Influence of the Electrolyte Composition of the Subphase on the Structure of 2D Films of Fullerene C_{60}

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Received April 12, 2006

Abstract—The morphology of 2D films of fullerene C_{60} on interfaces has been studied by Brewster angle microscopy and atomic force microscopy. Fullerene C_{60} tends to aggregate, forming supramolecular structures with a surface area per C_{60} molecule from 21.6 to 2900 Å^2. As the area per C_{60} molecule decreases, monomolecular clusters gradually transform into multiplayer structures. The introduction of an electrolyte into the system prevents the formation of fullerene globules and favors the formation of more homogeneous films.

In recent years, fullerenes and nanotubes and their derivatives have attracted attention from the standpoints of both basic research and technological use [1–4]. Well-ordered 2D layers of fullerene C_{60} transferred onto different substrates are of particular interest due to the possibility of using them as molecular devices in different areas of optoelectronics and nanotechnologies [5–7]. The first image of fullerene clusters on a gold substrate, obtained with a scanning tunneling microscope in 1990 [8], opened a radically new area of study of the behavior of nanostructures. Modern methods can provide information on the behavior of a substance at the interface, which makes it possible to compare the quality of films formed by different methods. One method of organization of fullerene films on the surface of a substrate is vacuum deposition [9, 10].

Scanning tunneling microscopy, as well as the study of the electrochemical properties of samples, has shown that the distribution of fullerene over the substrate surface is not uniform. We suggested a simple and efficient method of obtaining 2D films on the surface of the aqueous subphase followed by transfer of the films onto a solid substrate. The parameters of 2D films can be controlled by the Langmuir method, and the transfer of the resulting layers onto a solid substrate can be controlled by the Langmuir–Blodgett or Langmuir–Schaefer method, depending on the properties of the solid phase. The Langmuir method makes it possible to control film parameters, such as the area per fullerene molecule and the two-dimensional pressure at a fixed film surface area, for example, the pressure at which a 2D film sample is transferred onto another support [11, 12]. The technique of obtaining of 2D films on the energetically homogeneous surface of the aqueous subphase allows one to directly observe the change in the film structure with a change in its area by means of Brewster angle microscopy.

EXPERIMENTAL

Chromatographically pure grade fullerene C_{60}, and chemically pure $(NH_4)_2SO_4$ and NH_4OH were used. 2D films were produced and their parameters were controlled by the Langmuir method. Distilled water or a solution containing different amounts of ammonium sulfate was used as a subphase for obtaining films. The pH of the subphase (pH 6.7) was adjusted by adding an NH_4OH solution.

The morphology of the films on the subphase surface was studied by Brewster angle microscopy on BAM 2 and MiniBAM (at lower magnification) instruments. The structure of the 2D fullerene film transferred onto a silicon wafer was determined by atomic force microscopy (AFM). The images of the transferred 2D films were obtained on a Nanoscope III (United States) instrument in the tapping mode at a scan rate of 2.15 Hz. A TESP silicon cantilever (length, 225 μm; frequency, 300 kHz) was used. The samples for AFM studies were transferred by the Langmuir–Schaefer method.

Films were produced by applying a fullerene solution in toluene to the aqueous subphase surface. Preliminary experiments to select experimental conditions showed that the application of a solution containing 5.6×10^{-8} mol/L of C_{60} is optimal. The stationary parameters of the two-dimensional pressure isotherms for the systems under consideration were obtained at a film compression rate of 0.01309 m^2/min. The solvent was completely removed from the applied film within 25 min after the beginning of the experiment.

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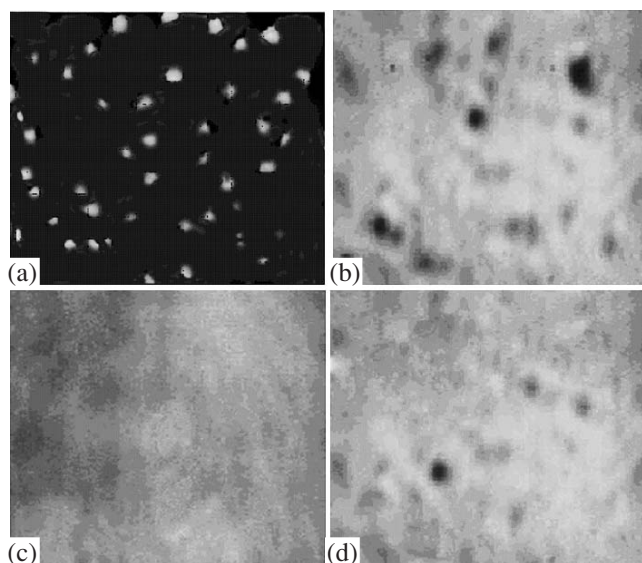
Fig. 1. Brewster angle microscopy images of 2D films of fullerene C_{60} on the surface of the water subphase ($T = 294$ K, pH 6.7), the surface area per molecule is (a) 2900 (gaseous layer), (b) 90, and (c) 30 $Å^2$; (d) films on the surface of a 0.01 M $(NH_4)_2SO_4$ aqueous solution with the surface area per molecule 90 $Å^2$.

RESULTS AND DISCUSSION

The structure of thin films of fullerene C_{60} molecules on interfaces was studied by Brewster angle microscopy and AFM. Brewster angle microscopy was used for studying the phase state of a sample in the course of formation of a 2D film on the surface of the aqueous subphase as the area of the deposited film changed. Figure 1a shows the image of the fullerene film in which the area per molecule exceeds the size of the fullerene globule by about a factor of 30. Under these conditions, classical surfactants form a gaseous film. Fullerene molecules exhibit a different behavior. As is seen, a considerable portion of C_{60} molecules deposited on the interface form aggregates. Supramolecular structures form immediately after the deposition of a fullerene solution as the solvent begins to evaporate. At a large area per C_{60} molecule (~2900 $Å^2$), the fullerene molecules are distributed between the aggregated species and separate molecules that form a gaseous layer (Fig. 1a). When the film is compressed to an area per fullerene molecule of ~200 $Å^2$, structures with higher aggregation levels appear. In this case, bilayer domains are likely formed. In this two-dimensional pressure range, the surface area free of fullerene molecules is ~10% of the total interface area in Fig. 1b. When the area per molecule becomes as small as 96 $Å^2$, which corresponds to the hexagonal packing of C_{60} molecules in a hypothetical monolayer, heterogeneous folded multilayers are observed. They are uniformly distributed over the subphase surface. The C_{60} molecules are distributed between 2D film regions with higher and lower densities (the latter occupy a major portion of the interface area (Fig. 1c)).

To control the structure of fullerene films, different amount of $(NH_4)_2SO_4$ were introduced into the aqueous subphase. Adsorption of cations on the surface of fullerene globules leads to the formation of a double electric layer, which prevents fullerene aggregation. Figure 1d shows the microphotograph of the C_{60} film with the surface area per molecule 90 $Å^2$ obtained at the two-dimensional pressure 20 mN/m on the surface of 0.01 M $(NH_4)_2SO_4$ solution. Comparison of the characteristics of the films formed on water and electrolyte solutions at given two-dimensional pressures demonstrates that the area free of fullerene molecules is smaller in the latter case. Hence, the introduction of an electrolyte favors a more uniform distribution of fullerene of the subphase surface.
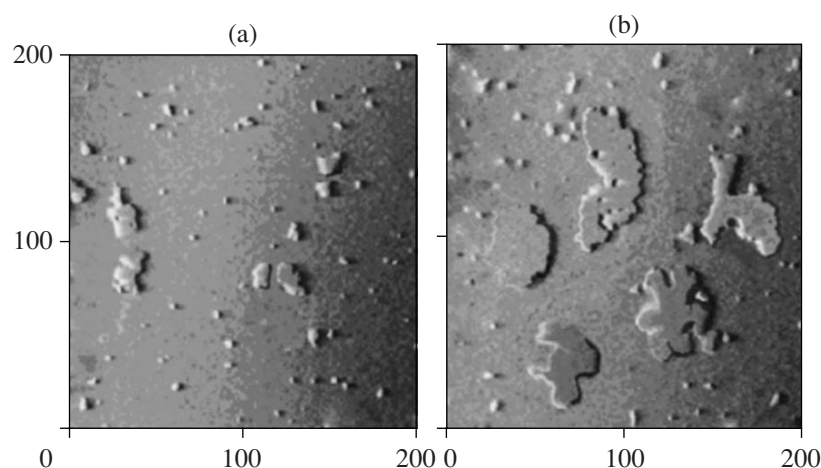

Fig. 2. AFM images of 2D films of fullerene C_{60} ($T = 295$ K, pH 6.7) transferred onto a silicon wafer: the surface area per molecule (a) 2900 and (b) 150 $Å^2$.
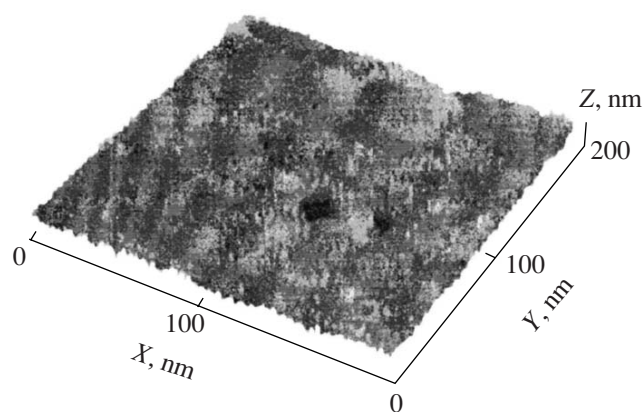
Fig. 3. AFM image of the 2D film of fullerene C_{60} transferred onto a silicon wafer at the surface area per molecule 90 Å^2, $T = 295$ K, pH 6.7.

AFM images of the surface of transferred fullerene C_{60} films were obtained. There is a correlation with the Brewster angle microscopy data, which make it possible to characterize the phase state of the 2D film at the surface of the aqueous subphase. The AFM images show that fullerene molecules are distributed between aggregates forming clusters and separate molecules. At surface areas per C_{60} molecule from 200 to 2900 Å^2, the films contain separate molecules, aggregates composed of two or three molecules and rather large clusters (Fig. 2a). The number of aggregates composed of two or three C_{60} molecules depends only slightly on the surface area per molecule in the 2D film. Conversely, the size (number of molecules) of clusters depends considerably on the surface area per molecule. At the surface area per molecule 200 Å^2, clusters containing 30–40 fullerene molecules are identified. Such a cluster has a round shape and is a hexagonal packing of globular molecules. A decrease in the surface area per molecule in the 2D fullerene film leads to enlargement of cluster structures and a change in their shape (Fig. 2b). These

structures consist of a central core with diverging asymmetric formations. At the same time, the monolayer structure of the films persists. Transfer of the 2D fullerene film at a two-dimensional pressure >1 mN/m under the conditions where the surface area per molecule is 90 Å^2 shows the formation of thicker structures. The film structure can be schematically represented as a monomolecular film with chaotically arranged two-layer clusters (Fig. 3). At the same time, there are regions at the water surface that are not occupied by fullerene molecules. At the initial portion of the two-dimensional pressure isotherm of the 2D fullerene film, the area of the "holes" is about 10% of the total surface area of the sample.

Upon compression of the fullerene film to the two-dimensional pressure 21.6 mN/m, a multilayer film is formed. Figure 4 shows the surface profile of this film. In this state, holes are absent and the thickness drop is 2–3 nm. Our findings allow us to conclude that rough six- and three-layer films are obtained. A further increase in two-dimensional pressure results in formation of thicker multilayer films.

The study of the structure of thin fullerene films applied to the aqueous subphase and the structure of films transferred onto a solid substrate showed that there is a good correlation between the results obtained. Brewster angle microscopy and AFM show the formation of cluster structures in a 2D film at surface areas per molecule considerably exceeding the geometric size of the fullerene molecule. Fullerene C_{60} globules at the interface have a strong tendency of aggregation. This property of complicated molecules, such as fullerene, leads to the formation of supramolecular structures immediately in the course of applying a dilute fullerene C_{60} solution to the surface of the aqueous subphase, which is accompanied by dissolution and evaporation of the organic solvent. This complicated process results in the formation of the statistically most probable distribution of fullerene globules—from free discrete molecules to clusters of different size—at the surface of the aqueous subphase. Direct observations
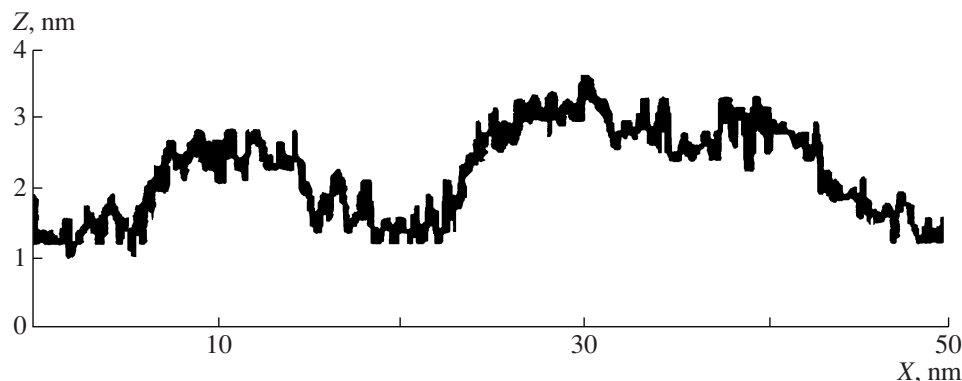

Fig. 4. Profile of the surface of the 2D film of fullerene C_{60} obtained by AFM. The 2D film ($T = 295$ K, pH 6.7) was transferred from the surface of the aqueous subphase onto a silicon wafer at the surface area per fullerene molecule 21.6 Å^2.

showed that this tendency of formation of complicated structures being in equilibrium with gaseous molecules at the air/water interface persists to the beginning of formation of a multilayer film. A decrease in the area per fullerene molecule results in a more complicated shape of aggregates and in an increase in the number of molecules involved in formation of supramolecular structures. Compression of the film to the area per molecule corresponding to the hexagonal packing in a hypothetical monolayer leads to the formation of a 2D film containing multilayer regions and regions of the subphase free of fullerene globules.

We determined the trend of the change in the structure of the 2D film with a change in the electrolyte composition of the subphase. For equal surface areas per molecule, the presence of a salt in the aqueous subphase changes the state of aggregation of films as compared with the films obtained on the aqueous subphase without addition of an electrolyte. The introduction of an ammonium sulfate solution into the subphase solution leads to a more uniform distribution of a substance over the subphase surface. This tendency is due to the appearance of the double electric layer formed by adsorbed cations, which prevents the aggregation of fullerene. Our findings show that the introduction of an electrolyte into the subphase can lead to a change in the structure of the fullerene 2D film applied to the aqueous subphase.

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