CHAPTER 6

Sliding Behavior of Water Drops on Spin Deposited Hydrophobic Silica Films
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6.1 Introduction

Non-wetting surfaces are very important for many biological processes and industrial applications. In nature, there are many plant leaves (such as lotus leaf) which are known for not being wetted by water and consequently to remain clean from any parasitic dust or debris leading to a self-cleaning effect. In 1997, Barthlott and coworkers showed that the self-cleaning property of lotus leaves was due to their specialized surface morphology and hydrophobicity [1]. Several studies have been reported that by finely controlling the micro/nanostructure and/or chemical composition of a surface, the adhesion between the water repellent surface and the water droplet can be changed, being either very weak or very strong [2-4]. Water repellent surfaces hold considerable promise for various potential applications, ranging from self-cleaning surfaces to microfluidic devices [5-7]. Beyond the existence of large contact angles, very low adhesion, characterized by a small sliding angle (i.e. roll-off behavior) is a prerequisite for many applications. This fact means that dynamic interaction between a solid surface and droplet of water must be distinguished from that of the static interaction. Several authors reported that it is possible to combine excellent optical transmission with high water contact angles [8-12], however, only a few studies report low contact angle hysteresis or a low sliding angle of water droplet [13-15]. These later characteristics are required if a surface is to exhibit true self-cleaning properties. Xu et al [16] prepared the superhydrophobic surface with sliding angle of only 1° by a simple sol-gel method involving removable nanometer-sized polymeric spheres. Zhang and Kwok [17] and Anantharaju et al [18] studied the effect of three-phase (air, water, and solid substrate) contact line on the dynamics of the sliding process of a water droplet on a superhydrophobic surface by simulation. To obtain hydrophobic sol-gel coatings, usually, hydrophobic additives are
mixed to a sol. In the present work, the sol-gel co-precursor method was followed because it is simple and less time consuming compared to the surface derivatization method. Besides, hydrophobic films can also be made by using different co-precursors via sol-gel process [19-21]. In this work, to improve the hydrophobicity and water sliding behavior of the MTES based silica films; the TMES is used as the hydrophobic additive.

6.2 Experimental
6.2.1 Preparation of silica films

Silica films were prepared by two step (acid-base) sol-gel process. The chemicals used were methyltriethoxysilane (MTES), trimethylethoxysilane (TMES) (Sigma-Aldrich chemie, Germany), methanol (s.d.fine-chem limited, Mumbai), ammonium hydroxide and oxalic acid (L.R. Grade from Qualigens, India). All the reagents were used as received.

The hydrophobic silica films have been prepared by sol-gel process using spin coating technique from an alcoholic solution containing silica precursor methyltriethoxysilane (MTES), co-precursor trimethylethoxysilane (TMES), methanol (MeOH), acidic water (0.01M, oxalic acid) and basic water (12 M, NH₄OH). The influence of TMES/MTES (M) molar ratio on the water repellent behavior of the silica films was studied by keeping the molar ratio of MTES, MeOH, oxalic acid (0.01 M) and ammonium hydroxide (12 M) constant at 1:12.73:3.58:3.58, respectively and the TMES / MTES molar ratio (M) was varied from 0 to 0.22. In the first step of experiment, MTES was diluted in the methanol along with the hydrophobic reagent, TMES. The oxalic acid (0.01M) was added to this solution, drop by drop, while stirring (~15 minutes). After 12 h of hydrolysis reaction, ammonium hydroxide (12M) was added to the solution, drop by drop, while stirring (~2 h). There are four distinct stages in the spin coating process. The first stage is the deposition of the coating fluid onto the substrate, and the second stage corresponds to the period approaching the desired rotation speed. The third stage is the fluid thinning period at a constant spinning rate, and finally at the fourth stage
thinning behavior is observed due to the solvent evaporation [22]. The coating solution was spin-deposited on glass substrates using a commercial spin coater (Chemat technology spin coater KW-4A, USA) at room temperature (~27°C). The spin coating condition was 2500 rpm for 10 seconds. The spin-deposited films were dried at room temperature (~27°C) for 1 h and annealed at 150°C for 2 h.

6.3 Results and discussion

6.3.1 Surface Morphological Studies

The two-dimensional morphological study of the TMES modified silica film (M=0.22) has been carried out using SEM image. Figure 6.1 (a and b) shows the SEM images of hydrophobic silica films at two different magnifications (1000x and 2000x respectively). The low magnification image (figure 6.1a) of the film reveals the aggregation of the spherical particles with diameter typically ranging from of 5 to 7 µm distributed on the substrate. For detailed investigation of these particles, high magnified image (figure 6.1b) was recorded. The high magnified SEM micrograph of the film shows narrow smooth trenches between the aggregated particles.
Figure 6.1 (a): Scanning electron micrograph of TMES modified silica film (M=0.22) at 1000x magnification.

Figure 6.1 (b): Scanning electron micrograph of TMES modified silica film (M=0.22) at 2000x magnification.
6.3.2 Atomic Force Microscopy (AFM)

The wettability of a solid surface is dependent not only on its chemical composition, but also on the surface topography. Figure 6.2 shows the typical three dimensional atomic force microscopy (AFM) image of the TMES modified silica film (M=0.22) on the glass substrate. The image was recorded at $1\times1 \, \mu m^2$ planar in contact mode. The root-mean-square (RMS) roughness value of the film modified by the TMES was analyzed with AFM. The silica film showed an RMS roughness value of 20 nm. The surface of the film has many spherical-shaped islands that are distributed on the film surface.

![Atomic force microscopy image of TMES modified silica film](image)

**Figure 6.2: Atomic force microscopy image of TMES modified (M=0.22) silica film**

6.3.3 Effect of TMES/MTES molar ratio (M) on the dynamic water contact angle of the silica films

In a macroscopic view, the sliding process can be controlled by two forces parallel to the surface: $F_1$ from the gravitation of the water droplet and $F_2$
from the flow resistance. If the driving force \( F_1 \) is equal to or larger than the flow resistance \( F_2 \), the water droplet could begin to slide [23]. The sliding process of the water droplets was observed by first placing the water droplet on a horizontal surface and then slowly tilting the film surface until the droplet starts moving. For \( M = 0.22 \), a water droplet of 10 mg could roll off very easily from the film surface, when the film was put at the sliding angle of 9°. Therefore, the maximum force required to slide the water droplet on the film surface was calculated to be around 15.33 µN. No visual water residue was left on the film surface and water droplets rolled off at all locations over the film surface. Such an extremely low sliding angle is caused by the narrow trench morphology of the silica film. When the film is tilted for a very small angle (9°), the air squashed in the narrow smooth trenches can expand, giving the water droplet a pushing force. Thus the water droplet can roll-off easily on the film surface. This observation suggests that the adhesion between the films surface and the water droplet is very weak. However the same water droplet will not slide away easily from the unmodified silica film (\( M = 0 \)). The water droplets are pinned on the unmodified film surface where there were possibly some defects on the surface and eventually these areas were wetted with water. The TMES modified silica film (\( M = 0.22 \)) showed lower sliding angle of 9°, whereas for the unmodified silica film (\( M = 0 \)) the water droplet still needs a sliding angle of 40°, before sliding. The maximum force required to slide the water droplet on the unmodified silica film surface was calculated to be around 62.99 µN. Figure 6.3 (a-c) shows the effect of increase in the molar ratio (\( M \)) from 0 to 0.22 on the water sliding angle of the silica film. The water sliding angle values decreased with an increase in \( M \) value. Most prominently, water droplets on the TMES modified film surface (\( M = 0.22 \)) freely roll-off the surface without becoming pinned, even after sitting on the surface for a long time. The unmodified silica films show strong adhesion with the water droplet and the water droplet can not slide off the film surface by gravity even when the substrate is tilted at 40°. However, for the TMES modified silica films, the
adhesion is very weak. As a result, the water droplet can roll off the tilted (9°) films surface effortlessly.

Figure 6.3 (a): Sliding angle (SA) of water droplet on silica film prepared at molar ratio of $M = 0$
Figure 6.3 (b): Sliding angle (SA) of water droplet on silica film prepared at molar ratio of M = 0.11

Figure 6.3 (c): Sliding angle (SA) of water droplet on silica film prepared at molar ratio of M = 0.22
6.3.4 Fourier Transform Infrared Studies

The surface chemical modification of the silica films spin-deposited on the glass substrate was investigated by FTIR spectroscopy using the KBr method in transmission mode. Several characteristic absorption bands were observed in the range between 450 to 4000 cm\(^{-1}\). These bands confirm the presence of organic species in the silica films. The FTIR spectra of the unmodified and TMES modified silica film (M = 0.22) are shown in figure 6.4 (a-b). In the figure of FTIR spectra, the absorption bands observed at around 2950 cm\(^{-1}\) and 1400 cm\(^{-1}\) are due to stretching and bending of C-H bonds and the peaks observed at 847 cm\(^{-1}\) are due to the Si-C bonding [24]. The peak at around 1600 cm\(^{-1}\) and the broad absorption band at around 3400 cm\(^{-1}\) are due to the Si–OH groups [25]. The strong absorption peak centered at 1050 cm\(^{-1}\) is an asymmetric stretching vibration of Si-O-Si bonds. The presence of this peak confirms the formation of a network structure inside the film [26]. In the case of the unmodified silica film, a strong peak at 3400 cm\(^{-1}\) indicates that a significant fraction of the silanol groups exist on the film surface, which is found to be disappearing for the TMES modified silica film. The number of C-H and Si-C peaks are quite notable for the TMES modified silica film, which are found to be less for the unmodified film. The intensity of the absorption peak of C-H in the surface modified silica films increases significantly, while the intensity of the absorption peak at 3400 cm\(^{-1}\) decreases. This indicates that the non associated –H bonds are well substituted by Si–CH\(_3\) bonds after the TMES modification. Even though the surface modified silica films show a strong water repellent behavior, the surface hydroxyls still exist in the FTIR spectra of TMES modified silica film.

As expected, when the organic moiety is removed by a thermal treatment in air, the hydrophobic character is irreversibly changed to the hydrophilic nature. However, the hydrophobicity must either be lost or much weaker after such a treatment, due to the oxidative removal of the organics from the surface. Decomposition of the organic groups occurs at a particular temperature. Thermal stability tests were conducted by putting the hydrophobic
silica films in a furnace (Vulcan, 3-550, USA) at various temperatures. When the TMES modified film (M=0.22) was cured at a temperature higher than 280°C, the film became superhydrophilic; the contact angle for water on the film was smaller than 5°. This is due to the fact that above these temperatures the methyl groups get oxidized into Si-OH groups leading to the adsorption of water.

Figure 6.4: The FTIR spectra of the (a) unmodified (M = 0) and (b)TMES modified (M = 0.22) silica films

6.3.5 Static water contact angle measurements

The hydrophobicity is usually determined by measuring the contact angle of a water droplet contacting a surface. Figures 6.5 (a-c) shows the images of water droplet on the silica film prepared with M = 0, 0.11, and 0.22, respectively. Raising the initial molar ratio (M) from 0 to 0.22, the water
contact angle increased from 86° to 120°, respectively. The contact angle measurements that were quickly repeated on the same spot gave similar values. The silyl groups present in the TMES contribute to the enhancement of water contact angle of the film. The highest water contact angle (in the present experiments) of 120° was observed for M=0.22 and MTES: MeOH: acidic water: basic water, molar ratio equal to 1:12.73:3.58:3.58 respectively. The photographs clearly indicate that the water contact angle on the film surface increased with an increase in the M values. The water droplet displayed a comparatively large contact angle (120°) on the TMES modified silica films than the contact angle (86°) on the unmodified silica films, which testified that the hydrophobic surface has been created. In the Cassie-Baxter’s model, the sliding water contact angle is extremely small, but this value becomes large in the Wenzel model. In the case of Cassie-Baxter’s model, the low surface energy of air reduces the frictional force when a water droplet moves. This strongly suggests that the contact model of a water droplet on the film prepared from M = 0.22 is the Cassie-Baxter’s model. However, the opposite trend is the resulting phenomenon in the Wenzel’s model, which favors the water droplet pinning and therefore leads to an increase in frictional force. In the case of unmodified silica film (M = 0), water sticks to the surface, making the water droplet in the state of Wenzel’s model.
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Figure 6.5 (a): Shape of water droplet on the silica films prepared at molar ratio of \( M = 0 \)

\[ \theta = 86^\circ \]

Figure 6.5 (a): Shape of water droplet on the silica films prepared at molar ratio of \( M = 0.11 \)

\[ \theta = 111^\circ \]
6.3.6 Effect of humidity on surface wettability

For artificial superhydrophobic surfaces, the water repellent capability gradually degrades during long-term outdoor exposure and accumulation of contamination. Humidity is a measure of the amount of water vapor in the air. The hydrophilic silica films contain –OH groups on their surfaces and they react with the atmospheric moisture, and hence the film structure gets deteriorated. For long term durability of the water repellent silica films, the surface of the film should be chemically modified with non-polar groups. The effect of humidity on the wetting properties of TMES modified (M=0.22) silica films was carried out at relative humidity of 90 % at 30°C temperature over 60 days. It was observed that there was no significant change in the static and dynamic water contact angles for the TMES modified films. This reveals that the TMES modified films are highly stable against the humidity.
6.3.7 Optical transmission studies

To achieve the integration of superhydrophobicity and optical transmission within the same surface, the dimensions of roughness should be lower than the wavelength of visible light (ca. 380-760nm) [27]. From the AFM study, the dimensions of roughness value for TMES modified film (M=0.22) is lower than the wavelength of visible light. Figure 6.6 shows the optical transmission spectra of the unmodified and TMES modified silica films. The unmodified films showed 80% optical transmission; whereas the TMES modified films showed an optical transmission of 85%.

Figure 6.6: The optical transmission spectra of the (A) unmodified (M=0) and (B) TMES (0.22) modified silica film.
6.4 Conclusions

Uniform, transparent and hydrophobic silica films based on methyltriethoxysilane (MTES) precursor with trimethylethoxysilane (TMES) as a co-precursor were synthesized by sol-gel process at room temperature (~27°C). Silica films with static water contact angle (θ) as high as 120° and water sliding angle as low as 9° have been produced by increasing the TMES/MTES molar ratios (M) to 0.22. The FTIR spectra showed an increase in the intensity of Si-C and C-H peaks and decrease in the intensity of O-H peaks with increase in M value, clearly indicating the increased chemical modification of the silica surface by the organic (silyl) groups. By modification of silica sols with trimethylethoxysilane, sol-gel coatings could be prepared on glass substrates at room temperature owning to excellent water repellent properties without any addition of fluorine containing compounds. In addition, the films are transparent to visible light. Therefore, the films could find application as self-cleaning windshields of automobiles, in which a high transmission of visible light is desirable.
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References

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