REVIEW

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Review

Superhydrophobic materials and coatings: a review

John T Simpson1,3, Scott R Hunter2 and Tolga Aytug2

1 University of Tennessee, Knoxville, TW 37996, USA
2 Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
E-mail: jsimpso4@utk.edu, huntersr@ornl.gov and aytugt@ornl.gov

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Abstract
Over the past few years, the scientific community, as well as the world’s coatings industry has seen the introduction of oxide/polymer-based superhydrophobic surfaces and coatings with exceptional water repellency. Online videos have caught the public’s imagination by showing people walking through mud puddles without getting their tennis shoes wet or muddy, and water literally flying off coated surfaces. This article attempts to explain the basics of this behavior and to discuss and explain the latest superhydrophobic technological breakthroughs. Since superhydrophobic surfaces and coatings can fundamentally change how water interacts with surfaces, and the fact that earth is a water world, it can legitimately be said that this technology has the potential to literally change the world.

Keywords: superhydrophobic, volumetric, superhydrophilic, oleophobic, desalination, anti-biofouling, anti-corrosion

(Some figures may appear in colour only in the online journal)

General discussion, definitions, and properties of hydrophobic/hydrophilic and superhydrophobic/superhydrophilic surfaces

Young’s static and dynamic contact angle equations [5] are the most common and relevant parameters describing the wetting property of a surface with respect to liquid water. Figure 1 pictorially shows Young’s equation related to a drop of water on a surface.

Young’s equation [4, 5]

For a drop of liquid water ‘L’ in coexistence with a vapor phase ‘V’ that is put on a substrate ‘S’, the key equation describing this situation is the Young’s equation which describes the force balance between the interfacial tensions formed at the solid–liquid–vapor contact line.

\[
\cos \theta_y = \frac{(\sigma_{sv} - \sigma_{sl})}{\sigma_{sv}}
\]

\(\theta_y\) = Young’s contact angle
\(\sigma_{sv}\) = surface tension (energy per unit surface) of the solid–vapor interface
\(\sigma_{sl}\) = surface tension of the solid–liquid interface
\(\sigma_{lv}\) = surface tension of the liquid–vapor interface

Static contact angle [47]
The ‘contact angle (CA), (\(\theta\)) measurement assumes a water droplet is on a smooth, planar, rigid, and homogeneous surface.

Wetting phenomena

Liquid water has a relatively large surface tension primarily due to its electrical dipole. One simple way of thinking...
about water’s dipole behavior is that water has a tendency to stick to things, including itself. A surface is classified as either hydrophilic (loving water) or hydrophobic (scared of water) by how it interacts, or sticks to water drops. A water drop will tend to wet a surface that has high surface energy chemistry (e.g. glass) and will tend to bead-up on a surface that has low surface energy chemistry (e.g. Teflon). If a water drop has a tendency to stick to itself more than it sticks to a given surface that surface is called hydrophobic and the water drop will bead up with a CA greater than 90°. Conversely, if a water drop tends to stick more to a given surface than it sticks to itself, that surface is called hydrophilic and the drop will have a contact angle of less than 90°. Note that a water drop that completely wets a surface will have a contact angle of ~0°, while a drop that has no interaction with a surface (no wetting) will bead up into a prefect sphere (ignoring gravity) and will have a contact angle of ~180°. The images in figure 2 show these conditions.

Dynamic contact angles (advancing and receding) [4, 47, 48]

Figure 3 shows a water drop on a tilted surface exhibiting advancing (θa) and receding (θr) contact angles. The difference between the advancing and receding CAs is known as the contact angle hysteresis (θΔ).

Roll-off angle [6, 48]

The angle at which a water drop rolls off a tilted flat surface is known as the roll-off angle (θR). Generally superhydrophobic surfaces exhibit roll-off angles less than 5 degrees, but very
high quality superhydrophobic surfaces can exhibit roll-off angles of less than 1 degree. Figure 4 shows a water drop with a roll-off angle of ~5 degrees.

**Effects of surface roughness or topology on contact angle [49]**

If a liquid water drop is placed on a flat, smooth, homogeneous surface (substrate), its localized contact angle will strictly be a function of the liquid’s surface tension and the surface’s chemistry (surface energy). But, with increased surface roughness, the effective contact angle will either decrease or increase, depending on the substrate’s surface chemistry. If the surface chemistry is hydrophilic, then roughening its surface will decrease its CA. While a surface with a hydrophobic surface chemistry will increase its CA if its surface is roughened. The first sequence shown in figure 5 below shows a water drop on a hydrophilic cone spike verses time. It shows the wicking effect of a water drop in contact with a hydrophilic glass cone spike. The second sequence in figure 6 shows how a water drop can be repelled from the cone spike if the cone spike’s surface chemistry is hydrophobic [11].

Note that the localized contact angle does not change with time, while the effective contact angle can change dramatically. In the first case, where the surface chemistry is hydrophilic, the effective contact angle goes from ~45° to ~0°. And in the case where the surface chemistry is hydrophobic, the effective contact angle goes from ~120° to ~180°. Note that a hydrophilic surface becomes more hydrophilic and a hydrophobic surface becomes more hydrophobic when the given surface is roughened or its topography is significantly increased.

**Wenzel and Cassie–Baxter regimes [9, 10, 48, 49]**

The increase of effective contact angle as a result of surface roughness and structure topography falls into two regimes, known as the Wenzel and Cassie–Baxter regimes. While both regimes describe an increase in contact angle with increasing surface roughness, the Cassie–Baxter regime comes into effect when there is a trapped air layer within the roughened or textured surface which causes a substantial increase in contact angle and a significant reduction in roll-off angle and contact angle hysteresis.

**Superhydrophobic, ultrahydrophobic [8, 44, 45], and contact angle hysteresis [48] definitions**

When the effective contact angle of water drops is 150° or higher, the surface is defined as superhydrophobic. The term ultrahydrophobic has been used to describe a surface that exhibits both advancing and receding contact angles of greater than 150°. The difference between advancing and receding contact angles is referred to as the contact angle hysteresis [4].

**Natural superhydrophobic (SH) surfaces [7, 50, 51]**

There are many examples of naturally occurring superhydrophobic surfaces. These include both plants and insects surfaces. The most notable natural superhydrophobic is that of the lotus leaf. The extreme water repellency exhibited by lotus leaves is what inspired scientists to initially pursue research into superhydrophobic phenomena. In fact, the term ‘lotus effect’ is still synonymous with superhydrophobic behavior. Figure 7 shows another superhydrophobic leaf from the tennessee state tree, the tulip poplar.

**Effects of superhydrophobic surface pinned air layer [9]**

In order for a surface to be superhydrophobic it must have a high contact angle (θ > 150°). That generally means that water drops on the surface have, at least some, air between them and the surface (i.e. Cassie–Baxter regime [9]). A high quality superhydrophobic surface will have a uniform layer of pinned or trapped air that produces a very high contact angle (approaching 180°), a very low roll-off angle (approaching 0°), small contact angle hysteresis (approaching 0°), and will produce an optical mirror effect when the surface is submerged in water due to total internal reflections of light reflecting off the pinned air layer. Figures 8(a) and (b) show the mirror effect on a piece of wood and a fabric treated with superhydrophobic coatings. Note that the pinned or trapped air in a high quality superhydrophobic surface acts as a physical barrier to liquid water or aqueous solutions but is not a barrier to the air, or gasses in general. Figure 9 shows a water drop beading up into a sphere while sitting on a superhydrophobic coated wire mesh.

**Examples of synthetic superhydrophobic surfaces**

*Engineered and ordered superhydrophobic arrays [1, 11]*

Various universities and research institutions [1] have fabricated synthetic superhydrophobic surfaces using microelectronics-based photolithography. Figure 10 is an example a photolithography-based array of silicon rods fabricated by Bell Labs. The array of one micron diameter silicon rods were treated with a hydrophobic solution giving them both the right surface chemistry and micro-structure to be superhydrophobic.
The result was a superhydrophobic surface with a static contact angle of approximately 160°.

In 2004 researchers at ORNL (Dr John Simpson and Dr Brian D’Urso) used glass fiber drawing techniques to fabricate an array of glass cone spikes (see figure 11). These cones had a periodicity of 7 microns and a height of 12 microns [11]. The glass cone array’s surface chemistry was changed from hydrophilic to hydrophobic by treating the glass array with a fluorinated silane solution. The silane solution produced a covalently bonded self-assembled-monolayer (SAM) on the cones’ surfaces. The treated cone tips were measured to be less than 10 nm in radius. This superhydrophobic array of nano-sharp glass cones is the world’s most water repellent surface ever reported, having a measured contact angle greater than 179°. Figure 12 shows an image of a 14 mm diameter glass disc having approximately 1 million cone spikes surrounded by water. Note the water meniscus surrounding the disc and that the SH treated cone array is so water repellent that virtually no wetting of the disc surface is observed. Researchers at Oak Ridge National Lab dubbed this phenomena the ‘Moses effect’.

Engineered disordered superhydrophobic surfaces [2, 3, 52]

The following micrographs are examples of engineered, disordered, nanotextured surfaces which are initially
superhydrophilic, but become superhydrophobic when their surface chemistries are changed from hydrophilic to hydrophobic by treating the surfaces with a hydrophobic self-assembled-monolayer (SAM). Figure 13 shows superhydrophobic nano-structured and nano-porous silica produced by differential etching phase separated borosilicate glass [3, 37]. This nano-textured superhydrophobic structure has shown contact angles as high as 178°. Figure 14 shows nano-strands of fluorinated polymers having contact angles of roughly 145°. Note that these polymer strands are easily matted down. When that happens the CA is quickly reduced to below 130°. Researchers from UCLA [2] fabricated a random array of cone spikes produced by asymmetrically etching a silicon wafer. Their random cone spike structure had a static CA of over 170°.

Superhydrophobic diatomaceous earth [12]

Figure 15 is a micrograph of diatomaceous earth (DE). Diatomaceous earth contains the microscopic skeletal remains
of a class of phytoplankton known as diatoms. Diatoms have a unique feature in that their skeletons are formed of hydrated silicon dioxide. DE is a natural and plentiful silica-based material which is easily mined throughout the entire world. It has both micro and nano-porosity and a nano-roughness that greatly increase either its water absorption or its water repellency, based on its surface chemistry. Since its natural surface chemistry is hydrophilic, it is naturally superhydrophilic. But, if DE is treated with a hydrophobic silane, it becomes superhydrophobic because of its hydrophobic surface chemistry and the amplification effect of its texture and nano-porosity. This superhydrophobic nano-porous powder is called superhydrophobic diatomaceous earth, or simply SHDE. A surface consisting of SHDE powder has a typical contact angle of from 160° to 170°, but can be as high as 175° (see figure 16).

**Historic limitations of superhydrophobic surfaces and coatings**

For the past ten years or so, researchers have been reporting on the amazing water repellency behavior of superhydrophobic materials and surfaces. But, until recently, none of these superhydrophobic materials or surface effects made it into any commercial products. The following is a list of the major reasons why.

1. Cost issues—Except for SHDE, the cost of superhydrophobic materials has been relatively high due to the amount of processing required to create the micro and nano-structures necessary for superhydrophobic behavior. For instance, most of the early superhydrophobic micro and nanostructured surfaces were produced using photolithography [13–15], which can itself be a very costly process. But when you combine the fact that nano-scale photolithography produces small chip dies that have to be stitched together in order to cover any significant area, the overall cost and performance can be prohibitive.

2. Nano structure stability—A high quality, high contact angle, superhydrophobic surface requires a hydrophobic surface chemistry with a stable micro and nano topography. This is generally not an easy set of requirements to achieve. For instance, polymers with nano-texture tend to act like ‘wet noodles’ at the nano-scale (see figure 14). These polymer strand ‘wet noodles’ tend to easily matted down and thus quickly lose their superhydrophobic behavior [16].

3. Durability issues—Even if you use high quality superhydrophobic particles (like SHDE or functionalized silica nano-particles), it’s still not easy to bond such particles to a substrate without significantly degrading or destroying the superhydrophobic behavior. This tends to be a classic trade-off condition between durability and superhydrophobic behavior [34].

4. Condensation issues—While superhydrophobic coatings and surfaces repel water, they do not repel water vapor. If the coating is in a condensation condition (i.e. the coating temperature is below the dew point) condensation will occur. When this occurs, the resulting condensate can result in substantial surface wetting [17, 18].

5. Impingement issues [22, 23]—The pinned air layer associated with superhydrophobic surfaces can be reduced or eliminated by localized high water pressure. This can be caused by a localized stream of water or by simply rubbing the surface while it is submerged in water. Because superhydrophobic behavior has historically been a simple surface effect, any significant surface impingement quickly produced defective superhydrophobic behavior at the impingement location.

6. Surfactant/oil wetting issues—Superhydrophobic behavior is a result of amplifying (via the surface topography) the effect of water’s surface tension. If the water’s surface tension is greatly reduced with a surfactant or with an oil, superhydrophobic behavior will be greatly reduced or eliminated and the surface is then easily wetted [24, 25].

**Phases of superhydrophobic technology**

The previous examples of superhydrophobic materials are associated with two technology phases of superhydrophobic surfaces. The first phase deals with basic research of superhydrophobic structures conducted at various universities, national laboratories, and research centers. While this first phase generated much excitement in the scientific community, none of the materials were commercially viable due to either their small scale, lack of durability, or their poor performance. The second superhydrophobic technology phase uses some of the first phase materials (e.g. functionalized nanoparticles [42]) to make superhydrophobic coatings in a loosely bound top-coat. Note that this top-coat type of superhydrophobic technology is strictly a surface effect and is exemplified by Rustoleum’s ‘NeverWet’ product. If the coating’s surface is removed or damaged, its superhydrophobic behavior is eliminated. While this technology has proven to be somewhat commercially viable, it is still lacking in applicability and durability. Recent superhydrophobic technology breakthroughs will likely produce a third and fourth generation of
superhydrophobic technologies, which could fulfill the promise of making superhydrophobic technologies widespread, if not ubiquitous.

Recent superhydrophobic technology breakthroughs

Volumetric SH coatings [26–28] (paints, epoxies, and silicones)

The creation and use of volumetric superhydrophobic coatings represent a new (third) phase of superhydrophobic technology. As of April 2015 there were no commercially available durable superhydrophobic paints, epoxies, silicones, or other such superhydrophobic products. That will likely soon change with the anticipated upcoming introduction of volumetric superhydrophobic paints and epoxies from some of the leading US paint companies (estimated to be available in the fall of 2015). What is meant by ‘volumetric superhydrophobic’ is a coating that is superhydrophobic throughout the coating’s entire volume, from its outer surface all the way to the underlying substrate. Such a coating will dramatically repel water even if the coating’s surface gets abraded away. This development represents a major breakthrough in superhydrophobic technology in that it virtually solves superhydrophobic coatings durability problem, which has been the major reason why superhydrophobic coatings have not achieved widespread commercial success. This development not only makes superhydrophobic coatings much more durable, but it also expands the capabilities of superhydrophobic coatings in entirely new ways (like reducing or eliminating the impingement issues).

The next section will attempt to explain how the creation of volumetric superhydrophobic came about and the principles behind it.

Water marbles [29, 46]

Since silica is naturally hydrophilic, nano-textured silica particles will be super-hydrophilic and are readily wetted by water drops. If the particles are fully functionalized with a hydrophobic silane, the particles will become superhydrophobic and they will not be wetted by water. Figure 17 shows a water drop beaded up on such fully functionalized superhydrophobic particles. But, if the particles are only partially functionalized, each particle can simultaneously have both superhydrophobic and superhydrophilic areas of behavior. When water drops interact with these particles, ‘water marbles’ are formed. A water marble is a drop of water that wets the superhydrophilic portion of such particles while not wetting the superhydrophobic portion of the particles. A water drop in contact with a large number of such partially functionalized particles will result in water drops with their outer surfaces covered with these hydrophilic/hydrophobic glass particles. The superhydrophilic portion of the particles stick to the water drop while its superhydrophobic portion resides on the outer part of the water drop. Since the drop’s outer surface is covered with the superhydrophobic portion of the silica, the water marble itself is superhydrophobic and will not be wetted by other water drops. See figure 18.

Resin marbles [26]

The interaction of superhydrophobic nano-textured silica (e.g. SHDE) with molten powder-coat resins can produce what researcher at Oak Ridge National Laboratory call ‘resin marbles’. The powder-coat process uses dry polymer resins to coat surfaces using an electrostatic process. Once an electrically grounded surface is sufficiently covered with charged resin particles, the coated surface is placed in an oven where the resin particles become molten forming a uniformly coated and cured powder resin surface. A blend of SHDE and powder-coat dry resins will not adversely affect the electrostatic application process, since the SHDE charges just like the dry resins particles. But during the curing process the interaction of the SHDE with molten resin acts much like the water marble forming process in that SHDE partially wets the resin while most of the SHDE repels the molten resin. If the proportion of SHDE to resin is great enough (e.g. 25% SHDE to resin), then complete resin marbles form and the molten resin cures without combining with other molten resins (see figure 19). The result is a surface containing cured resin marbles that are completely unbound to other resin marbles or the substrate. If the proportion of SHDE to resin is reduced (e.g. to 5%) then much of the molten resins will flow, but will not form a uniform coating due to the resin-phobic/philic nature of SHDE. As can be seen from the SEM micrograph image (figure 20), blended powder coat resins with SHDE can
produce a very porous interconnected surface having micro-porosity due to the limited interaction of the resin marbles. This micro-porosity extends throughout the entire volume of the coating. Furthermore, the micro-pore’s outer surfaces are covered with SHDE which creates a surface nano-porosity and superhydrophobic effect throughout the entire volume of the coating.

Creating a partial resin marble effect paint [28]

If SHDE were to be added to a solvent-based paint, the paint would easily wet the SHDE. As the paint dries, and the solvent evaporates, the SHDE’s pores and nano-structured surface would be completely filled and covered with the cured paint. No superhydrophobic behavior would therefore be present after the paint dries. But it is possible to create a volumetric superhydrophobic paint using the same type of phobic/philic ‘resin marble’ effect. Figure 21 shows such a paint surface. In order to create the phobic/philic ‘resin marble’ effect in regular paint one must recreate the same dual nature of adhesion and repulsion of the superhydrophobic material (in this case SHDE) to the particular type of paint being used. One way of achieving this dual repulsion and adhesion particle effect is with the use of inert solvents, like Fluorinert (3M brand name). If the SHDE is first wetted using a low surface energy inert solvent (like 3M’s Flouroinert), the solvent can effectively protect the SHDE from being totally engulfed by the paint, thus keeping its pores and some of its surface free of paint. The combination of fluoroinert and SHDE has the dual adhesion and repulsion characteristic needed to create a phobic/philic ‘resin marble’ effect. When the particular paint cures and the Fluorinert completely evaporates, the result is a volumetric superhydrophobic paint having both micro-porosity and

Figure 19. ‘Resin marbles’ and close-up image of ‘resin marble’.

Figure 20. Volumetric SH powder coat (left: SEM micrograph showing the micro porosity of the structure. Right: showing the superhydrophobic behavior of water drops on a 4″ × 4″ superhydrophobic powder coated surface).

Figure 21. Micrograph of volumetric SH paint.
 nano-porosity throughout its entire volume shown in figure 21. Figure 22 shows four volumetric superhydrophobic coated plates using different paint types (epoxy paint, oil-based enamel, acrylic latex, and water-based latex paint).

Oleophobic (oil repellant) surfaces using SLIPS [28, 38, 39, 43]

Slippery liquid-infused porous surface(s) (SLIPS) surfaces are surfaces with nano-porosity that have been infused with low surface energy liquids. These surfaces have shown exceptional liquid- and ice-repellency, pressure stability and enhanced optical transparency. It is generally agreed that the reason why these surfaces are so liquid and ice repellant is that they create super-smooth surfaces. One way of understanding SLIPS behavior is to consider that by infusing a low surface-energy fluid into a nano-textured and porous surface, you have effectively created a low surface-energy fluid-modified superhydrophobic surface. The reason why a SLIPS surface repels oil has to do with the oil having a higher surface-energy than the pinned infused fluid. As long as the low surface-energy fluid remains within the superhydrophobic nano-texture, any other (higher surface energy) fluid (like oil or water) will tend to slide off its surface. Note that a superhydrophobic surface can actually pin an infused liquid in its pores and on its surface if the infused liquid and superhydrophobic surface chemistries are compatible (e.g. if both chemistries are silicon based).

Durable superhydrophobic optical thin films [30–32] (superhydrophobic technology phase IV)

The fourth phase of superhydrophobic technology will likely be the development of commercially viable (i.e. durable) superhydrophobic optical thin films. The three properties required to make a durable superhydrophobic optical thin film (namely, durability, optical clarity, and superhydrophobic behavior) tend to be mutually exclusive making it inherently difficult to make such a coating. For instance, superhydrophobic behavior requires a rough textured surface which normally scatters light and thus prevents optical clarity. And, in order to make a durable thin film consisting of superhydrophobic nano-scale or micro-scale particles, a fair amount of binder (e.g. polyurethane) is required. But, generally binders will cover and/or fill-in the very pores and textured surfaces required for superhydrophobic behavior. It is relatively easy to make a superhydrophobic, optically clear thin film by either using hydrophobic functionalized silica nanoparticles suspended and dispersed in a solution containing a small amount of binder (e.g. polyurethane), or by using a hydrophobic sol-gel process [34]. If such a solution is uniformly sprayed or applied onto a clear surface (e.g. glass), the result is a clear superhydrophobic thin film. Unfortunately, such a film is easily removed with only a small amount of abrasion.

Recently, researchers at Oak Ridge National Lab (ORNL) showed that durable, optically transparent, superhydrophobic optical thin films are possible using nano-textured and nano-porous-based thin films instead of the typical fused silica nanoparticle-based thin films. ORNL’s superhydrophobic optical thin films require a series of process steps that include: glass sputtering or chemical vapor deposition (CVD), ion milling, glass phase differential etching, and a hydrophobic silane treatment. The result of these process steps is a volumetrically
superhydrophobic, atomically bonded (durable), optical thin film. Figure 23 shows a micrograph of such an optical thin film nano-structured surface. Figure 24 shows a glass plate with a superhydrophobic optical thin film surface. It is anticipated that this technology will be commercially available by the summer of 2016.

Applications of durable superhydrophobic surfaces and coatings

With the recent advances in durable superhydrophobic surfaces and coatings, there will soon be a large number of existing products converted into superhydrophobic products. And, since volumetric superhydrophobic technology adds new functionality to coatings, there will likely be many new products based on this new functionality.

Water repellency

Water repellency is the most obvious application of superhydrophobic coatings and surfaces. The complete list of possible water repellency applications would be extensive and too long to include in this paper. A partial list includes clothing that will be both breathable and water repellant, umbrellas that stayed completely dry, building materials, paints, epoxies, and silicones. Figure 25 shows a water drop being repelled and beading up by a superhydrophobic volumetric painted surface.

Self-cleaning optical windows and lenses [27, 53, 54]

Optically clear superhydrophobic coatings on glasses, windows, and optical lenses will make seeing in foul weather much easier and cleaning windows will be as simple as spraying them with water. Figure 26 shows a periscope window that first had its right side coated with an optical superhydrophobic thin film and then mud was applied to the entire window. The superhydrophobic area of the window (right side) repelled the mud and stayed clean, while the untreated side (left side) gets covered with mud.

Viscous drag reduction [35, 36]

Superhydrophobic paints and epoxies could greatly reduce the cost of transporting goods by ships and improve the efficiency of water craft of all kinds due to the reduction of water drag on the watercraft’s hull. Figure 27 (left and right) shows a toy boat with and without a thin superhydrophobic coating on its hull. Notice how high in the water the left boat sits when it’s treated with a superhydrophobic coating. While the buoyancy increase produced by coating toy boats with superhydrophobic paint doesn’t scale to large watercraft, there can still be a relatively large viscous water drag reduction due to the large slip length produced by the pinned layer of air.

The use of riblets on watercraft is a well-established drag reduction mechanism. When combined with superhydrophobic surfaces significant passive drag reduction is possible. A recent paper [36] presented by Charlotte Barbier describes a method to fabricate surfaces that combine both of these techniques in order to increase drag reduction properties. Samples have been tested with a cone-and-plate rheometer system, and have demonstrated significant drag reduction (even in the transitional-turbulent regime). A sample with 100 μm deep grooves showed drag reduction from 15 to 20% over a wide range of flow conditions (including laminar and turbulent regimes), and its slip length was estimated to be over 100 μm.

Anti-icing [17–21, 38]

Superhydrophobic coatings and oil-modified superhydrophobic coatings could greatly reduce or even eliminate many of the effects of ice storms and aircraft icing. Figure 28, top,
bottom left, and bottom right shows the results of superhydrophobic coatings on power lines in a simulated ice storm. The uncoated power lines (bottom right) quickly iced over and developed large icicles, while the superhydrophobic coatings (bottom left) prevented ice formation and showed no icicles.

Figure 28. SH coated power lines in simulated ice storm chamber.

Figure 29. Unfouled oil-modified SH treated 4” × 4” epoxy plate.

Figure 30. Fouled uncoated 4” × 4” epoxy plate.

Anti-fouling [37,38]
Superhydrophobic coatings and oil-modified superhydrophobic coatings could reduce or eliminate bio-fouling of ship hulls, piers, power plant intake systems and other surfaces.
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subject to bio-fouling, including barnacles and zebra mussels. The following pictures show how an oil modified superhydrophobic coating can prevent marine bio-fouling. These two Teflon epoxy plates were submerged in an estuary at Battelle’s immersion facility in Florida. The plate on the right (figure 29) was treated with an oil modified superhydrophobic thin film coating. After three months of submersion in an aggressive biofouling environment, the untreated plate (figure 30) was covered with algae and barnacles. The treated plate showed almost no biofouling with no barnacle attachment (the light areas are water drops).

Anti-corrosion [26, 28]

Low permeability paint, used as a water and vapor barrier, is the standard way of protecting metal surfaces from corrosion. Such paint works well until the paint develops micro-cracks. At that point, water seeps into the micro-cracks. From then on the paint, acting as a barrier, actually holds the water in the micro-cracks, which from that point on promotes corrosion. Volumetric superhydrophobic coatings prevent corrosion in an entirely different way. Volumetric superhydrophobic coatings are very porous with very high permeability. As such, one would believe that these paints would be terrible at preventing corrosion, but recent salt fog chamber testing has shown the opposite is actually true. And when one looks at the low surface-energy fluid (oil)-modified superhydrophobic coatings, the anti-corrosion results get even better [38]. As an example, figure 31 shows two plates, one coated with an epoxy paint and one coated with the same epoxy paint which has been modified to be volumetrically superhydrophobic. Both plates were placed into a salt-fog chamber and subjected to a salt fog for 1000h. While the standard epoxy paint coating showed heavy corrosion, the volumetric superhydrophobic epoxy coating showed no corrosion.

Figure 31. Two 6” × 8” plates subjected to 1000h of salt fog chamber testing. Left: shows an epoxy coated plate reference, Right: shows the same type of plate and coating with a volumetric porous superhydrophobic topcoat. Note that the volumetric superhydrophobic coating shows no corrosion even though the coating is extremely porous with high permeability.

Desalination [40, 41]

Evaporative desalination was the first and is generally acknowledged to be the easiest way of converting seawater into freshwater. But virtually all large scale desalination done in the world uses the more complicated and expensive method of reverse osmosis desalination. The reason why evaporative desalination has been abandoned has to do with the maintenance cost involved and corrosive effects of the salt residue generated by evaporation of saltwater. Volumetric superhydrophobic coatings are saltwater-based corrosion resistant and can greatly reduce or prevent any salt residue buildup. Therefore it is possible that the use of volumetric superhydrophobic coatings could finally make large scale evaporative desalination commercially viable. As an example, figure 32 left shows salt residue on an aluminum pan after seawater was poured into the pan and allowed to evaporate. Note that the salt residue climbed up and over the pan and was well bonded.

Figure 32. Left: evaporated seawater in aluminum plate. Right: evaporated seawater in SH treated aluminum plate.
to the pan after evaporation. Figure 32 shows another aluminium pan that was first coated with a superhydrophobic coating before adding seawater and letting it evaporate. After the salt evaporated, it was noticed that no salt residue climbed up the pan. In fact, none of the salt actually stuck to the pan, but instead forming a big salt crystal, which was easily removed from the pan and discarded.

**Summary/observations/predictions**

This superhydrophobic materials review paper started off with the basic nature and characteristics of hydrophobic and superhydrophobic behavior and then described four superhydrophobic technology phases. The first technology phase dealt with university, national lab, and corporate research groups looking into basic properties of superhydrophobic surfaces and their fabrication using photolithography. The second superhydrophobic technology phase began when the superhydrophobic spray-on surface-effect coatings became commercially available. These superhydrophobic surface-effect materials and coatings produced a lot of scientific and public interest in superhydrophobic materials, but resulted in a considerable amount of disappointment when the materials were shown to be either too expensive or lacked adequate durability. This paper describes a third and fourth superhydrophobic technology phase beginning in 2015 with the introduction of volumetric durable superhydrophobic paints, quickly followed by the introduction of durable and transparent superhydrophobic optical thin films. It is this author’s belief that the commercial introduction of durable superhydrophobic coatings, paints, and surfaces will have a dramatic world-wide effect on nearly every industry and possibly everyone on earth.

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  US Army—Picatinny Arsenal  
  DOE—EERE

ORNL’s superhydrophobic technology licensees
  Dry Surface Coatings, LLC—Stewart Kennedy  
  United Protective Technologies—Brent Barbee, Marty Efird  
  Lowes Corp.

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