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Structural investigation of *n*-hexadecanoic acid multilayers on mica surface: Atomic force microscopy study

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Abstract

The structure of *n*-hexadecanoic acid (HA) multilayers formed by spreading an ethanol solution containing this molecule onto a freshly cleaved mica surface has been studied by atomic force microscopy (AFM). AFM images of multilayers obtained with different coating time showed that HA molecules first formed some sporadic domains on mica surface. With the proceeding of the coating process, these domains gradually enlarged and coalesced, until formed a continuous film finally. It was observed that HA molecules were always adsorbed on mica surface with tilted even-numbered layers structure. The height of the repeated tilted bilayer film was measured to be approximately 3.8 ± 0.2 nm, which implied a $\sim 60^{\circ}$ tilt molecular conformation of the HA bilayers on mica surface. Phase image confirmed that the HA multilayers terminated with the hydrophilic carboxylic acid groups. The formation mechanism of the HA multilayers was discussed in detail. Thus, resulted hydrophilic surfaces are of special interest for further study in biological or man-made member systems.

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Keywords: *n*-Hexadecanoic acid (HA); Multilayers; Atomic force microscopy (AFM); Self-assembled monolayers (SAMs)

1. Introduction

Amphiphilic molecular films formed spontaneously on solid substrate by adsorption from the solution have been intensively studied for the last decade for their potential applications of surface modification and functionalization, for example, wetting, lubrication and adhesion, and molecular and biological recognition [1]. The structure and property of the molecule adsorbed on substrate can be influential to the subsequent application and study. Thus, understanding the formation process has been of considerable interest for the study of molecular adsorption. Most often, successful self-assembly process requires both balanced intermolecular interactions and favorable molecule–substrate interactions [2].

Although several groups have made important progress in understanding the SAMs structure and phase behavior [3–11], the initial growth process of SAMs is still incompletely understood. Early work on the formation of SAMs supported a homogenous growth mode [12]. However, recent ex situ infrared spectroscopy [13] and atomic force microscope (AFM) [14–16] studies on submonolayer SAMs indicated the presence of submonolayer islands on films removed from solution before completion. The ex situ AFM has been extensively used to investigate the formation mechanism of molecular monolayers on a solid surface owing to its extraordinary resolution and precision [17,18]. Although there are some disadvantages in ex situ AFM observation as previously mentioned [19,20], a lot of information on the formation process of the molecular monolayers could be still revealed by ex situ AFM studies.

Many phenomena of interest for wide range of fields are related to the adsorption of alkanes and amphiphilic alkyl derivatives on surfaces in ambient conditions, processes such as oxidation, lubrication, and catalysis are just a few examples. AFM had been applied to study the self-organization of physisorbed secondary alcohol molecules on graphite surface [21] and amphiphilic molecular layers formed by Langmuir–Blodgett (LB) technique [22–24]. AFM was also employed to study the formation mechanism of series of alcohol molecules on mica surface formed with immersion-coating technology [25–28]. Self-assembled monolayers, bilayers, and multilayers

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of OPA formed by spread-coating method on mica and silicon substrate were also studied by AFM [29–33].

In this work, the initial developing process of *n*-hexadecanoic acid (HA) multilayers on mica surface employing the spread-coating method was investigated using AFM. Although SAMs of this fatty acid on the surfaces of Ag, Cu, and Al [34], or Ti [35], as well as the corresponding oxides surfaces of Ag, Cu, and Al [36], have been investigated, no similar work deals with the HA multilayers structure on mica surface. The present results showed that bilayer was natural packing structures for HA molecules on mica surface. HA always adsorbed on mica surface as even-numbered multilayers providing a hydrophilic surface, and tended to transform from sporadic domains to integrated films in the whole developing process. The obtained information may improve our understanding in the development of theoretical models for molecular dynamics simulations of SAM formation processes. And we expect that such obtained hydrophilic surface would have a great potential for application in biological systems.

2. Experimental

2.1. Chemicals

n-Hexadecanoic acid (HA, the molecular structure was shown in Fig. 1a [37]) was purchased from Sigma and used without further purification. HA, when fully extended in the *trans* zigzag conformation is a linear-shaped amphiphilic molecule. Fig. 1b and c shows two different three-dimensional (3D) representations of the HA molecule. Fig. 1b represents a stereographic view of the molecule, identifying individual atom. The smallest spheres in light gray represent H atoms, and the medium-sized spheres in dark gray at the molecule body are C atoms, and the largest in black spheres corresponding to O atoms. Fig. 1c shows almost the same representation, but with atoms occupying their appropriate volumes in space. Ethanol (C_2H_5OH) of analytical-reagent grade was obtained from Beijing Chemical Reagent Factory (Beijing, China) and purified by redistillation before use.

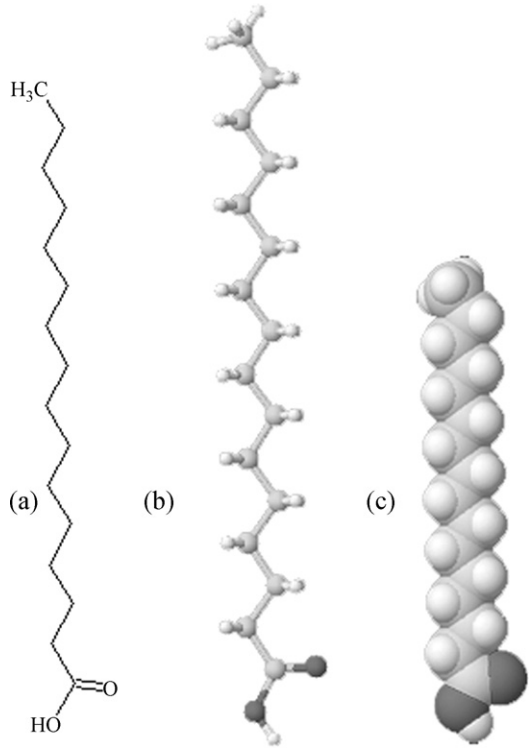

Fig. 1. (a) Molecule structure and (b, c) three-dimensional representations of the HA molecule. The smallest spheres in light gray represent H atoms, and the medium-sized spheres in dark gray at the molecule body are C atoms, and the black spheres correspond to O atoms.

2.2. Samples

Muscovite mica substrate ($KAl_2(AlSi_3)O_{10}(OH)_2$,) was cut into about 1.2 cm × 1.2 cm square pieces as the support for preparing HA samples. The spread-coating technique is employed to prepare the samples studied in this work and is very simple and reproducible [30,32]: a droplet (10 μL) of 0.1 wt% HA solution in ethanol is laid on a freshly cleaved mica surface, spreading over it. After a specific coating time, ultrapure (99.99%) nitrogen is used to blow the solution from the treated mica substrate, stopping the HA deposition process. The coating time is the time interval between the instant an HA droplet is put into contact with the mica surface and the instant it is blown from the mica substrate by a stream of nitrogen. In this work, the coating time varied from 2 to 240 s.

2.3. AFM imaging

A Nanoscope IIIa model from Digital Instruments (Santa Barbara, CA) was employed to image the samples at room temperature under ambient conditions. All images were recorded in tapping mode using silicon (Si) cantilevers (spring constant, 20–100 N/m) below its resonance frequency (typically, 200–400 kHz) and repeated several times with different samples and tips. Surface coverage was calculated using the height histogram of a given image [10,25,28,33].

3. Results and discussion

Representative AFM images for a series of samples prepared by using a 0.1 wt% HA (mM) solution in ethanol with varied coating time and their corresponding section analysis were shown in Fig. 2. All images were typical one obtained from at least five macroscopically separated regions on each sample. The coating times in Fig. 2 a–g were 2, 4, 10, 25, 60, 120, and 240 s, respectively.

Fig. 2a showed AFM image of HA modified mica with short coating time (2 s) and its corresponding section analysis, the dark regions in Fig. 2a indicated the mica surface, while the gray regions indicated the HA layers. It is obviously that the mica surface was covered sparsely with small round HA islands, and the average thickness of these islands was measured to be about 7.6 ± 0.2 nm. Since the length of one stand up HA molecules would be 2.2 nm (calculated from Van der Waals diameters, and energetic minimization based on