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Non-Wettable Surfaces – From Natural to Artificial and Applications: A Critical Review

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Abstract: Non-wettable surfaces have recently attracted significant attention due to their enormous promising applications. These applications are primarily due to their ability to repel liquid drops and remain unwetted. In this review, the various names used in describing non-wettable surfaces are given. This is followed by the fundamental theories of wetting. Natural non-wettable surfaces are then considered, along with their importance. Thereafter, we discuss how artificial non-wettable (biomimetic) surfaces are prepared. Next, the basic properties of non-wettable surfaces, which make them promising candidates for a wide range of applications, are discussed. Furthermore, the various applications of non-wettable surfaces are discussed, with references made to review articles with specific coverage of named applications. We conclude with a summary, challenges limiting the application of non-wettable surfaces to some real-life situations and possible suggestions to mitigate them as well as opportunities for future work.

Keywords: Wetting, biomimetic surfaces, non-wettable surfaces, contact angle, wetting theories

1 Introduction

By placing liquid drops on solid surfaces and observing the corresponding equilibrium apparent contact angle (also known as static contact angle), three kinds of solid surfaces have been distinguished. These surfaces are namely wettable, partially-wettable and non-wettable solid surfaces [1]. Consider placing a liquid drop on a relatively smooth solid surface at ambient conditions. The solid surface is said to be wettable by the liquid if the liquid drop spreads on it completely to form a thin liquid film with an associated equilibrium apparent contact angle θ value of 0° [Figure 1(i)]. If the liquid drop forms a hemispherical cap and

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$0 < \theta \leq 90^\circ$ [Figure 1(ii)], the solid surface is considered to be partially-wettable by the liquid. However, the solid surface is considered to be non-wettable by the liquid if the liquid drop forms a quasi-spherical cap with $\theta \gg 90^\circ$ [Figure 1(iii)] and can easily roll off. The spreading coefficient $S = \gamma_{sa} - \gamma_{sl} - \gamma_{la}$, where γ_{sa} , γ_{sl} and γ_{la} are the solid-air, solid-liquid and liquid-air interfacial tensions, respectively, determines whether a liquid drop will spread or not. For partial-wetting and non-wetting, $S < 0$ while S is positive for complete wetting [1]. Wettable surfaces are said to be “philic” with respect to the liquid under consideration [2]. When the liquid is water, the surface is said to be *hydrophilic* and *oleophilic* when the liquid is oil. Wettable surfaces have high affinity for the molecules of the liquid under consideration whereas non-wettable surfaces, which are the focus of this review paper, have little affinity for the molecules of the liquid under consideration [3]. Non-wettable surfaces are said to be “phobic” with respect to the liquid under consideration [2]. For example, the surface is said to be *hydrophobic* or *oleophobic* when the liquid is water or oil, respectively [4]. Some surfaces are both hydrophobic and oleophobic and are said to be omniphobic or panphobic. For these surfaces, θ is always higher than 90° . For cases where $\theta \gg 90^\circ$ (typically $\geq 150^\circ$), the surfaces are said to be superhydrophobic or superoleophobic when the liquid is water or oil, respectively [5]. Correspondingly, surfaces that are both superhydrophobic and superoleophobic are said to be superomniphobic [6]. Sometimes surfaces are also described as ultrahydrophobic, ultraoleophobic and ultraomniphobic when they display superhydrophobic, superoleophobic and superomniphobic characters, respectively [7]. Partially-wettable surfaces are said to be either partially-’philic or

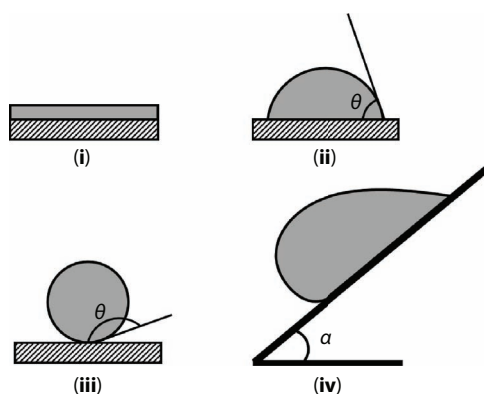


Figure 1 Schematics of (i) wetting, (ii) partial-wetting, and (iii) non-wetting solid surfaces. For wetting, the liquid drop spreads completely on the solid surface, forming a thin liquid film with an associated contact angle θ of 0° . The liquid drop partially wets the solid surface, giving rise to $\theta < 90^\circ$ for the partial-wetting case. The liquid drop insignificantly wets the solid surface with $\theta \gg 90^\circ$ for the non-wetting case. The schematic in (iv) shows the sliding angle α .

partially- ϕ phobic with respect to the liquid being considered. The suffixes “philic” and “phobic” stem from Greek meaning “having affinity for” and “lacking affinity for”, respectively. To denote the quality or condition of “having affinity for” or “lacking affinity for”, “philicity” and “phobicity”, respectively are used.

In addition to θ , the sliding angle α [Figure 1(iv)] is used to study the adhesion property of solid surfaces. The α is the minimum inclination angle required for a drop to slide on an inclined solid surface [8]. “Philic” surfaces have high sliding angles while “phobic” surfaces have low sliding angles. Lastly, the degree of surface roughness dictates the contact angle hysteresis $\Delta\theta$, the difference between the advancing θ_A and the receding contact angles θ_R [9]. The advancing contact angle is formed when the drop is advancing on the solid surface, Figure 2(i), while the receding contact angle is the angle formed when the drop is retracting from the solid surface, Figure 2(ii). For a liquid drop on a solid surface inclined at a certain angle, Figure 2(iii), the contact angle of the drop at the rear is the receding angle while that at the front is the advancing angle [10]. The magnitude of the advancing angle is always higher than that of the receding angle. Smooth surfaces have high hysteresis as opposed to rough surfaces which have low hysteresis. It must be remembered that the description of surface wettability with respect to contact angle is in terms of the advancing contact angle.

Non-wettable surfaces are relevant to many plants, animals and human beings. The non-wetting nature of the lotus (*Nelumbo nucifera*) and wild pansy (*Viola tricolor*) leaves is important for “self-cleaning”, i.e. the removal of dust particles and other unwanted solid substances from their surfaces by water drops that roll unhindered on them [11]. The superhydrophobic nature of the leaves of rice (*Oryza sativa*) enables them to hold gas under water, allowing the plant to photosynthesize, at least for three days, when submerged [12]. The superhydrophobicity of the wings of many insects like butterfly, dragonfly, termite, flies, cricket, mosquito and

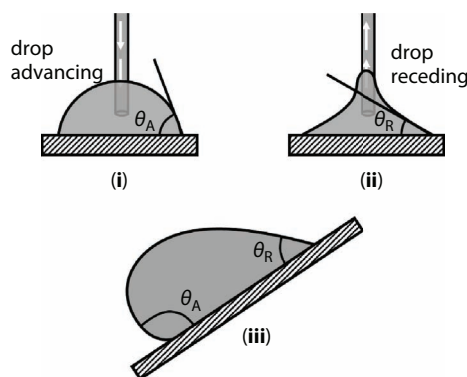


Figure 2 Schematics of (i) advancing θ_A and (ii) receding θ_R contact angles, and (iii) the advancing (front) and receding (rear) contact angles for a drop on an inclined plane.

mayfly ensures that they remain free from dust or particle contamination as well as are able to fly in humid environments [13]. Also, due to their superhydrophobic nature, the eyes of flies, cricket, mosquito and other insects are anti-reflective and anti-fogging and their vision is not affected by light intensity and humid weather [14]. The ability of insects to walk on water is supported by the superhydrophobic nature of their legs [14]. For mankind, non-wetting materials have attracted applications in the fabrication of self-cleaning surfaces, anti-fogging windows, anti-corrosive surfaces, drag reduction surfaces and efficient water transport channels. Therefore, this paper reviews non-wettable surfaces in nature as well as those fabricated (artificial) using various methods. The paper also highlights the properties and the numerous applications of these surfaces.

2 The Basic Wetting Models

There are three basic wetting models, namely the Young, the Wenzel and the Cassie-Baxter wetting models. These wetting models are also called “wetting theories” or “wetting states” and they relate the equilibrium apparent contact angle to the liquid-air, solid-air and solid-liquid interfacial tensions [Figure 3(i)] that come into play when a liquid drop rests on a solid surface. Let the equilibrium apparent contact angle for an atomically smooth surface be θ while that for a rough surface be θ^* . According to the Young wetting model, the relationship between θ and the interfacial tensions for a static liquid drop on an atomically smooth solid surface is given by Equation (1) [15,16].

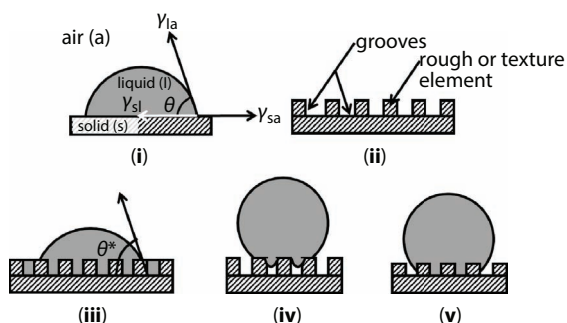


Figure 3 (i) Sketch of the action of the solid-liquid (γ_{sl}), liquid-air (γ_{la}) and solid-air (γ_{sa}) interfacial tension forces on a liquid drop placed on the surface of an atomically smooth solid substrate and how the forces are related to the equilibrium contact angle θ . (ii) Sketch of a rough surface showing the grooves and texture elements. Illustrations of the (iii) Wenzel and (iv) Cassie-Baxter wetting models. (v) Sketch of the impaled wetting state where the texture element spears the drop.

$$\cos\theta = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} \quad (1)$$

The γ_{sa} is also called the solid surface free energy while θ is also called the Young's angle. The "philic" surfaces ($\theta < 90^\circ$) have relatively high γ_{sa} while the "phobic" ones ($\theta > 90^\circ$) have relatively low γ_{sa} . For example, the surface free energy of glass (hydrophilic) is $\sim 96 \text{ mJ m}^{-2}$ while that for Teflon (hydrophobic) is $\sim 18 \text{ mJ m}^{-2}$ [17]. In the Young's wetting state, the contact angle hysteresis is very high and as a result the sliding angle is also high. Only very few solid surfaces are smooth in nature and for rough surfaces the Wenzel and the Cassie-Baxter wetting models are used to describe the relationship between θ^* and the interfacial tensions. Roughness modifies the equilibrium contact angle. Roughness lowers the equilibrium contact angle for "philic" surfaces, but increases it for "phobic" surfaces. Rough surfaces are also called "textured surfaces" and are characterized by grooves and texture elements, Figure 3(ii). According to the Wenzel wetting model, the liquid drop fills the spaces between the grooves, Figure 3(iii). The relationship between θ^* , due to roughness, in the Wenzel model, and θ in the Young model is given in Equation (2) [18],

$$\cos \theta^* = r \cos \theta \text{ where } \cos \theta = (\gamma_{sa} - \gamma_{sl}) / \gamma_{la} \quad (2)$$

in which r is the roughness factor characterizing the degree of roughness. The r (≥ 1) is the ratio of the total surface to the projected surface. Equation (2) indicates that for $\theta < 90^\circ$ ("philic" surfaces), θ^* decreases when r increases, but increases when r increases for $\theta > 90^\circ$ ("phobic" surfaces). It should be noted that Equation (2) changes to Equation (1) when $r = 1$ (smooth surfaces). When r is large, air is trapped within the grooves of the rough surface and the Wenzel wetting model transitions to the Cassie-Baxter model, Figure 3(iv). Drops in the Cassie-Baxter model are said to be in a 'fakir state' while those in the Wenzel model are said to be in 'inverse fakir state'. Intermediate between these models is the 'impaled state' where the rough elements on the solid surface spear the liquid drop as shown in Figure 3(v). According to the Cassie-Baxter wetting model, the liquid drop sits on top of the texture element and the relationship between θ^* due to roughness and the equilibrium contact angle in the Young model is [19]:

$$\cos \theta^* = \phi - 1 + \phi \cos \theta \quad (3)$$

The ϕ (< 1) is the ratio of the area of the rough element top to that of the total area of the surface. As ϕ approaches 0, $\cos \theta^*$ approaches -1 . In other words, θ^* approaches 180° . The Cassie-Baxter wetting state is important for the creation of non-wettable solid surfaces which repel liquid drops. However, a transition

from the Cassie-Baxter to the Wenzel wetting state is also possible. This occurs, for example, when a liquid drop in the Cassie-Baxter wetting state is pressed physically so that Equations (3) and (2) are obeyed before and after transition, respectively. The substitution of Equation (2) into (3) gives the threshold angle θ_{Th} [Equation (4)]:

$$\cos \theta_{\text{Th}} = \frac{\phi - 1}{r - \phi} \quad (4)$$

between the two wetting states. If $\theta < \theta_{\text{Th}}$, the trapped air pockets [shown in Figure 3(iv)] are metastable and the Wenzel wetting state results. The Cassie-Baxter wetting state results when the rough solid surface is “phobic”, $\theta > \theta_{\text{Th}}$ and the trapped air pockets are stable. Finally, contact angle hysteresis is quite small in the Cassie-Baxter wetting state and thus causes the sliding angle to be small. This can be compared with the Wenzel wetting state where both the hysteresis and the sliding angle are high.

3 Non-Wettable Surfaces

3.1 Non-Wettable Surfaces in Nature: Their Importance to Plants and Animals

The leaves of many plants [11] and many other surfaces of biological origin [20] have the inherent ability to repel water and remain unwetted. This is intriguing and it is now the basis for the fabrication of many non-wettable surfaces [21], frequently referred to, in scientific literature, as biomimetic surfaces as they are inspired by surfaces of biological origin. Biomimetic simply means mimicking biology or nature. Although, Bhushan and Jung [20] and Darmanin and Guittard [13] have given an extensive review of these surfaces, a brief summary will be given here so that the reader can have an idea about the basic nature of these surfaces. A common feature of these surfaces is that they are rough and hierarchical, with structural dimensions ranging from micrometres to nanometres. This is evident from the work of Neinhuis and Barthlott [22]. Using scanning electron microscopy (SEM), they studied the microstructure of the epidermal surfaces of 200 water-repellent plant leaves. Their study revealed the presence of convex papillae, coated with nanoscopic wax crystals (~10 to ~100 nm), on the plant leaves. This can be compared with plants with water-wettable leaves which have smooth surface and are not coated by wax crystals [23,24]. The wax crystals, composed of hydrocarbons, e.g. n-hexatriacontane [25], roughen the leaves surfaces. Values of θ^* ranging from 150 to 164° were recorded on the leaves surfaces for water drops (4–14 μL) [22]. For example, the lotus (*Nelumbo nucifera*) leaves are superhydrophobic, giving $\theta^* \sim 162^\circ$ [Figure 4(a)] with water drops, and hence repel water [25]. The leaves are reported to have a hydrophobic wax (composed of

nonacosane-10,15-diol and nonacosane-10-ol) [25] coating as well as rough and hierarchical “microbumps” superimposed with nanostructures [Figure 4(b-d)]. Water drops on the leaves are in the Cassie-Baxter wetting state. The leaves of rice (*Oryza sativa*) are also superhydrophobic [Figure 4(e)] with $\theta^* = 162^\circ$ for water drops [22, 26]. The leaves have parallel microgrooves with the epidermic layer decorated with papillae [Figure 4(f-g)] [27]. As a result, the leaves exhibit anisotropic or directional wetting property, such that water drops remain stuck to the leaves if inclined in the direction perpendicular to the microgrooves, but move if inclined in the direction parallel to the microgrooves. Due to the presence of wax-covered convex papillae, the leaves of the fossil tree (*Ginkgo biloba*), mottlecah (*Eucalyptus macrocarpa*) and bell-fruited mallee (*Eucalyptus preissiana*) are superhydrophobic ($\theta^* = 162^\circ$ for water drops) [22]. The leaves of cabbage (*Brassica oleracea*), wood spurge (*Euphorbia amygdaloides*) and cocoyam (*Colocasia esculenta*) possess wax-covered convex papillae and are also superhydrophobic. Similar observations were made on peanut (*Arachis hypogaea*) leaves [28]. The value of θ^* for water drops on the surfaces of these leaves ranges from 150 to 164° [22] with a relatively high adhesion force such that the drop remains stuck even if turned over. The rough and superhydrophobic nature of the leaves of these plants

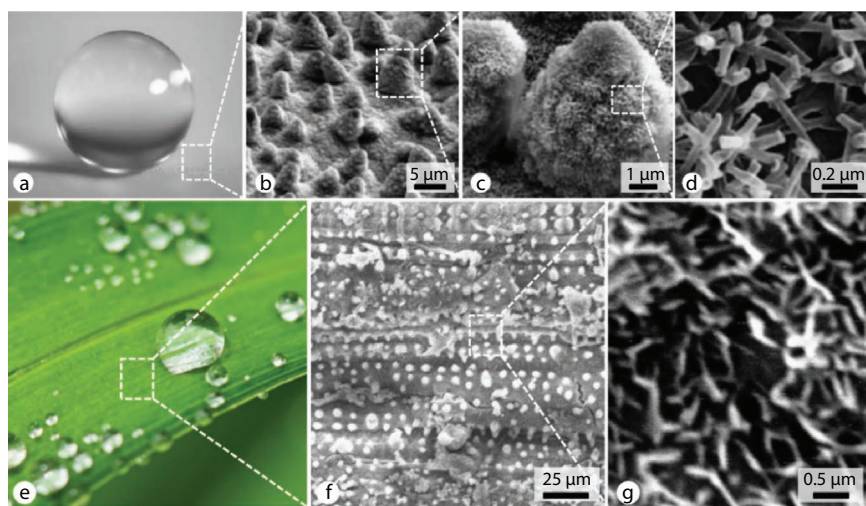


Figure 4 (a) Photograph of a quasi-spherical water drop on the surface of a Lotus leaf. (b)-(d) SEM micrographs of the Lotus leaf surface, at increasing magnifications, showing its rough hierarchical microstructure. Reprinted from ref. [25], with permission from the Royal Society Publishing, London. (e) Photograph of quasi-spherical water drops on the surface of a rice leaf. Reprinted from ref. [141], under the Creative Common Attribution License of MDPI. (f) and (g) SEM micrographs of the rice leaf at increasing magnifications, showing its rough hierarchical microstructure. Reprinted from ref. [135], with permission from Elsevier.

is important for “self-cleaning”: a water drop on the leaves surfaces rolls over, carrying along dust particles and other dirt and leaving them clean [11]. The dirt can be toxins, salts or other biologically unwanted species that arrive the leaves surfaces as aqueous solution. Self-cleaning keeps the surface free from pathogens, e.g. bacteria or fungal spores, minimizing the risk of infection. The removal of dust particles also reduces the risk of plant overheating [29].

Similarly, the feathers of many birds [30,31] and the wings of certain insects [32], the feet and bodies (e.g. legs) of certain reptiles and arthropods are also superhydrophobic [33] and have been observed to be textured, with hierarchical nano or microstructures [34]. Feathers primarily enable birds to fly. However, they also insulate them from cold and moisture. The coloration of feathers also provide birds with camouflage. Feathers are made up of a backbone (rachis) which supports numerous barbs, interlinked with millions of barbules [Figure 5(a)]. The hydrophobicity of bird feathers is primarily a function of the interplay of their hierarchical textural structure [Figure 5(b-d)] and the presence of oils produced by the spleen glands [30,31]. This oil is constantly applied to the plumage in birds. Unfortunately, external oils, e.g. those due to spillage are fatal to birds. Water drops on bird feathers are in the Cassie-Baxter state with high θ^* values (154–164°) as shown in Figure 5(e) for a pigeon feather and low hysteresis (5–7°), with a Cassie-Wenzel transition occurring as the drops evaporate [30]. Based on this, Liu *et al.* [31] have mimicked the microstructure of duck feathers on textile substrates so as to create water-repellent materials.

The wings of many insects like butterflies, *Parnassius glacialis*, Figure 6(a), and dragonflies are also rough with multiple hierarchical micro or nanostructures [Figure 6(b)] and are non-wetted by water drops [34–36]. Water drops on the wings are in the Cassie-Baxter state (with values of θ^* between 121 and 168°) with transition to the Wenzel state occurring when the ratio of the depth of the hierarchical structure to its size (average diameter or width) is above 20 [34]. Because they are non-wetted by water drops, the wings remain clean of dust and other particle contamination, via the self-cleaning mechanism, like plants with hydrophobic leaves. The hydrophobicity of the wings is also important in

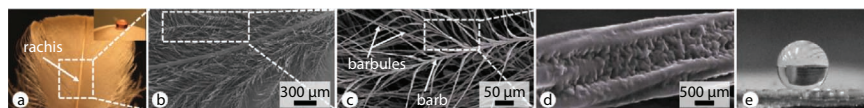


Figure 5 (a) Photograph of part of a duck feather, with a quasi-spherical water drop in the inset, showing the rachis. (b)–(d) SEM micrographs of the duck feather, at increasing magnifications, showing its rough hierarchical microstructure. Reprinted from ref. [31], with permission from the Institute of Physics. (e) An image of a water drop on the surface of a pigeon feather. The water drop is in the Cassie-Baxter wetting state. Reprinted from ref. [30], with permission from Elsevier.

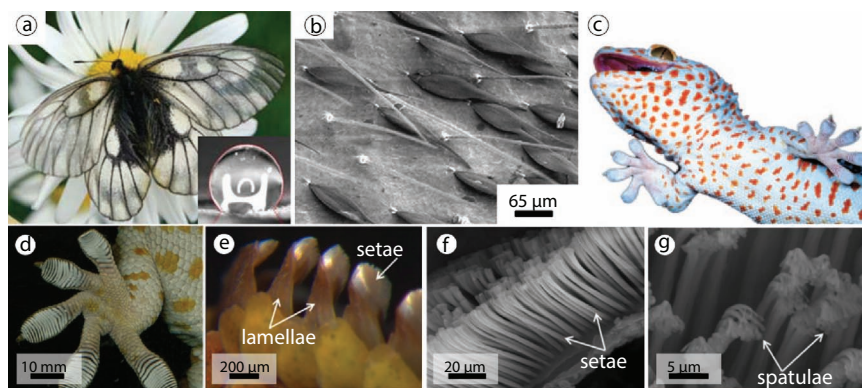


Figure 6 (a) Photograph of a transparent butterfly (*Parnassius glacialis*) with a water drop on one of its wings (inset). (b) SEM micrograph of a wing of *Parnassius glacialis* showing its textured microstructure. Reprinted from ref. [36], with permission from Springer. (c) Photograph (ventral view) of a gecko. Reprinted from ref. [39], © 2005 National Academy of Sciences USA. (d) Photograph of a gecko toe pad. (e)-(g) SEM micrographs of a gecko toe pad, showing its rough hierarchical microstructure. Reprinted from ref. [41], with permission from the Royal Society, London.

flight. In addition, the hierarchical microstructure is responsible for the beautiful coloration observed in some flies, e.g. butterflies, especially if they diffract light and induce interference. The color depends on the magnitude of the microstructure—the smaller the structure, the brighter the color and vice versa [36–38]. Lastly, for butterflies, the microstructures overlap in only one direction and leads to directional adhesion, i.e. a drop of water on a wing is able to roll only in the direction of overlap. The feet of reptiles, with gecko as a model example, are also hierarchical with thousands of keratinous hairs (setae). Each seta contains numerous submicrometer-sized textures (spatula ~ 200 nm) on its tip. This arrangement enables them to adhere to walls firmly, via van der Waals forces, as well as detach from them rapidly even if smooth and it is also responsible for their self-cleaning. Here, self-cleaning is not due to hydrophobicity, but because the setae are adhesive and can self-clean when dried [39] and this mechanism has inspired the creation of self-cleaning adhesives [40]. This notwithstanding, the hierarchical gecko toe pad is superhydrophobic, $\theta^* = 150\text{--}160^\circ$ with hysteresis of $2\text{--}3^\circ$ for water drops [41–44]. The water drop adheres strongly (with a force of $10\text{--}60\text{ }\mu\text{N}$) to the toes [44] and does not fall off even when turned upside down. The gecko's toes maintain a Cassie-Baxter state, even under water, and this is responsible for their ability to adhere to wet surfaces [41]. Geckos bodies are hierarchical and also hydrophobic and this protects them from water loss when on land and mechanical damage and enables them to keep clean [45].

The superhydrophobicity of the legs of pond skaters (*Gerris remigis*) is responsible for their ability to walk on water [Figure 7(a-b)] without becoming wet [46-48]. These insects are found on the surfaces of slow streams, ponds and quiet waters and are able to walk on them without sinking even when pushed by a rain drop that is heavier than their weight. Evidence from SEM [Figure 7(c-d)] shows that their legs are hierarchical with numerous hairs (setae) of diameter $\leq 3 \mu\text{m}$ and $\sim 50 \mu\text{m}$ long, nano-grooves and covered with cuticle wax. The setae are inclined to an angle of $\sim 20^\circ$ to the surface of the leg. The water contact angle of a water skater's leg is $\sim 167^\circ$. Although the maximum supporting force of a single leg of the insect is around $1.52 \times 10^{-3} \text{ N}$, about fifteen times its total body weight, it does not pierce the water surface unless a dimple of depth 4.4 mm is formed [32]. Water collection is a problem in the desert for many insects, e.g. the darkling beetle, and those with patterned non-wettable surfaces use this structural feature to surmount the problem. The darkling beetle lives in the Namib Desert (South Africa). The

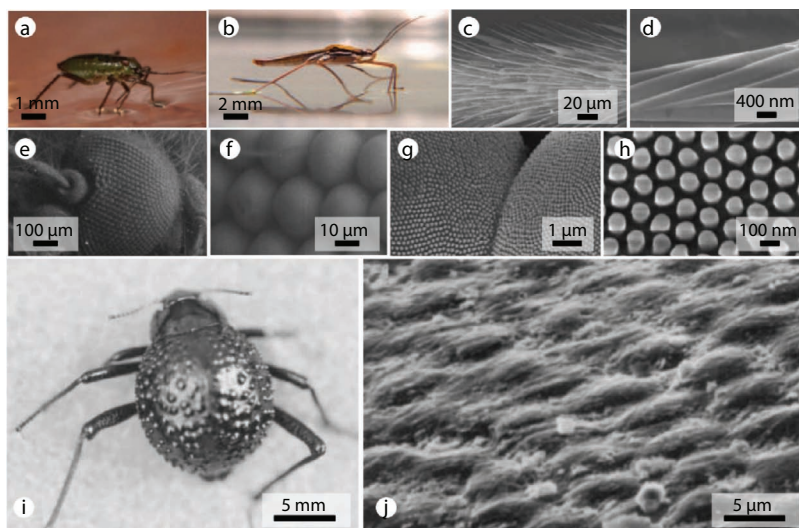


Figure 7 Photographs of water-walking arthropods on a water surface: (a) water measurer *Hydrometra stagnorum* and (b) water strider *Gerris*. Reprinted from ref. [48], with permission from Elsevier. (c)-(d) SEM micrographs of one of the legs of the insect in (b) at different magnifications revealing its rough microstructure. Reprinted from ref. [32], with permission from Nature Publishing Company. (e)-(h) SEM images of a mosquito eye at increasing magnifications, showing its inherent rough hierarchical microstructure. Reprinted from ref. [51], with permission from Wiley-VCH. (i) Photograph of the dorsal view of a female adult desert beetle (*Stenocara sp.*) showing peaks and troughs on the wings, and (j) SEM image of the insect's wing, where the rough microstructure is clearly visible. Reprinted from ref. [49], with permission from Nature Publishing Company.

body surfaces of the insect are bumpy with wax-coated alternating hydrophobic regions and hydrophilic regions not coated by wax. To collect water, the insect crouches, raising its back facing toward the wind during the wind-driven morning fog. The fog condenses on the front fused wings and the water collected rolls down the surfaces of the insect into its mouth. The collection of water is possible due to the bumpy non-wettable and wettable regions [49]. This mechanism of water collection has been confirmed by experiments consisting of surfaces with alternating hydrophobic and hydrophilic regions and artificial fog. Applications of such surfaces are said to range from biomedical applications [50], water-trapping tents and building coverings to anti-fogging coatings [33]. Another example of a natural non-wettable surface is the eye of a mosquito (*Culex pipiens*). Evidence from SEM micrographs [Figure 7(e-h)] shows that the eye is textured with numerous micrometer-sized spherical structures, known as ommatidium (diameter 26 μm), arranged in a hexagonal close-packed manner, which act as sensory units [51]. Each ommatidium is coated with nanometer-sized nipples (diameter 101 nm and pitch 47 nm). Due to this hierarchical arrangement, the mosquito eye is superhydrophobic and is non-wetted by fog [46,47]. This ensures a good vision even during fog [51].

Some natural surfaces are also non-wettable to oil. For example, the upper side of the lotus leaf exposed to air is superhydrophobic while the lower side exposed to water is superoleophobic ($\theta^* > 150^\circ$ for oil drops). This surface is made up of numerous textured (200–500 nm) tubular slightly convex micropapillae (length 30–50 μm and width 10–30 μm) [52]. On this basis, a Janus material, with the upper side non-wettable by water and the lower side non-wettable by oil has been fabricated. The upper and lower sides were mimicked by using poly(dimethylsiloxane) and epoxy resin, respectively. The Janus material was able to float on water just like the lotus leaf [52]. The scales on fishes are also superoleophobic and are not wettable by oil. This property protects them during oil spillage [53]. Leafhoppers are another example of superoleophobic structures in nature [54]. Leafhoppers are able to produce highly textured spherical (diameter 200–700 nm) honeycomb-shaped hollow particles known as bronchosomes as shown in Figure 8(a,b). These structures coat their integuments uniformly and densely. Because these structures are superoleophobic, they are not wettable by oil and protect them from contamination by plant sap. Also, because they are loosely attached to their bodies and thus erodible, they lower the risk of being captured by predators. The superoleophobic nature of these structures is due to a combination of their re-entrant curvature and protein coating. Although the bronchosomes-coated surfaces are wettable by ethanol, the values of θ^* for water, ethylene glycol and diiodomethane drops which do not wet them are reported to be $165\text{--}172^\circ$, $153\text{--}164^\circ$ and $148\text{--}156^\circ$, respectively [54]. The bodies of springtails, skin-breathing arthropods that live in the soil, are also not wettable by oils [55–59]. Their bodies are covered by cuticle with highly ordered hexagonal [Figure 8(c–e)] or rhombic comb-like [Figure 8(f–h)] micro/nano structures. Their surfaces are not wettable by polar liquids like

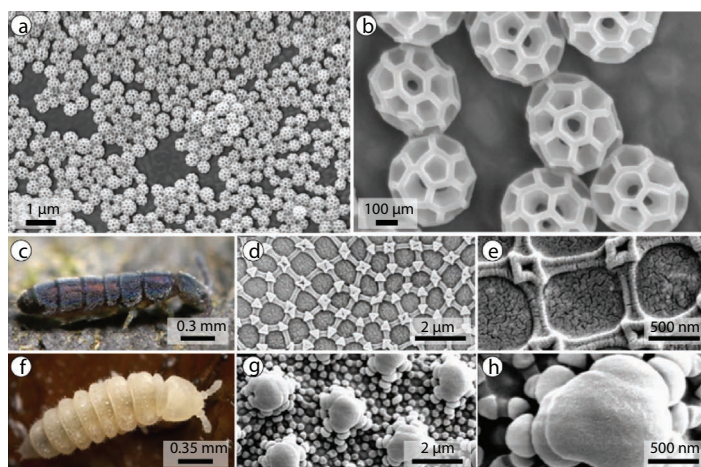


Figure 8 (a,b) SEM micrographs of the surface of leafhopper at a low and high magnification, showing the superoleophobic bronchosomes. Reprinted from ref. [54], with permission from Royal Society Publishing. (c) Photograph of a springtail (*Tetradontophora bilanensis*) and (d)-(e) corresponding SEM images of the springtail at a low and high magnification. (f) Photograph of a springtail (*Orthonychiurus stachianus*) and (g)-(h) corresponding SEM images of *Orthonychiurus stachianus* at a low and high magnification. The SEM images show the textured nature of the superoleophobic surfaces. Reprinted from ref. [56], with permission from Springer.

water, methanol, ethanol as well as many non-polar liquids (oils) like hexadecane and tridecane. The nanostructured cuticle of a springtail, e.g. *Tetradontophora bilanensis*, is reported [55] to be composed of three different layers, namely the inner, the epicuticular, and the outer cuticle layers. The inner layer is made up of lamellar chitin skeleton with numerous pore channels. The epicuticular layer is made up of chemicals like glycine, tyrosine and serine while the outer layer is made up of chemicals like hydrocarbon acids and esters, steroids and terpenes. The chemical composition of the cuticle as well as its nanostructure are responsible for the observed superoleophobicity of springtail [55].

3.2 Artificial Non-Wettable Surfaces

Artificial non-wettable surfaces are fabricated surfaces, i.e. not of biological origin, which are not wetted by liquid drops. Because they are inspired by biological species, plants and animals alike, whose surfaces are not wetted by liquid drops, they are often called 'bioinspired non-wetting' or biomimetic surfaces. Just like their biological counterparts, these surfaces are highly textured with micro or nanostructures. In addition, they are coated with non-polar groups like alkyl groups, silicones $-\text{Si}(\text{CH}_3)_2\text{O}-$ or fluorocarbons $-\text{C}_n\text{F}_{2n+1}$ and as a result they have low

surface free energy [60]. Due to their textured nature, liquid drops are either in the Wenzel or Cassie-Baxter wetting state. These surfaces have numerous applications. They are the basis for the creation of self-cleaning surfaces, anti-fog windows and drag-reduction systems. They also offer an efficient way for liquid transportation. Their applications in medicine range from high-throughput cell culture platforms to biomedical devices.

By extension, wettable powdered particles (nm– μ m) are also rendered non-wettable when coated with suitable organic groups. This has given rise to hydrophobic, oleophobic, omniphobic, superhydrophobic, superoleophobic and superomniphobic powdered particles. By contrast to their wettable (hydrophilic or oleophilic) counterparts which are wetted by liquids, these particles are unwetted and remain on the liquid surfaces [61]. The three-phase contact angle is 0° for wettable very hydrophilic or oleophilic particles, $0^\circ < \theta < 90^\circ$ for the hydrophilic or oleophilic particles and $>90^\circ$ for the hydrophobic, oleophobic or omniphobic non-wettable particles. For superhydrophobic, superoleophobic or superomniphobic non-wettable particles $\theta \gg 90^\circ$ (normally $\geq 150^\circ$). This is illustrated in Figure 9 for a spherical particle at a liquid-air interface [62]. Non-wettable particles are especially

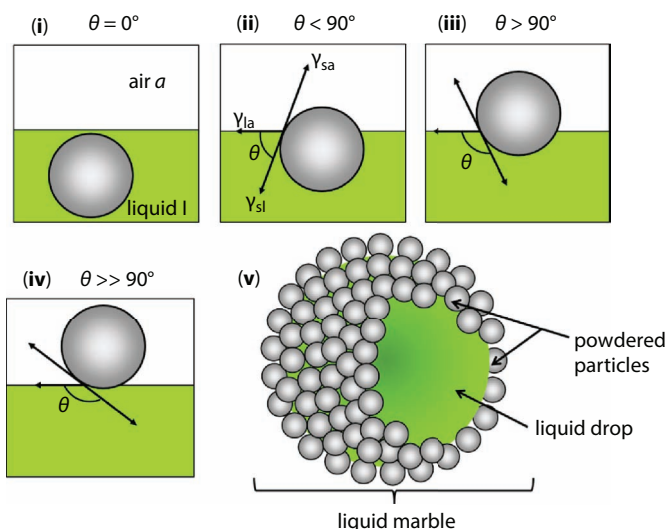


Figure 9 Sketches of a spherical particle at a liquid-air interface: (i) particle is very hydrophilic or oleophilic and is totally wetted by the liquid, (ii) particle is hydrophilic or oleophilic and is partially wetted by the liquid, (iii) particle is hydrophobic or oleophobic and is partially wetted by the liquid and (iv) particle is superhydrophobic or superoleophobic and is partially wetted by the liquid. (v) Schematic of a liquid marble showing the liquid drop and the enwrapping powdered particles.

important in the preparation of liquid marbles and other novel colloidal systems. Liquid marbles, Figure 9(v), are non-stick millimetre-sized liquid-in-air drops formed by wrapping liquid drops with powdered particles that poorly wet them [63]. Detailed information on the formation, characterization and applications of liquid marbles has been given by Tyowua [2].

3.3 Preparation of Non-Wettable Surfaces

In line with natural non-wettable surfaces, which are decorated with nano- and or microstructures with a wax overlaying film, the preparation of non-wettable surfaces from wettable ones involves the construction of nano- to microstructures on them [11, 22]. This is followed by surface chemistry modification using suitable organic or inorganic molecules that also decrease the surface free energy, crucial for achieving non-wettability [60]. The construction of nano- or microstructure is achieved via different methods like lithography, etching, deposition, deformation, and transfer [20]. Lithography is the art or a process of transferring a pattern onto a surface. The process includes photo (also called optical or ultraviolet) lithography, electron-beam (also E-beam) lithography, X-ray lithography, and soft lithography [64]. Photolithography uses light to pattern a surface, electron-beam lithography uses an electron beam to trace a pattern on a surface, X-ray lithography uses X-rays to make a geometric pattern on a surface while soft lithography imparts patterns of organic molecules or other materials like metals and ceramics on surfaces using mechanical processes like molding, embossing or printing [64]. Lithography has high accuracy and can be applied to a large surface. However, it is slow and expensive [20]. Etching refers to the process of making patterns on surfaces by removing part of them [65]. It involves plasma etching which uses plasma discharge [66], laser etching which uses laser beam [65], chemical etching which uses corrosive chemicals like concentrated acids and bases [67] and electrochemical etching which uses an electrolytic cell to etch the material [68]. Etching is fast, but it is difficult to control and the chances of chemical contamination are very high [20]. Deposition involves dip coating, spin-coating, spray-coating, adsorption, self-assembly, anodization, electrochemical, evaporation, plasma and chemical vapor deposition (CVD) [69]. Deposition is flexible and inexpensive, but it is difficult to control and often involves high temperature [20]. Deformation involves stretching or extension while transfer involves casting and nanoimprinting. Deformation is precise, but expensive. The choice of technique depends on the material or surface under consideration and availability of the necessary equipment.

Examples of different non-wettable surfaces reported in literature are summarized in Table 1, where the name of the material or surface, method of preparation, reagent, property and contact angle of liquid drops with the associated references are given. Although this is not a complete list of all the surfaces reported in the literature, it gives an idea of how various surfaces have been rendered non-

Table 1 Examples of materials or surfaces that have been rendered non-wettable by various methods and chemical coating and their property (in terms of texture) and the associated contact angle θ^* reported in literature.

Material/Surface	Method	Chemical coating	Surface property	$\theta^*/^\circ$		Reference(s)
				Water	Oil	
Teflon	Plasma lithography			168		[71]
	Extension			165		[72]
	Sanding (using sandpaper)			128–151		[73,74]
	Laser irradiation			170		[75]
Metal surfaces						
Oxidized Al & Ti	CVD	1,3,5,7-tetramethylcyclotetra-siloxane	Textured (500 nm–4 μ m)	163		[76]
Al, Cu & Zn	Chemical etching	Tridecafluorooctyl-triethoxysilane		>150		[79]
Cu	Electrodeposition		Textured with pillared structures (diameter and separation ~40 μ m)	160		[83]
Au	Electrochemical polymerization	Poly(3,4-ethylenedioxyppyrole)	Textured		153 (H)	[89]
Al	Anodic oxidation	Perfluorodecyl phosphate or perfluorododecyl phosphate	Hierarchically textured	>150	150 (R, H)	[82]
Si	Photolithography			170		[80]
Si	E-beam lithography			164		[81]

(continued)

Table 1 Examples of materials or surfaces that have been rendered non-wettable by various methods and chemical coating and their property (in terms of texture) and the associated contact angle θ^* reported in literature. (Continued)

Material/Surface	Method	Chemical coating	Surface property	$\theta^*/^\circ$		Reference(s)
				Water	Oil	
Si	X-ray lithography	Poly(methyl methacrylate)	Textured (25 nm)	>166		[84]
Si	Nanocasting	Poly(dimethylsiloxane)	Textured (6 μm)	158–160		[85,86]
Si	Au-assisted electroless etching	Perfluorooctyl trichlorosilane	Hierarchically textured	>150	151 (H)	[87]
Si	Ion etching + CVD	C_4F_8	Textured (nanonail structures)		~155 (Alc)	[88]
ZnO , TiO_2 nanorods	Sol-gel		Nanorods (length 0.2 μm)	161		[90]
TiO_2 nanotubes	Laser micromachining + anodization	Perfluorooctyl trichlorosilane	Micropillars		155 (H)	[91]
SiO_2	Lithography or dip-coating	Fluorodecyl POSS ¹ or fluorodecyl POSS ²	Textured with pillars (height 300 nm)	>150	>150 (P, H)	[78]
ZnO particles	Chemical modification	Perfluoroalkyl phosphate	Textured	127	120 (O)	[77]
ZnO on glass slide + polymer	Spray-casting	Perfluoroalkyl methacrylic copolymer	Hierarchically textured		154	[92]

(continued)



Table 1 Examples of materials or surfaces that have been rendered non-wettable by various methods and chemical coating and their property (in terms of texture) and the associated contact angle θ^* reported in literature. (Continued)

Material/Surface	Method	Chemical coating	Surface property	$\theta^*/^\circ$		Reference(s)
				Water	Oil	
Au clusters	Electrochemical deposition	Mixture of PDDA and PSS	Textured with dendritic structures	156–173		[93]
Carbon nanotubes	CVD	Poly(tetrafluoroethylene)	Textured with nanotubes (diameter 50 nm & height 2 μ m)	170		[94]
	CVD	ZnO	Hierarchically textured	159		[95]
	Replication and spray coating		Hierarchically textured	170		[96]
Silica	Acid etching with $\text{H}_2\text{SO}_4/\text{HNO}_3(1:1)$ + chemical treatment	Fluoroalkylsilane (HFDMS)	Hierarchically textured	171	161 (R)	[97]
	Sol-gel	Fluoroalkylsilane		150		[98]
	Layer-by-layer assembly	Fluoroalkylsilane (PFDT)	Hierarchically textured	160		[99]
Silica-polydopamine-silver hybrid particles coated surfaces	Coating	Fluoroalkylsilane (PFDE)	Hierarchically textured	155–172		[100]
Silica particles	Spin-coated on glass slides	Fluoroalkylsilane (TDF)		130–149	>136	[101]

(continued)



Table 1 Examples of materials or surfaces that have been rendered non-wettable by various methods and chemical coating and their property (in terms of texture) and the associated contact angle θ^* reported in literature. (*Continued*)

Material/Surface	Method	Chemical coating	Surface property	$\theta^*/^\circ$		Reference(s)
				Water	Oil	
	Spin-coating	Perfluoroalkyl methacrylic copolymer	Hierarchically textured		~150 (H)	[102]
Fabric materials						
Polyester fabrics	Dip-coating	Fluorodecyl POSS ¹	Highly textured	>150	150 (H)	[103]
PMMA mat	Electrospinning	Fluorodecyl POSS ³	Highly textured	>150	156 (H)	[78]
PMMA	Electrospinning	Fluorodecyl POSS ¹	Highly textured	150		[104]
Polystyrene web	Electrospinning	Polymers (over 30)	Highly textured	>150		[105]
Sericite (clay particles)	Chemical modification	Perfluoroalkyl phosphate	Textured	148	118 (H)	[106]

PDDA=Poly(diallyldimethylammoniumchloride), PSS=Poly(4-styrenesulfonate), PFDT=1H,1H,2H,2H-Perfluorodecyltriethoxysilane, PFDE=1H,1H,2H,2H-Perfluorodecanethiol, TDF= Tridecafluoro-1,1,2,2-tetrahydrooctyltrimethoxysilane, HFDMS = Heptadecafluorodecyltrimethoxysilane, Fluorodecyl POSS¹ = Perfluorodecyl polyhedral oligomeric silsesquioxane, Fluorodecyl POSS² = 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane, Fluorodecyl POSS³ = 1H, 1H, 2H, 2H-Heptadecafluorodecyl silsesquioxane, and PMMA = Poly(methyl methacrylate). Oils and Alcohols (surface tension at 20 °C/mN m⁻¹): (P) = Pentane (15.1), (R) = Rapeseed oil (27.5), (H) = Hexadecane (27.5), (O) = Olive oil (31.2); (Alc) = methanol (22.1), ethanol (21.8), 1-propanol (23.7), 1-butanol (26.2), 1-octanol (27.6) and 1-decanol (28.5).



wettable. The contact angle of a water drop on a Teflon surface does not exceed 120° [70], but contact angles between 128° and 170° have been reported when rendered superhydrophobic via plasma lithography [71], extension [72], sanding [73,74] or laser irradiation [75]. Metal oxides and metal surfaces have been rendered non-wettable. For example, aluminium oxide and titanium oxide surfaces were made non-wettable to water by CVD of 1,3,5,7-tetramethylcyclotetrasiloxane at 180°C for a day [76]. The surfaces became textured with structures of diameter 500 nm to $4\text{ }\mu\text{m}$ and gave a θ^* of 163° with water drops. Oxides of zinc [77] and silicon [78] were also reported to become non-wettable to water and oils following patterning and chemical modification with fluorocarbons. Qian and Shen [79] have rendered polycrystalline metals like aluminium, copper and zinc superhydrophobic by etching, using a dislocation etchant that preferentially dissolves the dislocation sites in the metals, followed by surface chemical modification with fluoroalkylsilane. Values of θ^* greater than 150° were observed with water drops on the metal surfaces. Many non-wettable silicon surfaces have also been reported [80–88]. The surfaces were reported to be textured and gave $\theta^* > 150^\circ$ with water and oils (e.g. hexadecane).

The preparation of non-wettable carbon nanotubes has also been reported [94–97]. These tubes were observed to exhibit θ^* as high as 161° with oils, e.g. rapeseed oil [97], and 170° with water [94, 97], with low hysteresis. Non-wettable surfaces have also been prepared from silica particles. These surfaces exhibited θ^* values $\geq 150^\circ$ and relatively low hysteresis with water drops [98–100]. In another study [101], glass slides were spin-coated with silica particles, treated with fluoroalkylsilane, and θ^* values between $130\text{--}149^\circ$ (water drops) and $>136^\circ$ (relatively low surface tension liquids like hexadecane) were reported with low hysteresis. The preparation of non-wettable surfaces has also been done with polymers in combination with suitable fluorocarbons, like fluorodecyl POSS, using either dip-coating [103] or electrospinning [78, 104]. The θ^* for water and oil drops, especially hexadecane, were observed to be above 150° with relatively low hysteresis. A detailed review on the preparation of superhydrophobic surfaces from polystyrene using electrospinning has been given by Sas *et al.* [105]. These surfaces were called polymer webs and exhibited θ^* above 150° and low hysteresis with water drops. Clay (sericite) powdered particles were treated with perfluoroalkyl phosphate and compressed to obtain a non-wettable surface [106]. The θ^* for water and hexadecane drops on the compressed powdered particles were observed to be 148° and 118° , respectively.

It should be noted that majority of the non-wettable surfaces listed in Table 1 underwent chemical modification with fluorocarbon compounds. This is especially important for oil-repellent surfaces (low surface free energy), which have been reviewed by Kota and Tuteja [107]. This is because fluorocarbons are known to lower the surface free energy of many surfaces [108].

3.4 Properties of Non-Wettable Surfaces

Non-wettable surfaces (natural or synthetic) are always textured (Figure 10 a,b) [109,110], with hierarchical multi-scale roughness in some cases (Figures 4-8), and coated with a thin film of wax or other organic or inorganic non-wetting chemical groups [111]. This arrangement is important for liquid repellence as it favors the Cassie-Baxter wetting state. Studies [8, 112-116] on the relationship between roughness and the wetting states have revealed that there is a critical value of the fraction of surface that is in contact with the liquid drop, below which the Cassie-Baxter state prevails and above which the Wenzel state is favored as illustrated in Figure 10 c-g. This transition corresponds to the threshold angle given in Equation (4). The stability or metastability of the two wetting states was also highlighted. It was shown that drops can exist in the Cassie state (metastable) on surfaces that thermodynamically favor the Wenzel state depending on the applied pressure, drop evaporation and mode of drop deposition. For example, a Cassie drop relaxed to the Wenzel state upon: (a) application of a certain minimum pressure and (b) evaporation. Also, the Wenzel state prevailed on a Cassie surface when the liquid was deposited in the form of mist rather than all at once.

Some non-wettable surfaces are non-sticky [117-120] while others are sticky [115,121,122]. The non-sticky surfaces are very important in the manufacture of the so-called “self-cleaning materials” like glass windows and car windscreens. Liquid drops roll freely on non-sticky surfaces even for small inclinations (sliding angles), but they will not in the case of sticky surfaces. Liquid drops are considered

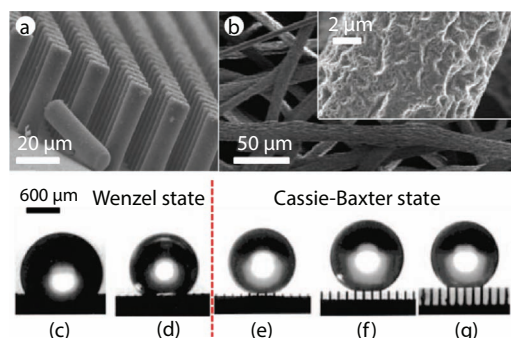


Figure 10 (upper) Examples of textured non-wettable surfaces. (a) SEM image of photoresist SU8 towers obtained by lithography. Reprinted from ref. [109], with permission from the Institute of Physics and (b) SEM image of electrospun polystyrene fibres. Reprinted from ref. [110], with permission from the Institute of Physics. (lower) Wetting transition of a water drop (1 μ L) on surfaces with increasing degree of roughness, quantified by the roughness factor r . The contact angle and the corresponding r are: (c) $114^\circ/1.0$, (d) $138^\circ/1.1$, (e) $155^\circ/1.2$, (f) $151^\circ/2$ and (g) $153^\circ/3.1$. Reprinted from ref. [116], with permission from the American Chemical Society.

to be in the Cassie-Baxter state for non-sticky surfaces and in the Wenzel state for sticky ones. The contact angle of liquid drops on non-sticky surfaces is normally higher, with low hysteresis, than on sticky ones with high hysteresis. This is because the high contact angle greatly reduces the solid-liquid contact area so that pinning of the drop in solid-liquid-air contact line is minimal. In terms of sliding angle, non-sticky surfaces have lower sliding angles compared with sticky surfaces [123]. For example, water drops stick (Wenzel state) to Teflon surface with $\theta^* \leq 120^\circ$ and roll when the sliding angle is between 10 to 30° . A transition to the Cassie-Baxter state occurs when it is textured by sanding. Here the contact angle is 151° with a hysteresis of 4° and the sliding angle decreases to $\leq 5^\circ$ [73]. This is consistent with other surfaces that water does not stick to [117-120] and can be compared with other surfaces that repel other liquids like oils where the sliding angle is $\leq 21^\circ$ [91, 124,125].

Another remarkable property of non-wettable surfaces is the ability of liquid drops to bounce on them. This is related to the wetting state of the drop upon arriving the surface, with the bouncing drops being in the Cassie-Baxter state and sticky ones being in the Wenzel state. This, in turn, depends on the height of fall and the velocity with which it impacts the surface. Liquid drops released from a relatively high distance to a Cassie surface arrive with a kinetic energy sufficient to push the drop into the asperities and induce the Wenzel state and remain stuck to the surface. This is also the case with drops released with a relatively high velocity. In fact the impact velocity increases with the height of fall. For a water drop ($\sim 4 \mu\text{L}$) impacting a textured poly(dimethylsiloxane) surface, composed of triangular arrays (pitch 42 or $50 \mu\text{m}$) and cylindrical pillars (radius 9 or $11 \mu\text{m}$) [126], bouncing was observed when the impact velocity was 0.27 m s^{-1} . However, the drop stuck to the surface when the velocity increased to 0.6 m s^{-1} [126] as shown in Figure 11(a,b).

For bouncing, the drop expands laterally before jetting-off the surface. Several bouncing events occur before the drop finally rests on the surface in the Cassie-Baxter state with a well-defined large contact angle. The degree to which a drop deforms upon impacting the surface depends on the impact velocity $V = \sqrt{2gh}$, which is embodied in the Weber number, $We = \rho V^2 R_o / \gamma_{la}$, with ρ being the liquid density [127]. (The Weber number compares the kinetic energy and surface tension of the liquid drop.) The larger the Weber number, the larger the drop deforms upon impact. There exists a speed threshold below which the drop does not bounce again [127]. This corresponds to the non-bouncing regime. Here, the drop expands weakly and undergoes damping oscillation after impact before reaching the Cassie state where it remains quasi-spherical. Unfortunately, surfaces that allow a broad spectrum of liquids, i.e. Newtonian, non-Newtonian, polar, non-polar, concentrated organic or inorganic acids and bases, to bounce on them are very rare. However, Pan *et al.* [128] electrospun a mixture of cross-linked poly(dimethylsiloxane) and fluorodecyl polyhedral oligomeric silsequioxane on stainless steel wire meshes to obtain a surface that was non-wettable [$\theta^* > 150^\circ$, low hysteresis ($\leq 7^\circ$), $\alpha \leq 2^\circ$] by

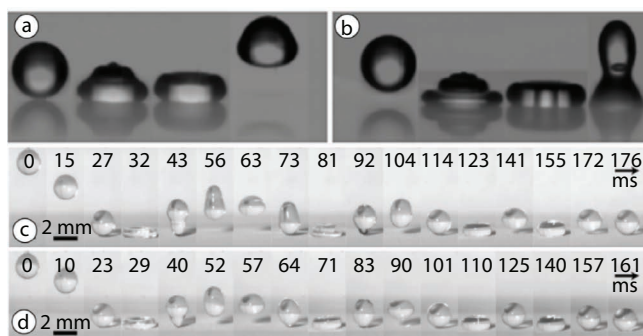


Figure 11 Dynamics of liquid drops upon impacting non-wettable surfaces. (a) Bouncing of a water drop (radius $R_0 \sim 1$ mm; impact velocity $V = 0.27$ m s⁻¹) on a textured poly(dimethylsiloxane) surface and (b) the sticking of the same water drop when $V = 0.6$ m s⁻¹. Reprinted from ref. [126], with permission from the Institute of Physics. (c, d) Images of acetic acid and hexylamine drops ($R_0 \sim 1$ mm), respectively, at various impact velocities bouncing on a textured non-wettable surface, tilted at 2° relative to the horizontal. Reprinted from ref. [128], with permission from the American Chemical Society.

these liquids. When released from a height of 4.5 mm, drops ($R_0 \sim 1$ mm) of these liquids ($\gamma_{la} \geq 19.8$ mN m⁻¹) were able to bounce even for impact velocities higher than 150 m s⁻¹ compared with the other surface where they did not bounce [126].

Another property of non-wettable surfaces is related to the so-called “smart surfaces” which are able to switch from non-wetting to wetting, e.g. ZnO particle-coated surfaces [90]. A glass wafer, spin coated with ZnO particles, was reported to be textured and non-wettable by water ($\theta^* \sim 161^\circ$). Upon irradiation with UV light from a 500 W Hg lamp, whose filter is centered at 365 ± 10 nm, for 2 h changed the contact angle to 0° , but its superhydrophobicity was recovered after placing it in the dark for seven days. This behavior was induced by the adsorption and desorption of surface hydroxyl groups at the outmost layer of ZnO film. UV irradiation generates electron-hole pairs in the ZnO surface and some of the holes can react with lattice oxygen to form surface oxygen vacancies. Water and oxygen compete to dissociatively adsorb on the surface oxygen vacancies. The defects are kinetically more favorable to hydroxyl adsorption than oxygen adsorption. The adsorption of the hydroxyl groups coupled with roughness improves the surface wettability. When placed in the dark, the adsorbed hydroxyl groups are gradually replaced by oxygen and superhydrophobicity is recovered. Similar results have been reported for TiO₂ particle-coated surfaces [129,130].

Lastly, it is important to note that although many non-wettable surfaces are opaque, a few transparent ones have also been created [131-134].

4 Applications of Non-Wettable Surfaces and Challenges

There are numerous applications of non-wettable surfaces as summarized by many authors [8,13,20,25,105,107,108,133,136-143]. These applications are in line with the properties of these surfaces. The applications include (i) anti-fog surfaces that prevent fog accumulation [144], (ii) anti-bacteria adhesion or anti-fouling surfaces that prevent bacteria and other fouling organisms from adhering as given in the review of Genzer and Efimenko [108], (iii) anti-icing surfaces that prevent the accumulation of snow and ice as reported in the review of Drelich and Marmur [4], (iv) anti-contamination packages that prevent contamination from biological stains and fingerprints [145,146], (v) stain-resistant surfaces that prevent staining from colored biological and synthetic molecules [147], (vi) oil-repellent coatings that repel oil [148], (vii) wax-resistant surfaces in fuel tanks that prevent wax formation, (viii) non-wettable clothing that are not wetted by liquids [149], (ix) droplet transfer in microfluidics for transporting liquids from one point to the other, (x) separation of oil-water dispersions, (xi) self-cleaning windshields for automobiles, airplanes and buildings that become clean as liquid drops roll on them carrying dirt along [4,5], (xi) drag reduction surfaces that reduce the effect of flow resistance during liquid flow [150], and (xii) corrosion-resistant surfaces that do not corrode easily [151,152]. In medicine, they are used for: (i) cell patterning for cellular interaction studies, (ii) functional cell spheroid culture, (iii) lab-on-a-chip for drop control, (iv) biomedical devices for liquid transportation, (v) high-throughput cell assay, (vi) anti-fouling slippery surfaces for biomedical implantable devices, and (vii) blood typing [153]. Medical applications of non-wettable surfaces are discussed in detail in the review of Shin *et al.* [141], Lima and Mano [154], Jokinen *et al.* [155] and Maani *et al.* [156]. Due to the enormous number of review articles on the applications of non-wettable surfaces, only highlights of recent applications will be given here. This will be accompanied by the challenges limiting the use of these surfaces in real life.

4.1 Non-Wettable Surfaces for Water Collection and Transportation

In areas where water is scarce, water is obtained from the condensation of moisture in air. In some cases, the collected water is required to be transported from one region to the other over long distances. Luo *et al.* [157] have shown that superhydrophobic surfaces can be used for water collection in air and transportation when necessary. Aluminium plates (thickness ~2 mm) were made superhydrophobic using electrochemical etching, electrochemical anodizing, low surface free energy modification and lubricant infusion followed by chemical modification with fluoroalkylsilane and used for the experiment. Although the surface was reported to be robust, stable over a wide range of pH and temperature, applying the technology to solve the problem of water scarcity in real life will require longer and

wider aluminium sheets compared with those used in the experiment. Obviously, the associated cost and time will also be high and long, respectively. This notwithstanding, lab-scale experiments demonstrating water collection and transportation using superhydrophobic surfaces are still emerging [158-166]. Conversely, Jiao and co-workers [167] and Chen *et al.* [168] have designed other non-wettable surfaces for underwater capturing and transportation of gas bubbles. Because these surfaces allow a free movement of liquid drops from one point to the other, they can potentially be used in microfluidic experiments and devices where the transportation of liquid from one point to the other is important as illustrated by Yang and co-workers [169].

4.2 Non-Wettable Surfaces as Self-Cleaning and Icephobic Surfaces

Surfaces that repel a wide range of liquids (from polar to apolar) are important in many industries because they are able to remain clean for a long period of time as a result of their self-cleaning ability. For example, they are important in the manufacture of solar panels, the so-called self-cleaning windows, wind turbines, automotive and aerospace components. The optimal capacity of solar panels is impaired when dirt accumulates [170]. This problem can be surmounted when they are made liquid repellent so that they can self-clean themselves. The same applies to wind turbines and automotive and aerospace components. Unfortunately, only few surfaces repel a range of different liquids and by extension may not repel biological waste like bird droppings, which are complex mixtures. Recognizing this, Bhushan and Multanen [171] have prepared a mechanically robust surface that repels a wide range of liquids even at low pH values, low ($-60\text{ }^{\circ}\text{C}$) and high temperature ($95\text{ }^{\circ}\text{C}$) conditions. The surface was said to have potential applications in the manufacture of self-cleaning, solar panels, satellite dish antennas, windows, windscreens, wind turbines, automotive and aerospace components. Other similar surfaces have also been reported [172-178]. Although, the approach used here gave surfaces with the desired properties, their fabrication requires a lengthy procedure that is time consuming and shorter routes are therefore solicited.

Surfaces with ice adhesion strength $\tau_{\text{ice}} < 100\text{ kPa}$ and which are able to repel ice are known as icephobic surfaces. They are useful in preventing ice accumulation on surfaces of wind turbines and airplane wings, which often damages them or make them ineffective [179]. Many superhydrophobic surfaces are also icephobic, i.e. not all superhydrophobic surfaces are icephobic [180]. For example, Jafari *et al.* [181] created a superhydrophobic and icephobic surface on aluminium alloy. The alloy surfaces were patterned by anodizing and then coated with Teflon particles. The fabricated surface displayed θ^* of $\sim 165^{\circ}$ with low hysteresis ($\sim 3^{\circ}$) and a low ice adhesion strength compared with a polished aluminium surface. Many icephobic surfaces with different properties have been created [182-196]. The passive removal of ice on many surfaces, e.g. on airplane wings and power lines

requires values of τ_{ice} lower than 20 kPa. Unfortunately, it is difficult to create such surfaces. However, Golovin *et al.* [197] have shown that by tailoring the cross-link density of different elastomeric coatings and by enabling interfacial slippage, surfaces with ice adhesion strength lower than 0.2 kPa can be realized irrespective of the material chemistry. The fabricated surfaces were reported to be durable with $\tau_{ice} < 10$ kPa after severe mechanical abrasion, acid/base exposure, hundred icing-deicing cycles, thermal cycling, accelerated corrosion and exposure to Michigan wintery conditions for several months. Details on the fabrication, characterization, properties and applications of icephobic surfaces can be found in the review of Jamil *et al.* [198].

4.3 Non-Wettable Surfaces for Biomedical Applications

Biological samples like blood are collected in small amounts in medical laboratories whenever they are required so that the patients do not develop problems in addition to the one being diagnosed. Microfluidics is the solution here as the amount of liquid required ranges between nanoliters to microliters, compared with the amount (≤ 20 mL) commonly required in many medical laboratories. The application of non-wettable surfaces in microfluidics for biomedical applications is well covered in the review of Oliveira and co-workers [199]. The authors described how biological specimens (liquids) are conveyed from one point to the other for analysis. They have also discussed the advantages and disadvantages of microfluidics over conventional methods of analysis. In addition to microfluidics, non-wettable surfaces have also been used for blood typing [153]. Using a simple printing technique, superhydrophobic surfaces were fabricated with Teflon powder and used for the experiment. Because blood does not wet the surface ($\theta^* = 149$ to 159°), quasi-spherical blood drops were formed on it. This allowed easy haemagglutination reaction after which the drop was photographed and images analyzed for blood grouping [153]. Compared with conventional lab procedures, the method requires small blood samples. In addition, the method is also capable of identifying blood samples with weak red blood cell antigens. The downside of this technique is the possibility of clotting and drying before the experiment is completed as the blood sample is very small. In another study, Li *et al.* [200] fabricated durable and flexible superhydrophobic and blood-repelling surfaces, from silicone and functionalized silica nanoparticles, for use in medical blood pumps. This technology circumvents the problem of blood damage or clotting (also known as hemolysis), associated with many extracorporeal blood pumps [200]. Because blood does not wet the surface ($\theta^* \sim 151^\circ$), the frictional force experienced by it, which leads to stress and damage, while flowing is significantly reduced. It has also been reported that non-wettable surfaces can be used to perform high-throughput assays to generate 3D cell environment, characterize and analyze the properties of biomaterials, and cell-cell and cell-biomaterial interactions [201]. Additionally, non-wettable materials have also been used as medical implants [155].

5 Summary and Future Prospects

Due to their ability to repel liquid drops and remain non-wetted, non-wettable surfaces have attracted significant attention. As a result, they can potentially serve as precursors for many industrial and biomedical applications. For example, non-wettable films can be applied to textile fabrics that need not to become wet during usage like raincoat and umbrella. Unfortunately, this application is still in the development state. For snowy areas, a combination of superhydrophobic and icephobic films will profit companies producing raincoats and umbrellas. In addition, such films are expected to be resistant to abrasion, temperature changes and pH. Sadly not all superhydrophobic films repel ice nor are resistant to abrasion, temperature changes and pH. Future fabrication of non-wettable surfaces can be tailored to films that repel both water and ice and are resistant to abrasion, temperature changes and pH. This also applies to non-wettable films required for the fabrication of non-wettable windows, windscreens, solar panels, satellite dishes and other related applications. Non-wettable surfaces are important for liquid transportation in microfluidics where only small quantities of liquids are required, but the chances of liquid contamination are high as the quantities of liquid involved are quite small. To overcome this, such surfaces should be kept clean at all times and preferably used in a closed system. This problem is similar to that encountered in biomedical applications where the samples of interest are also very small. Here, the chances of contamination and drying before the experiment is completed are high. This is in addition to the change in sample composition due to adsorption of biomolecules. Adsorption also alters the structural conformation of the biomolecules. The use of a closed chamber will reduce the chances of contamination and drying and the use of non-adsorptive surfaces will reduce the adsorption of biomolecules. It should be remembered that adsorption will be more in the Wenzel state, where the sample makes a significant contact with the surface, compared to the Cassie-Baxter state, where the sample makes less contact with the surface. Suffice it to say that non-adsorptive surfaces can be realized by fabricating Cassie-Baxter surfaces. Overall, the commercialization of non-wettable surfaces will involve the development of rapid and cost-effective fabrication routes for durable non-wettable films. For environmental concerns, “green” fabrication routes, involving the use of environmentally benign chemicals, are also encouraged.

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