Development of Super Hydrophobic Surfaces using Silica Nanoparticles

Muhammad Salman Saleem
CUNY City College

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Development of Super Hydrophobic Surfaces using Silica Nanoparticles

Thesis

Submitted in partial fulfillment of the requirement for the degree

Master of Engineering (Chemical)

at

The City College of New York

of the

City University of New York

By

Muhammad Salman Saleem

May 2015

Approved:

Professor Charles Maldarelli Thesis Advisor

Professor Jeff Morris Chairman
Department of Chemical Engineering

This thesis contains the research, theoretical & practical measures to understand the phenomenon of superhydrophobicity and fabrication of super hydrophobic surfaces using spin and dip coating.
Abstract

The development of surfaces that have high water contact angles and hysteresis has always been of great importance in industrial applications. Various methods and techniques have been introduced to fabricate surfaces at nano-scale to support super hydrophobicity. Some of these techniques are expensive, some are very complex, most can be used for selective materials and substrate and some form surfaces with very poor wear resistance. This document represents a systematic study on fabrication of super hydrophobic surfaces on glass substrate (SiO₂) using the functionalized silica (SiO₂) nano particles. SU8, Polydimethylsiloxane (PDMS) and Methylphenyl Resin SR355 polymer are being used as binder for Silica nanoparticles to stick on glass substrate. Measurements of contact angle and contact angle hysteresis are presented along with the wear resistance tests.
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Background and Motivation:
Crude oil has been the biggest and most leading source of energy since the mid of the 19th century because it offers high energy as well as it is very abundant. The increased high demand of energy through crude oil along with increased production cost has forced the oil industry to move towards offshore and deep-water reservoirs. The transportation of the oil from the offshore reservoirs to the offshore processing facilities has become one of the biggest challenges for the petroleum industries because of the formation of gas hydrates inside the pipeline. The mass production of gas hydrates results in the clogging of the petroleum pipeline and this problem sometimes becomes more intensive when the pressure inside the gas pipeline becomes so high that it gets rupture resulting in explosion, fire and oil spill, and ultimately whole operation process has to be stopped. The incident of BP Deep Water Horizon Oil Spill in Gulf of Mexico is major example where consequences resulting from hydrate formation were overtly showed up. The formation of gas hydrate in the petroleum pipeline is a very serious issue and it has to be addressed not only because it just stops the transportation of crude but also leads to fatal explosion risking human lives, effecting marine life, disturbing global economy and increasing global pollution.

Currently two methods are being used as standard to solve the blocking problem of the pipeline. i) By the introduction of chemical inhibitors in the pipeline. ii) By insulating and heating the pipeline with electricity. The use of chemical methods inhibits the formation of the hydrates in the gas pipeline but they offer poor environmental performance and they are really expensive as well. The second method which is a heating method is environmental friendly but it demands intensive energy requirements that may results in high increase of the production cost. Therefore, there is a need of highly effective method that prevents the adverse effect of clogging and provides excellent solution on inhibiting the hydrate formation. The factors that are directly involved in the formation of hydrates are dependent on the pipeline surface properties like surface roughness, porosity, surface energy and material type. My research is focused on designing such kind of surface which minimizes the formation of hydrates and their adhesion to the wall. The alteration in the wettability of the surfaces by changing their structure is the key factor in alleviating the flow problems. Building of microtextured array on the surface and then functionalizing them with low energy material (silane) can result in decrease in surface hysteresis and increase in contact angle. Another way of making the superhydrophobic surfaces is by depositing the nano particles on the surface and then hydrophobizing them with silane.

When a micro textured surface is submerged in the oil phase which has water drops, the mobility of the water droplet along the surface is increased and adhesion of water droplet decreases. Two types of techniques are mostly used for texturing the surfaces. The first one is the colloidal assembly technique and second one is the lithographic fabrication of micropost arrays. The reason water droplets get move very easily over the oil surface is because the surface is made hydrophobic by functionalizing it with some compound due to which oil gets absorb on the surface and a smooth cushion of saturated oil enable water drop to move very smoothly. The geometric parameters of the surface are used to measure the dynamic and static contact angles in order to indentify the minimal surface hysteresis. This thesis is based on partially solving a longstanding problem of how to remove water droplets which become stuck on surface in oils. The surface developed in this study will be useful to alleviate the problem regarding the formation of surface gas hydrate and flow assurance problem in petroleum industries as well as fouling and corrosion problems in the downstream unit operation equipments for refining.
The ultimate outcome of this research is to develop such a structure on the substrate surface that repels the water droplets when the surface is immersed in oil. Crude oils mostly have microscopic sized water present in them in the form of droplets having some dissolved salts too. When these drops come in contact with the surface of processing equipments and heat exchanger, it results in corrosion of the surfaces. For this reason the crude oil is mostly processed through a series of thermal, mechanical and chemical process to reduce the water level inside them. There are also some specific limits assigned by companies, ensuring the water content not greater than certain level, before crude is processed for unit operations.

Besides corrosion, at low temperatures and high pressures gas hydrates are also generally formed. The gas hydrates are the crystalline compounds having ice like structures consisting of gas molecules (methane, ethane, and propane) surrounded by hydrogen-bonded water cages. Generally, gas hydrates are formed when gas molecules contact water at ambient temperature, less than 300K, and moderate pressure (> 0.6 MPa or 5atm). The conditions for gas hydrates formation in petroleum transport are inevitable as warm crude oil from well-head cools as it moves over long distances (ten miles) from the ocean floor. Petroleum crudes are mostly mixture of oil, water and gas. Water becomes entrained in the oil as a water oil emulsion. Clathrate hydrates crystallize from these water droplets as gas molecules get dissolved in the oil. This hydrate crystallization and growth inside compromises the petroleum pipelines in two ways.

The first through the cohesive binding of hydrates particles through the capillary bridges that result into the formation of suspension of agglomerated particles. This increases the overall viscosity which in turn affects the flow and increases the energy requirements. The second is through the adhesion of water droplets to the pipe wall, and their subsequent crystallization to form the attached hydrate layers. The pipelines are mostly made from steel which is a polar material and it gets readily wet by the water in the presence of oil. This results in the water droplets to get stick to the surface and instead of passing downstream they get stuck to the walls, due to roughness of the pipe, where they crystallizes to form the hydrates. With the passage of time the hydrates also adheres the water droplets from the bulk through hydrate particle cohesion, leading to stenosis of pipeline and ultimately jamming due to enough build up of mass. This clogging of petroleum pipeline is the principle detriment to the flow assurance, forcing operations to be stopped until the obstacles are cleared. The treatment is really costly not in terms of only money but also of the downtime of the operations. The textured surfaces developed in this research help water droplets to get mobilize which restricts them from acting as a fixed capillary bridge point for immobilizing depositing hydrate crystals.

**Formation of gas hydrates:**

Turner suggested a four step mechanism to explain the influence of aggregation of hydrate plugging i) Water entrainment in oil phase ii) Growth of hydrate shell at water-oil interface iii) Aggregation due to capillary attraction\(^{[1,2]}\) iv) Catastrophic plugging of hydrate particles. The interfacial energies play a vital role in the hydrate particle aggregation phenomenon which is also considered to be a granulation phenomenon.\(^{[3]}\)
The Fig. 1 is completely showing one of the model by which formation of the gas hydrate in the petroleum pipeline can be showed. Initially water droplets, oil and gas molecules are separate. As bulk moves, hydrate shell growth starts. Due to capillary action, agglomeration of particle results in which the gas molecules get trap inside the hydrogen bond of the water molecule. In the final stage, there is plugging of the gas hydrates due to cohesive attraction between them resulting in the catastrophic plugging.

Clathrade hydrates are termed as gas hydrates or just the hydrates which are crystalline inclusion compounds hydrogen bonded from a cage with hexagonal or pentagonal faces. The gases in the crude like methane, propane and ethane are trapped inside them, termed as guest molecules, in order to stabilize the structure which is also thermodynamically stable structure at low temperature and high pressure conditions. The preference of the structure arises because of the ratio of the size of the gas molecule to the cage structure. The cage size of structure I (shown in Fig. 2) with diameter 5.86 Å is large for ethane molecule (5.5 Å diameter) but too small for propane molecule (6.28 Å).

![Fig. 1 Conceptual mechanism for hydrate plug formation in oil dominated flowlines, from Turner et al. (in collaboration with J. Abrahamson) where emulsified water droplets (black) may grow a thin hydrate shell (light grey) and aggregate in the oil phase (dark grey).](image1)

![Fig. 2 Molecular drawing of structure I (top), Structure II (middle), and structure H (bottom) hydrates](image2)
The adhesion forces of the hydrate-surface can be scaled up to the macroscopic parameters like the composite strength and moduli through an assumed packing.\textsuperscript{[4]} The apparatus like micromechanical force (MMF) has played a very vital role in understanding the interfacial behavior of hydrates. Generally cohesive forces information between the hydrate particle systems is based on the macroscopic parameters data (e.g slurry viscosity as a function of shear rate) for which there is a cohesive model where data can be fitted\textsuperscript{[45,62,63]}. The MMF apparatus is different in the way that it can directly measure the cohesive force between the particles. These methods conflated all the parameters into one parameter (cohesive forces) which helps in understanding of how the parameter like temperature, pressure, viscosity, system chemistry etc. can influence cohesive forces.

The temperature dependence of the cohesive forces was first studied by the Yang et al.\textsuperscript{[23]} using the tertrahydrofuran (THF). The further studies carried out by Taylor et al.\textsuperscript{[24]} and Dieker et al\textsuperscript{[5,25]} demonstrated that the hydrate has to be maintained below the ice point in order to keep the structure rigid due to which there was risk of getting the ice contamination in the cohesive force measurements and motivated for studying the pentane hydrate which is stable upto 7.7°C at ambient pressure.

Dieker et al\textsuperscript{[5,25]} studied cyclopentane hydrate cohesive forces and came on conclusion that nucleation of the cyclopentane hydrate from liquid water requires a lot of contact time greater than 10 hours. The formation of the cyclopentane hydrate was carried by melting the ice in the liquid cyclopentane. The measurement of the particle-particle forces was done and it was observed that the forces increases as the system warmed towards the melting temperature. The results were explained on the basis of the work done by Taylor and Yang which states that a large liquid layer will produce a larger and rigorous capillary bridge.

Further studies by Drake et al. on the cyclopentane hydrate in the presence of crude oil and various carboxylic acid checked the impact on the cohesive forces. It was concluded that in the presence of crude the inter particle-particle cohesive interaction tends to decrease and this decrease was directly linked with the presence of naphthenic acid amount present in the oil, with a particular focus on polyfunctional carboxylic acid. The studies lie on the fact that the inter particle interaction was dominated by cohesive attraction and surfactant weakens or decreases the liquid bridge between hydrate which decreases the cohesive force. The role of surfactant played in the field of cohesive attraction between the particles is one of the main topics in on-going studies.

The interaction between the hydrate particles is as important as the interaction between the hydrate and surface (adhesion). Taylor et al.\textsuperscript{[2]}, and Nicholas et al.\textsuperscript{[5, 6]} expanded the studies on MMF to the adhesion forces between the particles and surfaces. The process was carried to check the adhesion force of cyclopentane as a function of surface free energy of the various modeled surfaces by Aspenses et al.\textsuperscript{[7]}, It was determined that the surface forces increases with the increase in the surface energy and the magnitude of these forces becomes three times when the particles are interacting in the presence of water droplet. Further it was also concluded by Aspenses et al.\textsuperscript{[7]}, that with inclusion of 0.65% by weigh of naphthenic acid in bulk eliminates the adhesion force between hydrate and surface (steel) on the dry basis (without the presence of water) and by 50% when water droplets are present on the surface. These results are agreed with the previous experimental observation by Taylor et al.\textsuperscript{[8]}, Dieker et al.\textsuperscript{[11]}, and Aman et al.\textsuperscript{[10]}, and were partially explained by the extending the concept of capillary interaction to the particle-surface interaction.
Methods for micro-texturing:
The new synthetic methods have made it possible now to use the nano particles to forefront the need of making building blocks. The nano particles have played an important role in accessing the nano scale properties that once were only accessible through the expensive semiconductor type processing. Films of uniform and well ordered nano particles over large surfaces are used in coating for electronic and optical applications. A number of methods have developed for this purpose.

The surfaces formed by using the deposition of the nano particles were termed as hydrophobic surface that were not only repellent to water molecules but also helped in making less resistant towards fluid movement. The hydrophobic surface usually have water contact angle not more than 120°. But the lotus leaf has the water contact angle of more than 160°, and the phenomenon is known as superhydrophobicity and is also called as Lotus leaf effect. This effect is based on the roughness cause by the micro structured surface, cannot be seen by naked eye, together with the intrinsic properties. Due to intrinsic hydrophobic nature of the surface, water drops do not enter the surface and remain on the top leaving the air gap. This whole phenomenon is called as Cassie-Baxter Wetting. The origin of large contact angles on the Cassie-Baxter surfaces is theoretically explained by the Classical Young’s Equation and when there is change in the surface energy Wenzel’s Penetration Approach is best approach to check equilibrium angle.

A lot of theoretical as well as experimental studies are carried out in order to understand the behavior of water drop on the rough surfaces. The first it was studied by Wenzel and Adam back in mid 20th century where they proved that the apparent water contact angel increases with the increase in the surface roughness. The work performed by Wenzel was further extended by Cassie and Baxter [12] where they tried to proof that the apparent water contact will be more high if respective surfaces are rough as well as porous too. They found the theoretical expression for calculating the apparent contact angles for the porous surfaces. The summary of the calculations done to obtain the final expression is given by below:

Whenever a water droplet is places in the solids surfaces then it destroys the solid-air interface energy given by \( f_1 \lambda_{sv} \) and new \( f_1 \lambda_{sl} \), interface energy or solid-liquid is expended to form the solid liquid interface. Another energy \( f_2 \lambda_{lv} \) is also expended to from the liquid-air interface. The net energy \( E_D \), expended in forming the unit interfacial area of the interface is given by:

\[
E_D = f_1(\lambda_{sl} - \lambda_{sv}) + f_2\lambda_{lv} \tag{A}
\]

Where \( f_1 \) is the total area of the solid-liquid interface and \( f_2 \) is the total area of liquid-air interface in the plane area of unity parallel to the rough surface. If \( \theta_A \) is the advancing contact angle for the solid-liquid interface then

\[
\cos \theta_A = (\lambda_{sv} - \lambda_{sl})/ \lambda_{lv} \tag{B}
\]

Eq (A) can also be written as

\[
E_D = f_1(-\lambda_{lv} \cos \theta_A) + f_2\lambda_{lv}
\]

\[
E_D = \lambda_{lv} [f_2 - f_1(\cos \theta_A)]
\]

Eq (B) may be written as:
\[ \cos \theta_A = -\frac{E}{\lambda lv} \]

The apparent contact angle will be given by:

\[ \cos \theta_D = -\frac{E_D}{\lambda lv} = [f_1(\cos \theta_A) - f_2] \quad (C) \]

When the surfaces are only rough not porous then \( f_2 \) becomes zero and this equation approaches the Wenzel penetration equation for the apparent contact angle of the rough surface where \( f_1 \) would be the roughness factor. The above gives the advancing contact angle of water drop on the rough and porous surfaces. The equation for calculating the receding contact angle of the drop is given by:

\[ \cos \theta_W = -\frac{E_W}{\lambda lv} = [f_1(\cos \theta_R) - f_2] \]

where \( \theta_W \) is the apparent contact angle and \( \theta_R \) is the receding contact angle.

The Cassie-Baxter and Wenzel approach for the apparent contact angle is can be explain by the fig 3:

**Young-Dupre Balance of Forces at the Contact Line**

\[ \cos \theta_{eq} = \frac{\gamma_{s/v} - \gamma_{s/l}}{\gamma_{l/v}} \]

\( \gamma_{s/v} = \text{solid vapor tension} \)
\( \gamma_{s/l} = \text{solid/liquid tension} \)
\( \gamma_{l/v} = \text{liquid/vapor tension} \)
How Roughness Can Cause Hysteresis

\[ \theta_i \text{ intrinsic contact angle on flat surface of same material} \]
\[ \theta_a \text{ apparent advancing contact angle on rough surface} \]
\[ \theta_r \text{ apparent receding contact angle on rough surface} \]

Wenzel equation for equilibrium angle on rough surfaces

\[ d\Delta = r d\Delta \left( \gamma_{SV} - \gamma_{SV} \right) + d\Delta \gamma_{LV} \cos(\theta) \]
At equilibrium:
\[ d\Delta = 0 \Rightarrow \left( \gamma_{SV} - \gamma_{SV} \right) = \gamma_{LV} \cos \theta'_{eq} \]

Cassie-Baxter’s Wetting

Change in the Surface Energy.

\[ d\Delta = \left[ \gamma_{SV} - \gamma_{SV} \right] \phi_s d\Delta - \phi_s (1 - \phi_s) \gamma_{LV} d\Delta + \gamma_{LV} \cos \theta'_{eq} d\Delta \]
\[ \cos \theta'_{eq} = \frac{1 + \phi_s (1 + \cos \theta'_{eq})}{1} \]

\( \phi_s \text{ Solid area fraction} \)
Figure 3 (a) shows the interfacial force balance on the contact surface as explained by Young’s Dupree Model. The model also explains that in order to get maximum contact angle we need to maximize the solid-liquid interfacial forces. Fig 3 (b) shows the phenomenon how the roughness of the surface plays an important role in altering the apparent contact angle on it. Fig 3 (c) (d) shows the Wenzel penetration theory approach towards the contact angle change over the rough surface where it can be seen that the change in the angle will be totally dependent on the surface roughness factor which is given by the ratio of the actual surface to the geometric surface area. Fig 3(e) shows the Cassie-Baxter approach towards the contact angle altering and hysteresis which shows that in this approach contact angle is totally dependent on the solid area fraction which is actual contact area of the water droplet with the solid surface. In case of superhydrophobic surface the solid to liquid contact angle is minimum just at the point of elevations. Hence the Cassie-Baxter theoretical models shows that the when solid area fraction is minimum the apparent contact angle will be maximum. Fig 3 (f) shows the wetting behavior of water with the shape of droplet that will be formed over different surface. In pure hydrophilic surface the complete spreading of water drop will occur. When solid-liquid and solid-vapor interfacial forces become equal then contact angle of 90° will be obtained. In case of purely superhydrophobic surfaces the contact angle will be 180° and surface will completely be non-wetting. In pure superhydrophobic surfaces a single point of contact of liquid drop on the solid surface is assumed.

Lotus leaf self cleaning properties inspired the scientist and researcher to study in deep phenomenon and due to which recently significant progress has been made in the fabrication of the superhydrophobic surfaces on which the water droplets rest with the angle greater than 150° and get off the surface when surface is a little inclined to one side. The high contact angle and small hysteresis attributes of the superhydrophobic surface comes due to formation of air pocket between the water droplet and substrate.
surface which keeps water on the edges of the nano particles\cite{64-66}. The application of these surfaces is not only limited to the excellent water repellency but they are very good in resisting the formation of the snow and ice. Some observation and experimentation have been done on the attraction of snow on superhydrophobic surfaces and correlations have shown the high degree of success between the reduction of the adhesion of ice on the surfaces\cite{67-69}.

The contact angle can be used for checking the interfacial macroscopic and microscopic properties of the surfaces. There are different applications of contact angle. The contact angle can be measured using two different scales which are microscopic and macroscopic. The macroscopic contact angle calculations can be used to check the average wettability of different surfaces. The knowledge of the contact angle will not only help to predict whether water droplet will bend on the surface or will spread on the surface but also the shape of macroscopic fluid droplets on various geometries (e.g meniscus in capillary tube). In the laboratory environment, contact angle is the main factor which is used to measure the wettability. The microscopic contact angle measurements can be used to measure the physics and chemistry of the microscopic region at the contact line. These microscopic properties are used in condensation figures that are based on the droplets condensation on the surface. These can be used to diagnose the heterogeneous surface properties and structures\cite{13,16}. These two microscopic and macroscopic studies on the contact angles are intrinsically linked and they can be very useful in showing the connection between the static contact angle and precursor film thickness and with the help of asymptotic matching inner scale physics and dynamic contact angle can be defined.

It is very useful to measure the contact angle but at the same time it is also very difficult to measure them and even more difficult to interpret them. The homogenous surfaces that have almost zero hysteresis, the static contact angle can be measured. The force balance on the contact line\cite{17,18}, solid deformability \cite{19} and line tension issues are addressed using the static angle measurements. In heterogeneous surfaces having hysteresis, contact angle can take value in between the advancing and receding contact angles. Therefore, the hysteresis of the surface will also be a very pretty good indication of the heterogeneity of the surface and it also gives idea about the hydro dynamic motion of the water droplet over the heterogeneous surface. Currently no model is present which shows the quantitative relation between the contact angle and distribution of the surface chemistries or roughness on real surfaces.

Spin coating is one of the best well established technique used in the electronic industries for depositing the nano particles in the form of thin films of polymer for lithography. \textbf{ogi et al.} used the sapphire substrate with high surface coverage and deposited the coated films of submicron-sized SiO\textsubscript{2} particles from aqueous suspension. Spin coating is used for getting better surface uniformity and surface thickness can also be controlled using spin velocity but the uniformity and surface morphology is very dependent to the ambient conditions. Solvent used in the spreading the nano particles on the substrate surface are also very expensive too.

Dip coating technique which is relatively easy and fast is automated\cite{70}. It can be used for coating any kind of substrate. The 3D-assembly of photonic crystals referred as vertical evaporation is related to Dip coating. In the vertical evaporation\cite{71}, instead of moving the substrate out of the solvent, it is allowed to evaporate from the stationary substrate surface leaving behind a film. Similar to the dip coating, in vertical evaporation the film thickness can be increased by repeating the process.
Electronic deposition (EPD) is another technique in which the charged nano particles are attracted onto the charged substrate surface by applying the electric field to the suspension\cite{72,73} but this technique comes with one drawback which is that it cannot be applied to the insulating substrate surface. Magnetic field is also used to deposit nano particles onto the magnetically charged substrate surface\cite{74} but this approach is also limited.

Spray deposition is applied to the coating applications for many decades\cite{75} but getting a uniform thin and smooth coated surface is very difficult especially when surface thickness needs to be (<2um). The simplest and easiest one are the screen-printing and doctor blading but they do not offer the smooth and precise control on film thickness\cite{76}.

Langmuir-Blodgett (LB) uses the self assembly of nano particles at the gas-liquid interface which is then followed by compression by mechanical barrier and transfer of nano particles onto the solid surface. This technique is very suitable for the applications that requires the monolayer and for large surfaces applications\cite{77}. Similar to the gas-liquid interface, liquid-liquid interface can also be used and nano particles can be transferred to the solid substrate surface. In addition to this, different methods and techniques can be combined to get the desired surface thickness and other attributes, e.g by Tsai et al.\cite{78} successfully combined the LB and electrostatic assembly where a low dielectric constant solvent was used as a driving force to assemble for suspension onto the monolayer at air-water interface. All of these techniques are very efficient but they are limited in many different ways. Sometimes, the requirements can be for specific equipments, not applicable to large surfaces or limited to small surfaces, the morphology of the surface highly dependent on the ambient environment.

Adsorption is another technique which is one of the simplest techniques employed in the field of depositing the nano particles onto the substrate surface in the form of 2D and 3D network of arrays. The adsorption can be either physisorption or chemisorption. The most prominent advantage of the electrostatic adsorption on the other depositing techniques is its simplicity\cite{79}. In the electrostatic adsorption, electrostatic attraction is being established between the substrate surface and nano particles\cite{80-82}. Substrate surface is being dipped inside the nano particles for an optimized time for the adsorption and then it is withdrawn, rinsed and dried. The time for adsorption depends on the type of the layer on the substrate surface.

In some applications monolayer of nano particle (NP) is required and in these conditions big adsorption times are not favorable while for the case of multiple layers of structured arrays usually repeated steps are implemented to get the desired results. This is a kind of technique most commonly known as the Layer by Layer (LbL) assembly of the particles. Polyelectrolytes are often employed in the LbL to make the oppositely charged particles and substrate and not only electrostatic attraction but sometimes hydrogen bonding is also used in the LbL assembly\cite{83}. Li et al\cite{84} successfully coated the particles with the cross linked hydrogen bonded layer followed by polymer-on-polymer bonding. In the absence of the polyelectrolyte, LbL assembly can still take the advantage of the chemical nature of the substrate and particle. In case when the particles and substrate have the same surface charge then modification of the charge is required. There are two ways by which charge modification can be done. The first one is the self assembly of the monolayer, which is bi functional, on the substrate surface and then deposition of the NP on the monolayer. The second way involves itself the nano particles by bi-functional molecules\cite{85-89}.
Applications related to electrostatically driven adsorption of NP on the substrate surface have been developed at rapid pace and a lot of theoretical as well as experimental studies are present on it to get the deep inside understanding of the process. In some of the experimental studies it is being demonstrated that monolayer can be used to control the surface charge density of the nano particles or the substrate and parameter influencing adsorption of particle from the ionic strength of the solutions.

The maximum contact angle that can be obtained through the hydrophobic surface or flat surface with low surface energy coating is nearly 120°. In order to produce the super hydrophobic surface, roughness is required. The water droplets reside on the surface of the substrate in the form of either Wenzel regime or Cassie-Baxter wetting regime. In case of the Wenzel regime, there is full penetration of water inside the roughness which enables the full contact angle between the solid and liquid phase. Cassie-Baxter surfaces tend the water droplet to not enter the roughness and water droplets rest on the peak of the roughness features, with the air pocket filling the gap between. In addition to the high roughness, a low contact hysteresis is also required for the super hydrophobic surfaces especially for the self cleaning, which is resulted because of the high liquid-air fractional area. Application of the super hydrophobic surface in the optical surface is on high demand which requires the high transmittance of light through these surfaces too. However, the dual properties, super hydrophobicity and high transparency pose a challenge sometimes. The surface should be reasonably rough to obtain the high contact angles and low contact angle hysteresis while at the same time must has dimensions of the roughness small enough to keep the transmittance of light high and usually suggested size of the roughness must not exceed the half of the wavelength of the visible light which is around 100nm. Glass is most commonly used for architectural window and some other polymers such as polycarbonate (PC) and poly(methyl methacrylate) (PMMA) have also found great engineering importance in airplane canopies, solar panels, computer screens, optical high-performance electronic and medical devices.

In case of the glass substrate nano-structuring is generally achieved by using the technique of dip coating and spin coating. Another technique, plasma etching is also being used mostly for the polymer substrate surfaces. Several studies have shown with confirmation of high degree of transmittance of light thorough the coated surface and some have even showed the higher transmittance level as compared to the uncoated surface due to anti reflective effect but in order to achieve the super hydrophobicity, these surfaces requires the post treatment with the fluorosilane or other low energy surfaces. In some cases either higher contact angle or low contact angle hysteresis was absent. Polymer substrate instead of glass is also being used in a few studies. Mostly correlation and studies are developed on the basis of glass substrate. SiO₂ as nano particles are most commonly being used while ZnO use is also present but it is less common.

In order to utilize the unique properties that different nano particles have, fabrication technique should be developed in an optimize way that should be suitable for different variety of nano particles. Transparency and super hydrophobicity are two competitive factors which means that if super hydrophobicity is increased by increasing the surface roughness then surface transparency is decreased due to Mie scattering. Nano particles, especially silicon dioxide (SiO₂) are highly studied in different scope and areas. All of the nano particles can be used to form the nano-composites that are not very effective for the increasing the surface mechanical properties but they are very effective in making the surfaces as super hydrophobic. Polydimethylsiloxane (PDMS) is regularly used for the super hydrophobic surfaces.
The nano particles and polymers can also be used to form the super hydrophobic surfaces using the different fabrication techniques like dip coating, spin coating and imprinting\textsuperscript{32,33}.

The techniques which are being used in the making the super hydrophobic surfaces are sometime also used to make them antireflective in addition to super hydrophobic. It is being mentioned before too but now we will go in little detail. Self assembled monolayer or multiplayer colloidal crystals are widely used in the making the sacrificial masks to patterns the micro as well as nano structures for wide variety of applications that includes but not limited to biosensors and high density magnetic storage for plasmonic devices. It is a matter of fact that these techniques are useful in making these surfaces but they have some drawbacks like low throughput and incompatibility with standard microfabrication resulting in the mass production and on-chip integration of practical devices\textsuperscript{34, 35}. Moreover, it also usually takes hour to days to make a centimeter-sized colloidal crystal template using the current coating techniques. Some of these techniques also rely on the submicrometer and micrometer particles. The sub 100nm particles can be fabricated but the limited number density of the particles on the surface is always a problem. The close packed crystals are available through the traditional coating techniques while in applications of anti reflective and hydrophobic surfaces mostly non-close-packed surfaces are used. In my research, I have relied on the technique of spin and dip coating by which I was able to get the maximum contact angle and surface uniformity. Before we proceed to the results and experimentations, I would like to explain a little bit insight of the spin coating. This section will give an idea about how colloidal suspensions interact during the spin coating process, how whole surface structure is formed and how it gets interacted with the addition of different parameters.

**Spin coating in colloidal suspensions:**
Spin coated films formed by using very small particles, typically suspended in matrix of polymeric material or dispersed in an appropriate fluid, are used in wide variety of application including the dental coating, sensors, catalytic films and abrasion resistant surfaces. Recent studies have showed that the spin coating provides the most effective and simple technique for deposition of particles on the substrate. Choi et al.\textsuperscript{36} applied the simple method to show the deposition of nano particles on the vertically aligned nanotubes using the magnetic field. Quality and internal structure of the layers of the nano particles on the coated substrate is directly dependent on the distribution of the particles on the surface. Lithographically patterned surface can be formed using silica particles spin coating was first found by Xia and Brueck\textsuperscript{37}. It is also determined that the ability to distribute the nano particles on the surface depends on the rotational speed during spin coating, pH value of the suspension and surface of the substrate on which coated layer is being formed. Several methods\textsuperscript{38,39} have been employed for direct assembly of nano particles to fabricate the patterned surfaces. Mostly studies have been done of the particle of size ranging from 100 nm to 5 μm. Particle density distribution on the substrate surface can be altered by changing the rotation speed and concentration of the suspension. Generally, thickness of coating decreases with the increase in the speed of rotation and decrease in the average particle concentration. Most of the study that is based on the theoretical concepts is directed at application involving polymer solution. (Bornside et al., 1989, 1991; Lawrence, 1988, 1990; Ohara et al., 1989; Meyerhofer, 1978) and mostly they are based on low Reynolds number hydrodynamics. Much of the literature on spin coating of the colloidal suspension is based on the experimental work. The most notable work is of Tu\textsuperscript{40} and Potanin\textsuperscript{41} in which particle concentration equation is employed and treated aggregates as “effective sphere”. The studies on the spin coating of particles on substrate resulted into formation of two theories that relate to the film thickness on
the substrate with the rotation speed of the disk and physical properties of the solution used for the coating.

Meyerhofer (1978) and later modified by Bornside et al. (1991) assume for polymer systems that (i) the convective thinning rate of film is not affected by solvent evaporation rate (ii) the film thickness is determined when the convective thinning rate is equal to solvent evaporation rate.

The second theory, developed by Lawrence (1998, 1990), based on the assumption that when the concentration boundary layer spans the film thickness then the thinning due to radial flow ceases. We are unaware of the similar kind of study on colloidal suspension so one can assume that the similar assumptions can be applied to these too. But this is not the case. The structural behavior and morphologies of the coated surfaces are totally different from the polymer solution.

The objective is to develop the mathematical model to define the spin coating of colloidal suspensions based on the Navier-Stokes equation, convective diffusion and thermal energy equation. Two mathematical models are defined. J.S Marshall et al.[55] applied the theoretical approach to check the particle transport along the radial direction. This model is more fundamental as compared to previous studies on the spin coating and is focused on the specific part of spin coating process which is responsible for particle transport and deposition. Computation used in this modeling is based on the combination of discrete element method (DEM)[56] and previous lubrication method studies[57]. In this approach motion of every particle is traced and is solved for the collision and adhesion of the particles. Motion of the particles is calculated using combination of fluid-induced forces and torques, and forces and torques induced by particle collision and adhesion forces.

There are four stages involved in the development of spin coating layers. The time scale of the first two stages is short as compared to that of the latter two. The description of four stages is described as follow:

- First stage: There is deposition of the colloidal suspension of the substrate surface which is fixed.
- Second stage: Substrate is accelerated and colloidal suspension spreads on the surface and it has same rotation speed as that of rotating substrate.
- Third stage: In this stage the suspension starts spreading outwards and it is controlled by the centrifugal force and viscous shear force.
- Fourth stage: In this stage there is evaporation which starts as the film becomes so much thin that evaporation dominates.

In evaporation phase and for colloidal suspension the film thickness can be reduced to that of particle size at which the capillary forces are significant. The transfer from the third stage to fourth stage is dependent on the properties of the fluid and its volatility. For some applications, sometimes high temperature aids the evaporation which indirectly controls the chemical composition, film thickness and particle development.

Frasch and Saremski (1982) studied the protocols of spin coating for a polymer solution. They showed that slow substrate rotation rate for polymer solution results in radial striations. The same behavior is also observed in case of colloidal suspension[31].
J.S Marshall et al.\textsuperscript{[55]} developed a computational model in which the heat transfer effects are neglected and then an axisymmetric lubrication model of incompressible fluid is employed. Consequently, the effect of fingering of contact line\textsuperscript{[42,43]} interfacial waves\textsuperscript{[44]} and non-flat substrate surface\textsuperscript{[45]} were neglected. Another main assumption in this model is that the particle concentration is taken to be very small so that particles have negligible effect on the fluid flow. Non-Newtonian effects and shear thinning effects due to particles are also neglected. It is also assumed in this model that there is no chemical reaction during the process of spin coating and that the particles are present as a colloidal suspension which means that they do not precipitate out during the process of spin coating.

**Fluid flow:**
The computation of the fluid flow employs the axisymmetric lubrication model. In lubrication model, the product of Reynolds number and square of the interfacial slope is very small. The radial momentum equation for the frame spinning with the rotation speed of $\Omega_s$ is:

$$\mu d^2 u_r/dz^2 = dp/dr - \rho (\Omega^2 s) r$$

Here $u$ is the radial velocity, $\rho$ and $\mu$ are the fluid density and viscosity and pressure is independent of depth. The flow rate of per unit length is given by:

$$Q = h^3/3\mu (\rho_s\Omega_s r - dp/dr)$$

The pressure in here is the sum of the interfacial pressure and capillary pressure. The liquid film continuity equation is written by:

$$dh/dt + (1/r) d/dr(rQ) = 0$$

Putting the value of pressure in flow rate equation and then putting that value in above equation gives the value of height of film thickness in the form $dh/dt$.

**Particle Transport:**
The particle transport is calculated using the linear and angular momentum equation:

$$m_p dv/dt = F_F + F_A, \ I d\Omega/dt = M_F + M_A$$

$m_p$ is the mass of the particle mass, $d$ is particle diameter, $I$ is the particle momentum of inertia. The derivative shows the particle transport. $F_F$ and $F_A$ are the fluid forces and particle collision and adhesion forces respectively. $M_F$ and $M_A$ are the respective torque for the fluid and particles.

The forces on the particle is given by sum of centrifugal force, drag force, added mass force, lift force, Magnus force and centrifugal force which is given by difference between the particle centrifugal force and pressure gradient within the fluid. Gravity, Bassett history force and Brownian thermal force are neglected in this model. Using the different relation these forces can be calculated. Among these forces, drag force on the particle is the primary force which is given by formula:

$$F_d = -3\pi d\mu (v-u)$$
The particle collision and adhesion force act in the direction normal to the line joining the center of two particles. The force and torque is also generated due to sliding, twisting and rolling of particles over one another. The total collision and adhesion force and torque on particles are given by:

\[
F_A = F_n n + F_s t_s, \quad M_A = rF_s (N \times t_s) + M_r (t_R \times n) + M_n n
\]

The normal force in this particles collision is dominated by particle elastic response and adhesion is responded by the particle tangential motion is dominated by rolling motion. The normal force is further composed of particle elastic deformation and energy loss during the contact of the particles. These forces are calculated using the relation\textsuperscript{11, 12} and represented by \(F_{ne}\) and \(F_{nd}\). Similarly the sliding and twisting resistive forces and torque generated are calculated with the help of studies of Savkoor and Briggs\textsuperscript{[48]} and it was further simplified by Thornton\textsuperscript{[49,50]}. The value of these forces are calculated and putted in the main equations that are composed of sum of these forces and torques.

**Capillary force:**

The particles in the suspension that are present at the liquid-gas interface also experience an extra force that acts in the normal as well as tangential direction along the interface. The normal force attracts the particles towards the interface and tangential force pulls the particles at the interface towards each other. The Young Laplace equation can be numerically solved for the shape of the interface and can eventually serve as a means to calculate the capillary forces but this approach does not yield an analytical solution. Nicolson\textsuperscript{[51]} obtained an analytical expression for Capillary attractive force between the two bubbles and that force was calculated by solving the Linearized Young Laplace equation for each bubble and then superposing the individual solutions for bubbles. This is known widely as Linear preposition approximation (LSA). Chan et al.\textsuperscript{[52]} extended the work to cylinders and sphere in fluids. Vassileva et al.\textsuperscript{[53]} showed that the LSA can be used for the small particles (in the low Bond number limit) on an oil-water interface with very small separation through experimentations. The normal capillary force is given by:

\[
F_{cap,1} = -2\pi \sigma q \beta^2 q K_1(qr) n, \quad \text{where } Q_p = -\tan(\Theta_E - \Theta_o)/qK_1(0.5qdsin\beta_o)
\]

and tangential force is along the interface is experienced due to ambient slope. The force is given by:

\[
F_{cap,2} = 2\pi \sigma Q_p \mathbf{n} h \text{ which is given in terms of film thickness gradient.}
\]

Fig. 4 in this section is showing the trends of particle transport on the substrate surface during the spinning motion. The graphs have been plotted after regular intervals of times \(t=2, 6, 10\) and 20 for the top view and side view. The particle concentration in the film remains uniform in the start and then particles start to move outwards in the radial direction. The low particle concentration is formed close to the axis of rotation. A particle ridge is formed at the point just near the contact line and it is filled with the particles. A row of particles is formed at the low velocity region in the film at the bottom of the substrate surface.
In order to understand the particle transport, the Fig. 5 has to be observed. The particle velocity within the ridge experiences the strong radial velocity and then there is a low velocity part of the ridge near the substrate surface. The observed velocity pattern is similar to studies done on the rolling motion by Dussan\cite{58}. Figure 3 shows the concentration field which is obtained by plotting the graph between the average particle concentration which are in azimuthal direction on Y-axis and radius on the X-axis. These graphs are also showing the particles that are attached to the substrate surface as well. These particles are termed as wall attached particles.

The initial concentration in the start is uniform and no particle is touching the substrate surface. As the time goes on the particle get attached to the surface of substrate. It is also observed that the particle concentration is very low near the axis of rotation. The reason of this low concentration is that the centrifugal force acting on the particles is greater as compared to force acting on fluid. Due to this strong
force the particles disperse outward at a faster rate than the fluid that is why the region at the center of axis has very less particles. The particles cannot move beyond the ridge because of the rolling motion of the particles towards the low velocity region. Zhou et al\cite{54} also studied the same kind of motion for a particle-laden liquid film flow over the inclined surface. The peak of the particle concentration was found to be 0.04 near the film which is twice the average concentration of the particles.

The concentration of the wall attached particles also follows the same trend. At start no particles get attached to the surface of the substrate but with passage of time the concentration increases. It also follows the same trend of increase attached particle concentration near the contact line at the end of computation.

**Formation of Silica Particles:**
In many experimental studies, colloidal suspensions of matter, it is also desirable to have suspended phase of homogenous particles. The monodisperse particle are also used for the calibrating the analytical equipments. Investigations were done in order to get the monodisperse suspension of the silica sphere in the colloidal range. I am using the silica particles as the mean of getting the microstructure on the surface of glass substrate that is why I will define the procedure of the formation of the silica particles. Although, mostly during the experimentation phase, the silica particles were got from the outside companies instead of making them in order to save time and focus on the surface morphology and behaviors of water droplet on the super hydrophobic surfaces.

It is matter of fact that Werner Stober, Arthur Fink and Ernst Bohn\cite{62} did the investigation on the formation of the monodisperse silica particles with high level uniformity in distribution and characteristics. Their experimentation were based on the fact that silica particles can be produced by having a chemical reaction between tetraesters of silicic acid (tetraalkyl silicates) with certain solutions. Kolbe\cite{59} demonstrated that the silica particles can be made by reacting the alcoholic tetraalkyl silicates with water in the presence of some basic solution. He observed that under very slow reaction, if the reactants are pure, uniform spherical silica particles were formed. In order to duplicate the experiment results several attempts were made but most of them resulted in the formation of gel and a few resulted in the formation of ellipsoidal shape particles and a size range of 0.08μ. Due to this a systematic studies were organized and investigation were made on the parameters of the reactions. With changes in the experimental environmental, quasi-monodisperse suspension of the silica particles of size range of 2μ were formed. The time period for the reaction was nearly an hour and purity of the reactant should be of highest level for the ultimate particle distribution and characteristics.

Electrostatic effect plays a vital role in the particle distribution. The surface of the silica particles absorbs OH⁻ ions because of which there is generation of electrostatic effect due to which particles will repel each other. Therefore, particle will keep a certain distance from each other according to the electrostatic theory. This will result in the uniform distribution of the particles. Nucleation is another process which also depicts the particles size and distribution. It was found that the nucleation in the reaction takes place during the initial stage of the process for limited period of time\cite{60}. Eventually, growth starts and it dominates the nucleation process as the number of particles remains constant. This dynamics results in the competition between the nucleation reactor and growth. The balance between two competitive processes is defined by hydrolysis reaction which results in the release of slow addition of monomers. So basically,
the whole process can be defined as the monomer addition process in the presence of rate controlling reaction (hydrolysis). It was also observed that growth is reaction limited and diffusion limited.

But there is other side of the picture that the monomers are consumed during the nucleation process which inhibits the formation of large particles. There is another possibility if there is slow activation of the monomers. Only the hydrolyzed monomers will be available for the nucleation and slow release of the monomer will decrease the intensity of the nucleation process which in other word is the promotion of the growth of the large particles. Hendriks studied the relation of different parameters like initial concentration for monomer including the constant initial concentration, a constant source strength and infinite pool of the monomers. The results showed by him demonstrated the influence of different growth mechanism on the size as well as the moment of distribution of the particles.

The procedure for the silica particles is really simple but it requires high precision and accuracy in order to get the desired results. In the start of the experimental procedure, alcoholic mixture of pure alcohol is mixed with saturated alcoholic ammonium hydroxide solution in a flask having a kind of stopper on the top. Then water is also added depending on the desired concentration of ammonia and water in the solution. The water content of the solution is measured on the basis of the fractional amount added by individual component in the solution. Now alkyl silicate is added followed by mounting the flask on the shaker or in water bath in the presence of ultra sonic vibrations. The solution can also be agitated by the help of magnetic stirrer too. Whatever the technique is being used, the suspension of particles needs to be in agitation after the formation. Actually, during the experimentations performed by Stober, a series of different test run were done with different types of techniques, reactant concentration and experimental conditions. However, in this section I will only give a shot demonstration of only those that got back with optimum results. After the reaction has been started, condensation can be observed within ten minutes because of the formation of silicic acid and its condensation is being indicated by an increasing opalescence of the solution within 1-5 mins after the addition of tetraalkyl silicate.

The process ultimately ends up of forming white turbid suspension. In actual experimentation performed by Stober, the samples of the solution were observed after 120 mins but results of samples taken at different times showed that final size was reached by the particles in about 15 mins. The electron microscope was used to check the size distribution and shape of the particles. Stober et al. after careful observation of the samples come to conclusion that the reaction rates were fastest with methanol and slowest with n-butanol and particles size was also smallest in case of methanol while particle size was biggest when n-butanol was used. The tendency of the formation of wide size distribution with the usage of higher alcohols was seen in the results too. Similar results were also seen when particle size and reaction rate was compared with different alkyl silicates used. The smallest size particle of size less than 0.2μ and fastest reaction of about 1 min was seen when tetra-alkyl silicate was used. In case of tetra-pentyl ester reaction rate was slow, 24 hours, and with the use of n-propanol and n-butanol, size somewhat near to 2μ was obtained. More uniform surface was got when the ratio 1:3 of the methanol and n-propanol was used respectively. Detailed investigation on the influence of parameters like water, ammonia and ester concentration was made with the system of ethanol-ethyl ester system.
It was concluded that the condensation rate during the reaction was highly dependent on the initial water concentration. Irregular shaped particles with no spherical morphology were observed in the absence of ammonia while if the concentration of the ammonia was increased high then the bigger size particles were obtained. The biggest size silica particles were got when the saturated ammonia was used. Fig. 6 shows the silica particles morphology of ethanol-ethyl ester system under the electron microscope. Increasing in the molecular weight of the ester used in the reaction showed the decrease in the condensation reaction while at the same time bigger particles with the uniformity in the size were produced. Condensation reaction can be decreased further by increasing the alcohol molecular weight which is used in the reaction as a solvent but this would also directly increase the size distribution as well as median particle size. Fig. 7 shows the silica particles that were made using the ethanol-pentyl ester system. It can be seen that the size of the particles increased along with the increase in the size distribution.

Fig 6: Electron micrograph of sample of silica spheres obtained in the ethanol-ethyl ester system [62]
At very high concentration of the pentyl ester, there is the formation of separate surface on the bottom of the container by ester. This provides a substrate reservoir for the hydrolysis reaction occurring in the upper phase. This effects the particles growth during the formation. Apparently substrate reservoirs also provided the new condensation nuclei so that there was no uniformity at the end of the process. Stober et al. concluded after extensive studies that the particles sizes cannot be precisely reproduced, occasionally, usually high standard deviation of the size distribution come across. Generally, the particles size and distribution can be predicted within 30% of the limit from the experimental conditions.

**Pendent Drop Contact Angle Measurement:**

There are a lot of techniques by which the apparent contact angle of the liquid drop can be measured on the solid surface. Some of the most popular techniques include Sessile drop experimentation, pendent bubble method and pendent drop experimentation. The Sessile drop and pendent bubble methods are mostly used to measure the surface tension of the liquid in relation to different parameters. The pendant drop experimental apparatus is most widely used to measure the contact angles.
The pendent drop apparatus is really simple and it consists of an Illuminating system which can be anything a monochromatic light, Camera, Convex lens, Syringe, Vibration-proof table and a Computer system. The working of pendent drop apparatus initiates by putting the sample surface whose contact angle has to be measured in the experimental chamber. Then light is tuned on which is converged by a convex lens onto the sample on which liquid drop is placed with the help of syringe. The light that is coming from the Illuminating system is blocked by liquid drop and other light passes and it is directly analyzed by a camera that is connected with the computer. The black image of the drop will be formed which will be displayed on the computer screen. Actually black image shows the amount of light which is blocked by the liquid drop. A bright round circle will be shown at the middle of black image just because of the fact that convex lens converge all the light towards the center of the drop and the intensity at the drop center will be very high which shows up as bright round circle at the center. It is also very important to align sample surface very accurately with the light coming after passing through the lens. In case if there is not a proper alignment then the image of the drop that will be formed on the computer screen will not give accurate information and thus will vary the actual apparent contact angle measurements. For this purpose solid spherical balls can be used. The contact is measured on the computer screen using the different angle measuring tools. The assembly on pendent drop apparatus is shown in the fig. 8. The convex lens can be placed either before the experimental chamber or after the experimental chamber. Its sole purpose is to coverage the light to a single point.

![Fig. 8 General apparatus for contact angle measurement](image)
Experimental Section

In my research, I used different polymeric material as a binder for the nano particles and glass substrate. Some of the materials were totally not suited to my objective but most of them gave very useful results and I am adding their experimental work in this section.

**ETPTA (Ethoxylated trimethylolpropane triacrylate) as Binder:**
I started my experimental work by using the ETPTA (Ethoxylated trimethylolpropane triacrylate) as a binder for the nano particles.

**Materials and substrates:**
ETPTA (Ethoxylated trimethylolpropane triacrylate) and 60 nm microporous nano particles were purchased from Sigma Aldrich. The photo-initiator Darocur 1173 (2-hydroxyl-2methyl-1-phenyl-1-propanone) for initiating the polymerization of ETPTA stratomer was also obtained from Sigma Aldrich. The substrate used for this experimental work was silica glass (2.5 cm x 2.5 cm). It was obtained from corning.

**Instrumentation:**
Weight balance (Acculab) was used for taking the exact weight of the particles in the suspension. Centrifuge (HERMLE Labnet Z206A) was used for the cleaning of the silica nano particles. Sonicator (BRANSON 5510) and Vortex mixer (Fisher STD) were used for dispersing the colloidal suspension properly and uniformly. A Plasma Cleaner (PDC-32G) was used for oxidizing the surface of the silica substrate. The polymerization of the ETPTA was carried by UV system. The contact angle measurement was carried out using the pendent drop equipment. Spin coater of model (WS-400B-6NPP/LITE) was used for coating the colloidal suspension on the glass substrate.

**Preparation of the Colloidal Suspension and Glass Substrate:**
The glass substrate was first cut into the square shape of dimensions 2.5 cm x 2.5 cm. It was cleaned using the Piranha solution (3 parts H$_2$SO$_4$ and 1 part H$_2$O$_2$) where the substrate was kept in this solution for 2 days. The cleaning of substrate was done just for making it confirm that there is no organic layer or any other material present on substrate surface. Then substrate was cleaned with distilled water and dried using the inert nitrogen. Then substrate was kept in the plasma oxidizer in order to get charge on the surface.
The silica particles were silanized to make them hydrophobic. Fluoroalkyl silane drops were added in the silica 60nm particles along with ethanol as solvent. Then this suspension was properly mixed using the vortex mixer and then centrifuge to make them separate from the ethanol solvent. The hydrophobic 60nm particles were dried using the oven for 1 day. The dried silanized hydrophobic 60 nm particles were dispersed into the ETPTA solution. The solution was properly mixed using the vortex mixer and sonicator for 1 hour in order to get uniform colloidal suspension. 1% (weight) Darocur 1173 was also added as a photo-initiator. The final particle volume fraction was nearly 20%. After the filtration and separation of any larger aggregate, the colloidal suspension was left for some time for stability.

**Spin Coating and Polymerization:**
The 200 μL droplet of colloidal suspension was added onto the substrate using the pipette. The substrate was adjusted on the spin coater. The recipe for the spin coating was 200 rpm for 1 min, 300 rpm for 1 min, 1000 rpm for 30 s, 3000 rpm for 10 s, 6000 rpm for 10 s, 8000 rpm for 10 s\(^9\). The thickness of the coated layer is inversely proportional to that of the rpm of spin coater. The coated layer was then kept under the UV radiator for 4 s for the polymerization of monomer.

**Results and Discussion:**
The microemulsion process was used to develop coated silica surface. The 60nm micporesous silica particles were first made hydrophobic using the silane. The particles were added into the non-volatile ETPTA solution to get the final solution where final particle volume was maintained to be 20% of the solution. The Darocur 1173 photo-initiator was also added for the assisting the polymerization process. Colloidal suspension was added in the form of drop on the glass substrate and then it was rotated over the spin coater with gradual increase in rpm with maximum rpm of 8000. The monomer was photo-polymerized for 4 s under UV radiations. The transparent, smooth and firm coated layer of nano particles was obtained. Transparency was because the index between silica particles and polymer matrix was matched.

Visually the coated surface on the substrate seems to be pretty smooth and uniform. The water droplet was added onto the substrate surface and through naked eye the angle was not seemed to be more than 70°. When the contact angle was checked using the pendent drop apparatus it came out to be 75°-78°. The reason which came out for such a low angle was the hydrophilic nature of the ETPTA monomer. Although the silica particles were hydrophobic in nature but they were covered with the ETPTA monomer. The silica particles gave the reasonable roughness to the substrate surface thus making Wenzel surface but the hydrophilic nature of the ETPTA monomer allow the particle to get flat.

Fig. 9 and Fig. 10 shows the structural morphology of the substrate surface and contact angle respectively.
Glycerol & Water equilibrium on Flat PDMS surface

- Water and Glycerol have similar surface energies
- Glycerol viscosity is 1000 times that of water

Fig. 9 Contact angle for water and glycerol on flat surfaces

Fig. 10 Contact Angle for water drop in air for ETPTA monomer
The surface obtained using ETPTA were not able to give required contact angle greater than 150° but these surfaces can be used to get angle of 150° with the help of using the Chlorine RIE process operating at 3mTorr pressure and flowrate of 20 SCCM. The silica particles would act as an etching mask to Chlorine RIE process. The silica pillar will be formed with chlorine removing the ETPTA solution. Silica particles can also be removed by dissolving them into 2% hydrofluoric solution. However, this process is a bit complex one and required some extra equipment.

**Polydimethylsiloxane (PDMS) as Binder**

So I choose to go with PDMS solution as silica nano-particles and substrate binders. Polydimethylsiloxane (PDMS) belongs to the organosilicon polymeric compound which is more commonly known as Silicones. PDMS is most commonly used as silicone based organic polymer because of its excellent physical characteristics such as transparency, rheological, inert properties and non-flammable properties. The application of PDMS includes but not limited to medical devices and elastomers. Chemical formula for PDMS is given by \( CH_3[Si(CH_2O)_nSi(CH_3)_3 \) and \( n \) is the no. of repeating monomer \([SiO(CH_3)_2]\) units.

![Molecular Structure of PDMS](image)

In my research the surface chemical compatibility of PDMS allowed me to use it as the binder for the nano-particles and glass substrate. The external surface of the PDMS acts as hydrophobic when it is cross linked and polymerized that makes the water droplet to not stick on the PDMS surface. In fact, no polar solvent will get stick to the surface thus making the surface self cleaning and water proof. This property of the PDMS exhibits such characteristic which we were lacking in the previous ETPTA monomer where surface came out to be hydrophilic in nature that resulted in wetting of water droplet. So apparently it was very legitimate to say that PDMS should cover all the defect and problems that were faced in the initial
experimentation of my research and it also has a very good binding capabilities too. The surface of the PDMS can also be made hydrophilic by the help of plasma oxidizing. The oxidizing develops the SiOH linkage over the surface and surface chemistry is changed in such a way that it acts as hydrophilic. The conversion of the surface again to hydrophobic is inevitable in case of PDMS no matter whatever is surrounding environment (air, oil, vacuum). The stability time for the oxidized surface is only 30 mins.

**Materials and Substrates:**
In this experimentation, I used the 20 nm nano-particles that were purchased from SkySpring Nanomaterials, Inc. The 20 nm particles were brought as hydrophobic (Functionalized with Silane). The reason I used the 20 nm particles was to get greater ratio of particle volume to PDMS volume on the substrate surface. PDMS was made using base (SYLGARD 184 SILICONE ELASTOMER) and curing agent (SYLGARD 184 SILICONE ELASTOMER). The silicon glass was used as a substrate that was purchased from Corning. The solvent used for it was Toluene.

**Instrumentation:**
Weight balance (Acculab) was used for taking the exact weight of the particles in the suspension. Centrifuge (HERMLE Labnet Z206 A) was used for the cleaning of the silica nano particles. Sonicator (BRANSON 5510) and Vortex mixer (Fisher STD) were used for the dispersing the colloidal suspension properly and uniformly. A Plasma Cleaner (PDC-32G) was used for oxidizing the surface of the silica substrate.. The contact angle measurement was carried out using the pendent drop equipment. Spin coater of model (WS-400B-6NPP/LITE) was used for coating the colloidal suspension on the glass substrate.

**Formation of suspension and substrate:**
Colloidal suspension was made using a very simple method. The base and curing agent were added in the toluene. The ratio of base to curing agent was maintained to be 10:1. This mixture was added in 5ml toluene solution. The amount of toluene added into the solution does not matter much. It should be reasonable so that the mixture of base and curing agent (PDMS) get completely mixed inside the solvent. The reason we add solvent to the mixture is to decrease the viscosity of the PDMS so that it gets evenly distributed over the glass substrate. The final finished coated surface is obtained when all the toluene is evaporated from the substrate surface. After complete mixing of PDMS inside the toluene, Silica particles of size 20 nm are added inside the solution. I used three different ratio of the SiO$_2$: PDMS. The PDMS amount was maintained to be 2wt% in SiO$_2$:PDMS:Toluene. The ratio of the SiO$_2$ was changed keeping 2wt% of PDMS constant. The solutions were named as (2wt% PDMS---25% silica) having 25% by weight of Silica particles, (2wt% PDMS---50% silica) having 50% by weight of silica particles and (2wt% PDMS---75% silica) having 75% by weight of silica particles in the overall solution. Then the whole colloidal solution is sonicated for 1 hours. The glass substrate of size 2.5 cm x 2.5cm is cleaned using the Piranha solution (3 parts H$_2$SO$_4$ + 1 part H$_2$O$_2$) for 1 day. Then substrate is washed with the distilled water and then it is dried using the pure nitrogen gas purge.

**Spin Coating of suspension:**
The washed substrate was placed onto the spin coater and then 100μL drop of the suspension was added onto the suspension using the pipette. The recipe used this time for the spin coating was different as compared to the recipe used in the previous experimentation of ETPTA. This time the substrate was rotated at 3000 rpm for 20 s. After the spin coating, the coated sample was putted inside the oven for 80°C for 2 h in order to get the SiO$_2$/PDMS coating and it helps to increase the evaporation of the toluene. As
the toluene gets evaporated the coated surface becomes more and more stable and its adhesive strength against the glass substrate surface increases.

Results and Discussion:
The simple method of micro-emulsion was used to cover the glass substrate surface with colloidal suspension of 20 nm silica particles mixed with PDMS acting as a binder and toluene solution acting as a solvent. The suspension was made by first mixing the base and curing agent and then sonicating them after which silica particles were added into the mixture and again were sonicated and mixed using the vortex mixer. Three suspensions were made using different ratio of the silica particles to PDMS. After complete mixing of the particles inside the suspension, the substrate was spin coated using 100μL of suspension drop. The substrate was then placed inside the oven for 2 h for 80°C to complete the polymerization of PDMS and evaporation of toluene.

The samples obtained using different suspension had different optical as well as surface properties which was also very obvious owing to different amount of particles present inside them. The sample obtained from (2wt% PDMS—-25% silica) were transparent in nature and the coated layer was also very strong which was not easy to be rip off using the fingers. The contact angle coming out was not very high. It was nearly 122°. The sample obtained using the (2wt% PDMS—-50% silica) were also very stable, not as much as of the previous sample, but the contact angle obtained using this ratio was fairly high. It was nearly 137° which is showing the non-wetting behavior but still it was not good enough to give the desired angle that was above 150°. The third sample that was obtained using 75% of the silica particles came out with very good results. The water drop contact obtained on (2wt% PDMS---75% silica) was above 150°. The mean of the angles got at different points on the glass substrate surface came out to be 154° which was a very excellent result. The surface of the third sample was not transparent enough and it was lacking the optical properties. It was gloomy white and the patterns of the silica particles over the surface can be easily seen through the naked eye too.

Although the angle obtained using the third sample was high enough but the coated surface was lacking the strength and it was very weak. The reason was very obvious too. The particles present on the top were loose enough that they were not providing the extra strength to the surface. The binder was lacking on the top of surface. The particles were present in the high amount in the third sample due to which the multiple layers were present and top surface was only comprised of the particle with a very little amount of PDMS as binder present between them. Other high rpm schemes with high time duration were also used but results were same. The particles were easily getting of the surface with finger which was making it difficult to maintain the super hydrophobic nature of the surface. As the water droplets were placed on the surface using the syringe in order to check the contact angle, the particles were also removed when droplet was moved or removed from the surface. After careful and regressive experimentation, the surface strength was a bit increase with the help of change in the spin coating recipe. Although, the contact angle coming using PDMS and 20 nm silica particles were very high, showing that definitely there was the formation of Cassie-Baxter surface, but the strength of the surface was not up to the mark as those surfaces cannot be used for the desired objective.
**Reason for getting weak adhesive surface:**
The reasons for getting weak surface when high proportion of silica particles was present are not very explicit. After analysis of 10 to 15 samples of the PDMS that were formed using different rpm and time duration using the (2wt% PDMS---75% silica) suspension, it was predicted that there can be two reasons that can justify the weak surface behavior.

First of the all, we need to check the factors that can directly affect the binder power of the PDMS and glass substrate. The PDMS binding strength itself to the glass substrate, high particle ratio, multiple layer formation and improper suspension mixing can be some of the reasons that can affect the PDMS biding strength. The PDMS strength to the glass was checked by making the regular PDMS suspension in which silica particles were not added. The same procedure was followed with a result of getting a pure, transparent and very highly adhesive PDMS coated surface having the contact angle of 110°. It showed that the PDMS strength to the glass substrate was very good. Particle and PDMS suspension were mixed and sonicated in alternative manner for couple of hours in order to get surety that mixing is proper and even. The result was still a weak surface which means that improper mixing was not a problem. Multiple layer formation might be the problem so for that maximum rpm for 2 hours was set and all same procedure was carried out but again there was not much improvement in the strength. So the obvious conclusion from the above investigation was that the high proportion of the silica particles in the solution was making it difficult for PDMS to give enough strength to the coated silica particle to keep stick to the surface.

After further investigation it was found that actually the binding force between the silica-silica particles and that of silica and glass substrate were very different. Fig: 11 shows the typical bonding structure between the silica particles and glass substrate and structural morphology that would come out when coated surface is fully developed.

Fig. 11 (a) shows the top view of the coated substrate surface where you can see that PDMS is present inside the particles. PDMS is surrounding around the particles. Fig. 11 (b) shows the side view of the situation when particles are in high proportion. Due to high proportion we can consider that multiple layers are formed by particles. The top layer will have high amount of particle which will reduce the amount of PDMS between them and in some situation the ratio of surface area of PDMS to Particle will become negligible. This will cause the top of coated surface to become weak enough that particle will get removed from the surface with just the touch of the finger. The same logic can also be used for the monolayer coated surface. If mono layer has large number of particles then particles will have very less distance between them which will again result into very small ratio between the surface area of PDMS and Silica particles. Fig. 11 (c) shows the surface structure if particles are in small ratio. The surface has large amount of PDMS as compared to Silica particles that gave extra strength to the surface.
After getting some more insight of surface morphologies and series of spin coating cycles on same substrate sample the strength of the coated surface was a bit increased without compromise to contact angle. The coated surface was of such a strength that it was getting off when water drop was dropped on it with large height or high pressure. The contact angle results and surface hysteresis of the coated surface is shown in the Fig: 12.
Fig. 12 (a) Water contact angle in air over the coated glass substrate
Fig. 12 (b) Hexadecane contact angle in air over the coated glass
Fig. 12 (c) Water contact angle (advancing) in air over the coated glass.
Fig. 12 (d) Water contact angle (receding) in air over the coated glass
Fig. 12 (e) Water contact angle in oil over the coated glass substrate
Fig. 12 (f) Water contact angle (advancing) in oil over the coated glass substrate
So the conclusion was that we need to find such a material which has more adhesive strength as compared to PDMS. Basically, we need a material with such adhesive properties that even its small amount keeps the particles attached to the coated surface thus maintain the Cassie-Baxter surface structure. So I researched the material which was more stable and adhesive in nature as compared to PDMS.
Methylphenyl silicone resin as Binder

Methylphenyl silicone resin has all the properties that were required in order to get more stable and stronger surfaces. Moreover, Methylphenyl silicone resin is hydrophobic in nature that will support the coated surface in case of super hydrophobicity. Silicone resins are most widely use in different number of application all over the world. They are used in for the coating functions most commonly in ink and paint manufacturing which give extra adhesive strength to the suspension, paint or ink, to stick to the substrate.

Methyl phenyl silicone resins are mostly formed by mixing silicone resin in with phenyl and methyl molecules. The material which I am using in my research is SR355 formed by momentive. The material is 100% solid and it comes into dry form and it can be used as binder or in different moulding applications. SR355 can also be used in high temperature application where hard resin and low shrinkage is required after heating. Methyl phenyl silicone resin can be easy to handle and can be used in dry as well as wet mixes. The weight retention is greater than 80% for this compound at 900°C calculated using thermogravimetric analysis. The physical properties of the methyl phenyl silicone resin SR355 are as follow:

### Physical Properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Points</td>
<td>32°C becomes fluid at 93°C, has low viscosity at 120°C</td>
</tr>
<tr>
<td>Physical Form</td>
<td>Granular Particles</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.08</td>
</tr>
<tr>
<td>Shelf Life</td>
<td>6 months at 21°C</td>
</tr>
<tr>
<td>Color</td>
<td>Off White</td>
</tr>
<tr>
<td>Solid Content</td>
<td>100</td>
</tr>
</tbody>
</table>

Dry mixing as well as wet mixing can be used to dissolve the SR355 resin into the solvent solution, making the suspension, which can be used for different purposes including filling and coatings. In the process of wet mixing the resin is being added into the solvent like toluene or methyl-ethyl-ketone and then filler, in our case nano particles are added, in order to give even spreading of coating on the substrate surface. In order to make mould using the filler, the solvent is evaporated by putting the solution into the pan or by spray drying. Room temperature and high velocity air can be used for this purpose. After the solvent is evaporated, granulation might be required for making the sample shape into the form suitable for moulding. The temperature should be kept low during the granulation operations. In case of coatings the SR355 resin is added into the solvent, can be mixture of two different solvents, in order to dissolve the granular resin. If nano-structured coating is required then nano particle are added into the solution which is then thoroughly mixed in order to get the colloidal suspension. Dry mixing requires the grinding of the resin particles into smaller size like (325 mesh) in order to assure the uniform mixing. Sometimes lead carbonate is used as a catalyst in the range of 0.5 to 1% depending on the resin content mixed. The experiment that I followed in my research was taken from [90] and some of the modifications were made in it to get desired results. The experimental procedure is described below:

**Material and Substrate:**

Silica glass purchased from (Dow Corning) was used as the substrate that was being shaped into square with area of 2.5 x 2.5 cm². The silane modified super hydrophobic silica particles of size 60 nm were
used. The methylphenyl silicone resin was obtained from the Momentive Performance Material as a sample for the research. The Tetrahydrofuran (THF) and Isopropylpropane (IPA) were being used as a solvent for the colloidal suspension.

**Functionalization of nano-particles:**
Although, the particles we got were already silanized but still they were functionalized with fluoro silane to renew or confirm the hydrophobicity of the particles. With the passage of time, the coated silane surfaces get absorb some of moisture from the environment due to which the fluoride bonds transfer into the hydroxyl bonds. So the surface structure gets alter with the passage of time. So silanization of 60 nm particles was carried out by mixing the particles with toluene and then fluoro silane was added in the solution and then it was vortex mixed and sonicated. After three hours particles were filtered from the solution and then they were dried by the help of oven.

**Preparation of colloidal solution:**
The 60 nm particles were dispersed inside the 40% / 60% THF / IPA (by volume) solution respectively. The amount THF and IPA added into the solution is very important. If high amount of THF is added into the solution then the final solution will lose its transparency and the final coated surface will be off white. THF rapidly dissolves glass substrate that results in the loss of transparency. The amount of THF should not be increased from 50% by volume in order to keep the surface transparency. The IPA alone suspension would also not be suitable as the pure IPA coated surface would not be easily evaporated and homogeneity will also not be uniform along the surface. The optimal concentration of the silicone particles inside the solution is 30mg/mL of the solution. The increase in the particle concentration resulted in decrease in the transparency and decrease in particle concentration resulted in the loss of the super hydropobicity. However, we were only concerned with the super hydrophobicity of the surface not with the transparency that is why high ratio of the particle to solution were also used.

Initially 30 mL of the solution of THF/IPA was made with ratio of 40/60 percent by volume respectively. Using the 30 mg/mL solution, 300 mg of the 60 nm particles were weighed and then added into the beaker in which 30mL solution of THF/IPA was present. The solution was mixed properly and then it was sonicated in the sonicator for 4 mins. After which 150 mg of the methylphenyl silicone resin was added into the solution in order to maintain the silicone nano particles ratio to methylphenyl silicone resin as 2:1 respectively. In case if concentration of methyl resin is decreased it would result in poor adherence of the coated surface to glass substrate and if concentration is increased then it would result in loss of super hydropobicity. The reason for the loss of hydrophobicity would be engulfing of silica particles inside the coated surface which would results in the loss of the roughness that is provided by silica particles. In this way it would not be possible to achieve the Cassie-Baxter or Wenzel State for the coated surface. So the ratio has to be maintained to the desired but we can play with decreasing the concentration of methylphenyl silicone resin to compromise for surface adherence while at the same time will get increment in the contact angle. Initially the ratio was maintained to be 2:1 particle to resin respectively. After the addition of resin in particle and THF/IPA solution, again the whole solution is properly mixed and it is sonicated for 4 mins. After the sonication, nearly 10 mL of THF/IPA solution with 40:60 ratio respectively was added into the solution in order to compensate for the loss of solvent.
Coating of suspension over the substrate:
The glass substrate was properly cleaned using the Piranha solution (3H₂SO₄ + 1H₂O₂) and then it was dried using the inert nitrogen purge. After complete drying the glass substrate was plasma cleaned to oxide the surface. In this experimentation, Dip coater was used for providing the coating facilities. The Dip coater was set to the speed of 84 mm/min. The glass substrate was fixed inside the dippers and it was dipped inside the colloidal suspension using the speed of 84mm/min for one time. The substrate was dipped in the suspension in the way that substrate went into the suspension and when it got completely submerged inside the suspension it was brought out with no residence time. The coated sample was kept in the oven for 10 mins at 40°C. When the coated sample was observed then colloidal suspension was not completely covered on its surface therefore another round of dip coating was performed over the sample and again it was kept inside the oven for 10 mins at 40°C. The second sample visually seemed to be very good and surface adherence was also reasonable.

Results and conclusion:
The sample obtained using the above mentioned technique was resistive and the mean of the contact angles measured at different spots on the substrate surface, using the pendent drop experimental apparatus, came out to be 154°. However the surface the adherence was not as much good as desired but it was quite better that the surfaces that were obtained using the PDMS and SU8 polymer. In order to make surface adherence and contact angle more optimum the 300:100 mg by weight of silica:resin ratio was used using the whole above mentioned procedure. The contact angle for these surfaces were nearly 157° but the surface adherence was really poor i.e even finger touch was removing the particles from the surface. Similar results were seen with150:150 mg by weight of silica:resin ratio. However, in this case surface adherence was good but contact angle came down to 142°. So we proceeded with the optimum ratio 300:150 by weight of silica to resin.

Spin coating technique was also used using the methylphenyl silicone resin and 60 nm silica particle suspension. The recipe used for the spin coating was 100 rpm for 30 sec, 300 rpm for 30 sec and 1 min for 2000 rpm. The sample obtained was kept in the oven for 10 mins at 40°C. The contact angle of this coated surface was coming around 145° which was not less than desired.

The optimum results came when the 300:150 ratio was used and dip coating was done thrice on the glass substrate sample with the same speed of 84 mm/min. The dip coated sample was putted inside the oven after every coating cycle. The final coated sample was moderately transparent and the contact angle and contact angle hysteresis coming for this sample were 154° and 4° respectively. The surface adherence was also pretty good infact the surface was really resistive to the water flow and finger touch. The contact angle and contact angle hysteresis for this sample is being shown in the figure 13.
Fig. 13 (a) Water contact angle in air over the coated glass substrate
Fig. 13 (b) Hexadecane contact angle in air over the coated glass substrate
Fig. 13 (c) Water contact angle in oil (hexadecane) over the coated glass substrate
Fig. 13 (d) Advancing water contact angle in oil (hexadecane) over the coated glass substrate
Fig. 13 (e) Receding water contact angle in oil (hexadecane) over the coated glass substrate
The surface I developed in the study is fairly strong, particles remain in position when hydraulic water drop pressure is applied in the form of drop flow, and strongly super hydrophobic which was my main research objective. In future, I plan to enhance the surface adhesivity of the particles using hierarchical structural technique and structural modification of the binder.
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