Designing bioinspired superoleophobic surfaces

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Designing bioinspired superoleophobic surfaces

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Nature provides a range of functional surfaces, for example, water-repellent or superhydrophobic surfaces, most common among them the lotus leaf. While water-repellency is widespread in nature, oil-repellency is typically limited to surfaces submerged in water, such as fish scales. To achieve oleophobicity in air, inspiration must be taken from natural structures and chemistries that are not readily available in nature need to be introduced. Researchers usually turn to fluorinated materials to provide the low surface energy that, when combined with bioinspired surface topography, is the key to unlocking oil-repellency. This review presents the state-of-the-art in the fabrication of superoleophobic surfaces. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4935126]

Nature, over some three billion years, has evolved a range of surfaces optimized to handle a variety of challenges. For instance, the gecko’s foot contains hundreds of thousands of hairs to improve adhesion and enable climbing up vertical surfaces. Sharkskin scales contain riblets with micro-groves aligned to the direction of flow, which help reduce drag underwater. And there are numerous examples of water-repellent surfaces in plant and animal species. This review will investigate how lessons are being learnt from nature to develop surfaces that are repellent to not just water, but oils as well.

Oil repellency (superoleophobicity) is a desirable surface property for a range of different applications. Superoleophobic surfaces could find use in anti-fouling, self-cleaning, anti-smudge, and lab-on-chip applications. For instance, transparent, self-cleaning, and anti-smudge surfaces could find use in smart screens such as tablets and phones. Anti-fouling surfaces have use in the biomedical industry for non-fouling medical implants, and in oil pipelines, where high-drag sludge accumulation reduces pipeline productivity. Such surfaces are also relevant in transportation, as they could help prevent bio-fouling of ship hulls, reducing drag and resulting in decreased fuel consumption. The field of oil-repellency is becoming increasingly popular, since 2007 the number of publications that mention superoleophobicity has grown rapidly, Fig. 1. The advantages and disadvantages of the current techniques will be outlined and an outlook for the future of the field of superoleophobicity provided.

When designing oil-repellent materials, we must first understand how liquids interact with surfaces. When a finite amount of liquid comes into contact with a flat, solid surface, it forms a spherical droplet determined by a combination of interfacial tensions,

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}},$$

where $\gamma_{sv}$, $\gamma_{sl}$, and $\gamma_{lv}$ are the solid–vapor, solid–liquid, and liquid–vapor surface tensions, respectively, and $\theta$ is the contact angle, Fig. 2(a). For water, contact angles <90° and the surface is considered hydrophilic, whereas surfaces exhibiting angles >90° are hydrophobic. The corresponding surfaces for oil are referred to as oleophilic and oleophobic, respectively.

When a surface is roughened, contact angles change due to amplification of the solid–liquid interactions. Taking water as an example, hydrophilic surfaces become more hydrophilic and...
hydrophobic surfaces more hydrophobic. This is the Wenzel regime of wetting.\(^3\) Fig. 2(b). It is also possible for air pockets to become trapped between the solid and the liquid resulting in a composite interface and, since the liquid is resting partially on air, a more repellent surface.\(^4\) Fig. 2(c). This is known as the Cassie-Baxter state of wetting.

High contact angles are also achievable, even if the contact angle of a liquid on the flat surface (\(\theta_{\text{flat}}\)) is low, by creating re-entrant structures, where surface roughness features create an overhang\(^5\) (i.e., become narrower closer to the surface). For example, for a surface with inverse trapezoidal features, if the combination of the re-entrant angle (\(\alpha\)) and \(\theta_{\text{flat}}\) is \(\geq 90^\circ\), the geometry is able to support a favorable shape for the liquid–vapor interface (surface tension is pointing upward) and the liquid does not fully wet the surface (vapor pockets and a composite interface with a low liquid-solid contact fraction), Fig. 2(d).

Structures with re-entrant curvature (spherical, cylindrical, oval etc.) as shown in Fig. 2(e) are able to support high droplet contact angles for various liquids with flat contact angles \(< 90^\circ\) since it is possible to draw multiple tangents of a corresponding flat surface, as demonstrated in Fig. 2(f). Therefore, liquids with various flat contact angles can wet the re-entrant curvature to different extents to achieve a favorable liquid–vapor interface shape. The re-entrant structures in Fig. 2(g) are able to support low flat contact angles (\(0^\circ < \theta_{\text{flat}} < 90^\circ\)) and, while they could theoretically support flat contact angles of \(0^\circ\), the presence of positive pressure in the droplet means that a liquid–vapor interface shape with upward surface tension is required. This is possible with doubly re-entrant geometries, as shown in Fig. 2(h), which incorporate vertical overhangs normal to the surface in addition to the horizontal overhangs parallel to the surface found in Fig. 2(g). Here, tangents on the re-entrant curvature can be drawn beyond those parallel to the flat surface and so a favorable liquid–vapor interface shape where the surface tension is pointing upward can be supported, even with a fully wetting liquid.\(^6\) Such structures need to be designed to minimize the liquid-solid contact fraction to ensure the droplet is resting mostly on air pockets for the surface to be repellent. The structures therefore need to be as thin as possible.\(^6\) However, such surface features are fragile and difficult to fabricate on a large scale and therefore singly re-entrant geometries are more commonly used in liquid repellency.

One must also consider the way a droplet of liquid moves across a surface. A rough surface can exhibit contact angle hysteresis, where the contact angles of a mobile drop are different for the leading edge and the trailing edge. As the leading edge of a droplet moves downhill, it does so with a certain contact angle known as the advancing contact angle (\(\theta_{\text{adv}}\)). When the trailing edge begins to move, it will do so with a receding contact angle (\(\theta_{\text{rec}}\)). Advancing and receding may have different respective contact angles; this is the contact angle hysteresis. Typically, a low hysteresis is preferred to ensure liquid droplets roll away easily without contaminating the surface.

In nature, a high water angle and low hysteresis are evident in the lotus leaf.\(^7\) Lotus leaves are found in muddy ponds and yet the leaf is typically clean. This is achieved by the fact that the leaf surface is superhydrophobic. Water droplets falling on the leaf are found to exhibit high contact angle and a low hysteresis and therefore move easily across the leaf, collecting debris as they do and keeping the leaf clean for photosynthesis.
FIG. 2. (a) Liquid droplet displaying contact angle of $\theta$ on flat surface, (b) droplet exhibiting Wenzel state of wetting, (c) trapped air between droplet and surface in Cassie-Baxter state of wetting, (d) $\theta_{\text{flat}}$ angles of $<90^\circ$ on non-re-entrant and re-entrant geometries, liquid does not fully wet structure if $\theta_{\text{flat}} + \alpha \geq 90^\circ$ thanks to favorable shape of the liquid–vapor interface, (e) geometry with re-entrant curvature supporting a $\theta_{\text{flat}}$ angle of $70^\circ$, (f) geometry with re-entrant curvature supporting various $\theta_{\text{flat}}$ angles of $\leq 90^\circ$, (g) re-entrant geometry supporting $\theta_{\text{flat}}$ angles of $30^\circ$, and (h) doubly re-entrant geometry supporting $\theta_{\text{flat}}$ angles of $\approx 0^\circ$.

The superhydrophobic nature of the leaf is a result of its chemistry and topography. It is composed of a hierarchical structure of micropapillae and nanotubules. The nanotubules are made of a hydrophobic wax and, when combined with the micropapillae, result in a superhydrophobic surface.\cite{7,8}

While repelling water is common in nature, oil repellency is more difficult to accomplish, as the surface tensions of oils are much lower than that of water, Table I. This means that oils are more likely to spread out on a surface. Examples in nature are generally limited to underwater oil repellency; for example, sharkskin is oleophilic in air but superoleophobic underwater.\cite{9} This is due to a hydrophilic coating that would rather interact with water than oil. As mentioned above, the upper side of the lotus leaf is superhydrophobic due to wax nanotubules. However, the lower side of
TABLE I. Surface tension values of common liquids used to assess repellency of a surface.

| Liquid          | Surface tension (mN m\(^{-1}\)) |
|-----------------|----------------------------------|
| Water\(^a\)     | 71.99                            |
| Diiodomethane\(^a\) | 50.80                           |
| Ethylene glycol\(^b\) | 47.70                           |
| Rapeseed oil    | ca. 35                           |
| Peanut oil\(^b\) | 32.23                            |
| Olive oil\(^b\)  | 32.03                            |
| Soybean oil\(^b\) | 29.43                           |
| Hexadecane\(^a\) | 27.05                            |
| Tetradecane\(^a\) | 26.13                           |
| Dodecane\(^a\)  | 25.35                            |
| Cyclohexane\(^a\) | 24.95                           |
| Decane\(^e\)    | 23.37                            |
| Methanol\(^a\)  | 22.70                            |
| Ethanol\(^a\)   | 22.10                            |
| Octane\(^a\)    | 21.14                            |
| Hexane\(^a\)    | 18.43                            |
| Pentane\(^a\)   | 15.48                            |
| Silicone oils\(^c\) | 16–20                          |
| Perfluorohexane (FC-72)\(^d\) | 10                        |

\(^a\)Data compiled from Ref. 76.
\(^b\)Data compiled from Ref. 77.
\(^c\)Data compiled from Ref. 78.
\(^d\)Data compiled from Ref. 79.

the leaf has no such structures and is hydrophilic. When floating on water, the lower side of the leaf is therefore superoleophobic.\(^10\)

Natural surfaces exhibiting superoleophobicity in air are rare. However, certain species of leafhopper display high contact angle values for diiodomethane and ethylene glycol.\(^11\) Springtails are also oil-repellent, with a plastron layer being formed around their body when immersed in olive oil.\(^12\) In both cases, re-entrant geometries are responsible for the oil repellency. However, a natural surface with repellency to liquids with surface tensions <30 mN m\(^{-1}\) has yet to be found. Nature has a limited toolbox of materials, the ones it is able to utilize cannot easily repel oils with low surface tensions. To create oil-repellent surfaces, synthetic materials must be used.

When choosing such materials, the factors that affect surface energy must first be determined. Surface energy is a measure of work per unit area required to form a surface. In creating a new surface, disruption of bonds needs to occur, at some energy cost dependent on the cohesion of the material. In water, a single molecule can hydrogen bond to four adjacent water molecules resulting in a strong cohesive force and a high surface energy.

Cohesion and adhesion are typically dependent on van der Waal forces; for instance, oils are non-polar and so only exhibit interaction via a pair of induced dipoles (London dispersion force). Since this interaction occurs due to the polarization of molecules, it depends upon their polarizability. Polarizability depends upon the mobility of electrons; a low polarizability signifies tightly bound electrons and the least polarizable element is therefore fluorine. Fluorine is very electronegative; it has five electrons in the 2p electron shell and therefore only requires one more to achieve an ideal configuration. The low polarizability of fluorine results in a low susceptibility to London dispersion forces, which in turn leads to weak intermolecular forces, weak cohesive and adhesive forces, and low surface energies for fluorinated materials. Fluorinated materials are therefore a good choice for creating repellant surfaces.

In order to achieve oil-repellency, it is necessary to pair re-entrant geometries with low surface energy, fluorinated materials. We will now discuss a variety of different fluorination techniques which, when paired with appropriate surface topography, can result in superoleophobic surfaces. The
studies detailed below use a variety of liquids as listed in Table I in order to claim oil-repellency. This can make direct comparison between studies difficult. For instance, some studies claim a surface is superoleophobic and yet only investigate the contact angles for ethylene glycol (47 mN m\(^{-1}\)) without investigating other liquids with lower surface tensions. A more appropriate liquid for assessing oil-repellency is hexadecane (27 mN m\(^{-1}\)) and surfaces that repel a droplet of hexadecane should be considered superoleophobic. More in-depth studies will investigate multiple liquids covering a wide range of surface tension values. Surfaces found to repel a range of liquids are likely to be classified as superomniphobic (repels all).

Fluorinated materials are commonly used when a low-adhesive surface is desirable, most famously in Teflon® a derivative of polytetrafluoroethylene. However, low adhesion is also a disadvantage. It is difficult to apply a fluorinated coating to a substrate and the mechanical durability is typically poor. This, however, has not stopped research on fluorinated materials for liquid repellencies. When combining fluorine with surface topography, typically nanoparticles or patterned substrates, and using the lotus leaf and other natural surfaces as inspiration,\(^{13}\) it is possible to create water- and oil-repellent surfaces. There are several popular techniques, using various fluorinated materials, each with the aim to provide a superoleophobic surface as summarized in Fig. 3. The advantages and disadvantages of each method of fluorination will now be discussed.

Fluorinated polymers for low surface energy coatings are desirable as polymers can provide functionality and bind nanoparticles commonly used to increase surface roughness. An early

Fluoropolymer

Fluorosilane/Fluorothiol

Fluorosurfactant

Fluoroplasma

FIG. 3. Schematic of popular techniques for creation of fluorinated, superoleophobic surfaces. Fluoropolymer plus particles is straight-forward but mechanical durability is an issue, fluorosilane/fluorothiol layers are thin but require surface activation (e.g., via UV/plasma) for silanes or specific substrates (e.g., copper, silver) for thiols, fluorosurfactant layers provide a surface that repels oils but attracts water for oil–water separation but requires specific surface chemistry for bonding, and fluoroplasma accomplishes surface texturing and fluorination in one step but is difficult to scale.
example was created via spray coating a perfluoroalkyl methacrylic copolymer along with TiO$_2$ nanoparticles. This coating was found to have high contact angles for water and ethylene glycol. However, not only was hysteresis not reported but lower surface tension liquids were not tested and no durability experiments were performed.\(^\text{14}\)

Fluoropolymers have also been used with electrodeposited conductive polymers,\(^\text{15}\) ZnO nanoparticles,\(^\text{16}\) polydimethylsiloxane (PDMS) trapezoids,\(^\text{17}\) silica particles,\(^\text{18}\) carbon nanofibers,\(^\text{19}\) silica-modified fabrics,\(^\text{20}\) raspberry-shaped particles,\(^\text{21}\) and electrospun copolymers\(^\text{22}\) to result in oleophobic or superoleophobic surfaces. Fluoropolymers have also been spray cast with fluorinated silica particles resulting in good repellency towards water, diiodomethane, rapeseed oil, and hexadecane.\(^\text{23}\) However, the authors reported that durability was compromised to achieve optimum oil repellency and, similarly, more durable coatings were not as repellent.

One drawback of fluoropolymers is it can be difficult to achieve the necessary roughness from the polymer alone and additional materials must be added. Alternatively, the fluoropolymer can be deposited on a prefabricated substrate with the correct topography. However, if the coating is too thick, surface roughness features can be lost.

Fluorosilanes are another desirable method for creating superoleophobic surfaces as they can form thin, self-assembled layers that will not conceal small topographical features. Silanes typically require –OH groups on the surface for a covalently bonded layer to form. Unfortunately, many silanes are sensitive to moisture and form insoluble polymers in solution.\(^\text{24}\) When factored in with the requirement for surface activation, this can limit the use of silanes for industrial scale up.

Regardless, fluorosilane layers have been investigated on silicone nanofilaments,\(^\text{25}\) porous silicon,\(^\text{26}\) etched bulk metallic glasses,\(^\text{27}\) silica particle-functionalized cotton fibers,\(^\text{28}\) micro- and nanopatterned titania surfaces,\(^\text{29}\) fibrous substrates with vapor-phase polymerized polypyrrole,\(^\text{30}\) nanocellulose aerogel,\(^\text{31}\) titania-SWNT composites,\(^\text{32}\) polymer-silica composites,\(^\text{33}\) silica-encased carbon soot,\(^\text{34}\) hierarchical copper oxide,\(^\text{35}\) electrospun titania,\(^\text{36}\) nanostructured ferroselite,\(^\text{37}\) hierarchical zinc oxide,\(^\text{38}\) silica-MWNT composites,\(^\text{39}\) plasma-etched polymers,\(^\text{40}\) acid-etched aluminium,\(^\text{41}\) and nanofiber aerogels.\(^\text{42}\) Many examples also opt to create re-entrant patterns on silicon,\(^\text{6,43–45}\) Fig. 4. As mentioned

**FIG. 4.** Example of re-entrant geometry on fluorosilane-functionalized, patterned silica posts. The textured silica posts were found to be more repellent than the smooth posts. Adapted with permission from Zhao et al., Langmuir 27, 5927–5935 (2011). Copyright 2011 American Chemical Society.
previously, re-entrant structures enable high contact angles for liquids that typically exhibit low angles (<90°) on the corresponding flat surface. However, these structures are typically very fragile and difficult to manufacture.

Another method uses a cage-like organosilicon compound, functionalized with a fluorosilane and dip coated onto fabric. The treated fabric is repellent to water, oils and is durable against UV, acid and abrasion tests. These fluorosilane-functionalized silsesquioxanes have also been spray coated alongside poly(methyl methacrylate) (PMMA) to create superoleophobic coatings with high contact angles for water and hexadecane, though the hysteresis of the latter is high unless deposited on a steel mesh. The fluorinated silsesquioxane has also been combined with electrospun PDMS on a steel mesh to provide repellency against a wide range of liquids, including solvents able to dissolve PDMS.

It is possible to take advantage of existing natural structures and further functionalize them with materials not available in nature. For instance, a PDMS replica of the hydrophobic colocasia leaf was modified with silica nanoparticles and fluorosilane to result in an oleophobic surface. Despite good replication of the flower-shaped protuberances from the natural leaf, the group found it difficult to activate the PDMS for silane attachment. The oxidizing treatment chosen triggered the formation of silica nanoparticles leading to an increase in the roughness. It is therefore difficult to determine whether the topography of the natural leaf, when combined with the fluorosilane, is sufficient for creating an oleophobic surface since both chemistry and roughness were altered.

We have investigated a superomniphobic coating comprised of several layers, which are deposited individually in a layer-by-layer technique. A nanoparticle layer introduces roughness and increases the hardness to improve durability. Intermediate polymer layers (PDDA) are used to help bind the particles to the surface. The final layer in the coating contains the desired surface chemistry and can be easily swapped to produce a different functionality.

By adding a fluorosilane to the top of the layered stack, we were able to create superomniphobic coatings with contact angles >150° and tilt angles <10° for water, hexadecane, tetradecane, dodecane, and decane. The fact that the fluorinated material is only present at the solid–air interface, unlike in other examples, ensures that it does not compromise the durability of the coating.
Another species capable of forming a self-assembled, fluorinated layer are thiols. However, these display long term instability toward oxidation and only assemble on specific surfaces such as silver, gold, platinum, palladium, or copper. Fluorinated thiols have, however, been spray coated with silica nanoparticles and a photoinitiator to create UV-cured superomniphobic films. The films were repellent to water, hexadecane, methanol, ethanol, PDMS, and cyclohexane. However, the authors admit that durability remains a challenge. Fluorinated thiols have also been deposited on
silver coated, sand-blasted copper  and chemically etched copper. Finally, fluorinated thiols were also found to simultaneously etch and fluorinate Cu(OH)$_2$ nanostructures to result in high oil contact angles. It was also reported that the oil adhesion could be tuned by altering the nanostructure length and density.

Surfaces that repel oils also typically repel water, due to water having a higher surface tension (Table I). However, it is possible to create a coating that repels oils but attracts water. This can be achieved through the use of a fluorosurfactant, which contains a high surface energy head group and a low surface energy tail group. Fluorosurfactants are typically used as additives in paints or cleaners, however, the presence of the ionic head group common in many examples allows for them to become complexed, either in solution or on a coating, with electrolyte-containing polymers. In either case, after deposition the fluorinated tails segregate at the air interface resulting in a low surface energy barrier that repels oils. However, when droplets of water are placed on the surface, they are able to penetrate down through the tail groups to reach the high surface energy groups below, and thus the coating appears hydrophilic.

Such surfaces can be exploited for a variety of applications, including oil–water separation and anti-fouling. However, many examples of these surfaces have several drawbacks including poor oleophobicity or poor water penetration resulting in a coating that is initially hydrophobic.

We created superhydrophilic/superoleophobic coatings, through the use of the layered technique described above, by swapping the fluoroisilane for a fluorosurfactant. The coating displayed oil contact angles of $>150^\circ$ with low tilt angles and water contact angles of $<10^\circ$. By spraying this coating onto a stainless steel mesh, we created an oil–water separator, Fig. 6(c). When an oil/water mixture is poured onto the mesh, the oil is repelled and remains on top while the water spreads out and penetrates through the mesh to be collected on the other side, thereby separating the two liquids.

It is also possible to use fluorosurfactants to create superomniphobic surfaces where water is unable to penetrate. For instance, superomniphobic copper surfaces were created by spray coating copper acetate and perfluorooctanoic acid. The coating was superoleophobic with high contact angles reported for hexadecane, dodecane, rapeseed oil, and ethylene glycol. However, the lower surface tension oils exhibited high sliding angles. Perfluorooctanoic acid has also been used to functionalize acid-etched aluminium and electrochemically etched aluminium.

Another study utilized acetic acid and hydrogen peroxide to create microflower-like structures on the surface of cast iron. The micro and nanostructured surface, when treated with a perfluorocarboxylic acid, was superomniphobic and displayed anti-rust and anti-corrosion characteristics.

Finally, fluorinated thiols were also found to simultaneously etch and fluorinate CuO nanowires. Fluorinated materials are popular due to
their low adhesion. Fluoropolymers are used to form nanoparticle composites, however, they may not be suitable for pre-patterned surfaces and durability is usually poor. Fluorosilanes, fluoroethoxyls, and fluorosurfactants are able to produce thinner films, however, they require surface activation or specific chemistry. Finally, fluorination via plasma results in good surface coverage, however, such treatments require specialty chemicals and conditions not typically suitable for scale-up.

By taking inspiration from nature, and adding additional chemistries, it is relatively easy to achieve oil repellency. The challenge is designing a treatment or coating that is not only industrially viable (cost, safety, and scale-up) but also durable enough to be relevant for a range of applications. Many of the surfaces highlighted rely on delicate structures that are difficult to fabricate on a large scale. Additionally, the use of fluorinated materials makes durability a challenge due to poor adhesion. However, many studies are beginning to investigate mechanical durability in more detail and the outlook is improving.

Finally, studies are starting to investigate liquids beyond oils and are successfully repelling solvents, acids, and polymers. Future work will undoubtedly be focused on repelling ultra-low surface tension liquids such as fluorinated oils, which can be successfully repelled using specially designed, re-entrant structures. As more and more liquids are repelled, the number of applications for superoleophobic and superomniphobic surfaces increases and the field of liquid-repellency will continue to grow.

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