Construction of C_{60} Monolayer on the Water Surface

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A C_{60} monolayer was constructed on the water surface by the multi-step creep method for the first time. The surface morphology of the C_{60} monolayer was homogeneous and the C_{60} molecules in the monolayer were closely and regularly packed in hexagonal array.

Buckminsterfullerene (C_{60}) has attracted much attention because of its characteristic structure and interesting physical properties such as superconductivity at a high temperature[1] and high nonlinear optical coefficients.[2] For the application of the C_{60} monolayer as functional devices, it is inevitable to construct the defect-free or defect-diminished C_{60} ultra thin film. Amphiphilic molecules such as fatty acids and phospholipids are generally used for the construction of monolayer on the water surface. However, since the C_{60} molecule is not amphiphilic without any chemical modification and exhibits strong intermolecular attractive force, the C_{60} molecules easily aggregate in a 3-dimensional array without the formation of the C_{60} monolayer on the water surface.[3] The multi-step creep method[4] is one of the effective preparation methods for the formation of defect-diminished monolayer on the water surface. As the multi-step creep method is based on the structural relaxation phenomena in the monolayer, it might be useful for the construction of the morphologically and crystallographically homogeneous C_{60} monolayer.

In this study, the C_{60} monolayer prepared by the multi-step creep method on the water surface was investigated on the basis of the transmission electron microscopic (TEM) and the atomic force microscopic (AFM) observations.

A very dilute C_{60} benzene solution of 1×10^{-5} mol L^{-1} was spread on the pure water surface at the subphase temperature of 293 K. The surface pressure-molecular occupied area (π-A) isotherm measurement was carried out at the constant compressing rate of 120 mm^2 sec^{-1}. The prepared C_{60} film on the water surface was transferred onto a collodion substrate for TEM study (Hitachi, H-7000) and a freshly cleaved mica for AFM observation (Seiko Instruments Inc., SPI3700) by a horizontal drawing-up method.[5]

Figures 1(a) and (b) show the AFM image of the C_{60} film at 0 mN m^{-1}(a) and the height profile(b) along the straight line shown in Figure 1(a), respectively. The average height of an isolated circular C_{60} domain was ca. 0.9 nm which fairly corresponded to the diameter of C_{60} molecule including π electron cloud, ca. 1 nm.[6] Hence, it seems reasonable to consider that the C_{60} molecules form 2-dimensional domains right after spreading a sample solution on the water surface.

Figure 2 shows the π-A isotherm of the C_{60} film at 293 K and its AFM images at 10 and 20 mN m^{-1}. The voids among the C_{60} domains were observed from the AFM image. A limiting area evaluated from the π-A isotherm of the C_{60} film was 1.3 nm^2 $molecule^{-1}$. Also, the molecular occupied area in the 2-dimensional C_{60} crystal calculated from the lattice parameter of the 3-dimensional C_{60} one was 0.87 nm^2 $molecule^{-1}$. Therefore,

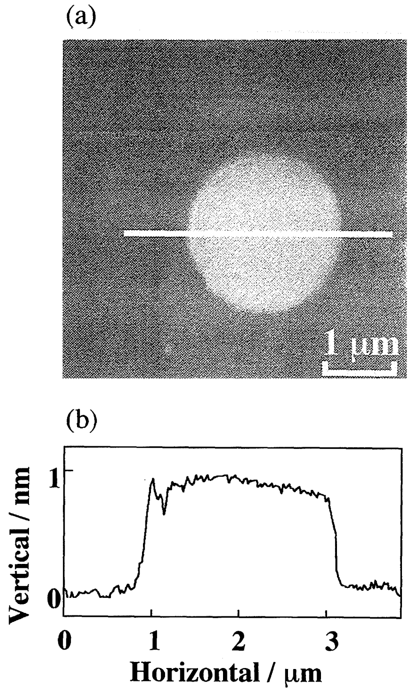

Figure 1. (a) AFM image of C60 film at a surface pressure of 0 mN m^{-1} and (b) its height profile under the line into (a).

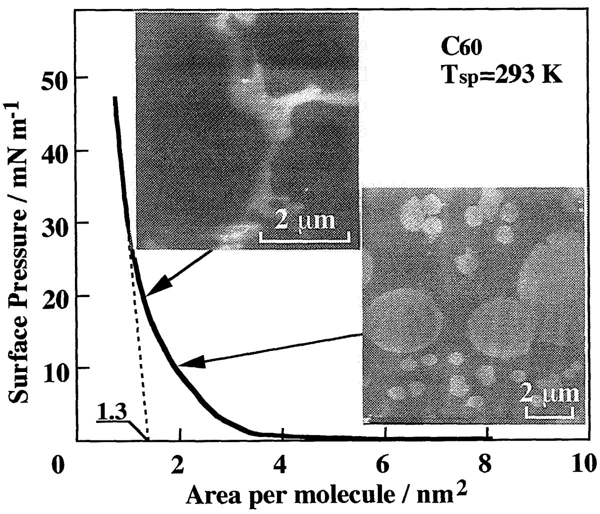

Figure 2. π-A isotherm of C60 film at Tsp of 293 K and AFM images of C60 film at the surface pressure of 10 and 20 mN m^{-1}.

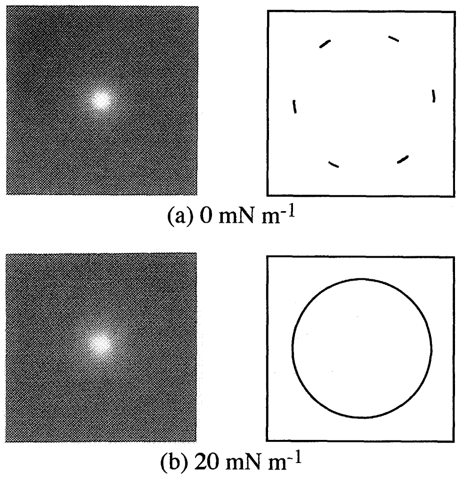

Figure 3. ED patterns of C60 film at the surface pressure of (a) 0 and (b) 20 mN m^{-1} and their schematic diffractions.

these results indicate that the C_{60} monolayer with much voids was prepared by aggregation of the 2-dimensional C_{60} domains the at least at a low surface pressure. However, the C_{60} film compressed to 20 mN m^{-1} by a continuous compression method collapsed into 3-dimensional aggregations in part, as shown in Figure 2. Therefore, Figure 2 indicates that in the case of the continuous compression to the high surface pressure of 20 mN m^{-1}, there was not enough time for the structural relaxation to rearrange in the 2-dimensional C_{60} film.

Figures 3(a) and (b) show the electron diffraction (ED) patterns of the C_{60} film at (a) 0 and (b) 20 mN m^{-1} prepared by the continuous compression method, respectively. The ED pattern for the C_{60} film prepared at 0 mN m^{-1} shows the crystalline hexagonal spots, and on the other hand, that for the C_{60} film prepared at 20 mN m^{-1} was the crystalline Debye ring. Therefore, Figure 3 revealed apparently that the C_{60} film was collapsed into small fragments during a continuous compression, maybe due to its rigidity and morphologically inhomogeneous aggregation of the C_{60} film fragments. Then, Figure 3 apparently indicates that the structural relaxation during a monolayer compression might be effective to construct the homogeneously large and defect-diminished C_{60} monolayer. Therefore, the multi-step creep method was proposed to construct the defect-diminished C_{60} monolayer.

In the case of the multi-step creep method, the C_{60} film was compressed to 15 mN m^{-1} and maintained at the surface pressure for a sufficient area-creep. After the area-creep at 15 mN m^{-1}, the alternative compression and area-creep was repeated several times, and then, the surface pressure of the C_{60} film was reached to 20 mN m^{-1}. The area-creep of the C_{60} film at each surface pressure was carried out until the molecular occupied area of the film was reached to the almost constant. The molecular occupied area of the C_{60} film at the surface pressure of 20 mN m^{-1} corresponded to the ideal value of the 2-dimensional C_{60} crystal due to the sufficient structural relaxation.

Figures 4(a) and (b) show the ED pattern and the AFM image of the C_{60} film at 20 mN m^{-1} prepared by the multi-step creep method, respectively. The AFM image showed that the C_{60} film was remarkably homogeneous, and the film thickness was ca. 0.8 nm which agreed well with the diameter of the C_{60} molecule with π electron cloud. Since the ED pattern of the C_{60} film was the sharp crystalline hexagonal spots, the C_{60} molecules were closely packed in 2-dimensional monolayer even at the high surface pressure of 20 mN m^{-1}. As shown in Figure 2, the C_{60} film prepared at 20 mN m^{-1} by the continuous compression method was easily collapsed. Therefore, it is reasonable to conclude that the C_{60} molecules in the C_{60} film prepared by the multi-step creep method was regularly packed in a hexagonal array and the defect-diminished C_{60} crystalline monolayer might have a high mechanical stability.

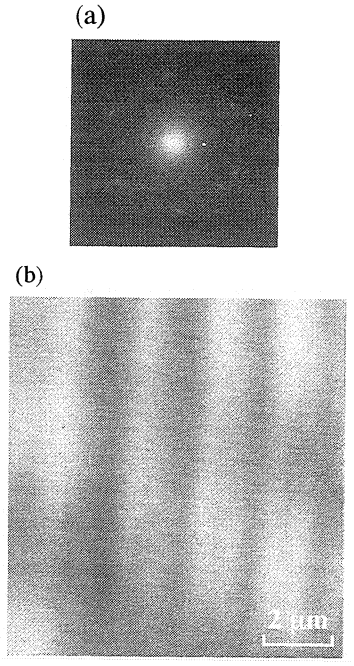

Figure 4. (a) ED pattern and (b) AFM image of C60 film prepared by multi-step creep method.

In conclusion, the C_{60} molecules without any chemical modification formed the 2-dimensional domains on the water surface. The multi-step creep method is useful for the construction of the defect-diminished C_{60} monolayer due to a sufficient structural relaxation.

Reference and Notes

1 A. F. Hebard, M. J. Rosseinsky, R. C. Haddron, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature*, **350**, 600 (1991).

2 Z. H. Kafafi, J. R. Lindle, R. G. Pong, F. J. Bartoli, L. J. Lingg, and J. Millile,*Chem. Phys. Lett.*, **188**, 492 (1992).

3 for example, T. Nakamura, H. Tachibana, M. Yumura, M. Matsumoto, R. Azumi, M. Tanaka, and Y. Kawabata, *Langmuir*, **8**, 4 (1992).

4 T. Kuri, Y. Oishi, and T. Kajiyama, *Tfans. Mat. Res. Soc. Jpn.*, **15A**, 567 (1994).

5 Y. Oishi, T. Kuri, Y. Takashima, and T. Kajiyama, *Chem. Lett.*, **1994**, 1445.

6 Diameter of the C_{60} molecule was calculated from (a)STM image and (b)molecular simulation ; (a) for example, J. L. Wragg, J. E. Chamberlain, H. W. White, W. Krätschmer, and D. R. Huffman, *Nature*, **348**, 623 (1990). : (b) S. Saito, and A. Oshiyama, *Phys. Rev. Lett.*, **66**, 2637 (1991).