Fabrication of Octyltriethoxysilane Langmuir–Blodgett thin film

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Fabrication of octyltriethoxysilane Langmuir-Blodgett thin film

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In the present work the monolayer properties at the air-water interface of Octyltriethoxysilane (C_8TES) molecules are investigated using Langmuir isotherm graphs. Uniform and high quality Langmuir-Blodgett films of these molecules are prepared and characterized by UV-visible, atomic force microscopy and quartz crystal microbalance measurements to determine the deposition quality of these films. High transfer ratio of about 0.99 at a deposition pressure of 11 mN/m was obtained. The contact angle of water was 93.17° with a surface free energy of 23.8 mN/m. The use of soluble triethoxy-based silane coupling agents under anhydrous conditions is shown to produce surfaces with a minimal number of surface defects. C_8TES material has been demonstrated to produce well organised LB films and is shown to be a good candidate for application in the field of biosensors.

1. Introduction

Thin organic films, which have a thickness of a few nanometers, are used in many practical and commercial applications such as sensors, displays and electronic circuit components. They are easily deposited on a solid substrate by various physical and chemical deposition methods such as thermal evaporation, adsorption from solution, self-assembly, and Langmuir–Blodgett (LB) techniques. Two methods, LB film deposition [1] and solution adsorption [2], are commonly used to prepare silanized surfaces. It is well known that LB technique allows the deposition of ultra thin films with a precise controlled thickness at a molecular level with different molecular orientation [3]. This technique offers the advantage of maintaining accurate control over surface pressure during the deposition process and it also allows the deposition of multilayer structures with varying layer composition at desired molecular architecture [4-5].

Long chain fatty acid/salts were extensively studied as LB monolayer and multilayer and were used as model systems for biomedical surfaces. Alkylalkoxysilanes have been widely used to modify surfaces due to their ability to undergo silane coupling reactions [6-7]. These deposited layers can display antibacterial properties and have been utilized in applications such as antibody and protein based sensors [8-9]. In addition, they are used in the manufacture of thin film transistors, liquid crystal displays [10], nanoparticles [11], sensing devices [12], surface modified powders [13], fibers [14], thermal imaging device [15], and in drug detoxification [16]. Organosilanes bind to each other and to the surface hydroxyl groups via the formation of Si-O bonds. The head group of the molecule usually contains either halogen or ester groups, which liberate corresponding halogen or ether groups and form hydroxyl groups (-OH). This in turn forms either a hydrogen bond to the surface water layer forming an adsorbate precursor or bonds directly to a surface hydroxyl group forming a Si-O-Si bond [17-18].
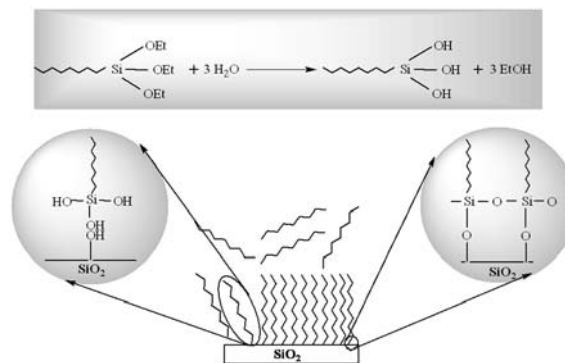

Fig. 1. A schematic diagram depicting the overall interaction of LB film with the glass surface.

In this study, C_8TES material (molecule's formula is shown in Fig. 1) is chosen to produce thin films using LB method. To the best of our knowledge this is the first time LB films of C_8TES are prepared and characterised using UV-vis, contact angle (CA), QCM and AFM techniques, with application as sensor elements in mind.

2. Experimental details

Glass substrates were cleaned using sonication bath (Bandelin Sonorex RK 255 H) The slides were sonicated

with detergent for 30 min at 70 °C and were rinsed with ultra pure water for about 15 min up to 5 times. The substrates were then blown dry using nitrogen gas. Contact angle (CA) measurements were performed at room temperature using a KSV CAM 200 (Finland) optical contact angle meter with an automatic liquid dispenser. Drops of volume 5 μL were formed on the tip of a vertically oriented Microliter[TM] syringe needle, which was subsequently brought into contact with the measuring surface, so that the fluid drop transferred onto the surface with a minimal velocity. The change in the value of the CA reveals the hydrophobic/hydrophilic character of the surface, which in turn can be related to silane LB deposition. To determine the hydrophobicity we have used ultra pure water while ethanol, hexane and carbon tetrachloride were used to determine the surface free energy.

A NIMA 622 alternate LB trough was employed to investigate the behaviour of the molecules at the air-water surface and to fabricate LB films. The temperature of the water subphase was controlled using Lauda Ecoline RE204 model temperature control unit and all experimental data were taken at room temperature. C_8TES molecules were dissolved in chloroform with the concentration of 1 mg mL^{-1} at pH=6 and 50 μL of the solution was spread onto the water subphase. A time period of 30 min was allowed for the solvent to evaporate before the area enclosed by the barriers was reduced. The pressure-area isotherm graph was obtained with the accuracy of 0.1 mN/m, as shown in Fig. 2. A monolayer of C_8TES molecules at the water surface was shown to be stable and surface pressure of 11 mN m^{-1} was selected for LB film deposition. Y-type LB deposition and a vertical dipping procedure was performed at the selected surface pressure with a dipping speed of $10\,\mathrm{mm\,min}^{-1}$ for both the down and up strokes. LB film sample was dried after each up stroke.

QCM measurements were performed at room temperature using an in-house designed oscillating circuit and a standard quartz crystal with a nominal resonance frequency of 7 MHz. Surface imaging was performed with a DME 2452 DualScope Scanner DS Atomic Force Microscope. Tapping mode imaging was performed and scans were carried out in AC mode under ambient conditions with a silicon microcantilever probe tips, using the following parameters; Force Constant=60.000 N/m, and Force= 0.11 nN.
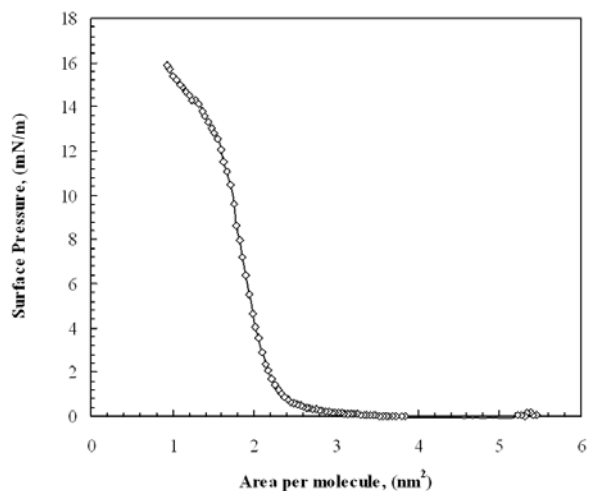

Fig. 2. An isotherm graph of C_8TES molecules during compression on water subphase.

3. Results and discussion

The CA was determined as the average value of measurements in five neighboring sites of the film. The active glass surface and LB film modified with pure component alkylsilane show water contact angles of 5.22° and 93.17°, respectively (Table 1). This increase indicates the formation of a partially grown hydrophobic surface.

Table 1. Contact angle measurements and calculated surface energies for glass surface and C_8TES LB film using four different liquids.

Sample	Water contact angle	Ethanol contact angle	Hexane contact angle	Carbon tetrachloride contact angle	Polar portion (mN/m)	Dispersive portion (mN/m)	Surface energy (mN/m)
Active glass surface	5.22°	2.34°	4.17°	7.83°	55.12	13.5	68.62
C_8TES LB film	93.17°	8.63°	5.55°	17.09°	3.4	20.4	23.8

The free energy of smooth, homogeneous surfaces is calculated via the following extension of the Young equation [19-20]:

$$(1+\cos\theta)\gamma_l = 2\sqrt{\gamma_s^d}\sqrt{\gamma_l^d} + 2\sqrt{\gamma_s^p}\sqrt{\gamma_l^p} \qquad (1)$$

where θ represents the wetting contact angle, γ_l and γ_s represent liquid and solid surface energies, and d and p denote dispersion and polar force components. Dispersive and polar surface free energy components are 21.8 and 51.0 mN/m for water, 17.5 and 4.6 mN/m for ethanol, 18.4 and 0 mN/m for hexane, and 26.7 and 0.3 mN/m for carbon, respectively [20]. Hydrophobic surface is indicated by higher contact angles and lower surface energy. Water has rather high surface energy by nature; it is polar in structure and forms hydrogen bonds. As seen in

Table 1, free energy of active glass surface which is hydrophilic surface is 68.62 mN/m while C_8TES LB film which is hydrophobic has surface free energy of 23.8 mN/m.

QCM measurement technique is often used to monitor the deposition and quality of a multilayer LB film on a quartz crystal because the resonant frequency of the crystal, Δf, is extremely sensitive to a small mass changes; this is described by Sauerbrey Equation:

$$\Delta f = \frac{-2f_0^2}{\rho_q^{1/2} \mu_q^{1/2} A} \Delta m \qquad (2)$$

where f_0 is the initial frequency of the crystal (Hz), Δm is the mass change (g), A is the piezo-electrically active area (cm^{-2}), ρ_q is the density of quartz (2.648 g cm^{-3}), and μ_q is the shear modulus of quartz (2.947×10^{11} g cm^{-1} s^{-2}). The linear relationship between the QCM frequency and the deposited mass changes can also be used to confirm the reproducibility of LB film multilayer deposition. Δf could be related directly to the deposited number of layers as described by the following equation:

$$\Delta f = \frac{-2f_0^2 \Delta m}{K_q} N \qquad (3)$$

where N is the number of layer, Δm is the mass per unit area per layer, and $K_q = (\rho_q \mu_q)^{1/2} A$.

Fig. 3 shows the change in resonant frequency of the quartz crystal as a function of layer number of C_8TES LB films. A linear relationship is clearly observed which demonstrate good reproducibility of LB film deposition of C_8TES molecules. Typical frequency shift of about 11 Hz per layer for C_8TES LB film is obtained from the gradient of the plot. This corresponds to an estimated bilayer mass of 105 ng of C_8TES LB film which is deposited onto the quartz crystal as depicted by Eq. (3) and demonstrated in Fig. 3.
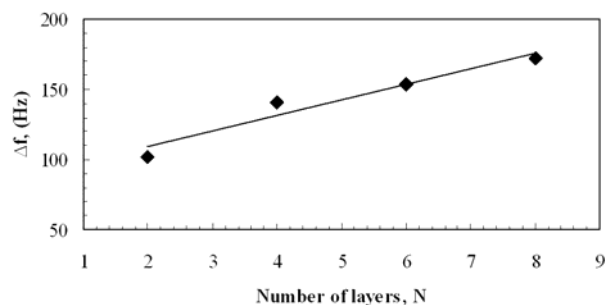

Fig. 3. The frequency shift of quarz crystal as a function of C_8TES LB film layers number.

Fig. 4 presents the AFM images for glass surface (a) and glass surface coated with C_8TES LB film (b). A root-mean-square (rms) roughness of 3.02 nm on a 10 x 10 μm scale is found for the glass substrate. An AFM image of the C_8TES LB film on the glass surface (Fig. 4b) is shown to have different topography from that of bare glass

substrate (Fig. 4a). This C_8TES LB film shows a uniform and homogeneous surface with some surface aggregates with an rms value of 8.61 nm on a 10 x 10 μm area.
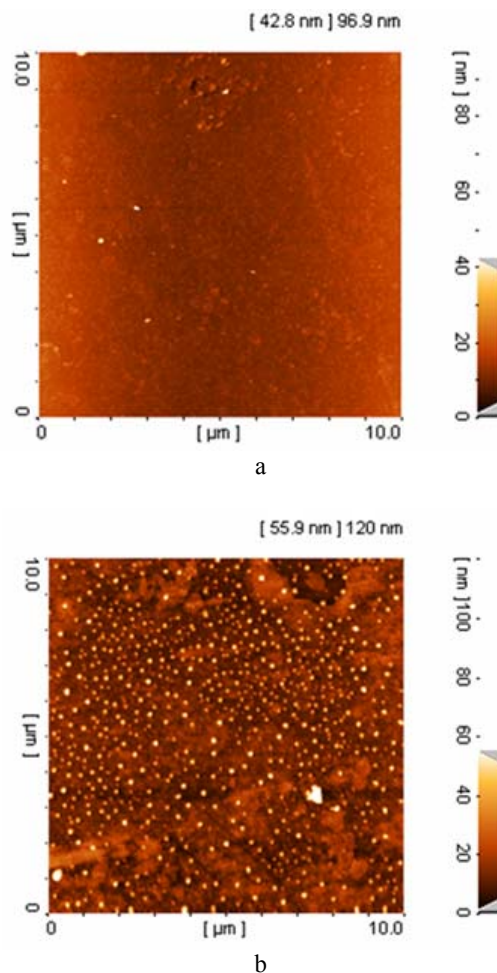

Fig. 4. AFM images of glass surface (a) and C_8TES LB film (b).

4. Conclusions

CA data of the modified glass showed hydrophobic character which has arisen from alkyl group of C_8TES molecules. The monolyer of C_8TES molecules was investigated at the air-water interface using an isotherm graph. Multilayers comprising this molecule were successfully deposited onto glass and quartz crystal substrate at the pressure of 11 mN m^{-1} with a transfer ration of about 0.99. QCM measurements were shown to give linear dependence of the frequency shift and number of deposited layers which demonstrate homogeneous and reproducible LB film deposition. AFM images of the C_8TES LB films show higher rms value than glass surface which explain the change in the surface properties of glass substrate as a result of LB film deposition. These results can be used to demonstrate that C_8TES material is suitable for thin film fabrication using LB technique with potential

for future application in bio and chemical sensors. Future work is aimed at investigating the sensor characteristics of this LB film and its layer structure.

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