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Review Article

Fluorine-free superhydrophobic characterized coatings: A mini review

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Abstract
The scientific fraternity and coating companies have researched and developed coatings with superhydrophobic features for a wide range of applications, varying from automotive, oceanic, pharmaceutical, and thermal and power sectors, over the preceding few years. The self-cleaning features of superhydrophobic surfaces exhibit pronounced dust repelling and lower dust adhesiveness qualities, along with incomparable water repellence for maritime, automotive, and pharmaceutical applications. The advancement of super-hydrophobic surfaces for averting the accrual of impurities on surfaces is an active space of exploration globally. A lesser hysteresis of contact angle leads to drops of water sliding effortlessly on such surfaces. The solid surfaces' surface energy can be weakened by fixing materials of lesser surface energy on the exterior, which can be performed by the following dual methods; either by fixing materials of reduced surface energy straight onto the exterior of a substrate in the form of a coating of that material, or by fixing materials of less surface energy on the exterior of nano-architectural structures and then dropping the coating of those nanoscale materials on the exterior of the substrate. The generation of nanoscale irregularities on substrates by dropping nanostructure layers on surfaces makes it an attractive option since, usually, nanomaterials have a minimum of one dimension, ranging from 1 - 100 nm. The nanostructures' sizes unveil exceptional physical and chemical characteristics, principally owing to their greater specific surface area to volume quotient. This review encompasses the non-fluorinated superhydrophobic coatings developed to date.

1. Introduction

The progress of coatings of a superhydrophobic nature, with distinctive configurations, features, and comprehensive applicability, in the arenas of anti-fogging (England et al., 2016; Howarter & Youngblood, 2007; Gan et al., 2007), anti-fouling (Banerjee et al., 2011; Chambers et al., 2006; Callow & Callow, 2009), anti-icing (Boinovich et al., 2013; Li et al., 2012; Peng et al., 2012), self-cleaning (Latthe et al., 2014; Ganesh et al., 2011), anti-corrosion (Wei et al., 2015; Isimjan et al., 2012; Mo et al., 2015; Chen et al., 2009), and other sectors (Xue et al., 2014; Zheng

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et al., 2010; Ball, 1999; Li et al., 2017), of late have grabbed the attention of scientists and industrialists. The key parameters to strategize a surface of a superhydrophobic nature are lesser surface energy characteristics and micro- and nanohierarchical coarseness of the surface. The theory of Wenzel highlighted that a lesser area of touch between a droplet of water and a solid surface results in an improved hydrophobic nature of a rough surface. The Cassie and Baxter prototype (Cassie & Baxter, 1944) highlighted that a lesser hysteresis of contact angle and a higher contact angle on a permeable exterior is owed to the entrapment of air in the apertures of a substrate, which has the consequences of declining the interaction between the droplet of water and the substrate. Additionally, the entrapped air diminishes the attachment amongst the consequent strata of accumulated dust and, thus, averts the accrual of dust more competently.

Commercially available superhydrophobic coatings lose their functionality subsequent to mechanical abrasion due to the methodology involved in the fabrication of these coatings, where generation of micro-/nanoscale rough surface morphology, as well as functionalization of the surface structures in order to diminish their surface energy, is carried out. However, the micro to nanoscale architectures of the surface are innately brittle and are detached effortlessly, resulting in the loss of the superhydrophobic nature (Ke et al., 2014).

The 4 different modes of wettability, distinguished on the basis of contact angle produced by a drop of water, are superhydrophilic, hydrophilic, hydrophobic and superhydrophobic (Marmur, 2012). The same is diagrammatically illustrated in **Figure 1**.

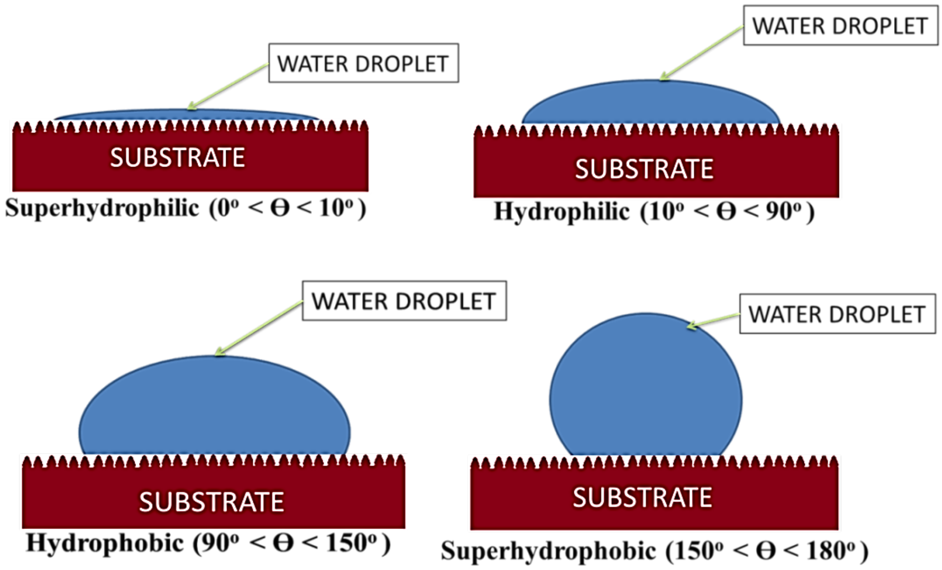

Figure 1 Graphic illustrations of superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic concepts on identical surfaces.

The long-established presence of natural superhydrophobicity is predominant and documented in various literature reports. There are innumerable natural resources, like the petals of lotus flowers and animal species and their precise parts, that have demonstrated superhydrophobic characteristics, which are schematically illustrated in **Figure 2**.

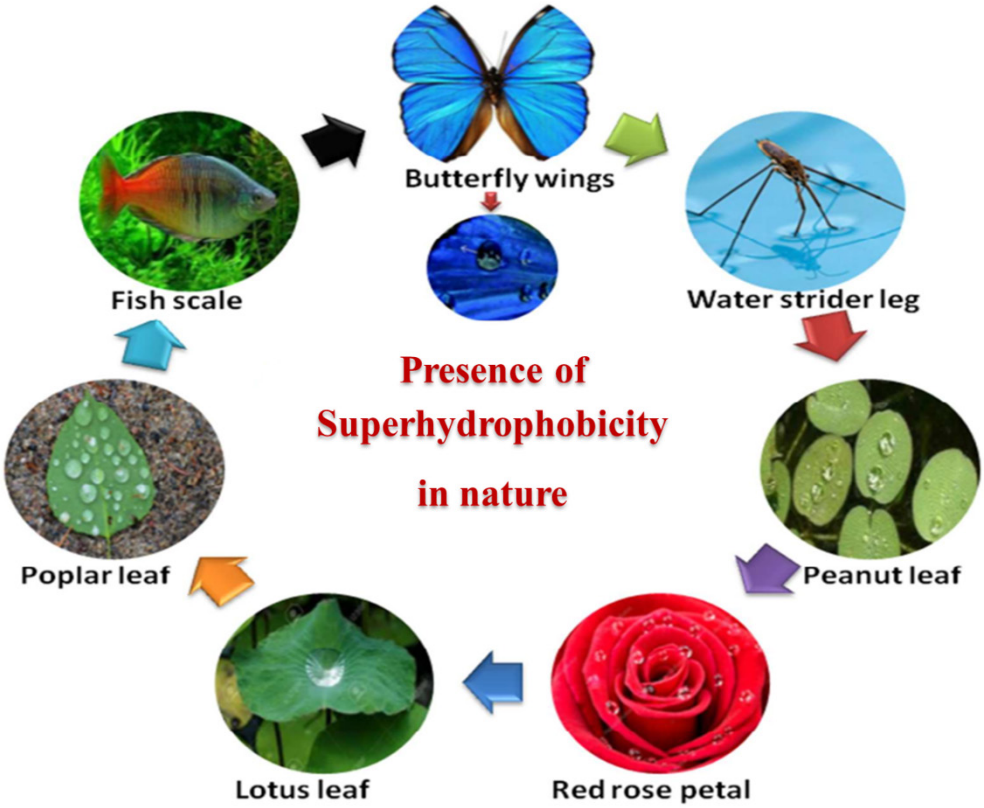

Figure 2 Prevalence of superhydrophobicity in nature. Reprinted with permission (Das et al., 2018).

Several researches have been carried out to identify the numerous influences accountable for determining superhydrophobic nature. The key parameters which have major influences are roughness, in terms of nanoscale, surface energy, depth of coating, mechanical steadiness, and bonding strength between the substrate and coating (Si & Guo, 2015). Tetrafluoroethylene and organopolysiloxane are coatings of polymeric origin, adapted with lesser surface energy, which establish a much lesser accrual of dust, and hence are deliberated as prospective contenders for coatings which are self-cleaning in nature. The augmentation of a solar panel's productivity by impeding the accrual of dust can be accomplished by a robust and ecologically benign coating of a superhydrophobic nature; the property of photosensitive transparency is a prerequisite for solar panels, as it augments solar radiation's transmissibility and, hence, escalates effectiveness. However, the presence of a higher proportion of surface roughness in coatings of a superhydrophobic nature results in a substantial scattering of light which impedes the productivity of the solar panels. Hence, the features of transparency and superhydrophobicity are contradictory to each other, leading to a precise regulation of roughness which is paramount during the fabrication of transparent coatings of a superhydrophobic nature (Hooda et al., 2020). The intensified awareness of manufacturing superhydrophobic surfaces with a focus on improvement of roughness from micro- to nanoscale is an effort to be applauded. Nanofillers, such as zinc oxide, titanium dioxide, and nanosilica, are employed in the production of superhydrophobic coatings for enormous-scale industrial applications (Das et al., 2018). In most superhydrophobic surfaces, the addition of poly- or per-fluoro-alkyl hydrophobic agents leads to a decline in surface energy, due to fluorocarbon's lesser affinity to water, even if paralleled with hydrophobic hydrocarbons. Nevertheless, fluorinated surfaces are seen as ecologically hazardous, due to their impending dangers towards the health of human (Zhang et al., 2018).

2. Progress in the fabrication of numerous fluorine free coatings of a superhydrophobic nature

De Nicola et al. (2015) manufactured coatings of a super-hydrophobic nature from a multi-walled carbon nanotube (MWCNT), specific to stainless steel substrates, by engaging the chemical vapor deposition procedure at temperatures of less than 1,000 °C, also devoid of additional catalysts. It was observed that MWCNT sheets of a super-hydrophobic nature on stainless steel substrate demonstrated both high contact angle values (154 °) and higher adhesive strength (high hysteresis of contact angle). The existence of dual morphology at both micro- and nanoscale levels, along with the lesser energy materials on the surfaces, manifested super-hydrophobicity features.

Zhu et al. (2014) testified about the production of carbon nanotube coating with a superhydrophobic nature that demonstrated worthy reusability and stress-free reparability by sputtering multiwalled carbon nanotubes on the substrate trailed by a floatation of surface technique. The lesser adhesion strength between the MWCNT coatings and water led to the formation of spherical droplets of water, which at a small tilt angle rolled off effortlessly from the coatings.

Zhang et al. (2015) highlighted the creation of polydimethylsiloxane-coupled carbon nanotube composite coatings of a superhydrophobic nature with the usage of a spray suspension technique. The achieved superhydrophobic nature of the coatings was correlated in relations of mass proportion of carbon nanotube to polydimethylsiloxane, which ranged from 0.1 to 0.5. The coating with mass ratio greater than 0.3 unveiled superhydrophobicity features with a contact angle of 163 °, a slide angle value of lesser range, less adhesive strength, and an elongated period of stability. The coating with mass ratio of less than 0.3 revealed a contact angle value of 128.3 °, which was a consequence of being devoid of nanoscale irregular structures and the presence of hair-like protuberances.

Junaidi et al. (2017) prepared a silica-oriented superhydrophobic coating with photoluminescence features which was synthesized from rice husk ash. The rice husk ash at 550 and 650 °C was calcined to produce particles of silica with a minor quantity of residual carbon. Nevertheless, this established coating with superhydrophobic characteristics could only be casted on glass plates and concrete. Notably, the coated concrete revealed a water contact angle value of 157.7 °

Liao et al. (2019) invented unique polybenzoxazine hybrid superhydrophobic surfaces strengthened with silica nanoparticles. It was also reported that the undeviating ultraviolet-aided replica molding process was applied to create locations of a superhydrophilic nature on the superhydrophobic-coated layer by incorporation of a shadow mask or an optical mask. Subsequently, ultraviolet exposure of 5 min on the coated surface promoted worthy bonding of droplets of water on the hybrid surface, and a contact angle of 161.1 ° was recorded.

The spin-coating of trimethylsiloxane silica suspension onto polyurethane (PU) layer by Jiang et al. (2013) resulted in the development of a superhydrophobic surface. The coated substrate unveiled extraordinary stability with time period and recorded a higher value of contact angle of 166.2 °, and even after half a year of interval, a noteworthy value of sliding angle of 6.6 ° was documented.

The incorporation of a spray coating technique to manufacture coatings of a superoleophobic nature by casting suspensions of nanoparticles of zinc oxide onto polymer was undertaken by Steele et al. (2009). This resulted in the generation of a surface morphology of categorized nanotextures which led to achieving multiscale roughness. The mass proportion of ZnO to PMC of 3.3 resulted in superoleophobicity, and a static contact angle of 157 ° was recorded, whereas the mass fraction of 1.7 led to superhydrophobic characteristics with 168 °.

The development and casting of fluorine-free resilient films of zinc oxide-coated mesh of a superhydrophobic nature on substrates of steel with the help of the hydrothermal route was undertaken by Wang et al. (2012). Subsequently, stearic acid was used to improve the coatings to amalgamate superhydrophobicity and superoleophilicity coated mesh films of zinc oxide for submerged and surface oil arrest and conveyance application. The application of hydrothermal treatment to a coating of mesh size 600 µm for 45 h revealed that the recorded contact angle was superior to 150 °, which was owed to the flower-type ZnO morphology possessing ultraviolet superhydrophobicity.

Fluorine-free zinc oxide/ polydimethylsiloxane composite coatings were developed by Zhang et al. (2010), which exhibited resistance to oil-fouling and possessed a superhydrophobic characteristic. Micrographs obtained by scanning electron microscopy (SEM) technique revealed the architecture of the nanostructure which is liable to incorporate both superoleophilic and superhydrophobic features; the contact angle value recorded was 160 °, with droplets of water rolling at a tilting angle of 3 °.

The non-fluorinated wet chemistry technique was chosen by Holtzinger et al. (2013) to design and manufacture superhydrophobic TiO_2 coatings based on a nanosphere lithography manner. This method uses spheres of polystyrene which are embedded with hexadecyl trimethoxysilane (C16), fabricating coatings exhibiting a higher contact angle of 160 ° and indicating a superhydrophobic characteristic.

The fabrication of polyurethane-organoclay nanocomposite coatings of a water-repelling nature by the dispersion of polyurethane which was moisture curable, along with altered montmorillonite clay by fatty amine/amino-silane in cyclomethicone in water emulsion, was done by Bayer et al. (2010). The polyurethane and organo-clay disseminated emulsions were layered onto aluminum substrates via a spray technique to achieve self-cleaning coatings of a water-repelling nature and exhibited a water contact angle of 155 °.

Gore and Kandasubramanian (2018) manufactured cellulosic substrate-based PLA Janus fabric, which was ecofriendly and was functionalized with surface-altered nanoclay. via the effective electrospinning procedure. This substrate demonstrated a water contact angle of 152 ^{o}, highlighting the superhydrophobic nature.

Sahoo and Kandasubramanian (2014) manufactured particles of carbon soot via manually regulating the combustion of camphor. This substrate revealed a water contact angle of 170 ^{o}, highlighting the superhydrophobic nature.

Gore et al. (2020) degummed silk fibers using both water and Na_2CO_3. Both of these exhibited 153 and 158 ° water contact angles, respectively, demonstrating a higher water repellency capability. Additionally, a superoleophilic nature was also observed, and 50 % efficacy was documented; however, this was restricted to 10 numbers of oil-water separation cycles.

Besides the above-documented progress, it has been seen that, due to the excellent thermal conductive nature and the inherent brilliant mechanical characteristics, various carbon materials, like nanofibers, nanotubes, and fullerene, and grapheme and its oxides, were employed for the production of a superhydrophobic surface (Sahoo & Kandasubramanian, 2014).

3. Limitations during the manufacture of coatings of superhydrophobic nature

3.1 Exorbitant pricing of superhydrophobic materials

The preparatory materials that are prerequisites for the creation of coatings of a superhydrophobic nature are on the higher side in terms of pricing. The techniques employed for generating both micro- and nano-architecture on coating surfaces are equally expensive (Feng et al., 2011).

3.2 Durability of the prepared coating

Uncertainty about the loss of superhydrophobic characteristics, even after usage of a high quality of material like nanosilica, is a cause of concern. This is due to the occurrence of chemical or physical linking with the solid substrate, resulting in the deterioration of the superhydrophobic features of the nanomaterial. This indicates that the superhydrophobic features and the strength of that coating are paired opposite to each other; hence, a suitable equilibrium is obligatory to cultivate a steady superhydrophobic coating (Aegerter et al., 2008).

3.3 Consistency of generated nanoscale architectures

Generally, a surface of lesser energy based on the feature of the repelling of water, entailing sturdy micro- to nanoscale structural topographies, is obligatory for accomplishing an outstanding superhydrophobic coating, i.e., occurrence of higher water contact angles. Attaining all of the crucial experimental constraints concurrently is a very complex state of affairs. For example, at nanoscale, it has been noted that specific polymers entailing nanotextural features perform like 'gluey noodles' which interweave down effortlessly and ultimately discontinue performing like a superhydrophobic surface (Bhushan & Jung, 2011).

3.4 Precipitation/condensation concerns

In an atmosphere where a coating is deployed, the occurrence of condensation can prevail if the surrounding temperature falls below the dew point. Due to the condensing process, a materialization of substantial wetting on the superhydrophobic coating happens, which leads to the loss of water-repelling characteristics; hence, highlighting that they are not water vapor-repulsive (Miljkovic et al., 2013).

3.5 Concern of wetting by emulsifier/oil

The usage of an emulsifier or oil significantly curtails a drop of water's surface tension, whereas an augmented surface tension of a droplet of water results in the superhydrophobicity of a surface. Hence, application of an emulsifier or oil on a solid substrate can lead to effortless wetting, due to the annihilation of the superhydrophobic performance of the substrate (Chang et al., 2007).

4. Methods to augment mechanical sturdiness of superhydrophobic surfaces

The mechanical robustness of a coating is reliant on the adhesive strength amid the substrate and the superhydrophobic coating, whereas the wearability of these coatings is principally governed by the nature of the polymer. The three techniques used to enhance the mechanical resilience of coatings are as follows (Zhang et al., 2018):

- The bonding of hydrophobic functionalized nanoparticles and adhesives is extensively applied by certain marketable coatings of a superhydrophobic nature, because the surface toughness is extremely reliant on the sturdiness of the adhesives.
- The usage of integrally abrasion-resistive substrates for superhydrophobic coatings, like flexible textiles or concrete, the approach for which is, however, is restricted by substrate-specific materials.

The generation of dense superhydrophobic film by the dispersion of hydrophobic nanoparticles in the polymer, done by the exposing of a fresh coat of the film when the preceding layer is damaged, thereby maintaining the nature of superhydrophobicity.

5. Evidence of innumerable applicability of polymer-based nanocoatings of superhydrophobic natures in versatile arenas

The design, development, and commercialization of superhydrophobic coatings have been matters of great attention over the past few years. The various fields of applicability are corrosion resistance, de-icing, defogging, auto-cleaning ability, the separation of oil from water, medicinal usage, and resistance to biological foulers. The same is illustrated in **Figure 3**.

Superhydrophobic coatings using nanoparticles incorporated with an anti-ice nature were fabricated by Cao et al. (2009) which was motivated by the self-cleaning nature of lotus petals. A sequence of nanocomposite polymeric coating, using acrylic as the matrix and nanofillers of silica of diameters varying from 20 nm to 20 μm on several substrates, together with glass and metal, were utilized. The superhydrophobic characteristics of the coatings were affected by the alteration of the silica nanoparticle sizes. The produced nanocomposites of various sizes from 20 nm to 10 µm possessed superhydrophobic features, with contact angles of greater than 150 °.

Figure 3 Applicability of superhydrophobic coatings. Reprinted with permission (Das et al., 2018).

The technique of solvothermal process was applied to fabricate nanoporous polydivinylbenzene materials unveiling both superoleophilic and superhydrophobic natures by Zhang et al. (2009). However, in comparison to conventionally-activated carbon absorbent, the nanoporous materials showed distinct discernment for several organic compounds.

Zhang and Seeger (2011), with the help of the chemical vapor deposition technique, prepared materials from polyester textiles of both superhydrophobic and superoleophilic natures. These materials demonstrated a reusable nature, flexible features, superwettability, and a higher segregation efficacy of oil/water.

Various coated devices, established on conjugated microporous polymers of a superhydrophobic nature, extremely effectual conjugated microporous polymer-coated sponge, and stainless steel, for the segregation of oil-water and trace organic pollutants, were designed by Xiao et al. (2017). The novel explored varieties of permeable materials of these conjugated microporous polymers that can be effortlessly manufactured by basic organic reactions. Conjugated microporous polymers exhibit a surface adaptable nature, decent stability, and a huge surface area, leading to momentous attention from researchers.

Tough multifunctional coatings with a superhydrophobic nature for self-cleaning, the superior separation of water/oil, corrosion resistance, and anti-bio adhesive features were developed by Cho et al. (2017). The usage of siloxane polymer and silica ormosil suspension in the preparation of extremely transparent and superhydrophobic nanocomposites was documented. The surface roughness parameter was enhanced by the amalgamation of silica ormosil suspension with polymethylhydroxysiloxane nanoparticles.

Three-dimensional superhydrophobic poly(ε-caprolactone) electrospun knits, comprising poly-(glycerol monostearate-co-ε-caprolactone) as a hydrophobic polymer dopant, were developed by Yohe et al. (2012). In the tunable drug release activity, this superhydrophobic mesh was used through the displacement of air to govern distribution percentage. The serum's durable existence for a longer period was revealed by the layer of air that was captured within the superhydrophobic meshes, displaying effectiveness counter to cancer cells in vitro for a period greater than two months.

6. Recent utilization of transition metals and their oxides as biomimetic surfaces of superhydrophobic natures

The contemporary advancement of the application of a sequence of transition metals and their oxide materials, including TiO_2, ZnO, Fe_3O_4, CuO, Ag, and Au, unveiling superhydrophobic natures, has been worth noticing. The incorporation of transition metals and their oxides in manufacturing superhydrophobic surfaces are not only due to their surface topographies, with governable microstructures resulting in diverse adhesion, water-repellency, and wettability adaptability, but also due to a diversity of distinct assets, like anti-bacterial properties, magnetism, optical performance, and transparency. The sensitivity of ZnO and TiO_2 to UV light, the antibacterial characteristics of silver, and the magnetic nature of iron oxide, are some of the specific properties which have led to the wide employment of transition metals for the production of superhydrophobic materials, aside from the ease of controlling morphological structures.

Ebert and Bhushan (2012) used several categories of nanoparticles (SiO_2, ZnO, and ITO) to formulate surfaces of superhydrophobic natures on various substrates like glass, PC, and PMMA. These surfaces revealed higher values of water contact angles, lesser adhesiveness, and higher transmissibility of visible light, along with exceptional resistance to wear and tear. A sol-gel technique was employed to prepare TiO_2-SiO_2-PDMS multipurpose hybrid films, and their superhydrophobic and photocatalytic characteristics led to the applicability of the printing of flamboyant designs and the separation of oil-water (Deng et al., 2014).

7. Conclusions

The assorted applicability of polymeric coatings unveiling superhydrophobic physiognomies has been perceived. The amplification of the superhydrophobic nature of the polymeric coatings has been also affirmed, solely after the addition of fillers of various scales. For the designated application of the segregation of oil-water, polymeric nanocoatings comprising ZnO are used, whereas polymeric nanocoatings comprising clay unveiled greater anti-wetting features with respectable self-cleaning characteristics. In acidic and alkaline solutions, superior chemical resistance properties were demonstrated by CNT and silica-based polymer. The production expertise should be comparatively cheaper and require less effort, such those large-scale industries can more easily undertake it. For the accomplishment of metallic surfaces displaying superhydrophobic natures, the roughness parameter of multiscale structures plays an imperative role; hence, a thorough knowledge and checking of it is a prerequisite. Low surface energy polymers, like PDMS, PS, and PET, are majorly incorporated for achieving water repellency and, so, designing non-fluorinated polymers is still a challenge.

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