A review on superhydrophobic materials and coating techniques

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Abstract- Since the recent year, we have seen the interest in scientist to mimic the natural behaviour, and they tried to mimic the nature’s property of superhydrophobicity artificially and very far they also get succeeded. This superhydrophobic property is very useful in many aspects of life as well as in industries as they have an extensive property to overcome wear, corrosion, biofouling etc. There are different ways to fabricate these coatings, some are chemical and some are physical. In this review paper, we have discussed the theoretical background of superhydrophobicity and discussed the need for a surface to become superhydrophobic like surface energy and roughness and also different ways of fabrication in which some are simple and cost-effective and some are very useful for industries. Also, there are different examples of materials that can show superhydrophobic properties.

Keywords- Superhydrophobicity, Coatings, Contact Angle, Surface Roughness, Surface Energy.

1. Introduction- Scientists always inspired by the natural phenomenon and try to replicate that artificially. In this term of events, they try to replicate the different leaves, wings of some insects found in nature that have the capability to repel water from its surface example sacred lotus leaves, cicada ornis’s wings etc, because they have exceptional self-cleaning property this property is associated with the superhydrophobicity [1]. Superhydrophobicity is a term we use generally for a surface that repels water and water droplet get a jump on it and roll on the surface. Also, to understand superhydrophobicity we can use the phenomenon of surface tension. As we know that molecules which are in the liquid have equal force all around it but the molecule that is on the surfaces faceless force that leads to the surface tension [2] and we know that due to surface tension the droplets always try to reduce their area and form a spherical shape. But as droplet gets in contact with the surface it changes its shape from spherical and gets distorted due to gravity [3]. Also, the cohesive force of the liquid should be more and adhesive force should be less for that surface, so for superhydrophobicity, with the help of surface roughness and surface chemistry, we try to reduce the adhesion force. In different culture, lotus leaves are known for its purity although it grows in muddy water [2]. Water on the leaves roll of from its surface including all the dirt particles along with it, this effect is called a lotus effect or self-cleaning property of lotus [2,3]. Due to this type of wetting property and self-cleaning this favoured topic for the scientists [4]. To indicate wettability, we use contact angle made by the water droplet on the surface [5]. Wetting of any surface depends on these factors, contact angle between and a droplet of water, chemical composition and surface roughness [6]. For wettability, it is said by the scientists that when the contact angle is less than 90 degree then it comes under hydrophilic surfaces and for greater than 90 degrees to 150 degrees it came under hydrophobic surfaces and contact angle greater than 150 degree comes under superhydrophobic surfaces [7,8]. Chemical composition describes the energy of the particular surface. For superhydrophobicity, the surface energy should be low. And the surface of the superhydrophobic substance should be rough [9, 10, 11]. We will discuss this property in this review further.

To get superhydrophobic surface we fabricate different layers on the surface that have to make superhydrophobic with different techniques. The main requirement for any fabrication technique is to
modify the surface and head to decrease surface energy and increase surface roughness [7,12].

Superhydrophobic surfaces are very useful for daily uses and industrial purpose also, it has different applications like self-cleaning, anti-biofouling, anti-icing, an increase of corrosion resistance, anti-fogging surface etc. We see the frying pans have coatings that make them anti-sticking, we can see the hydrophobic layers in textiles industries, in different industries where high corrosion resistance is required, in ships where we need to control the biofouling. These are some places where we use these layers for different purposes. In this review, we will discuss the layers to increase corrosion resistance and to increase the anti-biofouling characteristics and self-cleaning. And also, different techniques like electrochemical deposition method, sol-gel process, chemical fabrication method, spray coating fabrication method etc of fabrication will be discussed further in this paper.

Figure 1. Water contact angles for hydrophilic hydrophobic surfaces [6].

2. Theoretical Background

2.1. Contact Angle- The definition of contact angle is that the angle which is made by the edge of the droplet and solid surface is known as the contact angle. When droplet touches the surface there is a contact point if solid, liquid and gas phases, at this point the angle between solid phase surface and tangent to liquid droplet is the measurement of contact angle [13]. So, we can say that there are three-phase and all three phases solid-liquid, liquid-air, air-solid and have their surface tension forces are $\gamma_{SL}$, $\gamma_{LA}$, $\gamma_{SA}$ respectively [14] (fig 2). For contact angle measurement for wetting first model was given by Thomas Young in 1885 [15]. Derivation for contact angle by Thomas Young is in equation (1).

$$\cos \theta_Y = \frac{(\gamma_{SA} - \gamma_{SL})}{\gamma_{LA}}$$

(1)

here $\theta_Y$ is Young’s angle,

But this Young’s angle is derived for the smooth surfaces and we know that in actual superhydrophobic conditions the surfaces rough and this affects the contact angle. So, to get actual angle other models were proposed we will discuss the other two models in wetting models.

Figure 2. Young’s Water Contact Angle [15]
Superhydrophobicity traditionally implies not only a high contact angle as well as a low contact angle hysteresis. The minimal hysteresis of the superhydrophobic surface contact angle is accountable for the self-cleaning characteristics that ensure a drop of water can roll off the surface easily and eliminate dust from the surface. Self-cleaning is one of the most essential properties of superhydrophobic surface applications and functions. [16,17].

For superhydrophobicity, the only greater contact angle is not enough but the water should be roll off from the surfaces just by tilting the surface with a small angle. This slight tilting angle of the surface is known as the sliding angle. For superhydrophobic surface, this sliding surface should be very low generally less than 5 degrees [18].

2.2. Surface Energy- We know that for superhydrophobicity the surface energy should be low. Different chemicals or surfactants are used to lower the energy of the surface. These chemicals can be coated on the surface to reduce the surface energy. The surfactants and surface roughness combine to make the surface energy so low so that it can be used for the superhydrophobic substrate. Generally, the compound which has silane group in them have a great effect to reduce the surface energy of the surface. Among silane fluoroalkysilanes are most useful for lower surface energy. But these groups due to the presence of fluorine are hazardous for the environment in nature and are also very costly. So, there is a need for the substance that can replace these and can be used as an alternative, some substance like stearic acid and polymers can be chosen as the alternative [19].

2.3. Surface Roughness- A superhydrophobicity must have a rough surface. Due to this uneven surface air get caught in the between peaks of the roughness, so when water placed on the surface due to low surface energy and this air bubble restrict water to spread at all points of the surface, and due to this surface area get reduced and this leads to lower the friction that’s why the droplet gets slipped on the surface easily [20,21].

2.4. Wetting Models- Previously we have discussed young’s equation for contact angle but young’s equation is only valid for smooth surfaces. But we know that there are rough surfaces for the superhydrophobic surfaces and this roughness can be microstructured and nanostructured due to this roughness the contact angle gets increases. So, to calculate the contact angle for rough surfaces we use two models first is the Wenzel model and Cassie-Baxter model. Wenzel model is used for microstructure roughness. In figure 3 we can see the characteristics of water on both micro and nanostructures surface. Either Water droplet can penetrate in spikes on can be suspended over the peaks of roughness [5].

![Figure 3. Wenzel And Cassie Baxter State](image)

Wenzel published his model of wettability in 1936 for a rough surface. So, Wenzel introduced the factor of roughness R that is a ratio of rough surface area to the smooth surface area, the value of R is generally
greater than or equal to 1. The following equation provides the contact angle on a rough surface in the Wenzel model [22].

\[ \cos \theta_W = R \cos \theta_Y \]

*Roughness factor* \( R = \text{Actual surface area/Planar surface} \)

The surface roughness can enhance both hydrophobicities as well as hydrophilicity [23].

2.5. Cassie-Baxter Model- We know that due to roughness the air can be trapped in between them, but Wenzel model does not look into it, so we can say it works only for homogeneous surfaces. For heterogeneous surfaces, Cassie-Baxter came up with another formula for contact angle. In this Cassie-Baxter says that the droplet is only contacted at the top of the roughness but cannot wet the surface in which air is trapped [6]. The formula given by Cassie-Baxter is- [24,25]

\[ \cos \theta_{CB} = f (\cos \theta_W + 1) - 1 \]

here,

\( f= \text{fraction of area which touches the water} \)

\( \theta_{CB}= \text{Cassie-Baxter contact angle} \)

from the formula, we can see that the contact angle is increased in this state.

In the Wenzel model, the water driblet gets into the roughness grooves, but in the Cassie-Baxter model, it holds on the top of the roughness grooves as the air is trapped in the grooves [23,26,27].

3. Different Methods of Fabrication to Achieve High Corrosion and Anti-Biofouling Properties-

We have already discussed that two things (i) chemical composition and (ii) surface roughness is required to create the superhydrophobic layer. We can create a superhydrophobic surface by a association of the rough surface of lower energy material and by deposition of another material on low surface energy material [28,29]. So, different methods are used for the fabrication that uses base as we discussed above.

3.1. Electrodeposition Method- In the process of Electroplating, also known as electrodeposition there is a solution of ionic salts this salt is of the same material as depositing a material that has to be deposited on the conducting surface. We can use this method of fabrication to produce a thin film of metal on surfaces so that the properties of the surface can be enhanced. We can increase the corrosion resistance protection, abrasion resistance can be increased, also we can give lustrous property to surface. The main quality of this process is that we can use it in complicated parts which are not easy in some other methods. For example, in automotive part are electroplated by nickel-metal so that anti-corrosion property can be increased, also in the circuit board, we know that copper has lower resistance so it is plated on circuits so that resistance can be reduced. Another advantage of electroplating is that by this method we can electroplate alloys too on surfaces.

This method is very useful in managing the roughness morphology of coating. By this method we can produce a variety of morphologies like sheets, needles, tubes, cones, rods etc relatively fast There are several methods by which we can control both surface roughness and morphology but Electrochemical processes are way better than any other methods and are in capable of controlling these properties even on very large surfaces. [17].

Furthermore, micro-structures and nano-structures development can be easily controlled by regulating some electrodeposition parameters like current density, current type AC or DC, by using pulsed or non-pulsed current [30,31]. As an example, by using platinum anode and watts bath thin micro or
nanoparticles layer can be fabricated from a solution on the conductive surface and produce a pine cone-like hierarchical structure. [32].

Here is a fig. that shows the formation of nanostructure of ZnO by electrochemical anodization method by mixing hydrofluoric acid and methanol electrolyte on a large area surface. We can observe the difference in the formation of ZnO nanostructure that changes in nanodots, nanowires and nanoflower in less than an hour like fig “a” shows the formation after 30 seconds, “b” shows sample after 1 min, “c” shows sample after 5 min, “d” shows sample after 10 min, “e” shows sample after 15 min, “f” shows sample after 30 min [33].

![Figure 4](image.png)

**Figure 4.** According to different reaction times, the growth of ZnO nanostructure on Zn foil is shown by SEM image [33].

Using direct voltage supply and one-step deposition process Huang et al. prepare the superhydrophobic copper surface. They used a dilute ethanolic stearic acid solution in which copper plates were immersed. The reaction between copper and stearic acid takes place and a surface copper electrode on anode gets transformed to superhydrophobic with flower-like nanostructure of copper stearate film. This layer exhibits the water contact angle of 153 degrees [34].

Metals such as aluminium, zinc, nickel and iron and their following alloys like brass and Zn-Fe alloy etc shows their advantage of reaction with perfluorocarboxylic acid solution, they can make a very efficient superhydrophobic surface. By controlling process time and concentration of perfluorocarboxylic acid we can create a variety of different substrate [35].

3.2. Electrospinning Method- Electrospinning is a simple process that generally used for the making of polymer nanofibers. It is a very versatile process to fabricate continuous polymer fibres in nano and micrometre sizes. This process is something like the extrusion process but this extrusion is electrically controlled [36,37]. High voltage is applied to the raw material of electrospinning, this power is required to enhance the liquid electrostatic potential. There is a relationship between electric potential and surface tension of a liquid. So, if we vary the electric potential the surface tension, the volume of fluid can get
decrease or increase. But generally, oppositely surface charge to act as the electric potential get increase surface charge gets reduced and due to this change in surface charge fluid change, its shape and make the structure known as Taylor cone [38,39]. This method can be used in laboratories as well as in industries, it has a wide variety of application that’s why it became the most adaptable method for fabrication of nanofibers. Some examples of electrospinning are given below to understand the variety of this process.

Carbon nanotubes have many characteristics that can be used in mechanical works like higher tensile strength, higher modulus of elasticity etc [40]. Although when CNT reinforced to make composite then it became very hard so it can’t be made into string form so now this is not able to perform the mechanical properties so researchers try to synthesize CNTs into polymer nanofibers by electrospinning method [41]. A researcher found that electrospinning of CNT and polyaniline the are used as a fabrication composite and the conductivity of fibre got increases and it made a carbon sheet by electrospun method, this sheet was investigated and this layer was increasing the property of the base material [42].

Electrospinning can also use as a method to protect the wound. Fibres mat dressing can be used if the ultra-nano fibres produced using electric field and that directly spun on the wounded area of body [43,44].

Ma et al. combined PCL (polycaprolactone) by electrospinning which contains hierarchical roughness structure and PPFEMA (polymerized perfluoroalkyl ethyl methacrylate) by initial chemical vapour deposition process which has very low surface energy. So, this combination creates a very suitable state for the superhydrophobic film. This coating shows the contact angle of 175 degrees and 205 degrees of sliding angle [45].

PVDF (polyvinylidene difluoride) is well known for lower surface energy and used as a substance to lower the surface energy of the surface. It mixes with different substance like zirconia, alumina, silica etc and can make a compound that can create PVDF-ZnO, PVDF-Al2O3, PVDF-TiO2 coatings that can be used by electrospinning process [46,47,48].

3.3. Sol-Gel Method- In a typical sol-gel process a series reaction like hydrolysis and poly-condensation take place on the precursor and is transfigured into a glassy material. The surface roughness can be controlled by altering the precursor mixture and conditions. The transparent superhydrophobic layer can also be fabricated by this method as this is adaptable for glass [49,50,51]. Superhydrophobic sol-gel coatings usually present good reluctance to temperature. In this process gels and nanoparticles are synthesized on the substrate. By this method different types of layers can be formed like multi-layer films, thin layer, nanocomposites, porous roughness can be easily made [52,53]. Due to its advantages like process on low temperature, lower cost of fabrication, simple technique, and better control on the process it is used widely to fabricate superhydrophobic layer [54]. In this method generally metals oxides like silica, titanium oxide, zirconia etc are used to create a superhydrophobic layer that works on the theory of Wenzel and Cassie- Baxter [55,56].

Mahadik et al. prepared silica film by sol gel method with mixture of different chemicals like methyltriethoxysilane (MTES), methoxytrimethylsilane (TMMS), trimethylchlorosilane (TMCS), methanol, hexane and Ammonia, (MTES: TMMS:CH3OH: H2O- 1:0.09:12.71:3.58) and prepared transparent film that can we useful for goggles, specs, solar panels etc. they get best result in 25 hours deposition time in which they get contact angle of 172 degrees [57].
Lu et al. prepared sol gel coating with Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) and Methenamine (C$_6$H$_{12}$N$_4$) on aluminium substrate, stearic acid used to decrease the surface energy and they get water contact of 154.8 degrees [58].

![Figure 5. Sol-gel process [52].](image)

### 3.4. Etching Method

Etching is a method in which superhydrophobic surface is made by increasing in roughening of the surface. The metal surface can be etcher by the different etching method that can combine with acid to increase the roughness. There is a different kind of etching processes that increase roughness can be used together with acid to increase the roughness of the surface. For inorganic materials, plasma etching techniques and optical maser etching can be used. To make multiple roughness’s scales many techniques can be combined [59,60]. We can divide etching into two categories,

(a) Wet chemical Etching- in this acid or base solutions etch the surface and make the surface rougher [61,62].

(b) Dry etching- in this plasma, reaction etching like techniques are used. This generation of reactive atoms and particles takes place in gas discharge and they do an anisotropic etching of the surface [63,64]. The etching is a very simple and straight forward technique which can also be used on very large-scale surfaces but there is a demerit of this technique, due to use of corrosive acids like sulfuric acids phosphoric acids it leads to unsafe for use due to environmental issues [65].

### 3.5. Plasma Treatment

A plasma treatment of surfaces perpetually involves plasma etching. Plasma treatment of surfaces will cause a big modification within the surface micro-nanostructure attributable to the aeolotropic etching of the surface layers [66]. Plasma could be an uncomplicated and effective technique to fabricate hydrophobic surfaces. Increase in Surface roughness and reduction in surface energy both can get simultaneously. By using oxygen plasma, we can get Superhydrophobic surfaces simply. However, ageing is the main problem of superhydrophobic surfaces by plasma technique. Since the roughness of surfaces finished by plasma will be simply adjusted, this technique is a suitable way to fabricate superhydrophobic coatings with special optical properties, wherever the surface roughness of those coatings is the most vital factor [7]. Larger substrate and for continuous process plasma technique
is suitable because we can treat the large surfaces easily. After all, it doesn’t need vacuum instruments and can be used in inline mode rather than batch mode [67].

In one research using sound waves assisted nitric acid and cetyltrimethylammonium bromide (CTAB) Pan et al. made a rough surface on copper and made it superhydrophobic surface and get water contact angle of 155 degrees [68]. Ryu et al. created hydrophobic film by plasma method on polytetrafluoroethylene (PTFE) substrate and get spherical tips on surface that were nano structured. He get water contact angle of maximum 171 degrees [69].

3.6. Chemical Deposition- In this process generation of thin films on substrate take place. In a chemical reaction the deposition occurs and it self assembles itself and formed deposit on the substrate. It creates a crystalline structure on the substrate, we can use different materials like CdS, ZnS, CuSe etc. this deposition can be done by different processes like chemical vapour deposition, electrochemical deposition and chemical bath deposition. We can get a different type of morphologies and micro-nano structure can vary on basis of material and deposition conditions [5].

3.6.1 Chemical Vapour Deposition- In this chemical process the chemical gaseous substance(reactants) gets deposited on the substrate surface and forms a non-volatile solid film. In this process, the morphology of the layer is based on the morphology of the surface. But if change reactants and control the reaction conditions we can achieve a different kind of morphologies on the substrate [29]. Figure 7 shows by chemical vapour deposition techniques used by Mertaniemi et al. to coat FOTS (fluoro-octyl-trichloro-silane) onto the NFC (nano fibrillated cellulose) particles deposited on the surface and fabricated a superhydrophobic surface [70].

3.6.2 Electrochemical deposition- Electrochemical deposition can create a thin layer of metal or metallic alloys on the substrate. The main benefit of this method is that we can create a large verity of morphologies and structure on the surface and also at very low cost and thickness can also vary. Coating created by this method is very stable and can be achieved at room temperature. In this method, the cations of the electrodeposited metals get reduced by an electric current from electrodes to a conductive surface. For large area production, we generally used this method in preparation of photovoltaic solar panels [13]. In this method generally ZnO, gold cluster, silver aggregate used to prepare the superhydrophobic film. In an experiment of fabrication of hydrophobic film by chemical deposition, method researchers used aqueous compound of ZnCl$_2$ and KCl and ITO glass was used as substrate. After completing of process, we found that the layer was made up of zinc, oxygen and carbon. They found the contact angle of 128 degrees and the surface was relatively rough [71]. By this method, we can generate organic coatings like PEO-polyethylene oxide, PTFF-polytetrafluoroethylene [72]. In an experiment, myristic acid was used to create a stable layer and contact angle got by layer was 154 degree and this surface was also very good for corrosion protection [6].
3.6.3 Chemical bath deposition - Generally for fabrication for semiconductors there is no method that is simpler than the chemical bath method. We can fabricate thin film on a large area very easily, but in this method, we can use only some selected materials like Ag$_2$S, As$_2$S$_3$, Bi$_2$S$_3$, Ag$_2$Se, Bi$_2$Se$_3$, Ag$_2$O, AgO etc. In this we use a liquid bath containing suitable reagent and the temperature can vary from 0 degrees to 100 degrees [73,74]. The object is immersed in a solution containing the precursors in chemical bath deposition method. In this method nucleation and growth of particle is the two main steps that take place so that solid structure can be fabricated on the surface from the solution. Different parameters can affect the deposition like the temperature of the solution, the pH of the solution, concentration and time of bath. For the creation of nano pin type structure from CoCl$_2$ and NH$_2$CO in water, Hosono et al. used borosilicate glass. In thermodynamic equilibrium condition, every metal compound deposited singly on the substrate and make a crystalline-like structure. Lauric acid was used to adjust the nano pin. Here is a figure 8 shows a structure of nano pin. By this method the maximum contact angle was formed till now that is 178 degree also, we can see that there are 166 needles structures in a 9µm$^2$ area and apex of pins are of 6.5 nanometers.[75].

![Figure 7. A nano pin structure formed by film-coated with lauric acid [73].](image)

Hydroxide solution of a mixture of nickel sulphate, potassium persulfate and aqueous ammonia was used as a precursor for vapour bath method on Indium tin oxide coated glass. The precursor was deposited on the glass, firstly the colour was grey but after annealing, it became almost transparent and get adhere to the glass tightly. Even after annealing, the morphology was rarely changed, and it was found that this film has a porous structure [76].

Rezaei et al. used vapour deposition method to fabricate superhydrophobic layer that showed 160 degrees water contact angle by using Ammonium hydroxide (NH4OH), tetraethylorthosilicate (TEOS, P98%, Merck), vinyltrimethoxysilane (VTMS) and Ethanol on different substrates aluminium, glass and silicon slides. They also tried to fabricate the layer at minimum temperature that is 40 degrees [77].

4. Conclusion – In this review, an epitome of superhydrophobicity has been discussed with many examples. First of all, there is a discussion about natural superhydrophobicity in different natural things like flowers, insects etc. Then it covered the main aspect of wettability of surface and theoretical explanation of superhydrophobic property along with rough surface and low surface energy materials. An immense discussion of different kind of fabrication methods like electrodeposition method, electrospinning method, sol-gel method, a chemical etching method, chemical deposition methods were given. We know that there are very important and variety of applications of superhydrophobicity is there so, the properties as anti-icing, self-cleaning, anti-corrosion, anti-fogging etc. We have seen that there are many theoretical conflicts of superhydrophobicity but due to broad use of these coatings researchers and scientists showing a lot of interest in this field. With the help of micro and nanostructures, there can generate a large variety of surfaces. Now, still, we are very behind in making coatings on large areas and make it less costly so that it can be achievable to all. These coatings are also used in textile industries in fabrics to make waterproof cloths. There are some other uses of superhydrophobicity that is beyond normal superhydrophobicity like Leiden-Frost effect. In Leiden Frost effect we can see that water can
go up in the opposite direction if we can create proper patterning in micro and nanostructures. There is still a lot to do in the field of superhydrophobicity so that it can be used in different fields because it can make a change in the working processes of different fields.

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