air/water interface onto solid substrates [14]. The modified horizontal lifting method utilizes the upward movement of the substrate beneath the floating film keeping the substrate surface parallel to the air/water interface to lift up the film. The technique is basically the same as the well-known surface lowering method that utilizes drainage but more suitable for constructing multi-layered systems.

In this paper, we demonstrate that the conventional horizontal lifting technique can also transfer the C_{60} film efficiently onto solid substrate combining a diluted spreading solution of 0.1 mM and a high subphase temperature of 33 °C.

2. EXPERIMENTAL

The Fullerene (C_{60}) was purchased from Aldrich Chemical Company, Inc. and used without further purification. First, the C_{60} benzene solution (0.1 mM or 1.0 mM) was applied on the surface of pure water (Milli-Q). The floating C_{60} molecules were left on the water surface for 5-10 min and compressed up to 30 mN/m with the barrier compression speed of 41 cm^2/min. Then, the C_{60} film on the water surface was divided into

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†Present address: Department of Chemistry, The University of Georgia, Athens, GA 30602-2556, U.S.A

smaller fractions, which are 13×38 mm² in size, by placing a Teflon frame on the film surface. A USI type FSD-300C trough was used for the π-A isotherm measurement and film fabrication processes.

The fractionalized C_{60} sheets, which are 13×38 mm² in size, were transferred onto a quartz plate (1×13×38 mm³) by the conventional horizontal lifting method. The surface of the quartz plate was hydrophobized by keeping it in a container filled with vapor of 1,1,1,3,3,3-hexamethyldisilazane for more than a day prior to the transfer process. The UV-visible absorption spectra were recorded by a Shimadzu UV-2100 spectrophotometer.

3. RESULTS AND DISCUSSION

Figure 1(a) shows typical surface pressure (π)-area per molecule (A) isotherms measured at 17 °C. The solid and broken lines represent the isotherms obtained using spreading solution of 1.0 mM and 0.1 mM, respectively. Figure 1(b) shows the area per molecule at 30 mN/m on the subphase of 17 °C plotted against solution concentration. The plots at 0.1 mM and 1.0 mM are the averages of 72 and 42 data, respectively. The area per molecule is 0.076 ± 0.010 nm² in case the

concentration is 1.0 mM but it increases up to 0.131 ± 0.022 nm² using a diluted solution of 0.1 mM, as shown in Fig. 1(b).

Since the occupied area of each C_{60} molecule closely-packed in a two dimensional (2D) molecular assembly is estimated to be *ca.* 1 nm² according to the reported cell parameters of the crystals of C_{60} [15], the smaller value indicates a coagulated structure at the air/water interface. We have already reported that the C_{60} molecules form clusters at the air/water interface and that the film transferred onto a quartz plate by the modified horizontal lifting method consists of grains, which are 0.1-0.4 μm in lateral size, and 30-70 nm in thickness [14]. The granular C_{60} film at the air/water interface is considered to be 42 % thinner by diluting the C_{60} solution from 1.0 mM down to around 0.1 mM considering the increase of the occupied area.

Figure 2(a) shows typical π-A isotherms measured at 9°C, 17°C, 25°C and 33°C. Figure 2(b) shows the average area per molecule at 10 mN/m plotted against the subphase temperature. The average values of the area per molecule at 10 mN/m are from 12, 12, 21 and 23 different isotherms for 9°C, 17°C, 25°C and 33°C,
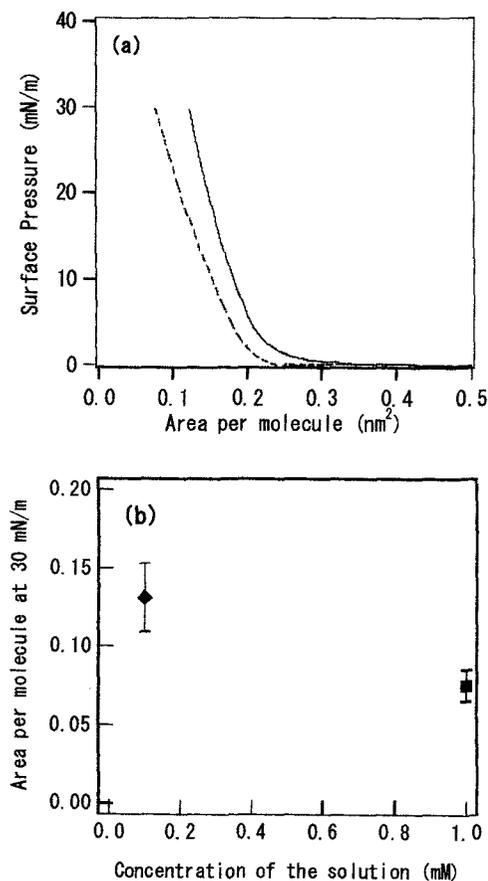

Fig. 1. (a)Typical surface pressure (π)-area per molecule (A) isotherms at 17 °C measured using spreading solution of 1.0 mM(----) and 0.1 mM(—). (b) The area per molecule plotted against the concentration of the spreading solution (17 °C).
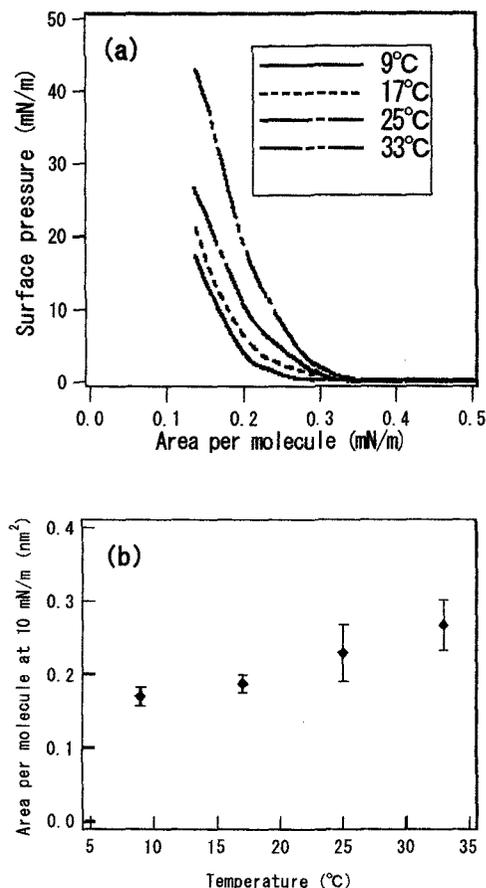
Fig. 2. (a) Typical surface pressure (π)-area per molecule (A) isotherms measured at 9°C, 17°C, 25°C and 33 °C using spreading solution of 0.1 mM; (b) area per molecule plotted against the concentration of the spreading solution (0.1 mM).

respectively. The average molecular areas are 0.169±0.013 nm², 0.187±0.012 nm, 0.229±0.039 nm² and 0.266±0.034 nm², at 9°C, 17°C, 25°C and 33 °C, respectively. The molecular area tends to expand appreciably by raising the subphase temperature. Here we also postulate that the granular C_{60} film at the air/water interface tends to become thinner by increasing the subphase temperature.

Obeng and Bard reported a π-A isotherm of the C_{60} molecules on water (Milli-Q) of 25 °C; the area per molecule is around 0.96 nm² at 10 mN/m, suggesting a formation of a monomolecular film [9]. In our data, however, the area per molecule is 0.229±0.039 nm² at 25 °C, which do not coincide with that of Obeng and Bard.*
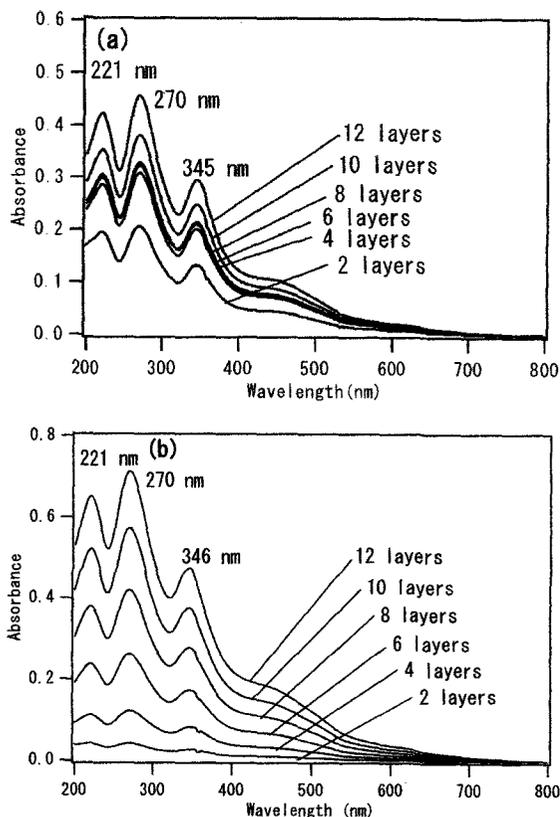

Fig. 3. Typical absorption spectra of the C_{60} LB films of 2-12 layers fabricated by horizontal lifting method at the subphase temperature of 17 °C (a) and 33 °C (b).

Figures 3(a) and 3(b) show typical absorption spectra of the C_{60} LB films of 2-12 layers fabricated by the conventional horizontal lifting method at the subphase temperature of 17°C and 33°C, respectively.

* In our experiment, 1 mL of a 0.1 mM benzene solution was introduced to 930 cm² of the air/water interface, while 100 μL of a 0.05-0.1 mM benzene solution was introduced to about 400 cm² of the air/water interface, as for the work by Obeng and Bard [9].
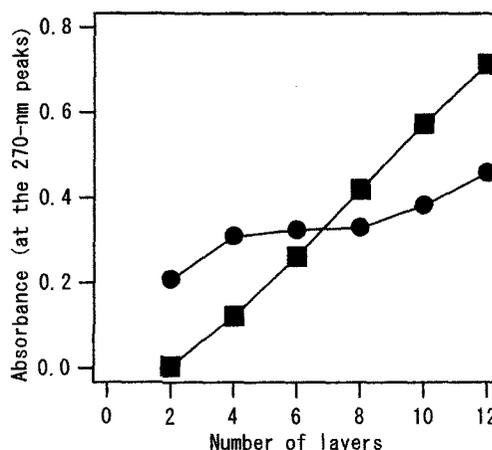

Fig. 4. The absorbance of 270-nm peaks vs. number of layers of the C_{60} LB films fabricated using subphase temperature of 17°C(●) and 33 °C(■).

Distinct absorption peaks have been observed at 221 nm, 270 nm and 345-346 nm, which are characteristics of C_{60}. All these peaks are red-shifted by *ca.* 10 nm compared to those of solution samples, which coincide well with the earlier works [10].

Figure 4 shows absorbance at the 270-nm peaks of the C_{60} LB films plotted against the number of layers. The closed circles and squares represent the absorbance of the C_{60} LB films fabricated using the subphase temperature of 17°C and 33 °C, respectively. In case the subphase temperature is 17°C, the increment of the absorbance is somewhat irregular, as shown in Fig. 3(a) and Fig. 4., suggesting a relatively poor reproducibility of the film transfer. On the other hand, in case the temperature is 33 °C, the increment of the absorbance is regular and the absorbance plotted against number of layers appears linear, although the absorbance of the first two layers is appreciably lower than those deposited over the two layers, as shown in Fig. 3(b) and Fig. 4.

Furthermore, in case the subphase temperature is 17°C, the absorbance changes drastically by moving the measuring spot on the samples, suggesting the macroscopic non-uniformity of the sample, while in case the temperature is 33 °C, the absorbance does not change appreciably by moving the measuring spot, suggesting the macroscopic uniformity. In case the subphase temperature is 33 °C, the absorbance of the 270-nm peak is 0.616±0.104, while it is 0.459±0.140 in case the subphase temperature is 17 °C. The absorbance is *ca.* 1.3 times higher in case the temperature is elevated from 17 °C up to 33 °C. Furthermore, as stated earlier, by raising the temperature from 17 °C up to 33 °C, the area per molecule increases from 0.187 nm² to 0.266 nm², suggesting that the average thickness of the floating C_{60} layer above the subphase of 33 °C is 30% thinner than that above the subhase of 17 °C. Therefore, it has been estimated that

the actual transfer ratio in case the subphase temperature is 33 ℃ is 1.9 times larger than that in case it is 17 ℃.

4. CONCLUSION

The experimental results are summarized : (1) the thickness of the C$_{60}$ film at the air/water interface becomes 42 % thinner by diluting the spreading solution from 1.0 mM to 0.1 mM in case the subphase temperature is 17 ℃, (2) the average thickness of the C$_{60}$ film at the air/water interface becomes 30 % thinner by raising the subphase temperature from 17 ℃ to 33 ℃, and, as a total, (3) the transfer ratio becomes 1.9 times higher by diluting the spreading solution from 1.0 mM to 0.1 mM and by raising the subphase temperature from 17 ℃ to 33 ℃.

We have already reported that the C$_{60}$ film at the air/water interface can be effectively transferred by a modified horizontal lifting method, where a hydrophobized substrate is lifted up beneath the floating layer keeping the substrate surface parallel to the floating film [14]. In this paper, it has been also demonstrated that the C$_{60}$ film at the air/water interface can be transferred efficiently by the conventional horizontal lifting method by elevating the subphase temperature up to 33 ℃ using a relatively diluted spreading solution of 0.1 mM.

ACKNOWLEDGMENT

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