

**“DYNAMIC BEHAVIOUR OF WATER DROPLET SMASHING
HYDROPHOBIC PLANT LEAVES.”**

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Dedicated to

My Beloved Family

*Without their love, support and constant
encouragement,
this would not have been possible*

DECLARATION

We undersigned, hereby declare that the work assimilated in the dissertation thesis entitled **“Dyanamic behaviour of water droplet smashing hydrophobic plant leaves”** has been carried out by us at Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India, under the supervision and Guidance of **Mr. Anand V. Khistariya, Assistant Professor** and **Dr. Mehulkumar L. Savaliya, Assistant Professor, Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India.**

To the best of our knowledge and belief, the work included in this thesis is quite original and has not submitted to any other Institution or University for the award of any degree either in this or any other form.

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1.0 ABSTRACT

We synthesize and deposit unsaturated carbon through wax and camphor flame synthesis on zinc plate, non-premixed flame locations to produce hydrophobic surfaces. The hydrophobicity is characterized through the contact angle for water droplets placed on the surface. The surface morphology of the nanoparticles is obtained from high-resolution HEIC images. The morphology and hydrophobicity of the unsaturated carbon surfaces depends upon the deposition, which differs at different flame locations. We determine the optimum flame location for the synthesis and deposition of surface unsaturated carbon that lead to maximum hydrophobicity. And we carried out Silica (SiO₂) powder and physical deposition technique were performed to fabricate superhydrophobic silicone rubber (SR) surfaces, in order to further demonstrate the superhydrophobic property of the surface of the sample, the horizontal bouncing test at room temperature (25 °C) and the tilted bouncing test at an angle of 40° with the horizontal plane were carried out. [1]

Keywords: Carbon nanostructures; Flame synthesis; Hydrophobicity; Surface roughness, silicone rubber (SR), Silica (SiO₂).

2.0 GRAPHICAL ABSTRACT:

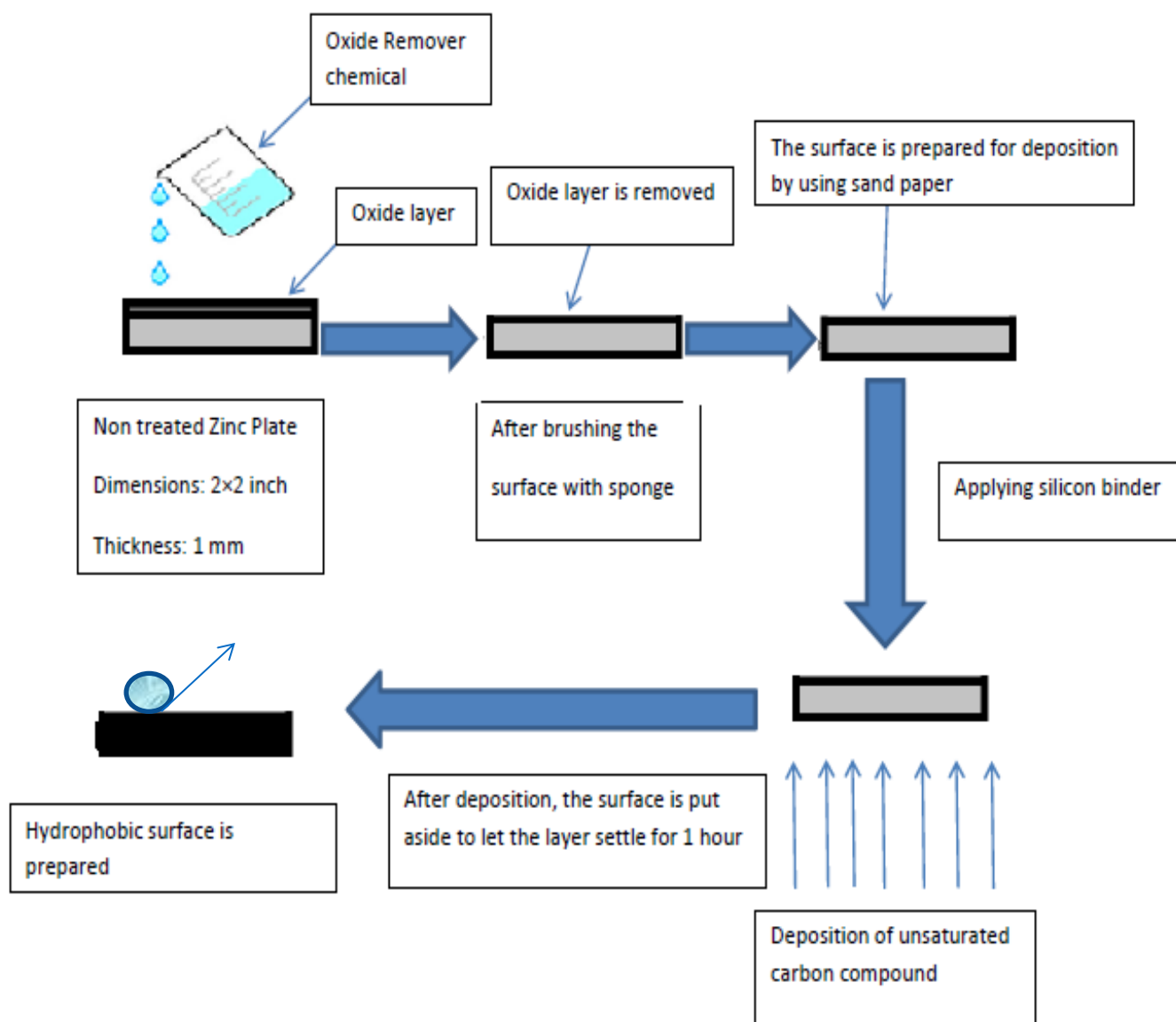


Figure 1. preparation of superhydrophobic surface with deposition of unsaturated carbon compounds. [2]

3.0 EXPLOITATION AND REVIEW OF LITERATURE:

3.1 SUPERHYDROPHOBIC SURFACES IN NATURE:

Superhydrophobic surfaces are often found in nature, such as on plant leaves, insect legs and wings. Water on these surfaces forms small beads with a high contact angle in excess of 150° and drips off rapidly when the surfaces are slightly inclined, while taking away powder-like contaminant. This interesting phenomenon has stimulated extensive research to make artificial superhydrophobic surfaces and to use them for a variety of applications. [3]



Figure 2. A Water droplet beads up on a lotus leaf due to the hydrophobic nanostructures



Figure 3. Effect of sacred lotus



Figure 4. Optical effect on lotus



Figure 5. Water's polarity on living things

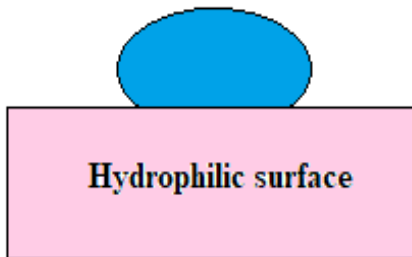
A “pond skater” replica (much heavier than a real one) can rest on the surface of water thanks to its superhydrophobic feet and the surface tension of water. Real-life pond skaters possess similar Nano-rough feet which are also hydrophobic.



Figure 6. Skatering effect on water layer

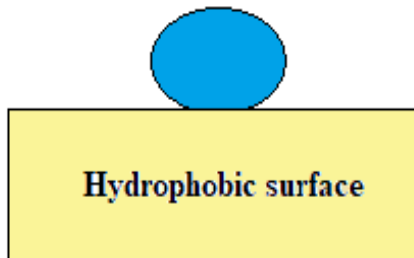
A live “pond skater” utilizing its superhydrophobic feet to rest on the surface of water. [3]

3.1.1 HYDROPHOBIC / SUPERHYDROPHOBIC HYDROPHILIC /



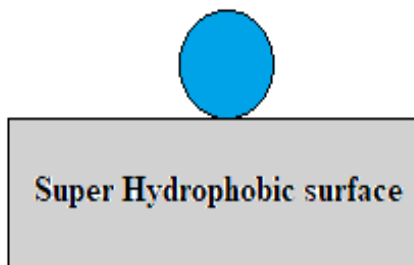
Hydrophilic surface:

- Surfaces with a contact angle $\theta_c < 90^\circ$
- Water spreads out on surface



Hydrophobic surface:

- Surfaces with a contact angle $\theta_c > 90^\circ$
- Water beads-up on the surface



Superhydrophobic surfaces:

- Surfaces with a contact angle $\theta_c > 150^\circ$
- Water is highly beaded (repelled)

Figure 7. (1) Hydrophilic Surface (2) Hydrophobic Surface (3) Superhydrophobic Surface

3.1.2 MAKING SUPERHYDROPHOBIC SURFACES

Nano-roughness creates superhydrophobic surfaces

- Lower water-solid contact area
- Water perched on hydrophobic posts containing trapped air
- Result: high contact angle



Figure 8. Nano roughened surface and water contact angle

Although it is a relatively simple and one-step process to make superhydrophobic surfaces by using intrinsically hydrophobic materials, unfortunately, many materials do not possess a low enough surface free energy to be intrinsically hydrophobic.[4] In order to make superhydrophobic surfaces on these intrinsically hydrophilic materials, a two-step process is usually required, *i.e.*, making a rough surface first and then modifying it with chemicals, such as alkanethiols, organic silanes, and fatty acids, which can offer a low surface free energy after linked to the surface.

Metal surfaces can be made superhydrophobic by first etching the surfaces to obtain roughness in both micrometre and nanometre scales and then modifying the roughened surfaces with a hydrophobic coating. Qian *et al.* have made superhydrophobic surfaces on aluminium, copper, and zinc polycrystalline substrates by first using chemical etching methods and then coating the substrates with a fluoroalkylamine. The key to the etching technique is the use of a dislocation etchant that preferentially dissolves the dislocation sites in the grains. [3] The etched metallic surfaces, after modified with the fluoroalkyl silane, exhibited superhydrophobic properties with water contact angles of larger than 150° , as well as sliding angles of less than 10° .

THE LOTUS EFFECT: Water droplets can interact with a surface in a variety of ways. The nature of the interaction is related to how well water bonds to the surface compared with how well it bonds to itself. It ranges from super-hydrophilic, in which the water can fully and effectively wet a surface to form a flat puddle due to a strong water–surface interaction, through to super-hydrophobic, in which water is effectively repelled from the surface to form a near-spherical droplet and in which there is a weak water–surface interaction. [4]

Super-hydrophobic surfaces are observed in nature, for example, in the lotus effect (named after the lotus plant, *Nelumbo nucifera*), which describes the self-cleaning action of some leaf surfaces. If the leaf shows high enough hydrophobicity, water will form near-spherical droplets that roll across the surface instead of sliding.

action increases the amount of foreign bodies picked up. Rougher surfaces tend to have the greatest self-cleaning action. The lotus leaf surface adopts this self-cleaning mechanism and facilitates the rolling of water droplets that collect

dirt particles as they move. The leaves themselves have a waxy surface coating that acts to repel water and also have protrusions that make the waxy surface highly rough. Both of these surface features combine to allow water droplets to roll and not slide. The rough, nanoscale, hair-like structures can also act to trap air underneath the water droplets, facilitating the rolling motion. Leaves that are waxy but do not have the rough microstructure observed in the lotus plant are less efficient at self-cleaning. Plants that possess both a waxy and highly rough surface has far superior self-cleaning properties than those with comparable smooth waxy surfaces.

Other examples of extreme hydrophobicity in nature include water strider legs, which have a highly defined microstructure that is coated by a layer of secreted wax. The wings of some insects also show hydrophobic properties brought about by surface microstructure and composition. Butterfly wings demonstrate super-hydrophobic properties, employing a directional rolling of water away from the body of the butterfly that is brought about by a network of microstructure scales on the wings surface. It is these surface characteristics that have proven inspirational in the design of artificial hydrophobic surface.

One nature-inspired method is to use a natural leaf surface for the imprint of polymer surfaces to render them hydrophobic. The lotus leaf and other surfaces that exhibit the lotus effect demonstrate a hierarchical micro- and nanoscale roughness. [5]



Figure 9. The water contact angle (θ) shown as the angle between the plane of a surface and the tangent at which the liquid droplet makes contact with the surface.

Surface roughness: The roughness of a surface can be defined by looking at the difference between the actual surface area, including peaks and valleys of surface morphology, and the planar or geometric area. The latter is the area of contact the water droplet makes with the surface assuming a totally smooth surface, whereas the actual surface area takes into account the protrusions. Both of these surfaces are used to calculate the roughness factor:

$$r = \text{roughness factor} = \text{actual surface area} / \text{planar area}.$$

Whereas the Cassie–Baxter model uses a comparable measurement (see below). The two models can be compared because they have many similar features and they deal with the same type of interactions; however, there are some fundamental differences. [5]

The Cassie–Baxter model uses both advancing and receding contact angles. They can be measured in experiments that use tilted surfaces (Figure 5a). The receding contact angle can also be measured by dropping a water droplet onto a horizontal surface, then removing some of the water from the droplet and noting the contact angle when the area of contact begins to decrease (Figure 5b). Advancing contact angles can also be measured by adding volume to the water droplet and noting when the area of contact starts to increase (Figure 5c).

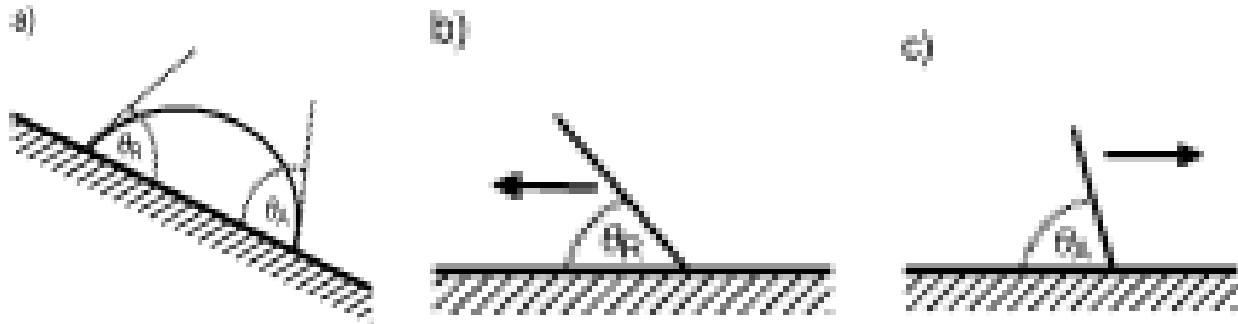


Figure 10. a) Determination of contact angles by tilting the surface until there is no further change in angle without movement of the droplet. b) Receding contact angle. c) Advancing contact angle [6].

The contact angle of the superhydrophobic surface with water is greater than 150° and the rolling angle is less than 10° . There are two main methods for preparing superhydrophobic surfaces: one is to construct micro-nano rough structures on the surface of low surface energy materials, and the other is to modify low surface energy materials on the rough structure surface. The current methods for preparing superhydrophobic materials mainly include template method, layer-by-layer self-assembly method, electrospinning method, phase separation method, chemical etching method, sol-gel method, deposition method, spray method, etc. Super hydrophobicity has been widely used in people's production and daily life. One of the important applications is self-cleaning. Superhydrophobic materials are applied to the surface of glass and wood. Rainwater or manual spraying can be used to achieve self-cleaning effect and decontamination. In addition, anti-freezing is another important application of superhydrophobic surface. Superhydrophobic materials can also be applied to solid surface anti-corrosion, oil-water separation, sewage treatment, and pipeline anti-fouling, anti-skid, drag reduction and other fields. Therefore, the preparation of superhydrophobic surfaces with excellent properties is of great significance.

Because of its excellent weather resistance, low toxicity, superb transparency and hydrophobicity, SR is very popular in the fields of electrical insulators, antifouling coatings, sealants, electronics, aerospace, biomedicine, machinery, food processing, etc. Due to its excellent hydrophobicity and low surface energy, SR has received extensive attention from scholars in the field of superhydrophobic surface preparation. Huang et al. reported a method for preparing superhydrophobic coatings of SR. Superhydrophobic zinc oxide film was obtained by adding Nano-zinc oxide to stearate alcohol solution, isopropanol and butanol. Yang et al. prepared a dodecane thiol modified ZnO/PDMS composite by a simple grinding method, and obtained a freezing-resistant superhydrophobic surface. Wang et al. used a template method to make a superhydrophobic surface with high temperature vulcanized (HTV) SR as a matrix material with a regular micron-level rough structure. They found that the as prepared superhydrophobic surface has extraordinary self-cleaning, anti-corrosion, droplet bouncing properties and mechanical stability. The method is simple with low cost, and is suitable for application in the field of outdoor insulating. Zhou et al. dispersed a layer of four-needle ZnO powder on the surface of room temperature vulcanized (RTV) SR and successfully prepared a superhydrophobic surface with excellent self-cleaning property and low water droplet adhesion property. RTV SR is an important series of SR products. It has the properties of electrical insulation, ultraviolet (UV) resistance, high and low temperature resistance, weather resistance, hydrophobicity and hydrophobic migration. It is widely used in electronics, aerospace, biomedicine, machinery, food processing and other fields. RTV SR can also be used for the preparation of superhydrophobic surfaces. The following research has been done related to the preparation of RTV SR on superhydrophobic surfaces. Tian et al. sprayed silicone sealant on the substrate and then covered the RTV SR, on which the particles generated by heating was deposited. The surface of the vulcanized SR formed a micro-rough structure with low surface energy, thereby forming a superhydrophobic surface. [7] Wang et al. used RTV SR to rub the papillary structure on the surface of the lotus

leaf, and generated Nano zinc oxide pillars on the surface, which was then modified with Fluor silane to prepare a superhydrophobic surface. Seyedmehdi et al. doped RTV SR with hydrophobic nanoparticles and aluminum hydroxide to obtain a surface close to super hydrophobicity, which has antifouling and UV resistance properties and could be used for high-voltage insulators. [6]

An et al. prepared a polyvinylidene fluoride (PVDF)/SR superhydrophobic film using electrospinning technique. In recent years, many kinds of materials have been applied to the preparation of superhydrophobic surfaces, such as SiO₂, TiO₂, ZnO, K₂TiO₃ and TEOS. In the process of preparing superhydrophobic surfaces, issues such as high cost and complicated preparation process are often occurring. For example, the sol-gel method has disadvantages such as complicated preparation process, poor controllability of the obtained surface structure, and solvent contamination. [7] The etching method has the disadvantages of higher cost and being not suitable for large area preparation. In this study, the superhydrophobic surface of SiO₂/SR has been obtained by physical deposition technique, which is simple in operation, low-cost, green and pollution-free, and no modification of low surface energy materials is required. In addition, the prepared SiO₂/SR superhydrophobic surface not only has excellent superhydrophobic and self-cleaning properties, but also has remarkable droplet bouncing performance. A high-speed camera is performed to study the droplet bouncing behavior on horizontal and tilted SiO₂/SR superhydrophobic surfaces.

4.0 LITERATURE REVIEW

4.1 METHODS USED FOR THE PREPARATION OF SUPERHYDROPHOBIC SURFACES: -

Both Wenzel and Cassie–Baxter theories have pointed out that a rough surface is essential for enhancing hydrophobicity and hydrophilicity. In practice, the approaches for superhydrophobic surface preparation can be basically categorized into two directions: top-down and bottom-up approaches. Top- down approaches encompass lithographic and template-based techniques, and plasma treatment of the surfaces. Bottom-up approaches involve mostly self-assembly and self-organization. Examples of bottom-up approaches include chemical deposition, layer-by-layer (LBL) deposition, hydrogen bonding, and colloidal assemblies. There are also methods based on the combination of both bottom-up and top-down approaches, for example, casting of polymer solution and phase separation, and electrospinning. In the following section, different approaches are addressed in detail. [8]

4.1.1 TOP-DOWN APPROACHES: -

Top-down approach is a general term in microelectronics referring to the fabrication of materials and devices by carving, moulding, or machining bulk materials with tools and lasers. For the generation of superhydrophobic surfaces, template and lithographic approaches, micromachining, and plasma treatments have been used. Temptation often involves moulding and replication steps. Thereafter, the template can be removed by lifting off or dissolution or even sublimation. In the lithographic approaches, light is irradiated through a mask with desired features onto the substrates (often silicon) with a photoresist. Subsequent etching steps yield the desired patterned surfaces. These surfaces are made hydro- phobic by salinization. In micromachining, surfaces are diced into the desired texture. In the plasma treatments, surfaces are etched anisotropic ally thus generating rough surfaces. Examples includes plasma treatment of poly (ethylene terephthalate) (PET), poly(tetrafluoroethylene) (PTFE), and polyethylene (PE). Pulse- laser treatments of poly- (dimethyl siloxane) (PDMS) for the generation of superhydrophobic surfaces have also been shown. [9]

4.1.2 TEMPLATION: -

Templation involves the use of a master with the desired features, replication of the features by molding and subsequent lifting off the replica or dissolution of the templates. Templation is used for the preparation of polymeric superhydrophobic coatings. Many materials can be used as a template ranging from natural lotus leaves, master prepared by lithographic processes, to commercial inorganic membranes.[10]

Sun *et al.* have used a lotus leaf as the template, where the replication process was denoted Nano casting. After casting and lifting off PDMS, a negative replication of the lotus leaf structure was obtained. This negative template was used further as a master for preparation of a positive replica of the lotus leaf. The positive replica has almost the same surface morphology on both the micro- and nanoscale as the natural lotus leaf. The SEM images of the positive replica showed small papillae hills with an average distance of 6 microns. Even the intricate Nano textures between the hills and in the valleys were clearly replicated. The positive replica exhibits the same superhydrophobic property as the natural lotus leaf with an advancing contact angle of 160°. On the other hand, the negative replica of the lotus leaf has a contact angle of 110°.

In a similar replication process, He *et al.* have fabricated PDMS structures with ~~its~~ of relatively big size (squared posts of 25 microns in width, 30 microns in depth, at varied distances from 8 to 80 microns). The replication process was based on a master prepared by micromachining. A water drop can both be suspended on top of the posts and wet the posts depending on how the water drop is deposited. In case of gentle deposition, a composite form is formed, and the observed contact angles are close to the CB theory prediction. When the water is dropped from some height, the gaps between the posts were wetted and the measured apparent contact angle follows the Wenzel Theory. [11]

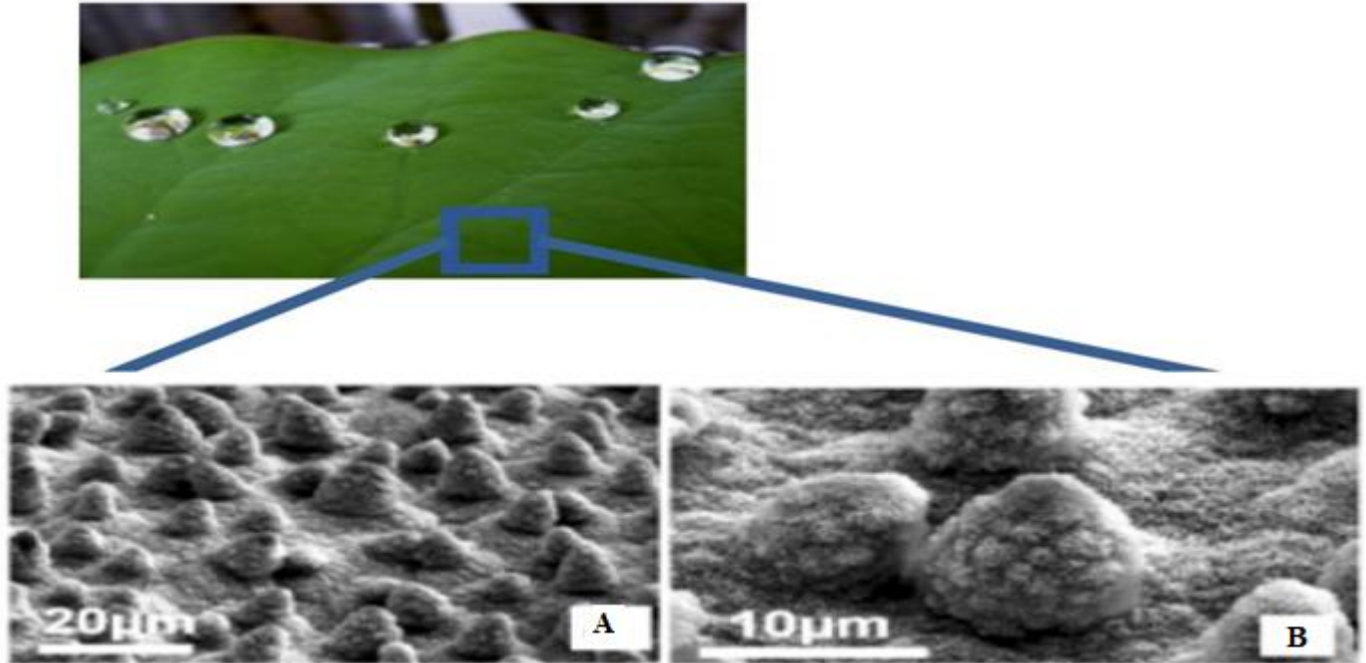


Figure. 11: Schematic illustration of Nano casting and SEM images of (a) a natural lotus leaf and (b) its positive PDMS replica.

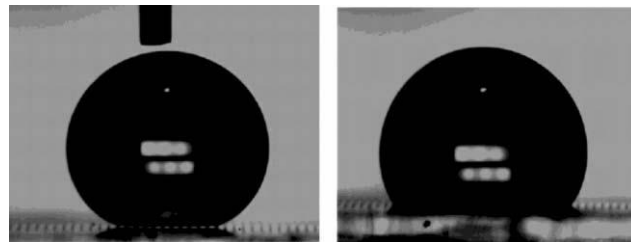


Figure. 12: Direct observation of a composite drop and a wetted situation on the surface depending on how the drop is deposited on the surface. Left, gentle deposition (suspension); right, water drop deposited from distance (collapsed). [12]

4.2 BOTTOM-UP APPROACHES: -

Contrary to the top-down approach, bottom-up methods involve the building (or designing) larger, more complex objects by integration of smaller building blocks or components. The bottom-up approach in nanofabrication involves often self-assembly and self-organization. Self-assembly is an integration method where components potentially assemble in solution or the gas phase until an unstable structure of minimum energy is reached. Bottom-up approaches that have been applied for the preparation of superhydrophobic surfaces include chemical deposition methods such as chemical bath deposition (CBD), chemical vapor deposition (CVD), and electrochemical deposition, layer-by-layer (LBL) deposition via electrostatic assembly, colloidal assembly, sol-gel methods, hydrogen bonding, and chemical synthesis. In the following paragraphs, some important examples will be given and discussed in detail [13].

4.2.1 CHEMICAL DEPOSITION: -

Chemical deposition takes place in a chemical reaction, where the product self-assembles and deposits on a suitable substrate. Chemical deposition is commonly used for generating thin films of crystalline inorganic materials, such as ZnS, CuSe, InS, CdSe, etc. Depending on the deposition conditions, several terms have been used such as chemical bath deposition (CBD), chemical vapor deposition (CVD), and electrochemical deposition. Depending on the material and the deposition conditions, different surface morphologies have been obtained from Nano pins, nanotubes to nanorods.

Hessoni *et al.* have used CBD for the creation of a Nano fin film from a solution of CoCl_2 and NH_2CO in water. The film was deposited on commercial borosilicate glass slides in an autoclave. Because each metal complex in the solution is singly deposited on the surface based on the hydrodynamic equilibrium conditions, single crystalline-like structures are formed. After deposition, the nano fin was modified with lauric acid (with $h = 75.1$). A picture of the Nano fin is shown in. The top of the

needle is very sharp with a diameter of 6.5 nm. The water CA of the resulted film is 178u, which is the highest contact angle that has been reported so far.[14]

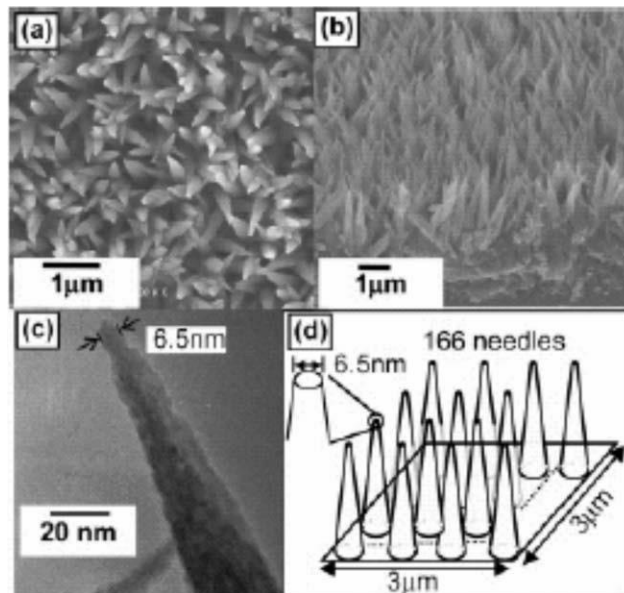


Figure. 13 (a, b) Field emission SEM images of the cobalt hydroxide films observed from the top and side, respectively. (c) TEM images of the cobalt hydroxide films. (d) A simple model of the film with the fractal structure.

4.2.2 LAYER-BY-LAYER DEPOSITION: -

Layer-by-layer (LBL) deposition takes advantages of the electrostatic charge interactions between the different layers such as polyanion and polycation. The LBL technique is easy to perform and allows controlling the thickness of the resulting layer with molecular precision. Polyelectrolytes are hydrophilic, therefore, a hydrophilization is always necessary. Nanoparticles are often incorporated into the multilayer system in order to enhance the roughness effects. However, the multilayer films can also be roughened by some additional treatment. Zhai *et al.* have prepared superhydrophobic silicon surfaces using polyallylamine hydrochloride (PAH)/poly (acrylic acid) (PAA) multilayers *via* LBL deposition. By using an appropriate combination of acidic treatments, pores on the order of 10 microns and a honeycomb-like structure were formed on the PAH/PAA films (Fig. 12(A) and (B)). The honeycomb-like polyelectrolyte multilayer surface was further coated with silica nanoparticles (Fig. 12(C)). Super hydrophobicity was achieved by coating this highly textured multilayer surface with semi fluorinated silane. The stability of the surface was tested by extended immersion in water. It was found that both the microstructure created by the combined acid treatments and the nanostructure induced by the deposition of silica nanoparticles are necessary to create stable superhydrophobic surfaces.[15]

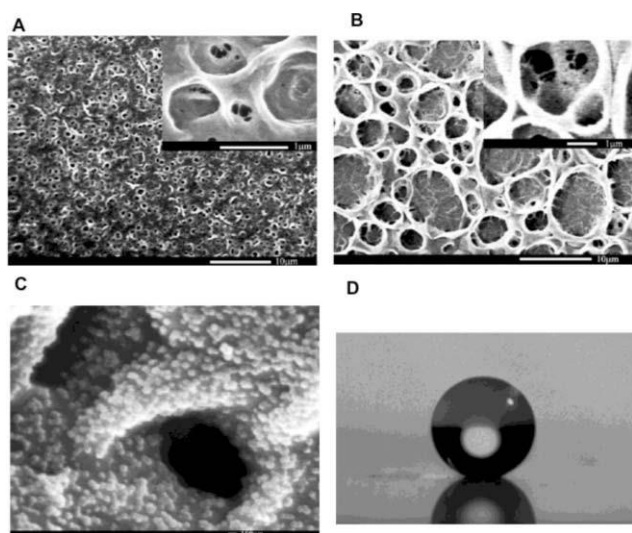


Figure 14.

SEM images of (PAH/PAA)_{100.5} films after a single acid treatment (A) and after a combined acid treatment (B). (C) SEM image of the fully treated structure (B) with silica nanoparticles. (D) Water droplet on this superhydrophobic surface. [16]

4.2.3 SOL–GEL METHODS:-

A sol is usually prepared by hydrolysis of the corresponding oxide in the presence of solvent. During the network formation process, a large number of solvents are also impregnated in the network and thus a gel is formed. Silica sols are normally prepared by hydrolysis and condensation of orthosilicate. The sol can be applied either directly or combined with fillers such as silica nanoparticles. The resulting surface property depends on how the sol was prepared and surface functional groups of the resulted gel.

Hikita *et al.* have used the sol–gel method for the preparation of super liquid repellent surfaces. Both surface energy and roughness were controlled using colloidal silica particles and fluoroalkyl silane. For films with optimal ratio between colloidal silica and fluoroalkyl silane, the surfaces exhibited repellency to both water and oil. This method provides a simple one-pot coating for a large area.

The advantages of the bottom-up approach are the molecular control of the chemistry, composition, even the thickness of the products. Nevertheless, it is difficult to predict the hydrophobic properties until the last step.[17]

4.3 COMBINATION OF BOTTOM-UP AND TOP-DOWN APPROACHES: -

The combination of bottom-up and top-down approaches might have the apparent advantages of both techniques. It is especially useful for the creation of architectures with a two-scale roughness, resembling the structure of the lotus leaf. The combination methods often consist of two stages. Typically, the first step is the top-down approach for the creation of a rough surface and the second step is bottom-up process for the creation of the fine roughness. However, some combination methods do not necessarily show a distinct two-stage process. For example, phase separation involves casting of thin film and subsequent phase separation by controlling the environmental conditions.[18]

5.0 MATERIALS AND METHODS:

5.1 MATERIALS:

The flame deposition of unsaturated carbon using the compounds that give flame of unsaturated compound on zinc plate of dimension (2×2) inch and 1mm thickness. Thereafter, special fullerene structures and nanotubes were discovered mixed within the soot agglomerates from low pressure premixed flames. The wax and camphor were used to generate the superhydrophobic layer on the surface. Carbon nanotubes and nanofibers were synthesized using metal catalysts in non-premixed and premixed flames. Detailed continuum and molecular models for metal-catalyzed graphitic carbon nanostructure flame synthesis are able to describe the inception and growth of these structures. The reader is directed to a comprehensive review for additional details. Unsaturated carbon deposition from flames can be used to modify hydrophilic surfaces so that they become superhydrophobic. [19] When unsaturated carbon is deposited upon a surface, they create a superhydrophobic topology that facilitates a water droplet to sit on the asperities of the roughness while air is entrapped in the structure below. In this Cassie equilibrium state, water droplets form very large contact angles (>150°) on the rough surfaces and also easily roll off them. This surface wettability, which is a function of roughness, can be exploited, for instance, for the self-cleaning of surfaces, manipulating hydrophobic interactions for protein adsorption and decreasing fluid resistance in microfluidic devices.

We employ flame synthesis to deposit carbon nanostructures on catalytic and inert substrates at various flame locations. Thereafter, we investigate the resulting variation in hydrophobicity and surface topology to determine an optimum synthesis location that produces maximum surface hydrophobicity.

5.2 METHOD:

5.2.1 SURFACE MORPHOLOGY AND MICROSTRUCTURE OF CVD MATERIALS

Surface morphology and microstructure of CVD materials are controlled by many factors that are often interrelated, such as substrate, temperature, supersaturation, deposition rate, impurities, temperature gradients, and gas flows. In this section a number of theories and classifications of CVD morphologies and microstructures are introduced. Van den Brekel and Jansen developed and applied a stability theory for single-phase vapor growth. If an arbitrary perturbation at the vapor/solid interface decreases with increased time, the interface is considered stable. However, the interface during CVD in an isothermal condition is unstable. On the other hand, because of the fact that relaxation times in films are much longer than deposition times (a few minutes) smooth layers can be grown even in unstable processes. The instability of the interface in a vapor growth process can also be described in the same terms as those used to explain dendritic growth from a melt in a negative temperature gradient. Random surface irregularities are frequently formed in growth processes. [20] Surface irregularities have a higher rate of growth if they extend into regions of higher supersaturation. In a CVD process, surface irregularities have better access to fresh reaction gas, which results in a higher supersaturation and hence a higher deposition rate. Also, a negative temperature gradient, as in the cold wall reactor, may result in a higher supersaturation for outgrowths. Blocher related the various microstructures formed in CVD to temperature and supersaturation process conditions. Epitaxial growth occurs at high temperature/low supersaturation. Decreasing temperature/increasing the supersaturation results in the formation of platelets, whiskers, etc. At high supersaturation, a powder resulting from the homogeneous nucleation in the vapor is obtained. Only comments on the growth of selected microstructures are given below. Epitaxial growth, which is frequently used in the microelectronics industry, occurs at relatively low growth rates. It is affected by the deposit–substrate crystallographic misfit, substrate surface quality, thermal stresses over the substrate, and polycrystalline regions in the substrate. High surface mobility of adsorbed species is required for epitaxial growth, i.e. usually enhanced by a high temperature. [21]

Columnar grains are common in CVD films, which can exhibit a high degree of texture. During initial nucleation, nuclei of different crystallographic orientations are formed. Depending on the anisotropy in the growth rate of various crystal surfaces, nuclei will grow at different rates. This preferential growth results in a characteristic columnar growth. Numerous examples of columnar growth in CVD can be found in Proceedings of the International CVD Conference series published by the Electrochemical Society. Surfaces grow by incorporating surface-diffusing adatoms into surface steps.

However, preferential adsorption of molecules at surface steps prevents surface-diffusing adatoms from being captured. Thus, a new growth mechanism is required. Throughout the years, the structure of CVD materials has been modified by adding small amounts of foreign substances (growth modifiers) to the reaction gas mixture. [22]

5.2.2 SELECTIVE DEPOSITION:

CVD can readily be scaled up to a large-area deposition technique. However, CVD is also well adapted for local deposition or *selective deposition*, where deposition occurs only on specific regions of the substrate surface. Selectivity is achieved by using various focused beams (photons, electrons, or ions). Energetic beams induce local CVD reactions on those areas which are incident. It is also possible to irradiate the substrate surface through a mask with, for example, a laser. Openings in the mask define the substrate areas where the deposition takes place. Selective CVD can also be achieved on patterned substrates. Selectivity in this case is based on differences in the initial interfacial reactions between the different substrate materials and vapor. Interfacial reactions on one substrate material should be inhibited completely to avoid nucleation, while deposition reactions should be stimulated on those substrate areas where deposition is required. [23]

Several major categories of selective deposition systems exist. In the system described above, deposition takes place on one substrate material while no deposition takes place on the other. However, different phases can also be deposited simultaneously and selectively on different materials, resulting in phase-selective deposition. Analogous to phase-selective deposition, films of different microstructures or different chemical compositions can be deposited on different substrate materials, and hence selectivity in microstructure or chemical composition is attained. Selective deposition is an emerging field and the demand is great for these processes in many application areas. With the continuous miniaturization of integrated circuit feature sizes there is a need for self-aligned processes. Examples are selective tungsten metallization in very large-scale integration (VLSI) and selective gallium arsenide (GaAs) epitaxy for monolithic integration of optoelectronic devices. Other applications include Micronics, heterogeneous catalysis, engineering of film/substrate interfaces, and growth of artificial 2D and 3D materials (e.g. photonic crystals). Since selective deposition on patterned substrates is based on interfacial chemistry, there are practically no restrictions on the dimensions of the deposited material islands. This opens up a fascinating perspective of constructing materials with microstructures without thermodynamic or kinetics limitations. The underlying principles of selective deposition are briefly discussed below. [24]

5.2.3 PROCESS OF CHEMICAL VAPOUR DEPOSITION ON ZINC PLATE:-

The zinc plate was taken with dimension of (2×2) inch and 1 mm thickness. The residue oxides were removed from the surface with the help of oxide remover chemical and polish agent while brushing with the sponge on the surface. Then the zinc plate surface was further polished using sand paper (no.2500). Then the zinc plate was put in acetone for 5 minutes to remove the remaining oxides. The zinc plate was then put in ambience for 2 minutes to let the acetone on the surface evaporate. The silicon binder was applied on the surface of the polished zinc plate and was let in ambience to settle the layer of binder for 5 minutes. The zinc plate-1 was then put above the burning wax to accumulate the layer of unsaturated carbon compounds. And the zinc plate-2 was put above the burning camphor to accumulate the layer of unsaturated compounds in the camphor. [25] After the deposition of the unsaturated carbon compounds on the zinc plates, the zinc plates were put in ambience for 1 hour to let the layer of unsaturated carbon compounds to settle on the surface of zinc plate. The unsaturated carbon compounds create nanostructured surface with the air bound on the surface the surface gives super hydrophobicity due to air bound the nanostructured surface. [26]

The contact angle of the water is (>150).

5.2.4 THE PREPARATION OF SiO₂ LAYER ON FABRIC:

The fabric is dipped in water for better wettability in solvent for 10 minutes. Hexane is used as solvent to dissolve SiO₂ and silicon binder is used for better binding capacity of SiO₂ on fabric. The solution is stirred for 15 minutes in magnetic stirrer to get homogenous solution. The fabric is dipped in solution for 20 minutes to let the layer of SiO₂ settle on the fabric. [27]

The contact angle measured is >130° for water

6.0 RESULT:

One of the limitations in the application of superhydrophobic surface coatings to commercial products is the lack of abrasion resistance. Because of the presence of surface micro- and nanostructures, the roughness can be altered readily due to surface abrasion-induced destruction of small surface structures. In addition, abrasion may also result in removal of the hydrophobic layer on the rough surface. Both of these effects result in a failure of the self-cleaning surface properties. [28]

6.1 THE DISCUSSION AND RESULT OF GLASS SURFACE:

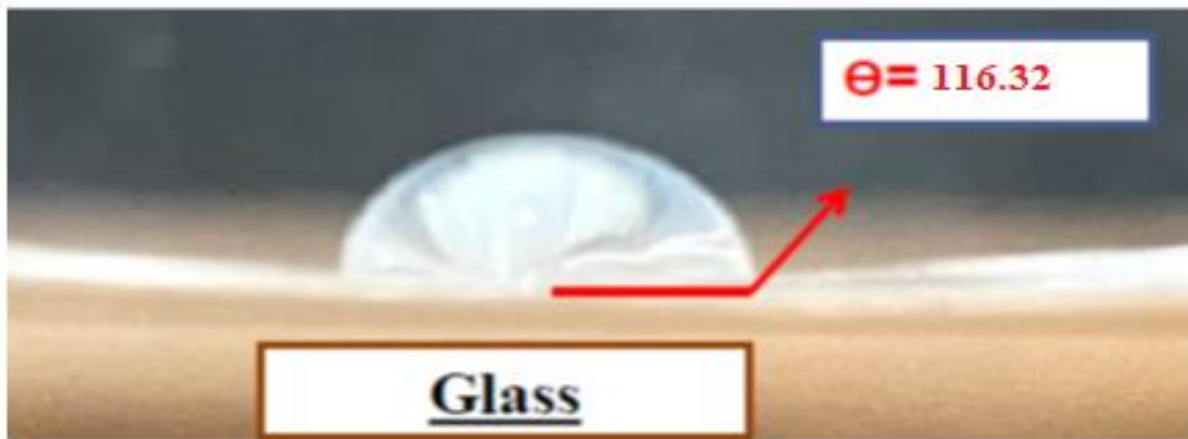


Figure 15.

The glass surface was treated with tetraethyl orthosilicate and acetic acid as curing agents and layer of liquid silicon rubber was prepared on the glass. further layer SiO_2 of 1mm was formed on the surface of silicon rubber layer. The hydrophobicity generated by the glass was not as good as required. [29]

The contact angle generated by glass was $>110.5 \pm 0.06$.

Dibutyltin dilaurate as a curing agent gives better results for hydrophobicity than acetic acid. But the substitute of dibutyltin dilaurate was not good enough to make the surface superhydrophobic. [30]

6.2 THE DISCUSSION AND RESULT OF ZINC PLATE SURFACE:



Treated zinc plate without chemical deposition

Figure 16.

The zinc plate was treated with oxide remover process and sanding process to give better results on the binding capacity and hydrophobicity. [31]

6.2.1 SURFACE PREPARATION FOR ZINC WITH CVD OF CAMPHOR:

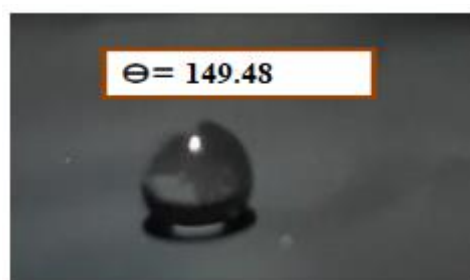


Zinc plate with deposition of camphor unsaturated carbon compounds without binder

Figure 17.

The deposition of camphor on the zinc plate was carried out using chemical vapor deposition technique. The contact angle for the surface was $>150.60 \pm 0.09$. The limitation of this surface was that it was easily removable from zinc plate.

To overcome this limitation, we decided to use binder for better surface adhesiveness of the camphor. [32]



Zinc plate with binder and deposition of camphor unsaturated carbon compounds

Figure 18.

The silicon binder was applied to another treated zinc plate and then the chemical vapour deposition of camphor was carried out. The silicon binder was suitable to zinc plate and increase the hydrophobicity more than just camphor deposition. [33]

The contact angle was $>153.0 \pm 0.3$.

6.2.2 SURFACE PREPARATION FOR ZINC WITH CVD OF WAX:



Zinc plate with deposition of wax unsaturated carbon compounds without binder

Figure 19.

The deposition of wax on the zinc plate was carried out using chemical vapor deposition technique. The contact angle for the surface was $>149.0 \pm 0.3$. The limitation of this surface was that it was easily removable from zinc plate.

To overcome this limitation, we decided to use binder for better surface adhesiveness of the wax. [34]

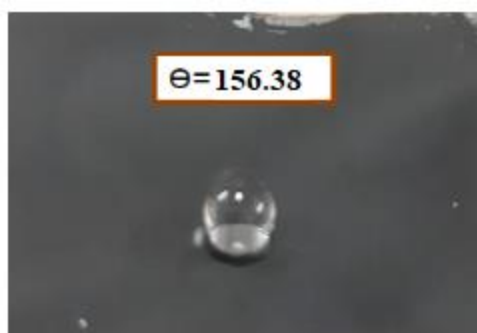


Figure 20.

The silicon binder was applied to another treated zinc plate and then the chemical vapor deposition of wax was carried out. The silicon binder was suitable to zinc plate and increase the hydrophobicity more than just wax deposition.

The contact angle was $>150.0 \pm 0.9$. [35]

6.3 THE DISCUSSION AND RESULT OF FABRIC SURFACE:



Fabric coated with layer of silicon oxide (SiO_2) and silicon binder.

Figure 21.

The fabric surface with the deposition of SiO_2 was prepared by layer by layer technique and give good hydrophobicity to the fabric. [36]

The contact angle was $>134.0 \pm 0.8$.

Table 1: the contact angle of the surfaces in the dissertation and average contact angles:

SURFACES	Contact angle 1	Contact angle 2	Contact angle 3	Average contact angle
3.5 cm	110.56	109.47	110.39	110.14
3.5 cm	112.86	110.23	111.53	111.54
3.5 cm	150.69	149.95	150.32	150.32
7 cm	153.31	153.67	152.98	153.32
7 cm	149.28	148.78	149.27	149.11
7 cm	150.87	150.42	150.65	150.64

7. CONCLUSION:

In this dissertation, we included different techniques for creating superhydrophobic surfaces.

The techniques used in our dissertation is (1) layer by layer method (LBL) (2)chemical vapor deposition. While have discussed about techniques such as (1) sol gel technique (2) Templation technique.

The air pockets generated with the formation of SiO_2 layer on the surface makes the water repel from the surface. And the surface is protected from outer water bodies making the surface usable for anti-fog coating, anti-freeze surfaces, oil and water separation, anti-bacterial surfaces, and medical applications.

The chemical deposition technique drastically increases the contact angle between the water and surface of metal. The increased contact angle generates properties like self-cleaning, stain resistance, rust stain resistance, anti-water absorption, and antibacterial properties. Zinc is used as a coating to protect iron and steel from corrosion (galvanized metal), so super hydrophobicity gives the surface more durability or sustainability.

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