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Adhesion force spectroscopy of model surfaces with wettability gradient

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ABSTRACT

Model surfaces with controllable wettability gradient are made by adjusting the feed mole ratio of 11-mercapto-1-undecanol and 1-octadecanethiol to form mixed self-assembled monolayers on gold. The surface adhesion spectra were obtained by force volume analysis at nanometer scale with atomic force microscopy and direct force measurement of droplets on surfaces with a microbalance. The results from direct measurement of liquid droplet-substrate adhesion are in good agreement with the measurements of force volume statistics and contact angle. It can thus be a useful supplement approach to understand surface wetting and adhesion property.

1. Introduction

Understanding a surface adhesion property is very important in a variety of areas, e.g., in enhancing oil recovery, microfluidic devices and protein–substrate interaction, etc. [1–3]. The adhesion can be varied upon absorption of molecular layers on surfaces. For example, in surfactant-based oil recovery, the wettability and adhesion properties of reservoir rocks are related to the efficiency of oil recovery, which controls how fluids flow and where fluids remain in the reservoir [3,4]. Meanwhile, surfactant absorption on reservoir rocks will change rock wetting property, adhesion and loss of surfactants [5,6]. Wettability and adhesion properties might be changed when reservoir rocks are exposed to crude oil and driving agents by the absorption of oil components and surfactants [7,8]. In addition, wettability and adhesion should be taken into account in spilled oil contamination. Spilled oil would spread and adhere wherever wet by oil and cause damage to ecosystem. Therefore, surface wettability and adhesion control is efficient to prevent solid surfaces from being contaminated.

Contact angle measurement is one of the most widely used techniques for measuring wettability of a solid surface [2], but the approach is only conceptually easy to understand for a smooth surface [8]. Some of other surface techniques have been applied for their ability to measure properties that related to empirical tests of wetting, such as X-ray photoelectron spectrometry (XPS) [9], Fourier transform infra-red (FTIR) spectroscopy [10]. Atomic force microscopy (AFM) has allowed a molecular level study on adhesion along with the morphology information [11]. Force–distance curve can be used for mapping surface forces with very high chemical and force resolution by measuring a force volume (FV) [12]. The measured FV coupled with friction force allows us to predict the wettability state of surfaces [13].

Theoretically, the adhesion force can be evaluated by directly measuring the force between droplet and surfaces from force–displacement curves. Measurement of adhesive force between a droplet and superhydrophobic surface has been reported by Jiang and co-workers [14]. Lai et al. reported a great consistence between water adhesive force and the contact angle measurement [15]. The method gives an insight into the ability of measuring adhesive force relating to empirical wetting tests of various liquids. However, in order to gain deeper insight into the real effect of surface wettability on enhanced oil recovery and spilled oil contamination, more precisely controlled model surfaces with a continuous wettability gradient are required.

Self-assembled monolayers (SAMs) of alkanethiols have been widely used as ideal platform for further binding reaction, not only because they can form well ordered monolayers [16], but it is also known as a facile way to fabricate energy gradient surfaces by tailoring different functional terminal groups of alkanethiols [17]. Methyl and hydroxyl terminated alkanethiols give a large difference in the wetting property of the resulting SAMs on gold surface, thus a wide range of tunable wettability gradient surfaces can be prepared by mixing these two thiols with different feed mole ratios in solution [18]. The wettability gradient surfaces of alkanethiol

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SAMs have been used to study the adsorption behaviors of cell, protein [19], surfactant [20] and polymer [21].

The objective of this paper is to fabricate model wettability gradient surfaces as an ideal platform for adhesion behavior study and present a novel system to precisely characterize wettability from a series of liquids on a variety of solid surfaces. Wettability gradient surfaces were modulated by adjusting the feed mole ratio of hydroxyl (11-mercapto-1-undecanol, MUOH) and methyl (1-octadecanethiol, ODT) terminated alkanethiols. The reliability and adaptability of the approach were also compared with other parallel characterizations e.g., atomic force microscopy (AFM), and contact angle measurement.

2. Materials and methods

2.1. Materials

Gold (99.99% purity) films were deposited on freshly cleaned Si wafers (100) by Magnetron sputtering (JZCL-450SC, Liaoning, China) at room temperature. The thickness of Au films was 100 nm (with 5 nm Ti underlayer). 11-Mercapto-1-undecanol (MUOH, 97%) was purchased from Aldrich (USA), 1-octadecanethiol (ODT, 96%) was purchased from ACROS (USA) and used without further purification. All chemicals were of analytic grade and used as-received. Deionized water was used throughout the experiments.

2.2. Preparation of alkanethiol SAMs

The wettability gradient of SAMs on the Au-coated substrates was controlled by adjusting the feed mole ratio of the two alkanethiols [18]. Au-coated substrates were firstly cleaned with O_2 plasma (Femto, diener electronic) for 30 s (the power is 99 W), then immersed in 5 μL freshly prepared pure solutions of MUOH, ODT and binary mixture of ODT/[ODT + MUOH] = 0.3, 0.5 and 0.7 (mol/mol) in ethanol with a total alkanethiol concentration of 5 mM for 12 h. After incubation, the substrates were thoroughly rinsed with ethanol and water, and then dried under nitrogen.

2.3. Contact angle measurements

The static water contact angles of SAMs were measured using the contact angle goniometry (DSA100, Kruss) under ambient laboratory conditions. A droplet of 5 μL Milli-Q water or diiodomethane was utilized for all measurements with five replicate measurements for each specimen.

2.4. Atomic force microscopy

AFM measurements were performed using a commercial Multimode AFM (Nanoscope IIIa, Veeco Instrument, Santa Barbara, CA) under ambient laboratory conditions of 20–23 °C and 30–35% relative humidity. In order to measure friction and adhesive force, standard commercially available 100 μm long, wide-legged, V-shaped Si_3N_4 cantilevers with a nominal spring constant of 0.58 N/m (NP-10, Digital Instrument) were used. The spring constant for individual silicon nitride cantilevers was calculated from the measurements of their resonant frequencies using the microscope software and based on the method reported by Hutter and Bechhoefer [22].

Adhesive forces between the AFM tip and specimen were determined from the measurements of typical force–distance curves. Herein, we used the force–volume map technique to obtain the adhesive force per unit area and the statistical distribution. Total 4096 (64×64 pixels) force curves were measured over $1\,\mu m \times 1\,\mu m$ surface area. The force curves were collected at a 3.99 Hz extending–retracting rate with a relative trigger mode. The total recording time for a complete image was about 30 min. The collected data were then analyzed by using a Matlab®-based program (Mathworks™).

Friction force was measured under a constant load using 90° scan angle. The scan length was 1 μm and the scan frequency was 1 Hz. The output voltages in friction loop were the lateral deflection signals of forward and reverse scans of the cantilever, which represents the friction force. The pure friction voltage signals were determined by subtracting the mean signals of retrace from trace and then dividing by two [23]. The applied normal load was controlled by transforming the "setpoint voltage". The value was converted to unit of force (nN) according to Ref. [24]. At least five separate locations were selected to collect the friction signals under variable applied loads for each sample.

2.5. Adhesion measurements

The adhesion of different liquids were determined with a dynamic contact angle measurement system (DCAT11, DataPhysics, Germany) and used to test the force–displacement curve between a droplet of liquid and sample surface, as shown in Fig. 1. The apparatus was reconfigured to measure wetting of variable liquids by setting an O-ring, under the microelectronic balance that is used for holding the liquid droplets. The microelectronic balance which has a high degree of accuracy of 0.01 mg is fixed on the top of the system. A sample stage is immobilized on the upper side of lift, and is driven by a computer controlled motor. When the system starts to work, the microelectronic balance is initialized to zero. Then the stage is lifted upward under a given speed of 0.3 mm/s, the sample is approaching suspended liquid droplet, and the software controlled system would sense the pull-on force between liquid droplet and sample surface when they are connected. After the pull-on force is detected, the stage starts to move back, the separation force increases to the largest until the droplet pulls off from sample surface, and the stage moves back to the initial position. During the whole process, stage movement versus force change is recorded by instrument matched software. And a high speed CCD camera is employed to record the process at the same time. At least five replicate measurements were performed for each specimen.

3. Results and discussion

3.1. Formation of SAMs with wettability gradient

Alkanethiols with –SH terminal groups are easily grafted onto Au surfaces by forming S–Au covalent bond. Mixed alkanethiols with different terminal groups perform the same way of assembly. Water and diiodomethane were used to measure surface wettability of the SAMs. The former has a high surface tension of 72.8 mN/m, and the latter possesses a lower surface tension of 50.8 mN/m which has been widely used as model probing oil [25]. The water contact angle of bare Au is $50.6 \pm 0.8°$ after cleaning by O_2 plasma, which is lower than the as-deposited Au surface [26]. The water contact angle of the MUOH modified Au surface is $19.7 \pm 1.6°$, which is more hydrophilic compared to bare Au surface. With the increase of feed mole ratio of ODT to 0.3, 0.5 and 0.7, surface –OH density of grafted alkanethiols decreases, and the contact angles thus increased to $97.3 \pm 1.0°$, $102.3 \pm 3.9°$, and $105.8 \pm 1.2°$. The pure ODT modified Au surface becomes very hydrophobic with a water contact angle of $118.5 \pm 3.8°$. The result does not coincide with Cassie's equation [27], as the composition of SAMs is not equal to the composition of solution, and the chain lengths of grafted alkanethiols are different. Though we do not know the actual mole fraction of the two components in mixed SAMs, the proportion of exposed –OH on mixed alkanethiols modified Au surfaces are quite lower as the alteration of water contact angles of these sur-