

## **Chapter - 5**

### **Analysis of Newline Nano Engineered Hydrophobic Surfaces**

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## Analysis of Newline Nano Engineered Hydrophobic Surfaces

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### Abstract

Hydrophobicity means the tendency of a substance to repel water and to avoid wetting of surface. A surface is super hydrophobic if it has a water contact angle above  $150^\circ$ . These surfaces are water repellent. These surfaces with low contact angle hysteresis (less than  $10^\circ$ ) also have a self-cleaning effect. Water droplets roll off the surface and take contaminants with them. Due to non-wetting of surfaces, hydrophobic surfaces have attracted much attention of researchers as there being potential applications in microfluidics, lab-on-chip, as functional surfaces and in self-cleaning of glasses and clothes, anti-snow sticking and monument protection are only some of them.

The self-cleaning surfaces are of interest in various applications, e.g., self-cleaning windows, windshields, exterior paints for buildings, navigation-ships and utensils, roof tiles, textiles, solar panels and reduction of drag in fluid flow, e. g. in micro/nano-channels. Also, super hydrophobic surface can be used for energy conservation and energy conversion. When two hydrophilic surfaces come into contact, condensation of water vapour from environment forms meniscus bridges at asperity contacts which lead to an intrinsic attractive force. This may lead to high adhesion. Therefore, super hydrophobic surfaces are desirable.

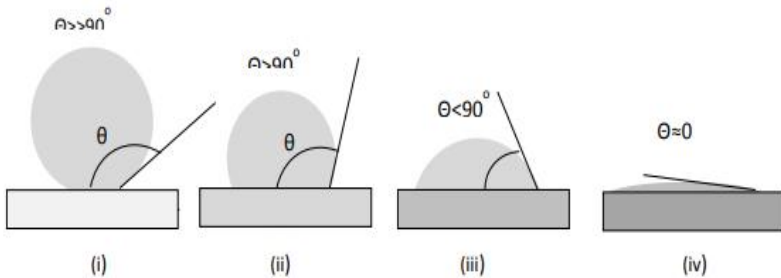
**Keywords:** Hydrophobic surfaces, contact angle, hierarchical microstructure

### 1. Introduction

Hydrophobicity refers to the non-wettability of surfaces, when they are in contact with a particular liquid. The surface has the property of repelling the liquid, instead of allowing it to become wet. Generally, in the study, the liquid is water and the wettability is in terms of effect of water droplet on the surface. On the other hand, if the surface allows wetting itself and liquid is not repelled, the surface is called to be a hydrophilic surface. The degree of

hydrophobicity or hydrophilicity depends on a number of factors and conditions of surface texture, surrounding medium etc. It will be decided on the basis of contact angle made by the surface on the droplet, when the droplet sits on the surface. At a very high contact angle ( $>150^\circ$ ) the tendency of repelling the liquid is also high and sufficient to roll the droplet away at a very low angle of tilt, resulting in leaving without wetting the surface. Such surfaces are known as ‘Superhydrophobic Surfaces’ and the phenomenon as ‘Superhydrophobicity’. In case of liquid being oil, the surface with such property is known as ‘Superoleophobic’ Surface’. The phenomena of superhydrophobicity is covered and understood under the field of science known as “wetting” of solid surfaces by fluids and the history of the related research is over 200 years old. In year 1805, Thomas Young <sup>[10]</sup> and Pierre Simon de Laplace <sup>[11]</sup> propounded by intuition that an interface has a specific energy, the so-called interfacial energy, which is proportional to the number of molecules present at that interface and thus to the surface area of this interface <sup>[10-11]</sup>. From the shape of the drop sitting on a solid, Young determined the size of the solid/liquid contact in terms of the contact angle made by the liquid on the solid as shown in Fig.1. The contact angle (CA) that the fluid develops with its substrate, provides a complete description of the drop behavior in respect to its ability to spread on the solid substrate or not.

The above behavior at a solid/liquid interface has been studied since long as wetting science, as referred above. The wetting property of the solid surface is specified by the contact angle that a drop of fluid makes at the surface. The schematic in Fig.1 illustrates the wetting behavior of various solid surfaces in four classes, the contact angle ( $\theta$ ) defined by a fluid (here, water as fluid) droplet forms on the solid surface. A given solid substrate of certain surface free energy, will exhibit varied wetting property with varying contact angle for fluids of differing surface free energy or surface tension and the contact angle. The contact angle (CA) is a unit for measuring and specifying the wettability of surfaces. Basically, there are only two well-defined categories of wetting; the one of a CA of less than  $90^\circ$  when the fluid is attracted to spread on solid surface and the other with CA higher than  $90^\circ$  when the fluid is repelled to bead out to a spherical shape. One can see that wetting is a fundamental property of surfaces and can be central to innumerable natural processes as well as day-to-day human life and in industry.



**Fig 1:** Schematic of various class of wetting; contact angle (CA)  $\theta$ , for a water drop placed on surfaces of different hydrophobicities (i) highly hydrophobic,  $\theta \gg 90^\circ$ , for  $\theta \geq 150^\circ$  the surface may become superhydrophobic (ii) hydrophobic,  $\theta > 90^\circ$  (iii) hydrophilic-  $\theta$ .

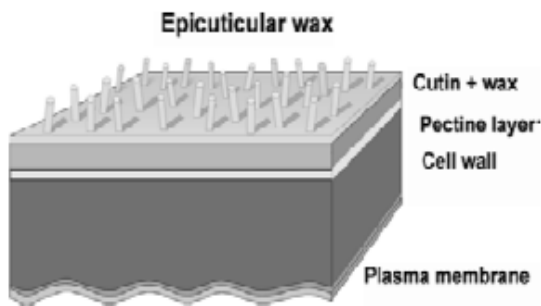
Further, when the droplet rolls off easily from those superhydrophobic surfaces due to a small inclination  $< 10^\circ$  of the surface, they are superhydrophobic and can provide a self-cleaning property similar to observed in lotus leaf. A schematic in Fig.1 demonstrates how the self cleaning is affected. The above definition of superhydrophobic surfaces with  $WCA \geq 150^\circ$  with SA.

### 1.1 Significance of superhydrophobicity to metals

Metals are important and indispensable materials. The innumerable applications of metals extend to most of the spheres of human activities from industrial, agricultural, structural, and scientific, to household consumer goods and utilities. Endowed with unique properties, the metals however present some limitations, for example, corrosion being one of them. Corrosion is a progressive and destructive process that compromises structural integrity and represents an enormous economic loss. Every year, the economic importance of rusting is such that it has been estimated that the cost of corrosion is over 1% of the world's economy. The corrosion by moisture and other harsh environment remains a matter of concern though protection of metal surface by coating the non-metallic materials has been commonly in practice, of course, with limited success. Perhaps, one of the most important applications for super hydrophobic surface is corrosion resistance for metals and alloys. In the past decade as the superhydrophobicity research progressed, super hydrophobic surfaces for metals have been an active area of research and development owing not alone to the potential that non-wetting ability holds for imparting anti-corrosion properties but also in enhancing the performance of metals.

## 1.2 The features on plant surfaces that help non-wetting

In respect to our interest in the present description related to hydrophobic or water repelling behavior of plant leaf surfaces, it is worthwhile to briefly explore their certain features relevant in the present context. The plants need a protective outer coverage to survive which is a continuous extracellular membrane, called cuticle. A schematic of outer protective layer of epidermis of a plant cell is shown in Fig.2 [7]. The referred protective layer is comprised of epicuticular wax tubules (epicuticular waxes can be of other morphology as well e.g., rod, tubules, platelets, hairs etc.) and the cutin backed with a pectin protein layer. Cutin performs a transpiration barrier function. The cuticle also serves as a multifunctional interface of nearly all primary tissues of land-living higher plants. One of the most important attributes of the cuticle is its hydrophobicity, which enables plants to overcome the physical and physiological problems connected to an ambient environment, such as desiccation. The protective outer coverage that as said above, is composed of hydrophobic material made basically of a polymer (cutin) and integrated or superimposed over it are the lipids usually referred as “waxes”.

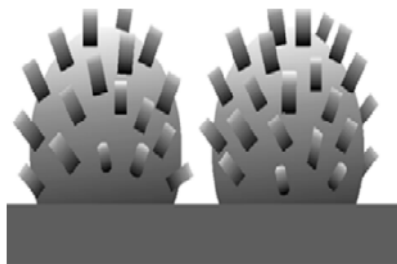


**Fig 2:** A simplified model of structure of the outermost layers

## 1.3 Lotus leaf surface: Hierarchical microstructure

The lotus leaf is one of the most well-known and studied examples of natural superhydrophobicity owing to its self-cleaning effect. For Lotus leaves, the static water contact angle is about  $160^\circ$  and hysteresis angle is  $< 4^\circ$ . Raindrops roll easily across the lotus leaf surface, carrying away dirt and debris. The morphological characteristics of lotus leaves have been found to possess a hierarchical surface structure of convex nodules of micro scale papillae epidermal cells with a very dense arrangement of nano scale three-dimensional epicuticular waxes, where single or every epidermal cell formed a papilla. Hierarchical surface structures are formed by a combination of two

structures in different sizes. A schematic model for hierarchical structure from the observed microscopic studies for lotus leaf can be represented as in Fig 3 [6-7]. These structural features appear akin to the features of outermost layer plant surface as shown and discussed earlier for Fig.3. The unique superhydrophobic and self-cleaning property of the lotus leaves has been attributed to the micro–nano scale hierarchical architectures in the form of the cilium-like nano -structures.



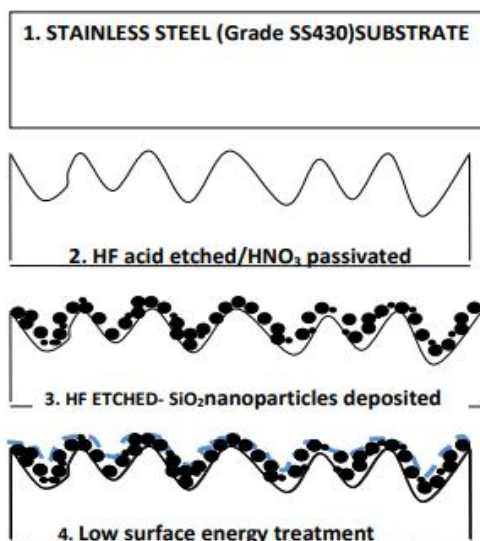
**Fig 3:** Schematic model of Hierarchical microstructure of super hydrophobic plant surfaces

## **2. Development of superhydrophobic steel**

### **2.1 Methodology**

A super hydrophobic structure, as discussed theoretically in essentially requires a dual/multiscale hierarchical structure. This inference has been drawn in past literature from observations on lotus leaf and many other natural plant and animal surfaces. A design concept for a potentially superhydrophobic surface based on the hierarchical nano/microstructure was proposed as described in chapter2. A large number of studies as surveyed in chapter 3 have established the concepts for creating the superhydrophobic surfaces by a variety of methods and using various material surfaces. The developing superhydrophobic stainless steel substrates have determined the optimal parameters of chemical (HF acid) etch showing that a microscale roughness could be created by a simple method. In this chapter we have determined optimal chemical etch method to get microscale roughness. It was also investigated by a model silica particle deposited surface to create nanoscale roughness. However, the criterion of superhydrophobicity namely, a Water contact angle of  $>150^\circ$  and a contact angle hysteresis or the slide angle (SA) First, we create a microscale roughness on steel substrates using the methods. On so roughened surface, we deposit nanoscale silica  $\text{SiO}_2$  particles. Expectedly, the microscale rough steel with nanoscale particles overlaid on its top may provide desired structure of hierarchical nature. This

surface then can be treated by low surface energy fluoro /chloro siloxane compounds or organosilanes as usual to obtain superhydrophobicity. The schematic of above proposed methodology is illustrated in Fig 5.



**Fig 5:** Preparing Superhydrophobic stainless steel surface (see text). 1. Substrate - Stainless steel Grade SS430, 2. The HF acid etched and  $\text{HNO}_3$  acid passivated substrate to obtain microscale roughness, 3. Silica nanoparticles (black dots) deposited by colloidal self assembly on etched substrate to get a hierarchical nano/microstructure, 4. Low surface energy fluoro/chloro compound treatment (in blue colour).

## 2.2 Low surface energy treatment

The method for coating the low surface energy is same as described the hydrophobicity agent fluoro carbon compound trichloro (1H,1H,2H,2Hperfluorooctyl) silane (PFOS). A diluted solution of PFOS 1-2 wt % in ethanol was prepared using magnetic- stirrer with the help of a magnetic-spin bar. The mixture of solvent fluoro compound was kept in capped bottles and vigorously stirred for 24 hours at room temperature. The etched and silica deposited SS specimen as prepared above were immersed for duration of 1hour and after withdrawing from solution were dried in oven at 70-80 °C. For adequate coverage of rough surface, the immersion dipping procedure was repeated for 2-3 cycles. Besides the fluoro compound PFOS, we have also investigated three other chlorosilane compound as low surface energy coating for comparison of efficiency of fluoro silanes and chlorosilanes. The following chlorosilanes are experimented:



TFPS [trichloro (3,3,3-trifluoropropyl) silane], DDTS (n-dodecyl trichlorosilane), and ODTS (octadecyl trichlorosilane). Now the used solvent for above chlorosilanes is n-hexane (in place of ethyl alcohol for the fluorosilanes). As a result of soaking in a 5 mM solution of chlorosilane/n-hexane, a silylated hydrophobic layer was adsorbed onto the silica surface. After heat treatment at 150 °C for 1 hr and 220 °C for 5 min, a uniform layer of silylating agent was formed on the silica particle surfaces with the hydrophobic chains protruding outward. Using the above methods 4 numbers each of hierarchically structured and fluorinated/ chlorinated SS430 specimen were prepared. The process in brief for obtaining SiO<sub>2</sub>-np: The tetraethylorthosilicate (TEOS) (6ml) (Sigma Aldrich) was added to the mixture of the co-solvent 80 ml ethanol (Merck), 4 ml DI water and 2.5 ml of saturated ammonia solution (28-30%) (Fisher Scientific). The mixture was stirred at 150 rpm for 2h at 35 °C using magnetic stirrer with a hot plate. The particle sizes were controlled by adjusting the pH from 9-9.5 by the ammonia catalyst and the cosolvent of the sol. The obtained milky solution, which contains the silica nano particle precipitate, was then added to the rotary evaporator (IKA- RV 10) at 60 °C and rotation speed of 120 rpm for around 40 minutes. To remove any residual solvents, nano particles were dried in vacuum at 70 °C overnight. After drying, the nano particle, were initially tested for extent of dispersion and for detecting heavier non dispersed particulates in acetone or ethyl alcohol. Whenever suspected, such particulates and agglomerate were removed by centrifuging at 2000rpm for 5-10 min and decanting the sol. The dried nano particles were washed and dispersed in ethanol typically using 5wt% SiO<sub>2</sub> in 30-50ml ethanol. The dispersion of colloidal SiO<sub>2</sub> kept in capped vial was ultrasonicated for about 10 minutes. The so dispersed sol was kept in an oil bath maintained at about 60 °C.

The etched and passivated SS430 substrate prepared earlier were dried in N<sub>2</sub> and were dip coated using single dip coater (SDC 2007C, Apex instruments Co., India). The substrates were immersed in the dispersed silica sol kept in heated state as above and withdrawn. The dipping and withdrawal rate of 50 mm/min were used with holding time of 15 min immersion in the colloidal SiO<sub>2</sub> nano particle. The dip-coating was repeated for 3 cycles to get large area coverage by the siO<sub>2</sub> nano particles. In between the coating cycle, the substrate was allowed to cool at room temperature. The ethanol was allowed to evaporate by covering the vials with a petridish while avoiding convection cooling by the room temperature environment. The SS substrates with deposited silica are heated at 250-3000 °C in an oven for 4-6 hours for

complete evaporation of solvent and also to help improve the adhesion of silica on the substrate by partial sintering.

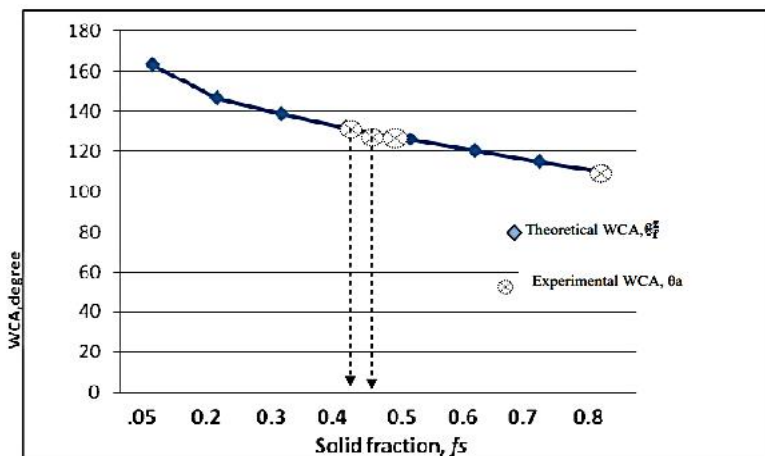
### 3. Results and discussion of mono-modal silica surface

The object of Task2 has been to determine the nano roughness due to deposited SiO<sub>2</sub> nano particles for the purposes to create super hydrophobic steel. The SEM images of the SiO<sub>2</sub> nano particles deposited on the glass substrate are shown in Fig, respectively, for the targeted 80-100nm and 140-160nm diameter spherical particles. It is observed for both of these targeted dimensions SiO<sub>2</sub> particles, the particles are spherical. A small deviation has been noticed in diameters for both the cases of observed SEM images. The smaller dimensioned particles (80-100nm) in Fig.6 appear with smaller deviations in diameters, which is higher for larger dimensioned particles (140-160nm,). The results of dimensional analysis carried out with the help of image-pro software as described in the preceding section is revealed by the SEM image in Fig. It is clear that over 80% of the identified particles are measured approximately close to the targeted range of 80- 100nm. The prepared SiO<sub>2</sub> particles thus appear within reasonable error bars of ±10nm and are similar to abundant results in literature. The results of SEM images show well prepared spherical SiO<sub>2</sub> nano particles as meant for this investigation in Task.

**Table 1:** The solid fraction  $f_s$  and theoretically predictable WCA, from CB equation\

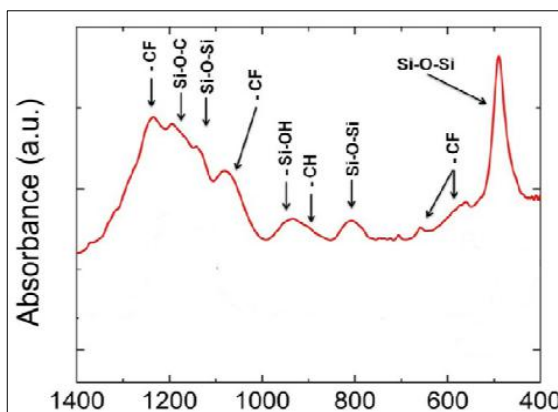
Solid fraction, $f_s$	$(1-f_s)$	$\text{Cos}\theta_f^*$	WCA $\theta_f$
0.05	0.95	-0.9587	163.5
0.2	0.8	-0.8348	146.6
0.3	0.7	-0.7529	138.79
0.4	0.6	-0.6697	132.04
0.5	0.5	-0.5871	125.9
0.6	0.4	-0.5046	120.3
0.7	0.3	-0.4221	114.96
0.8	0.2	-0.3395	109.84

The theoretically predictable values of WCA, in equation for various solid fractions are tabulated in Table 1 and plotted in Fig.6 As expected, reduces as the solid fraction value increases as seen in the plot figure.



**Fig 6:** The theoretically predicted WCA, by Cassie-Baxter equation for solid-fractions

The chemical nature of prepared SS nano/micro-structured specimen has been examined by Fourier Transform Infra-red (FTIR) spectra. The FTIR spectra were recorded at room temperature with a Bruker spectrophotometer (model VERTEX-70). The experimental conditions were set to ensure a spectral resolution of 1 cm<sup>-1</sup>. The FTIR for post low surface energy treated specimen have been obtained and presented in Fig 7.



**Fig 7:** FTIR spectrum of Fluorosilane (PFOS) treated SiO<sub>2</sub> nano particle surface

## Conclusion

In industry, super-hydrophobic coatings are used in ultra-dry surface applications. The coating causes an almost imperceptibly thin layer of air to form on top of a surface. Super-hydrophobic coatings are also found in

nature; they appear on plant leaves, such as the Lotus leaf, and some insect wings. The coating can be sprayed onto objects to make them waterproof. The spray is anti-corrosive and anti-icing; has cleaning capabilities; and can be used to protect circuits and grids. Super hydrophobic coatings have important applications in maritime industry. They can yield skin friction drag reduction for ships' hulls, thus increasing fuel efficiency. Such a coating would allow ships to increase their speed or range while reducing fuel costs. They can also reduce corrosion and prevent marine organisms from growing on a ship's hull.

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