Measurements on hydrophobic and hydrophilic surfaces using porous gamma alumina nanoparticle aggregate mounted on Atomic Force Microscopy cantilevers

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Abstract

Atomic Force Microscopy (AFM) measurements are extensively used for a detailed understanding of molecular and surface forces. In this study, we present a technique for measuring such forces, using an AFM cantilever attached with a porous gamma alumina nanoparticle aggregate. The modified cantilever was used to measure the forces of interaction of the aggregate with hydrophilic and hydrophobic surfaces. Strong force of attraction was observed between the aggregate and hydrophilic surfaces when the aggregate was kept dry. However, force of interaction on the aggregate in wet form (water filled in pores) was larger when the adjoining surface had hydrophobic characteristics. The results presented in this study show the versatility of the current technique and indicate its

usefulness in directly characterizing hydrophilic/hydrophobic properties of nano-scale surfaces and patterns.

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1. Introduction

The explosive growth of lithographic and patterning techniques in the past decade has paved way for the fabrication of various complex nano-scale patterns. High quality patterns and structures with dimension in the nanometer order could now be prepared by various routes. These complex patterns find more and more applications in areas ranging from optoelectronics to micro-fluidics [1-3]. The complete application of nanoscale patterns requires the ability to characterize them in terms of geometry as well as surface and molecular forces exerted by them. Atomic Force Microscopy (AFM) and its various modifications allows to measure molecular, surfaces forces and interactions between various surfaces, which helps to improve understanding of these forces, as well as their implications.

Patterns with well defined hydrophilic and hydrophobic regions are one of the most important nanostructures with several micro-fluidic applications as these structures allow virtual confinement and transport of liquids within pre-defined one or two dimensional arrays. Hence, the characterization of these surfaces and study of their interactions with water and other solvents are of utmost importance. AFM helps to do this based on the interaction between AFM tip and various surfaces. When the AFM tip approaches the sample there is a ~~dip~~ deflection in the cantilever causes the tip in contact to the surface and further scanning (forward and backward) with the tip in contact ~~on~~ to the surface and ends in retraction of the tip from the surface. During the retraction process, the negative force required to pull-off the tip from the sample surface is called as Adhesion Force [4]. In short, the adhesion force value is obtained from the retraction force distance curve.

A number of AFM based studies have been reported in the literature on various types of hydrophilic and hydrophobic surfaces and their interactions with water and other solvents [5-23]. In particular, surface force measurements between wet solid-solid surfaces performed inside liquid medium were reported by several groups [5-8, 10, 11, 13-23]. Surface forces have been measured and compelling theoretical models have been presented in these studies. For e.g. experimental measurements by Ducker *et al*. [5], on forces between gas bubbles and various solid hydrophilic and hydrophobic surfaces in aqueous   salt solutions suggested that apart from double layer and van der Waals forces, strong long-range attractive forces are responsible for such interactions. Ducker *et al*. [5] also proposed that a nonzero water contact angle on hydrophilic silica surfaces is only related to Derjaguin Landau Verwey Overbeek (DLVO) forces, and not to any hydrophobic

component. It has also been suggested in the literature that the force of attraction between macroscopic hydrophobic and hydrophilic surfaces and water are due to the intermolecular forces and dispersion forces/van der Waals forces [24].

As mentioned, the developments associated with AFM have helped to study the nanoscopic interactions between liquid films and surfaces in recent years [23]. A significant part of the measurements so far were performed in selected liquid medium or in saturated/humid environment. One of the reasons for conducting experiments in liquid medium was due to the short lifespan of very small water droplets on the AFM tip or substrate surface when exposed to atmosphere due to evaporation.

In this paper, we have described a direct method of measuring the surface properties of hydrophilic and hydrophobic surfaces. The results we have measured are comparable with those in published literature, but our method is considerably simple. We have mounted a mesoporous gamma alumina nanoparticle aggregate at the end of an AFM cantilever and switched the properties of the porous aggregate from dry to wet and consequently measured the differences in its interactions with hydrophilic and hydrophobic surfaces. The nano-porous aggregate has the ability to absorb water and retain it in its pores for long time without depleting water at ambient temperature easily.

Based on the force measurements, we tried to clarify the magnitude of forces that exist between various substrates of different surface properties. It is important to note that in most of the cases the repeated force measurements values between various surfaces and the

particle showed good consistency. This consistency in <mark>force</mark> showed that the technique would help in the understanding the microscopic variations in surface properties. Furthermore, when the substrates to be analyzed consist of microscopic regions of hydrophilic and hydrophobic nature, it would be best to switch the properties of the AFM tip, to identify the microscopic profile of the surface precisely. Also through this technique, surface characteristics of the nano-porous particle attached to the AFM cantilever could be defined in parallel with the substrates to be analyzed.

2. Experimental details

Gamma alumina nanoparticles used in the study were prepared by the sol-gel method. Boehmite sol for this was prepared by the controlled hydrolysis of aluminum-tri-*sec*-butoxide. Details of this sol-gel synthesis are reported elsewhere [25, 26]. The sol was dried at 50 ºC to obtain gel pieces of boehmite. These boehmite gel pieces were heat-treated at 600 ºC to make gamma alumina, which was then crushed into small aggregates of about 2-20 µm. Aggregates selected from such gamma alumina particles were attached to the tip of the AFM cantilever for force measurements.

Silica sol was synthesized by a process similar to the Stöber process [27]. For this, 10 ml of NH_3 solution was initially stirred with 84 ml of ethanol in a round bottom flask. To this 6 ml of tetraethyl orthosilicate was added. The mixture was stirred for 2 hours at room temperature to obtain silica sol. <mark>To coat thin film, solution</mark> was prepared by mixing this silica sol with ethanol as in the case of other silica thin films reported in literature [28]. The silica concentration of the coating solution was 0.5 wt. %. A small

portion of the coating solution was dropped on to a freshly cleaved mica substrate, allowing it to spread immediately on the surface forming a thin layer. The substrate was then dried in an oven at 50 ºC for about 5 hours to obtain the silica thin film. A portion of the silica thin film coated surface was made hydrophobic by coating with a solution of Decyltrichlorosilane ($C_{10}H_{21}C1_3Si$).

The AFM facility available at Nanochemistry Research Institute of Curtin University of Technology was used for imaging the surface of the nanoparticles and thin films. Forces of interactions between surfaces have also been measured. All these measurements were done using a Digital Instruments Dimension 3000 AFM (Nanoscope IIIa controller with Extender) and data were calculated using software "nanoscope V6. 12 r2". The force were determined by the motion of the laser-beam reflected from the back of a Si_3N_4 Contact Mode cantilever with a spring constant of 0.58 N m^{-1}.

For the measurements, a porous gamma alumina nanoparticle aggregate was mounted on the cantilever. A single alumina aggregate of about 10 µm selected using a microscope was glued using commercially available Araldite (SELLEYS, New South Wales, Australia) to the end of the cantilever and left undisturbed at ambient temperature for 1 hour to ensure that the glue is completely dried and the particle is well attached to the cantilever end (Fig. 1). This cantilever was then used for the force measurements. In some measurements, the nanoparticle aggregate was used in wet condition. This was achieved by filling the aggregates pores with water. For this, the nanoparticle aggregate attached to the cantilever was immersed in de-ionized water. The container was then de-aerated by

vacuuming in order to ensure complete filling of the aggregate pores with water. The hydration of the nanoparticle aggregate could be reversed by heat-treating. Dehydration and hydration gravimetric experiments performed on unattached gamma alumina gel pieces have shown that consistent water release and take-up values could be obtained at room temperature. Thus the reproducibility of the nanoparticle aggregate water take up is not an issue in the experimental procedure and the same cantilever could be used for repeated cycles of measurements.

The force-distance curve measurements on various hydrophilic and hydrophobic surfaces were done using an AFM cantilever mounted with nanoparticle aggregate as described earlier. The force measurements were done at ambient temperature under consistent relative humidity ranging from 55-60% for all the measurements. About 50-60 force-distance measurements were measured on each surface. The averaged adhesion force value with standard deviation is reported in this study.

Water contact angle measurements of all the surfaces such as gamma alumina particle in dry and wet conditions and Decyltrichlorosilane coated silica film were performed by screening an enlarged image of a water droplet resting over the given surface and extracting the contact angle from the profile on screen.

3. Results and discussions

3.1 Characterization of the surfaces and the gamma alumina particle

Synthesis of silica sol and preparation of thin silica films were discussed earlier in experimental section. These thin films consist of silica clusters with sizes ranging from 150-450 nm. The physical, chemical and adsorption properties of silica depend on several parameters like geometrical structure of the particles and their surface chemistry. In general, the presence of surface functional groups in the form of silanol groups ($\equiv$Si-OH) or siloxane ($\equiv$Si-O-Si$\equiv$), establish the hydrophilic and hydrophobic properties of silica [29, 30]. In this work, the intrinsic hydrophilic nature of silica thin films surfaces is due to the silanol groups ($\equiv$Si-OH), and is the main chemical feature of silica surfaces. Generally, when a surfactant, which possesses "silane" molecules, is coated over a hydrophilic surface, the silane molecules adsorb at the silica surface and create covalent bonds with silanol groups and thus siloxane groups are formed. During the formation of siloxane groups, the silanol groups of silica get depleted and the hydrocarbon tail of the silanes covers the silica surface. Treatment like this is widely used to convert hydrophilic silica surface to hydrophobic for studying hydrophobic interactions [31] and for practical applications. In this study, we have modified the hydrophilic silica surface to hydrophobic by coating with Decyltrichlorosilane.

As mentioned earlier we have used mica as the substrate for silica thin film coating. It is well known that the surface of freshly cleaved mica is highly hydrophilic and when exposed to air, a thin layer of water (with thickness of few nanometers or less), forms on the surface [20]. Such exposure generally contaminates the mica surface and makes the surface behave less hydrophilic in nature. We also have observed a change in the behavior

of the substrate mica surface on exposure to atmosphere after cleaving. A drop in force of interaction with the AFM tip evidenced the change of mica surface to less hydrophilic as will be shown later. Although we have not thoroughly characterized the change in state of the mica surface, we have included the force of interaction values of the mica substrate with the AFM tip in the following sections for comparison purpose (as all the other surfaces used in the study were prepared in our laboratory).

The preparation of gamma alumina gel was discussed in the experimental section. Gamma alumina gel was crushed to obtain aggregates to mount on the AFM cantilever. The surface area of gamma alumina nanoparticle was measured as $\underline{197 \text{ m}^2 \text{ gm}^{-1}}$ and the pore size was measured as 3.96 nm by nitrogen adsorption. The sizes of the individual gamma-alumina nanoparticles were <10 nm as in <u>Fig. 2</u> but were aggregated to form clusters of nanoparticles with sizes in 20-30 nm ranges. In general, the porous gamma alumina nanoparticle surface acted highly hydrophilic in nature (water droplet on surface was unstable). But when these porous gamma alumina particles were pre-filled with water, the nano-pores lost their capillary action and therefore a stable droplet with a water contact angle of 45-55 ° was measured (Table 1).

The difference in surface characteristics of porous gamma alumina nanoparticle aggregate on wetting had also been visualized in force measurements with a standard Si_3N_4 tip. <u>Fig. 3</u> shows the force measurement curves using standard Si_3N_4 tip on dry and wet gamma alumina nanoparticle aggregate. As shown in <u>Fig. 3</u>, an adhesion force of <u>63 nN</u>

was measured on the dry particle, whereas the wet particle showed only 39 nN. These results show a trend similar to the contact angle results in Table 1 and indicate that the water saturated alumina aggregate surface acts less hydrophilic compared to the dry surface.

Such porous aggregates could act as a reservoir of water with some degree of stability unlike nano-bubbles on dense surfaces, which decays very fast. This characteristic feature of porous gamma-alumina particle helped us to measure some interesting data on adhesion between the particle mounted tip and various solid surfaces by giving us some degree of control in planning and executing AFM measurements with the same tip but with different characteristics, by changing the condition of the aggregate from dry to wet.

3.2 Force measurements using dry gamma alumina particle mounted on a cantilever

Interactions between two hydrophilic surfaces, for e.g. silica surface *vs*. dry porous gamma alumina particle, featured a strong force of attraction as in Fig. 4. Table 2 lists the calculated force of interaction values between three measured surfaces and the dry tip. Fig. 5 (a-c) shows the force values for several sets of measurements. It is shown that reasonably consistent measurement results could be obtained in all the cases.

As shown in Fig. 4, Table 2 and Fig. 5, the attraction is smaller in the case of a mica surface compared to a silica surface. It should be noted that freshly cleaved mica surface gave a much higher adhesion force value of 97 nN. As mentioned earlier, the surface of freshly cleaved mica is highly hydrophilic, but in this case the cleaved mica surface was

contaminated by exposing to ambient temperature, resulting in less hydrophilic effect and therefore a lower interaction force of 46 nN.

The adhesion force measured in the asymmetric system; viz. between a dry hydrophilic porous gamma alumina particle and hydrophobic surface (water contact angle = 140-150 °), was much lower (only 30 nN). The surface was rendered hydrophobic by the adsorption of surfactant, Decyltrichlorosilane, on hydrophilic silica surface. A reason for the weak adhesion is due to the intrinsic property of the hydrophobic surface, where the thickness of the water film formed on the surface is very limited when compared to water layer thickness on a hydrophilic surface, which would result in a relatively small capillary force.

3.3 Force measurements using wet gamma alumina particle mounted on an AFM cantilever

In contrast to the results of force measurements using a dry particle, totally opposite results have been obtained when a wet gamma-alumina particle underwent interaction with various hydrophilic and hydrophobic surfaces (Table 3 and Fig. 6 & 7).

The interaction between a wet particle and a hydrophilic silica surface (or hydrophilic mica substrate) exhibited a weak adhesion force in comparison to the result shown in Fig. 4 and Table 2, i.e. between a dry particle and hydrophilic surfaces. A possible reason for this behavior is a smaller capillary force as discussed earlier.

Fig. 7 (a-c) clearly shows that the force measurements with the wet tip had good repeatability. A large difference in force of interaction values have been consistently measured between the hydrophilic and hydrophobic surfaces.

Recent studies by Christenson and Claesson [12], on various kinds of hydrophobic surfaces (mica and silica surfaces rendered hydrophobic by surfactant adsorption) showed similar sort of attractions. An interesting behavior was observed when the hydrophobic silica surface interacted with the wet tip, i.e. interaction between Decyltrichlorosilane coated surface of silica thin film and wet porous gamma-alumina particle. The force observed in this case was larger (48 nN) than the force measured for the interaction of the wet particle with hydrophilic silica surface (12 nN).

It should be noted that instabilities in some force measurements have been observed at different spots on the surface, which may be due to the different separation encountered by the AFM cantilever/particle with the surface or also could be due to the non-uniform coating of surfactant over the silica surface. Similar behavior of force curves has been reported earlier [5]. In addition to that, a major limitation of this study is the irregular shape of the porous gamma-alumina particle attached to the AFM cantilever. Due to the particle irregularity a variation in the shape of the retract curve was encountered while doing force measurements. This made the measurement of force range between various interactions difficult as the portion of a particle in contact with a given surface during force measurements could vary between different measurements due to this irregularity.

However, as shown in <u>Fig. 5 and 7</u> the force values reported in this paper showed good consistency on different sets of measurements. This consistency of the measured force values on any given surface at various times shows that the values reported in this paper and more importantly their comparisons are meaningful.

In short, by using a mesoporous gamma alumina aggregate, we <u>have</u> stabilized the water content on the tip of the AFM cantliver and have used the cantilever to make force measurements on hydrophilic and hydrophobic surfaces. The irregular shape of the gamma alumina particle, used for the present set of experiments was a drawback of the present study. Yet, consistent results have shown the benefits of the method to directly characterize hydrophilic/hydrophobic properties of surfaces. The strength of the method is in its ability to characterize microscopic differences in surfaces including any nano-patterns with a simple change in water content of the nanoparticle mounted at the tip. This direct technique should help to screen out any possible effect of other measurements parameters on surface characterization with AFM. The method should also allow the characterization of surfaces with unusual microscopic profile such as surfaces with gradients in free energy [32]. Other uses including applications in nano-manipulation of hydrophilic and hydrophobic gates with the same AFM tip should also be possible with some modifications in the experimental procedure.

4. Conclusions

In this study, we have presented results of force measurements made on various hydrophilic and hydrophobic surfaces, using an AFM cantilever attached with a porous gamma alumina nanoparticle aggregate. Strong force of attraction was observed between

the aggregate and hydrophilic surfaces such as mica and silica thin film surfaces. By wetting the nanoparticle aggregate we have switched its behavior and hence its interaction with specific surfaces. Interestingly, the wet aggregate showed strong adhesion force when interacted with hydrophobic surfaces. The results presented here show the versatility of the technique used in this study and indicate its usefulness in directly characterizing complex nano-scale patterns made of hydrophilic and hydrophobic surfaces.

Acknowledgments

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Figures and Tables captions

Fig. 1. Optical microscopy image showing a typical porous gamma-alumina nanoparticle aggregate, attached to the AFM cantilever. The nanoparticle aggregate size is about 10 μm.

Fig. 2. FESEM image of a porous a typical gamma-alumina aggregate showing the distribution of nanoparticles. Each individual nanoparticle size was <10 nm and pore size was measured by N_2 adsorption method was 3.96 nm.

Fig. 3. Force-distance curves showing adhesion forces of dry and wet porous gamma alumina aggregate measured with a standard Si_3N_4 tip.

Fig. 4. Data showing the interactions between dry porous gamma-alumina particle and various hydrophilic and hydrophobic surfaces. The adhesion force is obtained from the minimum of the (retractive) force-distance curve.

Fig. 5. Force histogram (The force values for several sets of measurements) showing the interactions between dry porous gamma-alumina particle and various hydrophilic and hydrophobic surfaces. It is shown that reasonably consistent measurement results could be obtained in all the cases. **(a)** Interactions between dry gamma-alumina particle and silica surface, **(b)** Interactions between dry gamma-alumina particle and Mica surface and **(c)** Interactions between dry gamma-alumina particle and hydrophobic surface.

Fig. 6. Data showing the interactions between wet porous gamma-alumina particle and various hydrophilic and hydrophobic surfaces. The adhesions force is obtained from the minimum of the (retractive) force-distance curve.

Fig. 7. Force histogram (The force values for several sets of measurements) showing the interactions between wet porous gamma-alumina particle and various hydrophilic and hydrophobic surfaces. It is shown that reasonably consistent measurement results could be obtained in all the cases. **(a)** Interactions between wet gamma-alumina particle and silica surface, **(b)** Interactions between wet gamma-alumina particle and Mica surface and **(c)** Interactions between wet gamma-alumina particle and hydrophobic (coating) surface.

Table 1

Water contact angle measurement data on the gamma alumina particle. The contact angle values indicate the change in the surface property of the particle. For comparison the contact angle value of the Decyltrichlorosilane treated hydrophobic surface is also given. All the measurements were done at ambient temperature.

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Table 2

Measurements of adhesion force between various hydrophilic and hydrophobic surfaces and AFM cantilever mounted with a dry porous gamma alumina particle. Adhesion force value reported is the average and the ± value represents the standard deviation over 50-60 adhesion force measurements from two sets of independent adhesion force experiments.

Table 3

Measurements of adhesion force between various hydrophilic and hydrophobic surfaces and AFM cantilever mounted with a wet porous gamma alumina particle. Adhesion force value reported is the average and the ± value represents the standard deviation over 50-60 adhesion force measurements from two sets of independent adhesion force experiments.