



e-ISSN: 2319-8753 | p-ISSN: 2347-6710

# IJRSET

International Journal of Innovative Research in  
**SCIENCE | ENGINEERING | TECHNOLOGY**



# INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 13, Issue 8, August 2024

**ISSN** INTERNATIONAL  
STANDARD  
SERIAL  
NUMBER  
INDIA

Impact Factor: 8.524

9940 572 462

6381 907 438

[ijirset@gmail.com](mailto:ijirset@gmail.com)

[www.ijirset.com](http://www.ijirset.com)

# Review Paper on Nano Engineered Hydrophobic Surfaces

**Gautam Kunal<sup>1</sup>, Prof. Sachin Jain<sup>2</sup>, Dr. Piyush Jain<sup>3</sup>**

M. Tech. Scholar, Department of Mechanical Engineering, Bansal Institute of Science and Technology,  
Bhopal (M.P.), India<sup>1</sup>

Assistant Professor, Department of Mechanical Engineering, Bansal Institute of Science and Technology,  
Bhopal (M.P.), India<sup>2</sup>

Head of Dept., Department of Mechanical Engineering, Bansal Institute of Science and Technology,  
Bhopal (M.P.), India<sup>3</sup>

**ABSTRACT:** Hydrophobicity means the tendency of substance to repel water and to avoid wetting of surface. A surface is super hydrophobic if it has a water contact angle above 150°. These surfaces are water repellent. These surfaces with low contact angle hysteresis (less than 10°) 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 micro-fluidics, 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:** Hydrophobicity, Surface, Micro/Nano, Surface

## I. 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°) 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’.

### 1.1 Superhydrophobic Surfaces

In the year 1997, Barthlott and Neinhuis discovered remarkable phenomena of nature on Lotus leaf [1]. On Lotus leaves, water droplets falling on the surface bead up and are repelled to roll off the surface instantaneously, carrying away dirt and debris and thus self-cleaning the lotus leaf surface (Fig1.1a-c). The phenomenon has come to be popularly known as “Lotus-Effect”. In the pioneering study of Barthlott and Neinhuis, detailed microscopy of the surface of lotus leaves revealed protruding bumps or nubs of about sizes 5-10 µm apart by 20–40 µm and each covered with a smaller nano scale rough surface of epicuticular wax crystalloids (Fig1,d-e).



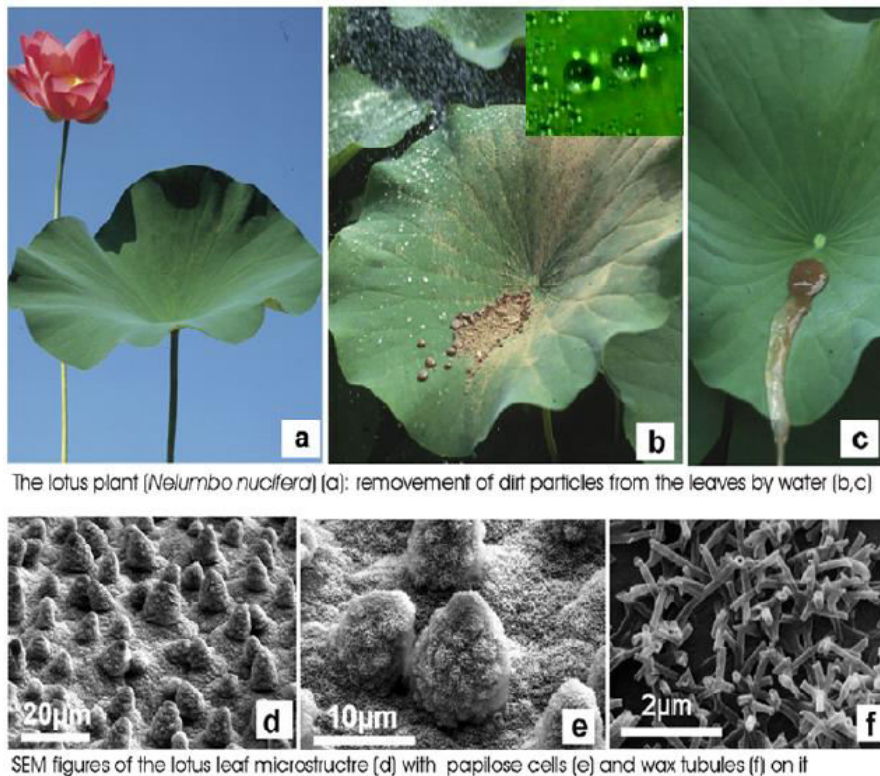


Fig1.1: Superhydrophobic and self-cleaning Lotus surface. (a) A flowering plant of Lotus (*Nelumbo nucifera*) (b) Lotus leaf contaminated with clay; the inset shows spherical water drops on leaf surface (c) shows the adhering particles getting removed by water. The SEM micrographs (d–f) show the lotus leaf surface at different magnifications: (d) shows randomly distributed cell papilla; (e) shows a detail of the cell papilla and in (f) the epicuticular wax tubules on the cell [Acknowledgement: (d) - (e) Bhushan B.

This observed dual scale microstructure with micro scale roughness topped with nano scale roughness has been aptly called as a *hierarchical* structure. Since this pioneering study, over 200 plant leaves, insects and other animals also have been found to exhibit remarkable water repelling properties [2-5]. Indeed, the lotus effect formed the basis for coining the term superhydrophobicity (i.e., ultra-hydrophobicity) and spurred the related research. In the past decade, the attributes of ‘lotus effect’, the self cleaning and the excellent low adhesion capability of superhydrophobic surfaces, have motivated intensive research on bio-mimicking such surfaces. It may however be added that prior to discovery of super-hydrophobicity in nature (Lotus effect) and when the phenomenon was widely.

It can be traced back to more than a century ago, when Ollivier et al., achieved a contact angle close to 180° by coating a substrate with soot [6]. In 1986, Sacher et al. had reported that very water repellent films could be obtained by depositing an organosiloxane (hexamethyldisiloxane) on silicon chips in high-energy plasma at low temperature [7]. Further, Morra et al. had prepared highly hydrophobic surface by O<sub>2</sub> plasma etching on polytetrafluoroethylene (PTFE) surfaces in year 1989[8]. The first ultrahydrophobic (super hydrophobic) surface was reported by Onda et al.[9] on fractal rough surface. Though, at the time of the study in the year 1996, the term superhydrophobic was yet to be coined and was acknowledged as such only later in year 1997.

## II. WETTING ON FLAT AND SMOOTH SURFACES

When a small droplet of liquid is deposited on solid surface, it may *spread* to form a film or may form a spherical cap shape. This spreading behavior in general is said as the *wetting* property of a solid surface. Wetting is a fundamental property of solid surfaces where a fluid may be attracted (wetting) or repelled (non-wetting). Thomas Young [10] first described in 1805 that surface energy is the interaction between the forces of cohesion and adhesion which determines

whether or not the wetting i.e., the spreading of a liquid over a surface occurs. If complete wetting does not occur, then a bead of liquid while in contact will form an angle with the solid surface which is a function of the surface energies of the system. The wetting property of the solid surface is specified by the contact angle that a drop of fluid makes at the solid surface. The hypothesis of Young assumed an idealized smooth and inert surface that also did not interact with fluid coming in contact with it. The significant phenomenon of contact angle has been widely studied later on non-ideal rough surfaces from both academic and practical perspectives. The theories of Wenzel [12] and Cassie-Baxter [13] have been mostly applied to explain and understand the wetting behavior of rough solid surfaces. The hydrophilic or hydrophobic nature of surfaces is fully understood by these theories. In the extreme case of non-wetting, the surface is said as *superhydrophobic* (or, superoleophobic for oil as fluid; conversely, for the case of extreme wetting the surfaces are called superhydrophilic or superoleophilic, depending on the fluid being water or oil). The extent of attracting or repelling property is conveniently defined by the contact angle. On a superhydrophobic surface, the water contact angle (WCA) is close to 180° when the drop is near spherical. Further, the definition of superhydrophobicity will be complete when such a spherical drop, rolls-off or slides away with a small tilt of surface defined as the *slide angle* (SA). Generally, superhydrophobicity is specified when  $WCA \geq 150^\circ$  and  $SA \leq 10^\circ$ . As described in the introductory chapter, the phenomena of superhydrophobicity was first observed in the year 1997 in nature in Lotus plant leaves and subsequently in over 200 plants where spherical water drops will just slide away from the lotus leaves and in process cleaning the leaf surface [1]. For understanding and explaining the phenomena of ultrahydrophobicity or superhydrophobicity, initially the classical wetting theory for wetting on rough surfaces by Cassie-Baxter [13] had been found to be generally adequate. Experimental evidence showed that though the WCA were sufficiently high, the drop has tendency to pin-down to the rough surface and a phenomenon of hysteresis, requiring other considerations beyond the classical theories. More later theories have proposed coexistence and transition between the Wenzel and Cassie-Baxter states and a Cassie-Baxter metastable state of non-wetting appears to explain extreme non-wetting on rough surfaces with certain special micro/nano scale structures. Though, there have been questions on the validity of the classical theories of Wenzel and Cassie-Baxter for fully (high WCA and the roll-off of water drop) explaining superhydrophobicity and controversy on such questioning. There have been significant developments in the past decade that put forward the explanation for the superhydrophobicity by laying down the criterion for such surfaces. These newer explanations, concepts and wetting models provide an avenue for the design of functional superhydrophobic surfaces with special wettability.

### III. SUPERHYDROPHOBIC SURFACES

Based on these concepts a general strategy for preparation of superhydrophobic surfaces can be presented as in Fig. 2. The techniques to make superhydrophobic surfaces can be simply divided into two categories: making a rough surface from a low surface energy material and modifying a rough surface with a material of low surface energy. In the figure we can see that the methods can be a single step or two step processes. In the single step process (Fig. 2a), a low surface energy material substrate is roughened to obtain a desired nano/microstructure by certain methods. Thus, strategy may be classified as one step top down preparation method. Whereas, in Fig. 2b, first on a substrate a nano/microstructure is created by depositing nano-scale/micro-scale features and in the second step a low surface energy material is overlaid on the micro structured surface prepared previously in the first step. It is obvious that this is a two-step process and a bottom-up approach. There yet may be methods where a high surface energy material surface may be roughened (by a top-down step) and over this roughened surface a low surface energy material may be deposited (a bottom-up step). Thus, this method combines a top-down and bottom-up steps. The most practical methods involving large area nano/micro structuring in repeatable cycles tend to combine both the 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. A variety of materials and methods have been used in the so-referred one step/top-down and two step/bottom-up approaches.

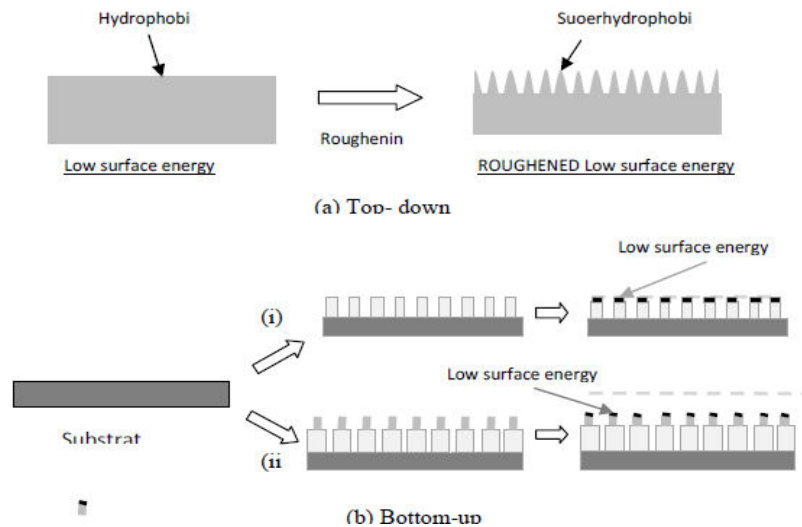


Fig. 2: Strategy for preparing rough superhydrophobic surfaces: (a) Top-down method of roughening a hydrophobic substrate (b) Bottom-up method of roughening (i) deposition of microstructure (ii) deposition of hierarchical nano/microstructure. The top surface of these structures (i) and (ii) overlaid with a low surface energy material.

#### IV. ROUGHENING METHODS

Methods to make superhydrophobic surfaces by roughening low surface energy materials are mostly one-step processes and have the advantage of simplicity. But they are always limited to a small set of materials that are hydrophobic and have  $WCA > 90^\circ$ . In more generalized top down methods, various hydrophilic material substrates can be used. The micro-structured surfaces however may still be hydrophilic and may need a low surface energy treatment to be made superhydrophobic. For the generation of structures, surfaces for superhydrophobicity, the methods such as lithography, templating, micromachining, plasma treatments have been used. In the lithographic approaches in general, light is irradiated through a mask with desired features onto the substrates (often silicon) coated with a photo resist film. Templating is a multistep process that often involves molding and replication steps. Thereafter, the template can be removed by lifting off or by dissolution or even sublimation. Subsequent etching steps yield the desired patterned surfaces. In micromachining, surfaces are diced into the desired texture. These technologies are not necessarily independent on each other, and rather, can be used as a combination to realize a superhydrophobic surface. To illustrate, a surface processed by lithography can be treated further by plasma etching to achieve complex roughness and then used as a featured template to produce replicas. However, for the creation of a superhydrophobic surface, the object always remains to make the process as uncomplicated as possible.

**Lithography:** The lithographic process is a well-established technique in delineating certain features on a surface. As a general statement, lithography prepares superhydrophobic surface structures by copying the information from a master, which can be either rigid or soft, and then transferring it to a replica in an opposite form. Lithography can be subdivided in various techniques that include optical lithography (photolithography). The photolithography is further classified as X-ray lithography, electron beam lithography (EBL). More recently, for creating nano/microstructures, soft lithography, nano imprint lithography (NIL), capillary force lithography [168], and colloidal lithography have been used in making superhydrophobic surfaces. These techniques are somewhat different though still perform similar to lithography. However, combining photolithography with various above variant lithography is increasingly being practiced in recent studies to obtain hierarchical superhydrophobic nano/micro-structured surfaces.

**Photolithography** Conventional lithography normally uses a flat plate as the master surface. Now the lithography is often referred to as photolithography, which transfers the entire geometric pattern from an optical mask to a thin film of photoresist sensitive to light (mostly ultraviolet). In this photolithographic approach, light is irradiated through the mask with desired patterns or features to the substrates with a photoresist coated on its surface. Due to irradiation the photoresist is cured. Subsequent developing and etching of non-irradiated area yield the desired patterned surfaces. The photolithography is the general term and is further sub classified depending on the light source (radiation/ electrons), as



X-ray lithography and e-beam lithography. For the preparation of superhydrophobic surfaces, an extra surface treatment step is needed to render the surfaces hydrophobic.

**X-ray lithography** X-ray beam lithography is similar to photolithography in its procedure. That also needs mask and photoresist; the difference is in the type of radiation. Compared to optical light radiation, now the X-ray radiations are used. As a special feature, the x-ray radiations are selectively absorbed by the resist to create the desired features. The resist materials thus are different than conventional photolithography. Using X-ray lithography, Furstner et al. [162] created regular patterns of spikes of 1 to 4 microns height (h) on silicon wafers. The spikes were of width (d) of 1 or 2 microns, with the distance between the spikes (a) varied from 1 to 5 microns. The structured wafer was hydrophobicized by sputtering a layer of gold and subsequent immersion in a hexadecanethiol solution and the height of the spikes (h) was also varied from. WCA of the surfaces varied from 113° to 161° depending on the pillar size, the clearance and the height of the spikes. A best self-cleaning surface was found with  $d/a = 2$  and  $h/d = 4$ .

## V. CONCLUSION

Not alone the plants, the superhydrophobic research has been extended to animals, insects and marine life as well, where a variety of microstructural features have been revealed and correlated to the observed wetting characteristics, including superhydrophobicity. The wetting related research on insects, spiders, lizards and frogs, other aquatic animals such as fish, sharks and birds, as reviewed in has revealed and confirmed the role of microstructure on the superhydrophobicity and related functionalities. Certain other interesting functionalities such as colour iridescences on butterfly wings or superhydrophilicity and superoleophobicity on fish scale, anti-fogging property on a moth eye and many others are described.

## REFERENCES

- [1] R.J. Daniello, N.E. Waterhouse, J.P. Rothstein, Drag reduction in turbulent flows over superhydrophobic surfaces, *Phys. Fluids*. 21 (2009). <https://doi.org/10.1063/1.3207885>.
- [2] B.J. Lee, Z. Zhang, S. Baek, S. Kim, D. Kim, K. Yong, Bio-inspired dewetted surfaces based on SiC/Si interlocked structures for enhanced-underwater stability and regenerative-drag reduction capability, *Sci. Rep.* 6 (2016) 1-11. <https://doi.org/10.1038/srep24653>.
- [3] F. Van Breugel, M.H. Dickinson, J. Meinwald, Superhydrophobic diving flies (*Ephydra hians*) and the hypersaline waters of Mono Lake, *Proc. Natl. Acad. Sci. U. S. A.* 114 (2017) 13483-13488. <https://doi.org/10.1073/pnas.1714874114>
- [4] F. Lin, L. Shuhong, L. Yingshun, L. Huanjun, Z. Lingjuan, Z. Jin, S. Yanlin, L. Biqian, J. Lei, Z. Daoben, Super-Hydrophobic Surfaces: From Natural to Artificial, *Adv. Mater.* (2002). <https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.200290020>.
- [5] A.B.D. Cassie, S. Baxter, WETTABILITY OF POROUS SURFACES, *Trans. Faraday Soc.* 40 (1944).
- [6] T. Kamegawa, Y. Shimizu, H. Yamashita, Superhydrophobic surfaces with photocatalytic self cleaning properties by nanocomposite coating of TiO<sub>2</sub> and polytetrafluoroethylene, *Adv. Mater.* 24 (2012) 3697-3700. <https://doi.org/10.1002/adma.201201037>.
- [7] S.S. Lathe, P. Sudhagar, A. Devadoss, A.M. Kumar, S. Liu, C. Terashima, K. Nakata, A. Fujishim, Mechanically bendable superhydrophobic steel surface with its self-cleaning and corrosion-resistant properties, *J Mater. Chem. A* 3 (2015) 10715-10722. <https://doi.org/10.1039/b000000x>.
- [8] J.F. Ou, X.Z. Fang, W.J. Zhao, S. Lei, M.S. Xue, F.J. Wang, C.Q. Li, Y.L. Lu, W. Li, Influence of Hydrostatic Pressure on the Corrosion Behavior of Superhydrophobic Surfaces on Bare and Oxidized 5807-5812. *Aluminum Substrates*, *Langmuir*. 34 (2018) <https://doi.org/10.1021/acs.langmuir.8b01100>.
- [9] K. Jayaramulu, K.K.R. Datta, C. Rösler, M. Petr, M. Otyepka, R. Zboril, R.A. Fischer, Biomimetic superhydrophobic/superoleophilic highly fluorinated graphene oxide and ZIF-8 composites for oil separation, *Angew. Chemie Int. Ed* 55 (2016) 1178-1182. <https://doi.org/10.1002/anie.201507692>.
- [10] H. Liu, J. Huang, Z. Chen, G. Chen, K.Q. Zhang, S.S. Al-Deyab, Y. Lai, Robust translucent superhydrophobic PDMS/PMMA film by facile one-step spray for self-cleaning and efficient emulsion separation, *Chem. Eng. J.* 330 (2017) 26-35. <https://doi.org/10.1016/j.cej.2017.07.114>.
- [11] M. Kharati-Koopae, M.R. Akhtari, Numerical study of fluid flow and heat transfer phenomenon within microchannels comprising different superhydrophobic structures, *Int. J. Therm. Sci.* 124 (2018) S36-546. <https://doi.org/10.1016/j.ijthermalsci.2017.11.004>.

- [12] J.P. Rothstein, Slip on superhydrophobic surfaces, *Annu. Rev. Fluid Mech.* 42 (2010) 89-109. <https://doi.org/10.1146/annurev-fluid-121108-145558>.
- [13] H. Ling, S. Srinivasan, K. Golovin, G.H. McKinley, A. Tuteja, J. Katz, High-resolution velocity measurement in the inner part of turbulent boundary layers over super-hydrophobic surfaces, *J. Fluid Mech.* 801 (2016) 670-703. <https://doi.org/10.1017/jfm.2016.450>.
- [14] H. Park, C.H. Choi, C.J. Kim, Superhydrophobic drag reduction in turbulent flows: a critical review, *Exp. Fluids.* 62 (2021) 1-29. <https://doi.org/10.1007/s00348-021-03322-4>.
- [15] C.W. Extrand, Repellency of the Lotus Leaf: Resistance to Water Intrusion under Hydrostatic Pressure, *Langmuir.* 27 (2011) 6920-6925. <https://doi.org/10.1021/Na201032p>.
- [16] P. Papadopoulos, L. Mammen, X. Deng, D. Vollmer, H.-J. Butt, How superhydrophobicity breaks down, *Proc. Natl. Acad. Sci. U S A* 110 (2013) 3254-3258. <https://doi.org/10.1073/pnas.1218673110>.



INTERNATIONAL  
STANDARD  
SERIAL  
NUMBER  
INDIA



# INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

 9940 572 462  6381 907 438  [ijirset@gmail.com](mailto:ijirset@gmail.com)



[www.ijirset.com](http://www.ijirset.com)

Scan to save the contact details