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Molecular Resolution Image of Lignoceric Acid Monolayer with Atomic Force Microscope

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A molecular resolution image of lignoceric acid monolayer, which was prepared on the water surface at a subphase temperature of 293 K and transferred onto a mica substrate, was successfully observed with an atomic force microscope(AFM) for the first time. The AFM image of the monolayer showed two-dimensional regular array with locally disordered molecular arrangements.

Langmuir-Blodgett(LB) films have been applied for various important functional characteristics, such as electric conductive and photoelectrical properties.[1] The ultimate functional properties of LB films can be attained by using a defect-free monolayer.[2] It is, therefore, indispensable for preparing a defect-free or defect-diminished monolayer to estimate molecular arrangement and structural defects in a monolayer. AFM with a molecular resolution has been applied to investigate the molecular arrangement and defects in the LB films of fatty acid salt.[3-5] In this study, a molecular resolution image of lignoceric acid monolayer on a mica surface was successfully observed for the first time.

A benzene solution of lignoceric acid($CH_3(CH_2)_{22}COOH$) with a concentration of 1×10^{-3} mol/l was spread on the water surface at a subphase temperature, T_{sp} of 293 K. Since T_{sp} is below the melting temperature of lignoceric acid monolayer, the monolayer is in a crystalline state.[6-8] The subphase water was purified with Milli-Q II® system. The lignoceric acid monolayer was compressed to a surface pressure of 5 mN/m at a barrier speed of 0.8 mm/sec and then, transferred onto a freshly cleaved mica by a vertical dipping method. The transfer ratio was unity, which implies that a mica substrate is completely covered with the monolayer. The AFM image of the monolayer was obtained with a SFA300(Seiko Instruments, Inc.) in air, using a silicon nitride tip on a cantilever with a spring constant of 0.027 N/m. The force applied between tip and sample was about 10^{-10} N.

Figure 1(a) shows a nonfiltered AFM image of the lignoceric acid monolayer on a scan area of 8×8 nm^2. The AFM image is given in a top-view presentation in which the brighter and darker portions correspond to higher and lower regions of the monolayer surface, respectively. Though scanning was done repeatedly, the monolayer was not damaged by a tip. However, a hole could be artificially pierced through the monolayer with a stronger applied force. The hole was about 2 nm deep, being comparable with the thickness of the lignoceric acid monolayer. It is reasonably expected that the brighter portion in the AFM image represents the individual methyl group of lignoceric acid molecule, because the hydrophobic part of lignoceric acid molecule in the monolayer on a mica surface was oriented toward air by transferring the monolayer onto a hydrophilic mica surface by the vertical dipping method. The AFM image exhibits that lignoceric acid molecules are regularly arranged with a hexagonal array. It was clarified from a large-area scan that a regularly periodic hexagonal array was extended over tens of

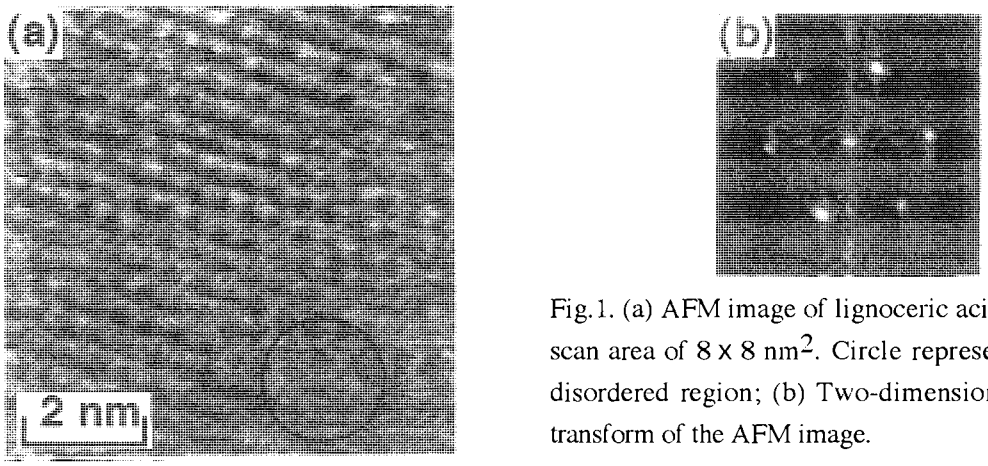

Fig.1. (a) AFM image of lignoceric acid monolayer at a scan area of 8 x 8 nm^2. Circle represents a molecular disordered region; (b) Two-dimensional fast Fourier transform of the AFM image.

square nanometers. The range of a periodic hexagonal array was comparable to the magnitude of crystallographical continuity which was evaluated by a single line method based on Fourier analysis of the electron diffraction profile.[6] As shown in the circle of Fig. 1(a), the hexagonal array of lignoceric acid molecules was locally disordered. In order to clarify the molecular arrangement in the monolayer, two-dimensional fast Fourier transform(FFT) treatment was carried out.

Figure 1(b) shows the FFT spectrum of the image shown in Fig. 1(a). The bright spots in the FFT spectrum exhibited a hexagonal pattern with the (1 0)[9] spacing of 0.43 nm. This magnitude agrees with the spacing of 0.43 nm which was estimated from the electron diffraction pattern of the lignoceric acid monolayer.[6] Therefore, it is reasonable to conclude from Figs. 1(a) and 1(b) that the lighter portion in the AFM image represents the individual methyl group of lignoceric acid molecule in the monolayer and also, that lignoceric acid molecules are regularly arranged with a hexagonal array.

It was speculated that the monolayer was in a fluid or disordered state, since no molecular resolution image fatty acid salt monolayer could be obtained owing to damage of the monolayer at scanning.[4] It is the first time that the molecular resolution image of the lignoceric acid monolayer has been obtained by scanning with the small magnitude of applied force of about 10^{-10} N and also, that the AFM image has clarified a distinct periodic array of lignoceric acid molecules in the monolayer.

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9) (1 0) represents the two-dimensional lattice plane with Miller indices of h=1, k=0.

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