Direct observation of C_{60} LB film with scanning tunneling microscopy

Jun Guo, Yu Xu, Yuliang Li, Chun Yang, Youxin Yao, Daoben Zhu and Chunli Bai
Institute of Chemistry, Chinese Academy of Sciences, Beijing, People's Republic of China

Received 6 April 1992

We report the direct imaging of monolayer LB film of C_{60}. The LB film was prepared onto an Au(100) surface by the vertical dipping method for scanning tunneling microscopy (STM) measurements. Ordered arrays of C_{60} molecules and close-packed molecular aggregation in the film are shown on the STM images. The calculated diameters along two mutually perpendicular directions in the arrays are 0.635 ± 0.013 and 0.572 ± 0.024 nm, respectively. Our results demonstrate that the molecular shape of C_{60} is easily compressed into an ellipsoid while forming the LB film.

1. Introduction

Following the efficient synthesis of macroscopic amounts of C_{60} and C_{70} clusters, intense interest in the spectroscopic and microscopic studies of these species has been shown [1]. A variety of experimental methods has been employed to investigate the structures of both individual molecules and their occurrence on crystal surfaces. The presence of C_{60} was first discovered by mass spectroscopy in studies of gas-phase carbon clusters. Regarding scanning tunneling microscope studies on the direct topography of C_{60} molecules, American scientists first obtained the STM images of C_{60} under the environments of vacuum and air in December 1990 [2,3], and the sample they used was C_{60} powder. After that Li et al. at Minnesota University observed different morphologies of thin film structures of pure and potassium-doped C_{60} grown on a GaAs (110) surface [4]. However, it has not been reported studying Langmuir–Blodgett (LB) film composed of C_{60} with STM.

Although C_{60} is not a self-assembling amphiphilic molecule of the type usually used to form LB films, according to our investigation and the result of Obeng et al. [5], its stable Langmuir film could be formed at the air–water interface.

Correspondence to: J. Guo, Institute of Chemistry, Chinese Academy of Sciences, Beijing, People's Republic of China.

We prepared a monolayer LB film with C_{60} with a purity of 99.90% onto a single crystal surface of gold substrate taking advantage of the LB film formation technique, then observed the surface topography using a scanning tunneling microscope and obtained clear top view images.

2. Experimental

Our production technique is similar to the Krätschmer–Huffman method [6,7]. The efficient macroscopic preparation of C_{60} was performed by the vaporization of graphite rods in 100–150 Torr of helium. After separating the solid reside by HPLC the C_{60} fraction was found to have a satisfactory purity of 99.90%. The measurement of pressure-area isotherms (Π–A curve) and deposition experiments were performed on a computer-controlled KSV 5000 instrument (made in Finland).

The purified C_{60} powder was dissolved in benzene (G.R.) using ultrasonic waves to form a solution with a concentration of 0.9–1.0 mM. 200 μl of the solution was carefully spread on a 0.01 M KCl aqueous solution or a freshly distilled water surface in a LB trough (707 cm^2) at 19°C. After evaporation of the solvent, the floating layer at the air–water interface was compressed by a mobile teflon barrier at a speed of 20 mm/min and the surface pressure was simul-

taneously monitored by a Wilhelmy balance while getting a Π–A curve of the sample.

The Langmuir film thus formed was kept at a surface pressure of 18 mN/m for 1 h, after which stability was reached. The film was transferred onto a single crystal surface of Au(100) by vertical dipping at a speed of 1–2 mm/min for STM measurement under room temperature and air pressure. We used a CSTM-9000 scanning tunneling microscope developed by ourselves to image the samples in the constant-current mode. The bias voltage was typically 29 mV, and the tunneling current was 0.84 nA.

3. Results and discussion

Fig. 1 shows the surface pressure-area isotherms (Π–A curve) of C_{60}. It can be seen from the curve that a stable Langmuir film was formed at the air–water interface and that it did not collapse until 40 mN/m. The limiting molecular area of C_{60} is 0.285 nm^2 on 0.01 M KCl solution and 0.310 nm^2 on pure water, respectively.

Figs. 2 and 3 are STM images obtained from different areas of C_{60} LB film on the Au(100) surface, with their scanning areas of 4.78×4.84 and 1.70×4.27 nm^2. In the middle area of fig. 2 two rows of C_{60} molecules in ordered arrays are clearly shown. In the upper-right rectangle a cross line is drawn along the direction of line AB in the figure. There are five

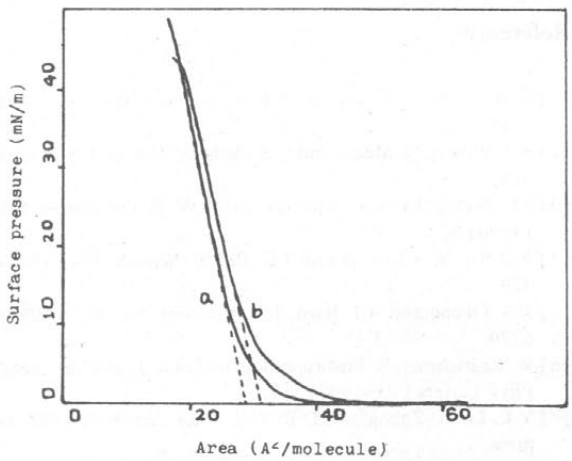

Fig. 1. Surface pressure-area isotherms (Π–A curve) of C_{60} at 19°C (a) on 0.01 M KCl solution, (b) on pure water.

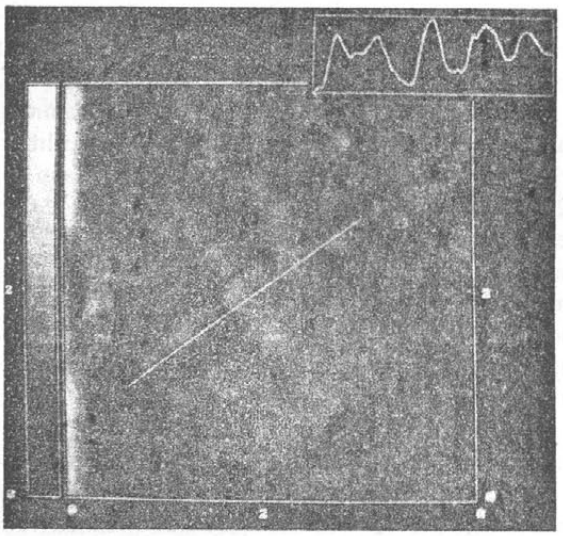

Fig. 2. STM image of the C_{60} LB film on an Au(100) surface ($I_T=0.84$ nA, $V_T=29$ mV, scanning area 4.78×4.84 nm^2).

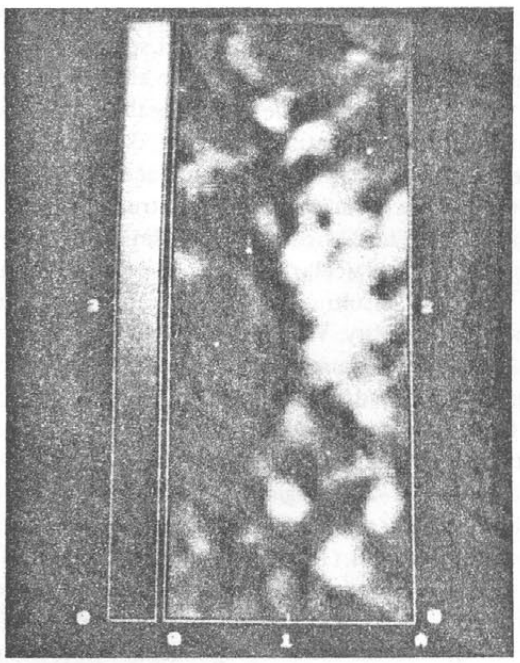

Fig. 3. STM image of the C_{60} LB film, showing molecular aggregation of close-packed C_{60} ($I_T=0.84$ nA, $V_T=29$ mV, scanning area 1.70×4.27 nm^2).

peaks in the cross line indicating that five C_{60} molecules exist in the cross section, which is consistent with the directly perceived result shown in fig. 2.

A STM image of cleaved graphite with a scanning area of $\approx 4 \times 4$ nm^2 was used for geometric calibration to calculate the diameter of C_{60} molecules in fig. 2. The statistically averaged results have proved that each diameter along the two directions which are mutually perpendicular has a different value. The one along the direction of line AB is 0.635 ± 0.013 nm long, while the other along the perpendicular direction is 0.572 ± 0.025 nm. This result demonstrates that the molecular shape of C_{60} is easily transformed into an ellipsoid when compressed to form a monolayer film. The calculated result of average area occupied by a single molecule is $S = \pi ab = 0.285 \pm 0.004$ nm^2, which accords with the area value obtained from the Π–A curve very well, and thus proved the truthfulness of the measured images.

According to the report of literature [8], X-ray powder diffraction data of C_{60} show an average radius of 0.351 nm and the diameter calculated from the carbon cage itself is 0.71 nm, while in this paper the largest radius of C_{60} was calculated to be 0.318 nm from the STM image. This smaller result than above values is due to the fact that spherical hydrophobic molecules of C_{60} which are easy to roll lead to aggregation easily while spreading the solution and compressing the floating layer. Fig. 3 shows the aggregation of close-packed C_{60} molecules in the LB film. Because of limitations of the structural features it is difficult to fabricate the LB film of C_{60} by vertical dipping particularly in case of using pure water as subphase, resulting in a small transfer ratio and poor repeatability. When 0.01 M KCl solution was used instead of pure water, a transfer ratio of 0.4 could be reached.

Generally, it is not suitable for STM to image such a thick molecule in its crystalline state, which by virtue of the 1.5–2.0 eV gap between its highest occupied molecular orbital (HOMO) and lowest unfilled molecular orbital (LUMO) might be thought of as insulating. However, experimental results demonstrated that C_{60} molecules could be scanned imaging by STM, whereas the imaging mechanism is not entirely clear. Some researchers suggested [2,3], the C_{60} ionization potential is in the range of 7.50–7.72 eV, so the LUMO is not far from the metal Fermi level (E_F). Moreover, interactions of the Au surface with neighbouring clusters will shift, split and broaden the molecular orbital, thus providing some density of states $p(E_F)$ at E_F, while STM is quite sensitive to $p(E_F)$ on the topmost atoms in the molecule. On the other hand, the presence of the tunneling tip may perturb the molecule in such a way that suitable electronic states become available for occupation. Experimentally the molecules were clearly detected by STM. In spite of this, proper instrumental parameters must be adjusted to perform the experiments, e.g. the range of the tunneling current and bias voltage.

We have observed clean Au(100) surfaces systematically and found that in case of large scanning area (more than 20×20 nm^2), some specks with irregular shapes were shown on the surface. But the surface was quite flat in a scanning area of less than 10×10 nm^2 at least. For the C_{60} sample with a molecular diameter of 0.7 nm or so, a single crystal of gold can be considered as a suitable substrate by any means.

Acknowledgement

The authors would like to thank Professor Youchang Xie from the Department of Chemistry of Peking University for his careful examination of this paper. This project was supported by the National Natural Science Foundation of China.

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