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Superhydrophobic Self-cleaning Surfaces in Nature

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Abstract: A global interest was awarded to study the natural superhydrophobic surfaces since the description of the Lotus Effect by Barthlott and Neinhuis in 1997. Natural biomimetic surface merits of micro/nano-roughness, water contact > 150°, sliding angles <10°, and minimized free-energy characteristics would motivate the dynamic fabrication of superhydrophobic surfaces. This critical review introduces an architectural panorama of numerous structural designs of natural superhydrophobic surfaces. Also, it discussed the fundamentals of self-cleaning and wetting theories to develop superhydrophobic structures. This progress review concentrates on superhydrophobic materials' applications for self-cleaning marine antifouling surfaces. It introduced an in-depth understanding of the structural design-superhydrophobic property relationship of the natural nano-wettable surfaces. It is technically first to shed light on the inner basics and platform for surface non-wettability and facilitates the way for design biomimetic self-cleaning antifouling surfaces.
Keywords**:** Superhydrophobic surfaces, Lotus Effect, self-cleaning, coating materials, antifouling

1. Introduction

Superhydrophobic surfaces have established cost-effective and eco-friendly solutions for different fields such as antifouling coatings, anti-icing, anti-corrosion, and textiles [1]. Learning from nature, one of the first lessons is the self-cleaning property of Lotus leaves, under investigation in the last decades for their particularly strong water repellency of its unique structure with a highly hydrophobic character [2]. Lotus plant leaves (Nelumbo nucifera) are the most famous superhydrophobic self-cleaning surface with the micro-roughness structure of epicuticular wax formed with 20-40 μm protruding ganglion [3]. Butterfly's wings and the leaves of cabbage and Indian cress plants are examples of superhydrophobicity in nature [4]. Superhydrophobic surfaces exhibited static water contact angle (WCA) >150° and contact angle hysteresis (CAH) <5°; which provided by low free energy and micro-/nano-patterned rough topology of the surface [5]. The exploitations of structural properties of plant or animal surfaces have generated new biomimetic approaches starting from micro- or nanoscopic observations and structural designs to a wide range of basic research and industrial fields. The first synthetic superhydrophobic surface, demonstrated in the 1990s, based on creating rough surface [6]. Superhydrophobicity provides a pathway toward protecting sensitive surface characteristics [7]. The roughness effect on the wettability properties of a solid surface can be interpreted by the models of Wenzel and Cassie-Baxter [8]. The increase in the solid-liquid interface can increase both the surface roughness and its hydrophobicity by air trapping within the surface grooves [9]. Such roughness of the surface and air-entrapping can provide the superhydrophobic character since the contact angle of air is 180° [10]. Micro-nano structured surface and the low surface free energy (SFE) are thus responsible for superhydrophobicity [11,12]. Superhydrophobic surfaces are extensively used in engineering applications. Among the different technological fields operating in and with seawater, in this work the application of superhydrophobic technology to protect boat and ship hulls against fouling organisms was considered. As an effective non-toxic fouling release (FR) coating, insertion of different nanofillers with controlled sizes and morphologies in silicone matrixes can increase the resistance against micro-organisms attack. In this review, the advanced self-cleaning FR nano-surfaces are highlighted. Therefore, the platform for developing superhydrophobic technology as a relatively young method for the protection of surfaces against marine fouling considered the biomimetic self-cleaning surface designs as an effective and cost-saving technology.

2. Surfaces with natural superhydrophobicity

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Superhydrophobic phenomena of many natural plants' surfaces have driven much attention [13]. Lotuses leaves (Fig. 1(a-c), butterflies wings (Fig. 1(d and e) and water striders' legs (Fig. 1(f and g)) possess superhydrophobic surfaces [14]. Roughness in the water strider's leg contains nano-grooves with high water non-wettability as reported by Gao et al. [15]

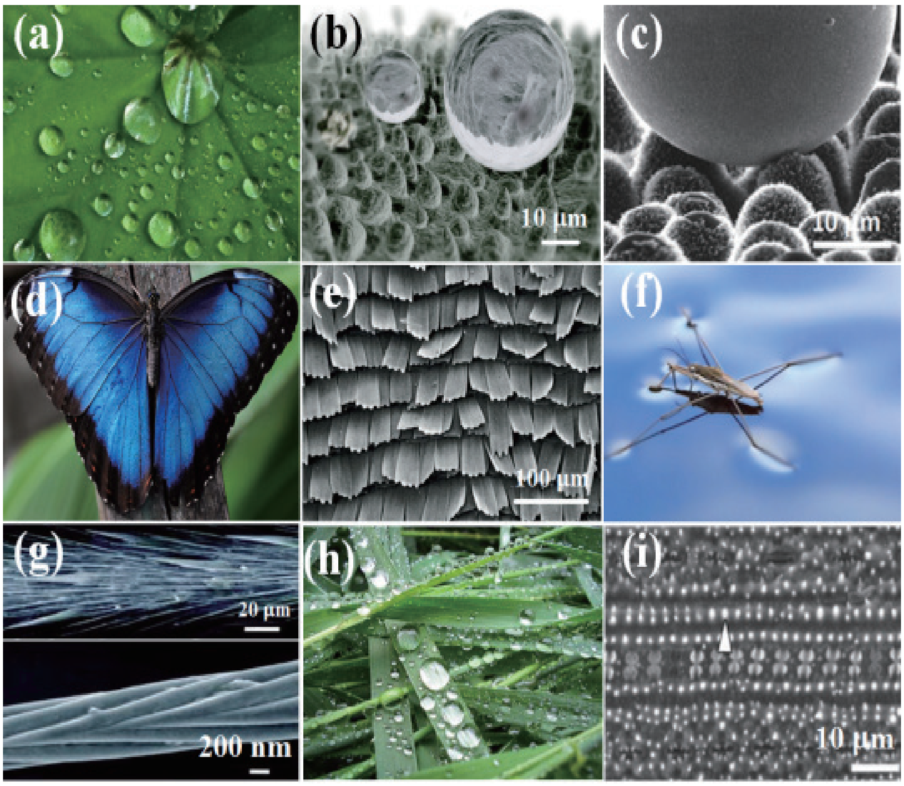
The legs' superhydrophobicity (WCA of 167˚) is caused by trapping the air in the surfaces' nano-grooves. This permits the survival of water striders on the water surface. The skin of the shark is wrapped with fine tooth-shaped dermal surfaces that have longitudinal grooves with ribbed structures as reported by Bechert et al [16]. Such grooves decrease the whirlpools formed on the ultrasmooth shark's skin which afford superhydrophobicity. The WCAs of nearly 200 plants were reported and their surface morphologies were demonstrated by Neinhuis and Barthlott [17].

The results excluded two different kinds of non-wettable leaves surfaces. These kinds are leaves with hair covered (ex. lady's mantle) and those with macroscopically-smooth (ex. Lotus) surfaces [18].

The lotus leaves possess a stable superhydrophobic surface as compared to many other plants that exhibit WCA of 160˚ [19, 20]. Lotus effect is an ideal model for superhydrophobic self-cleaning derived from lotus plant characteristics. Not only WCA is enough to compare the performance of superhydrophobic surfaces, but also other factors such as (1) The shape of the epidermal microstructure.; (2) The nanoscopic epicuticular wax crystals of the leaves; (3) Leaves' nanoscopic epicuticular wax crystals; (4) Superhydrophobic stability under moisture condensation conditions [21].

No significant loss of the property of water repellency was observed for Lotus plant under these conditions, therefore lotus leaves represent an outstanding model for fabricating superhydrophobic structured surfaces. Lotus leaves' superhydrophobic character possess micro- and nanostructured surfaces [22]. The results indicated that the surface of lotus leaves covered with protrusions (of 10 μm) and the distance between them is nearly 20 μm. These protrusions are covered with 100 nm nanotube-diameter and 500 nm height. Also, hydrophobic surfaces with micro- and nanostructured surfaces of the leaves possess reduced free energy of the surface with a waxy crystalloid hydrophobic surface. High WCA (> 160˚) and reduced CAH (3˚) are characteristics for lotus leaves' surfaces. Not only lotus leaves' surface has water non-wettability characteristics, but also other plants leaves (eg. rice leaf (Fig. 1(h and i), taro leaf (Fig.1 (j and k), as well as wings of butterfly and dragonfly insects [23], possess superhydrophobicity owing to their micro/nano-structured surface. Such waxy nano-bumps on rice leaves surface and microgrooves over butterfly wings afford a rough surface with superhydrophobic character and low adhesion and thus, enhanced self-cleaning ability.

The eyes of mosquito exhibited superhydrophobic self-cleaning with nearly 100 nm roughness Fig. 1 (l) at the microstructured surface. The surface also exhibited superhydrophobicity with WCA of ≥ 160˚ as well as low adhesion with a CAH of 10˚ is inevitable.



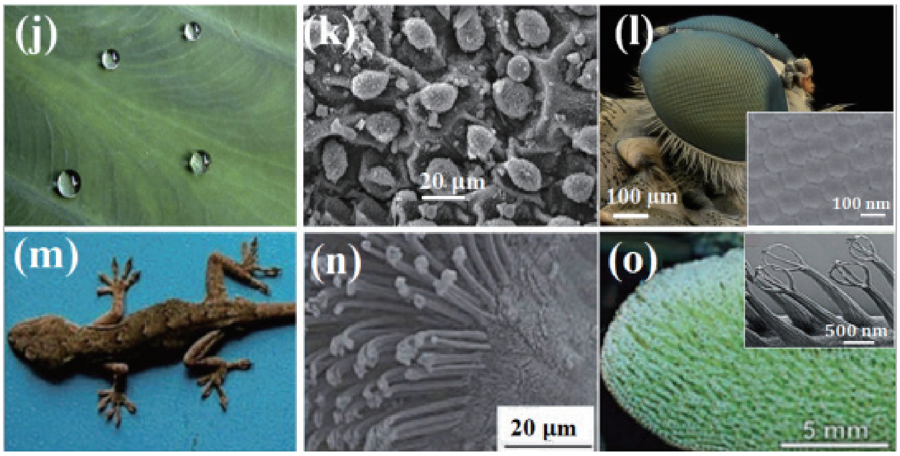


Figure 1. (a) Superhydrophobicity and self-clean ability of lotus leaves surfaces [23, 42]; (b) a spherical water drop over the leaf of lotus plant; (c) SEM capture for lotus leaf surface at high magnification power [11, 32]; (Copyright from Elsevier Ltd. 2019); (d) Wings of butterflies; (e) SEM image of the wings of butterflies with directional adhesion having radial outward direction; (f) Legs of water striders over the surface of water, (g) The Leg's SEM indicating the oriented microsetae covered with needle morphology and grooved nanostructures; (h) Rice leaf superhydrophobic surface structure with water droplets resting on the surfaces, and (i) SEM of rice leaves with longitudinal grooves and transverse sinusoidal structure for superhydrophobicity [11,23]; (Copyright from the American Chemical Society, 2005); (j and k) Taro leaf (Colocasia) and SEM of Taro leaf; (l) the eye of mosquito with its SEM capture covered with micro-spheres and nano-nipples; (m and n) a gecko on the wall and SEM image of setaes on the gecko foot and spatulas of a single seta [23]; and (o) The superhydrophobic surface of Salvinia molesta covered with hairs and inside the SEM image of the hair structure with an eggbeater shape [23]. (Copyright 2017, reproduced with permission from Elsevier Ltd. 2017)

SEM of mosquito eye reported by Gao et al. [24] showed that it is composed of hundreds of microscale hemispheres (about 26 nm) in its hexagonal structure. Also, other superhydrophobic surfaces in nature include rose petals, garlic, and scallions leaves [25].

The gecko species are able to stay firmly attaching on the wall surface even walk free on straight metopes like flat and climb on almost any rough or smooth surface because of their superhydrophobic feet [23, 26]. SEM images Fig. 1(m and n), indicated that the surface of the gecko foot is made up of a great number of well-ordered setae in micron scales and every hair has smaller spatulas in nanoscales. The presence of a multiscale structure and high-density nanopillars enable the gecko to endow both superhydrophobicity (a WCA of >160.9°) and a high adhesive force towards the water.

Also, Salvinia paradox exhibits superhydrophobicity because its surface covered by a mass of multi-cellular hairs, and the eggbeater-shaped structure with four branches appeared on the top of every hair (Fig.1 (o)) [27]. Thus, these superhydrophobic hairs with microscale eggbeater structures can hold air films for a long term underwater which enables this plant to survive in case of being dipped in water. Natural superhydrophobic surfaces have driven research to develop new superhydrophobic and biomimetic surfaces for various applications.

3. Characteristics of surfaces with superhydrophobicity

Superhydrophobic surfaces can be applied as self-cleaning, anti-sticking and antifouling applications. Superhydrophobic self-cleaning artificial surfaces are produced by the combination of micro/nano-structured surface and low surface free energy. Many environmental problems especially the biofouling in marine eco-system can be solved by developing superhydrophobic surfaces. As a result, it is inevitable to study the main parameters of the surface non-wettability for developing biomimetic self-cleaning surfaces.

3.1 Wetting property

This property of wettability represents liquid molecule-substance interactions [28]. Strong interaction between liquid molecules and solid surface, produce surface wetting and liquid spreading over the surface. Wetting occurs at higher surface free energy for different fields including coatings, dyes, anticorrosion and antibacterial applications [29-31]. Liquid molecules are attracted to each other's far away from the surface, which indicates the superhydrophobicity with water drops condensed in a spherical shape such as the mercury drops.

3.2 Contact angle and non-wetting theories

Imperfect wettability means there is no liquid-solid surface interaction. The contact angle is used to express the degree of wettability and is defined as the angle at the edge of the drop with the solid surface which facilitates the determination of surface free energy. Its evaluation is measured through the liquid drop tangent at the contact between the gas (G), liquid (L), and solid (S) in the three-boundary phase. The water contact angle and surface wettability on an ideal smooth surface are discussed by Thomas Young in 1805. Different surfaces are classified based on their wettability into hydrophilic ($0° < \theta \leq 90°$), hydrophobic ($90° < \theta \leq 150°$), and superhydrophobic ($150° < \theta \leq 180°$) surfaces (Fig. 2) [32]. On the other hand, the sliding angle is < 10° [33, 34].

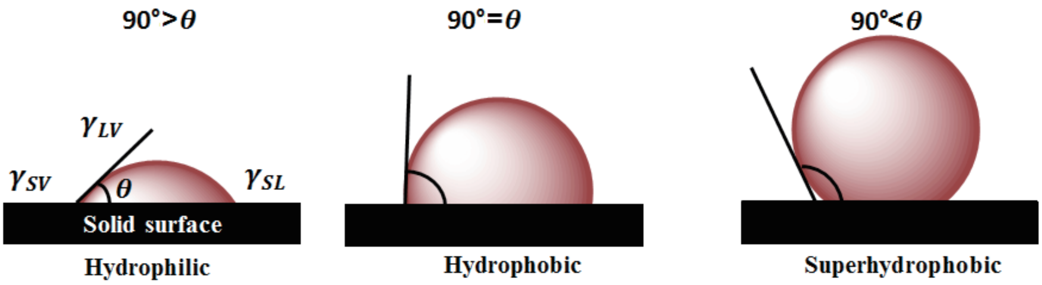


Figure 2. Various wettability behaviors for the contact between a solid surface and liquid drop according to Young's model including hydrophilic, hydrophobic, and superhydrophobic surfaces [32]. (Copyright 2019, reproduced with permission from Elsevier Ltd. 2019)

Atoms on the surface possess higher free energy than those in the interior because of their fewer bonds with their neighboring atoms. The current work can create surface area at standard conditions (temperature and pressure) expressed as the SFE (mJ/m^2). The certain angle obtained by contacting a drop of a liquid with a solid surface is expressed as static WCA (θ_0) as illustrated in Fig. 3a and discussed through Young's model (Eq. 1) [35].

$$Cos\theta_0 = \left(\frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}}\right) \tag{1}$$

Where the SFE for solid-liquid, solid-air, and liquid-air phases are represented as$_{SL}$, $_{SA}$, and $_{LA}$, respectively. Young's model deals with smooth surfaces and is not applied for rough surfaces. Decreasing the energy variation for solid-air and solid-liquid interfaces that enhances WCA determinations. WCA and CAH were used for investigating the hydrophobicity of the surface. The difference between the advancing and the receding WCAs is stated as CAH [36]. At low CAH, water drops can facilely roll-off on the superhydrophobic surface. CAH is greatly affected by the surface's rough topology, chemical homogeneity, and hydrophobicity.

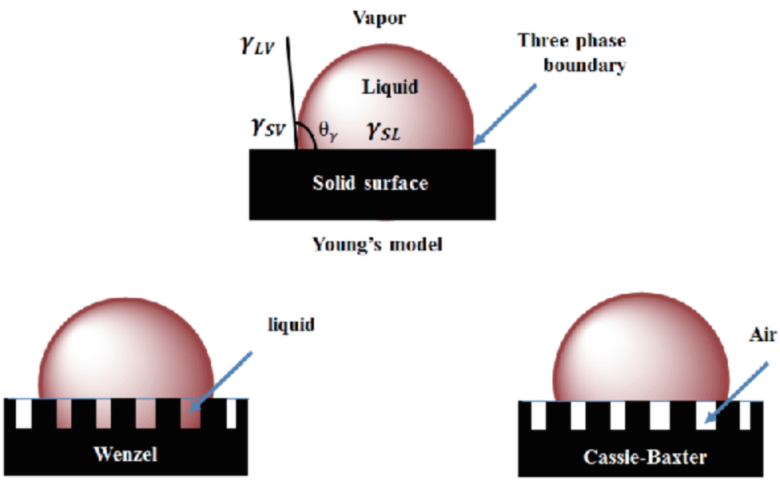


Figure 3. Three-phase boundary with the acting forces between solid, vapour, and liquid. Reproduced with permission from Ref [36]. (Copyright from Elsevier Ltd. 2019). While, (b) represents the Wenzel model for the homogeneous interface, and (c) Cassie and Baxter model for heterogenous phase [41]. Copyright 2019, reproduced with permission from Elsevier

The CAH variations may perform surfaces with a natural slippery or sticky topology. Although Young's equation assumes that all the surfaces are smooth, the topological disorders and roughness may affect the non-wetting state [37]. These effects were studied by the models of Wenzel [38] and Cassie-Baxter [39].

For the surfaces with rough topology, the model of Young cannot be applied [38, 40]. For a rough surface, Wenzel (1936, 1949) through his model expressed WCA θ (in relation with θ_0 of a flat surface. Wenzel model can be expressed as follow (Eq. 2):

$$Cos\ \theta = (\frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}}) = r\ Cos\ \theta_0 \quad (2)$$

where r represents the factor of non-dimensional surface roughness and calculated as illustrated in Eq. 3:

$$r = A_{SL}/A_F \quad (3)$$

where the actual area and projected area of a rough surface are expressed as A_{SL} and A_F, respectively. Surface superhydrophobicity roughness rises the θ for affording ultrahydrophobic character, since $r > 1$. While the roughness of a hydrophilic surface withdecrease the value for producing ultrahydrophilicity. Cassie and Baxter [41] model (for a heterogenous surface) is based on:

The fractional area (f_1) as well as WCA (θ_1)

The (f_2) and (θ_2);

where $f_1 + f_2 = 1$. WCA can be calculated as follow (Eq. 4):

$$Cos\ \theta = f_1 Cos\ \theta_1 + f_2 Cos\ \theta_2 \quad (4)$$

in cased of a composite interface (Fig. 3c), $f_1 = f_{SL}$; (θ_1) = θ_0 and $f_2 = f_{SL} = 1\ f_{SL}$; $\theta_2 = 180$. Cassie & Baxter equation can be expressed as follow (Eq. 5):

$$Cos\ \theta = rCos\ \theta_0 - f_{LA}(rCos\ \theta_0 + 1) \quad (5)$$

If $\theta_2 = 0$ for water/water contact angle (Fig. 4c) (The rough surface's holes filled with water not with air), the following equation of Cassie model was produced (Eq. 6).

$$Cos\ \theta = 1 + f_{SL}(Cos\ \theta_0 - 1) \quad (6)$$

For $\theta_0 > 90$, WCA increased yielding superhydrophobic surface with increasing f_{LA}. On the other hand, the WCA increased (with changing from hydrophilic to the hydrophobic surface) with increasing f_{LA}, for $\theta_0 < 90$ [42].

Wenzel state, or the homogenous wetting, produces higher CAH and a greater adhesion of the droplets to the surface than Cassie state [43]. The CAH of water drops was compared in both models using a surface with a micro-textured topology as reported previously [44]. In Wenzel state, the drops of water were condensed onto the surface, while in Cassie's model they were distributed in a gentle way. The Cassie model exhibit higher advancing CA and considerably lower CAH as compared to the model of Wenzel. and can be applied for various surfaces [45].

3.3 Free energy of the surface

The energy needed for enlarging an interface between two various phases without volume changing is considered as the surface energy (γ). Atoms at the surface are in contact with fewer molecules than others in the bulk phase, so the surface molecules have high potential energy than inside the material. Solid surfaces are intending to minimize the higher energy zone. At the minimum surface area/volume ratio, the liquid droplet seems to be spherical in shape [45]. The free energy of the surface must be measured from the set of contact angles for liquid/solid using liquids with definite surface tensions. Changing the chosen liquid may change vary the surface free energy [46]. Polar and nonpolar liquids are used to determine the surface free energy by using different techniques such as Van-Oss-Chaudry-Good equation. Polar liquids focus on specific molecular interactions within the surface energy components, however, for the non-polar surfaces; there is no focus on these surfaces. Nonpolar interactions include Van der Waals forces and hydrophobic interactions, while polar interactions focus on OH, C=O, amide, and nitrate units.

3.4 Dynamic wetting features

According to the Wenzel and Cassie–Baxter models, only one static contact angle value can be measured on a horizontal surface and equilibrium state; which is not completely true. Apparent contact angles are usually present between the minimal angle (termed receding contact angle, θ_{rec}) and maximal angle (termed advancing contact angle, θ_{adv}). The contact angle hysteresis (CAH) represents the difference between the advancing and receding contact angles (Eq. 7) [47].

$$CAH = \theta_{adv} - \theta_{rec} \tag{7}$$

The method of the dynamic sessile drop can determine the CAH for a water droplet on a horizontal surface before it begins to slide downward (Fig. 4).

Also, the sliding angle (SA) is important to determine the slippery nature of a surface and its antifogging characteristics within the surface on a raised horizontal plane interface [48]. Eq. 8 can be used to calculate the SA based on θ_{adv} and θ_{rec} values [49]:

$$mg\sin\alpha = \gamma_{LV} d(\cos\theta_{rec} - \cos\theta_{adv}) \tag{8}$$

Where α, m, d, and g express the SA, circumference's mass and diameter, and gravitational acceleration of the fog drag over a solid surface, respectively.

According to the equation, the lower the CAH (the difference between θ_{adv} and θ_{rec}), the less interaction within the liquid/solid interface, the higher hydrophobicity and slippery action. So, the tiny CAH with the minimum surface area can reduce the drop-contact to the solid and also with easy sliding features.

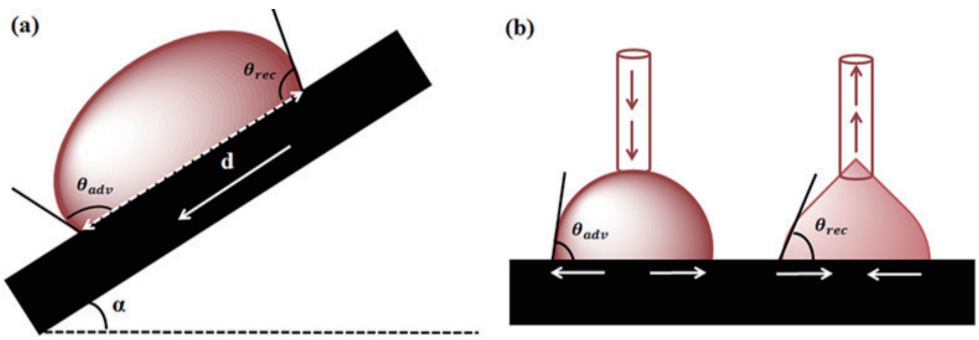


Figure 4. (a) Dynamic sessile drop method for contact angle determination; where θ_{adv} represent the maximal WCA before the droplet movement, while θ_{rec} represents minimal contact angle; (b) expresses the contact angles (θ_{adv} and θ_{rec}) were gotten by the tilting base method; thus, the CAH on a horizontal surface can be calculated [47]. Copyright 2019, reproduced after permission from the Elsevier

4. Application of ultrahydrophobic surfaces

Superhydrophobic surfaces have great importance for applications in various fields, especially for clean and sustainable chemistry. Superhydrophobic surfaces were extensively applied as self-cleaning and FR coatings [50-52]. Superhydrophobic nanocomposites with high WCA > 150˚, low CAH <5˚, micro-nano roughness, and reduced SFE are promising surfaces for eco-friendly antifouling applications [53].

PDMS nanocomposite films offer excellent physicomechanical and surface properties [54]. Advances of nanocomposite paints are growing rapidly to develop superhydrophobic self-cleaning materials with high antifouling performance [55].

5. Self-cleaning nanocomposites for fouling release coatings

Biofouling represents a nightmare for maritime navigation which causes several problems (Figure 5) [56,57]. Shipping accounts for 90% of the worldwide trade [58]. The friction drag and fuel consumption increase by fouling layers which reduces the velocity of the ship [11]. Several negative economic and ecological impacts such as increased shipping costs and environmental hazards are produced by fouling adhesion [59].

Figure 5. Costs of fouling on the marine environment and economy [8]. Copyright 2017, reproduced after permission from the Elsevier

Traditionally, biofouling is prohibited by using biocidal anti-fouling (AF) coating. Such leaching coatings can release toxicants to the maritime environment; thus can also harm non-target species such as fishes and dolphins [60]. It also can cause short-lasting, short dry-docking time, pollution of the marine environment and high cost as well as high frictional resistance and low fuel savings. Moreover, the International Maritime Organization (IMO, 2003) banned the use of tin-related compounds for fouling resistance on ship hull coatings. The worldwide ban accompanied by utilizing toxic antifouling paints have driven modern research toward eco-friendly solutions particularly, FR technology [61-67]. Controlling the size and morphology of nanomaterials can improve the performance of nanocomposite [68-70]. The Prevention of fouling attachments and reduction of fouling-coating adhesion strength are the mechanisms employed by FR self-cleaning surfaces [32,71,72] (Figure 6). Non-toxic FR nanocomposite is a new trend toward robust eco-friendly self-cleaning coatings for vessel bottoms and the shipping industry. For maritime navigation, superhydrophobic surfaces can introduce antibacterial and anti-biofouling materials [73,74]. However, the drawback of weak mechanical features is a major challenge nowadays for superhydrophobic and self-cleaning antifouling surfaces [75]. PDMS has widely utilized to synthesis superhydrophobic coating. Surface hydrophobicity, low SFE, micro-nano roughness, and chemical functionality are among the requirements to develop coatings with superhydrophobic character [76].

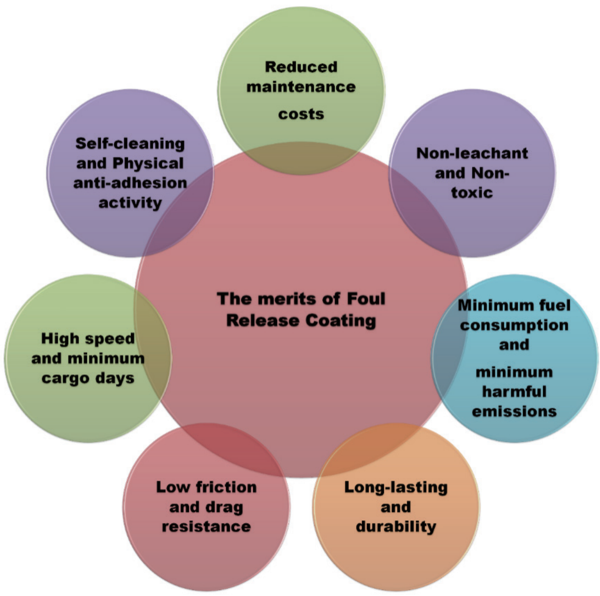
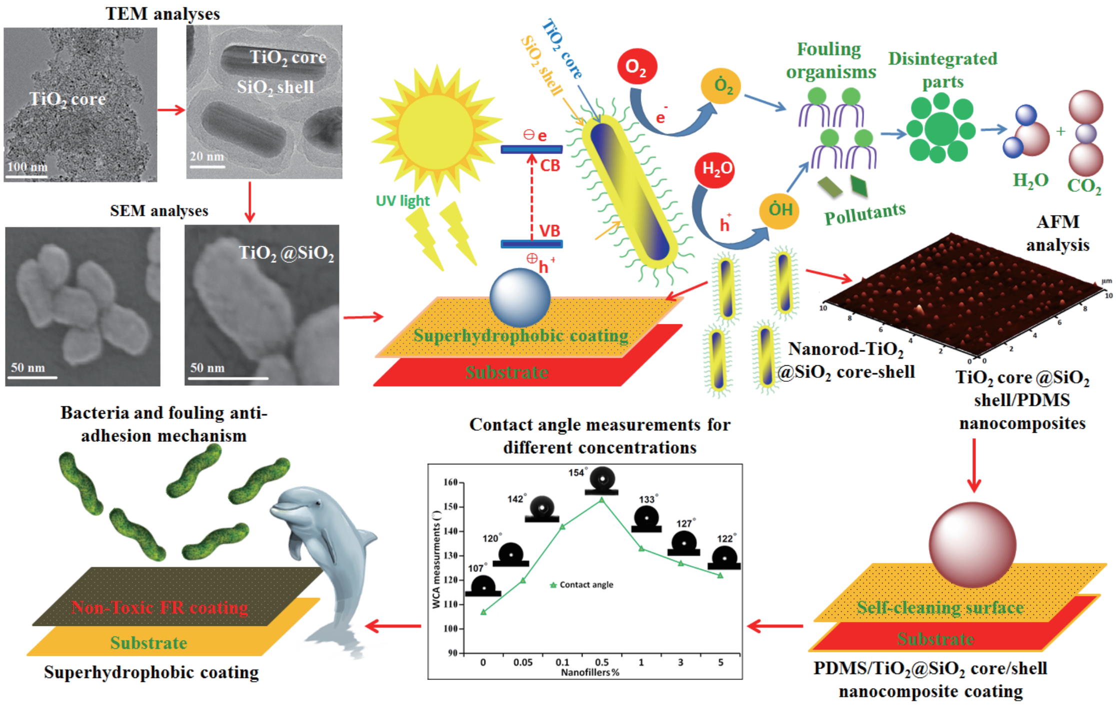


Figure 6. The merits of FR coatings for improving the antifouling and self-cleaning coatings [32,72]. Copyright from Elsevier Ltd. 2006

Efficient superhydrophobic antifouling coatings possess self-cleaning and cost-effective materials with high surface durability. This develops strong protective and self-cleaning antifouling coating material. FR self-cleaning, mechanical durability, cost-savings are characteristics provided by PDMS nanocomposite coatings as organic/inorganic hybrids [77-81]. Selim et al. projected a superior trend of $TiO_2@SiO_2$ core-shell enriched in silicone composites as smart photo-induced FR nanopaints (Figure 7) [64].



Figue 7. Illustration of the TEM and SEM of controlled-synthesis process carried out through hydrothermal and Stöber methods to yield $TiO_2@SiO_2$ core-shell; also contain the SEM and TEM captures of β-MnO_2 nanorods. Also, PDMS/ $TiO_2@SiO_2$ nanorod (0.5 wt.%) composite was fabricated through the in-situ process to produce self-cleaning and fouling release coatings. AFM was elucidated to indicate the preparation of the micro/nano-rough surface. Superhydrophobicity of the nanocomposite and self-cleaning design was illustrated. Contact angle test was performed on a series of nanocomposites prepared through different nanofiller percentages; where high self-cleaning effect was reflected for the well-dispersed nanocomposite (0.5 wt.% nanofiller concentration). High fouling-resistance for the well-dispersed sample was illustrated through bacterial antiadhesion mechanism [64]. Copyright 2019, reproduced with permission from Wiley

Also, nanocomposites are introduced as eminent nanofillers for various applications.
(1) Employed as an efficient photocatalyst to hinder recombining the photo-holes.
(2) Possess two-dimensional structured form and an extremely large area to the surface.
(3) Low energy band gap, robust and highly conductive.
Anchored graphene materials were reported as well-defined photo-catalysts and can fabricate outstanding surface materials with superhydrophobic, self-cleaning and photocatalytic features [82]. The utilization of superhydrophobic designs for robust FR coatings is an effective and eco-friendly trend.

6. Conclusions and Outlook

Studying the structures of natural superhydrophobic surfaces had driven research to develop novel self-cleaning surfaces because of their promising characteristics. Various methods were used for inspiring biomimetic surfaces from natural plants and animals through imitating the surface superhydrophobicity. Water repellency and superhydrophobicity of the biomimetic surfaces were greatly affected by surface roughness, chemical compositions, and morphology. Understanding the key functions of nanoscale filler tectonics in terms of its surfaces, atomic-scale crystal structures, architectures, parameters designated function models were inevitable for developing super-smart antifouling coatings. We provided evidence of the effect of nanoscale filler tectonics to fabricate structurally folded nanocomposite materials. Natural and biomimetic superhydrophobic surfaces were discussed to develop novel self-cleaning, superhydrophobic/ hydrophilic, and sustainable nanostructured materials. A detailed discussion of the subtle structural changes in the nanomaterials that yielded great improvement in surface self-cleaning performance was beyond the scope of this review. This review introduced an in-depth understanding of the surface structure-superhydrophobic property relationship of the designed nanocomposite surfaces. It provided new insights into the manufacturing of scalable, cost-effective, and reliable self-cleaning nano-based formulation coating. Developing advanced antifouling coatings by mimicking the natural superhydrophobic surfaces of plants and animals was necessary for a sustainable environment and for saving billions of dollars annually.

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Conflicts of Interest

The authors declare no conflict of interest.

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