A facile approach towards fabrication of super hydrophobic surface from functionalized silica particles

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Abstract. A facile and cost effective method for fabrication of super hydrophobic surface on a glass substrate is studied. The surface is fabricated from surface functionalized silica particles, synthesized by sol-gel process with the average size of 200±10nm. These particles were functionalized with stearic acid to induce hydrophobicity followed by coating on a glass substrate. After coating, substrate was dried to remove excess solvent. The drying temperature was optimized and its effect on contact angle of hydrophobic surface was studied. It was observed that surface exhibits higher contact angle with increased drying temperature till the decomposition temperature of Stearic acid. Silica particles were characterized by using Scanning electron microscopy (SEM), thermal analysis was performed with Thermo gravimetric analysis (TGA) while the coated surface was studied using SEM and Contact Angle (CA) measurement.

1. Introduction
Super hydrophobic surfaces have gained importance due to their non-adhesive and non-wetting characteristics. These properties make them useful for many applications including self-cleaning, anti-corrosion and anti-icing [1]. Super hydrophobic surfaces exhibit contact angle greater than 150°[2] which make them non-wetting and non-adhesive. The increased water contact angle of a surface is due to its characteristic low surface energy and rough morphology. Surface roughness not only increases the contact angle but also decreases the solid liquid adhesion by creating air pockets between solid and the liquid interface [3-4].

Polymers [5], metal oxides [6-7] and nanoparticles [8-9] including titania and silica particles are being used for the fabrication of super hydrophobic surfaces. Silica based coatings offer multiple benefits which are: ease of fabrication, cost effectiveness, better adhesion and thermal stability[10]. Silica particles are generally synthesized by sol-gel process which allows regulating the particle size by changing reaction parameters. Previously, it has been studied that particle size can be tuned by changing the reaction temperature, concentration of precursor and co-solvent [11]. The synthesized silica particles are hydrophilic due to attached hydroxyl group. Fluorinated hydrocarbons are being used to alter the hydrophilic nature of silica particles to hydrophobic by replacing the hydroxyl group[12-13]. However, modification with fluorinated hydrocarbons is expensive and hazardous to health and environment. Stearic acid is another modifying agent which can be utilized for the modification purpose.

In this study, we have prepared and characterized silica particles to prepare hydrophobic surfaces.
2. Materials and methods
2.1. Reagents
Tetraethoxysilane (TEOS, 98%) was purchased from Sigma Aldrich, Ethanol (99.8%) and Stearic acid was obtained from BDH Laboratory suppliers. Aqueous ammonia (33%) was supplied by Honeywell Burdick and Johnson and Methanol (HPLC) was purchased from LAB scan Analytical sciences.

2.2 Synthesis of silica particles
Silica particles were synthesized by taking inspiration from previously reported method [14]. 250 ml of methanol and 250 ml ammonium hydroxide solution were mixed for 10 min in a 1000 ml beaker using a magnetic stirrer. 5 ml of TEOS was added drop wise to the mixture and reaction was left to proceed for 30 min at 25°C. The product was centrifuged for 30 min at 4000 rpm followed by rinsing with methanol and drying.

2.3 Surface modification of silica particles
0.2g of the silica particle were added in 50ml ethanol in 100ml beaker. The mixture was sonicated using a probe ultra sonicator for 20 min. After sonication, 1g of stearic acid was added in the mixture in molten form followed by heating at 60°C for 2 hr.

2.4 Fabrication of super hydrophobic surfaces
The glass substrates were cleaned by rinsing with acetone followed by sonication to remove impurities. After that, the prepared solution of modified silica particles was dropped the substrate. The samples were subjected to different drying temperatures of 100°C, 180°C and 260°C to study the effect of temperature on contact angle.

2.5 Characterizations
Field Emission Scanning Electron Microscopy (SEM) (MIRA 3 TESCAN) was used to study the particle size, particles size distribution and the surface morphology of fabricated super hydrophobic surfaces. Thermal analysis of stearic acid, silica particles and modified silica particles was performed using TGA (METTLER TOLEDO). For contact angle measurement, an appropriate volume of water was dropped on the surfaces and captured using Nikon DSLR camera.

3. Results and discussion
Figure 1 shows the SEM micrographs of silica particles at two different magnifications. Non agglomerated and spherically shaped silica particles of size 200±10nm were synthesized using TEOS as precursor, ethanol as co-solvent and ammonia as catalyst. Previously it has been studied that changing the ratios of co-solvent and catalyst affects the particle size. Increased amount of ammonia increases the rate of hydrolysis and condensation and provides less time for nucleation which results in smaller particle size [11]. In the present study, spherically shape silica particles of size 200±10nm are produced by using the equal amount of ethanol and ammonia.

![Figure 1. SEM images showing silica particles at two different magnifications](image-url)
Figure 3 shows the thermogravimetric analysis of stearic acid, silica particles and modified silica particles. The TGA results indicated that decomposition of stearic acid starts at about 200°C and completes at 310°C with 95% weight loss whereas the weight loss in pure silica particles is only due to evaporation of water molecules. However, the presence of stearic acid in modified silica particles was confirmed through the weight loss starting from 250° and completing at 370°. The initial weight loss which is observed in the as synthesized silica particles is not present in the modified particles due to evaporation of water as these particles were scratched from coatings subjected to drying temperature of 180°C. The water content would have been removed during drying. In a previous study, modification of anatase with stearic has been studied and weight loss in the range of 200°C to 450°C was recognized as the decomposition of stearic acid [15]. In another study, a significant weight loss of stearic acid modified tourmaline was observed in temperature range of 138°C - 380°C [16]. In the present work, thermal degradation in modified silica particles is observed in temperature range of 300°C-440°C. So it can be inferred from thermal analysis that coatings fabricated with these modified silica nanoparticles are stable up to 300°C.

**Figure 2.** SEM images showing the surface morphology of substrate coated with modified silica particles at two different magnifications

**Figure 3.** TGA profiles of (a) stearic acid, (b) silica particles, (c) modified silica particle

In Figure 2, the SEM micrographs show the morphologies of coated glass substrates. Coating of modified silica particles have produced the rough surface as indicated in the SEM images. Surface roughness plays very important role in hydrophobic characteristics of a surface [17]. The hydrophobicity in naturally occurring surfaces is thought to be because of rough hierarchical structure which creates repellence with water and makes the contact angle of water droplet greater than 150° [10]. The role of surface roughness is explained by Wenzel and Cassie models, the first relates the wetting properties of a surface with roughness while the latter attributes it to the air pockets formed between surface grooves and liquid [10]. In the present study, it is observed that coating of silica
particles has created roughness on glass substrate which contributes towards the hydrophobicity of surface as shown in Figure 5.

![Figure 4. Variation in Contact angle with increasing drying temperature](image)

Figure 4. Variation in Contact angle with increasing drying temperature

![Figure 5. The contact angle of water droplet with (a) uncoated glass substrate, (b) coated glass substrate and dried at 100°C, (c) 180°C, and (d) 260°C](image)

Figure 5. The contact angle of water droplet with (a) uncoated glass substrate, (b) coated glass substrate and dried at 100°C, (c) 180°C, and (d) 260°C.

Figure 4 graphically shows the trend of contact angle with increasing drying temperature. Figure 5 shows the contact angles of glass substrate before and after coating. Three samples were prepared and subjected to the drying temperatures of 100°C, 180°C, and 260°C. It can be seen that the water contact angle is 130° at drying temperature of 100°C. The contact angle is increased to 150° when drying temperature was increased to 180°C. The contact angle dropped to 65° when drying temperature was increased to 260°C. The hydrophobic character of silica particles is owing to the long alkyl chain of stearic acid; the hydroxyl group attached to silica particle reacted with carboxyl group of stearic acid during modification [12].

4. Conclusion

Super hydrophobic surface has been prepared by coating modified silica particles on glass substrate. Silica particles were synthesized by sol gel process using TEOS as precursor. The prepared particles were modified with stearic acid followed by coating using dip coating process. Super hydrophobic surface with a maximum contact angle of 150° is produced in this study. Contact angle initially increases with increasing drying temperature then drops at 260°C. This drop is attributed to thermal destruction of alkyl chains attached to silica particles.
5. References

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