REVIEW

Recent Progress in Superhydrophobic Coatings Using Molecular Dynamics Simulations and Experimental Techniques

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ABSTRACT

Superhydrophobic (SH) coatings are intended to resist a surface from corrosion and thereby increases the product life duration. It is also a promising solution to save cleaning costs and time by providing self-clean nature to the surface. This review article provides the most recent updates in designing SH surfaces and their characterizations adopted both in experimental and computational techniques. To gain a comprehensive perspective, the SH surfaces present in nature those are inspiring human beings to mimic such surfaces are introduced at the beginning of this article. Subsequently, different fabrication techniques undertaken recently to design artificial SH surfaces are briefly discussed. Recent progress in computations employed in the development of SH surfaces is then discussed. Next, the limitations in SH surfaces are addressed. Finally, perceptiveness of different strategies and their limitations are presented in the concluding remarks and outlook. Overall, this mini review article brings together and highlights the significant advancements in fabrication of superhydrophobic surfaces which may surely help the early-stage researchers/scientists to plan their work accordingly.

1. Introduction

Superhydrophobic (SH) surfaces in nature demonstrating water contact angle (WCA) > 150° have enticed substantial topical research attention owing to their potential applications in many industrial sectors [1-4]. Fundamentally, this SH nature is a physicochemical phenomenon, wherein the physical appearance (surface texture) of a surface in combination with its chemical nature (low surface energy) combinedly helps to enhance the phobic nature of repelling water [15]. Before fabricating any artificial SH surface, it is better to first understand the self-clean surfaces present in nature. Lotus leaf [4,6,7], rice leaf [8,9], taro leaf [10,11], butterfly wings [12-14], water-strider legs [15], rose petals [16-18], and gecko feet [19-21] are the most exemplary cases present in nature exhibiting SH characteristics. Barthlott et al. [7] have investigated the self-clean nature of lotus leaf and found that there is a presence of (nano-scaled) epicuticular waxes superimposed over (micro-scaled) epidermal cells

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combinedly provide a dual scale surface to surface. Both these textures are hydrophobic in nature and hence enable the surface to provide sufficient repellence nature against water. When water drops fall on the lotus leaf surface, it forms a completely spherical shape which can easily be rolled down the surface taking the dirt particles along with it. Likewise, the rice leaf surface is consisted of micro papillae that is superimposed by epicuticular waxy nano bumps and in butterfly wings the presence of hierarchical scales with micro grooves. Such surfaces demonstrate SH characteristics simultaneously providing drag reduction with several fluids. Basically this super hydrophobicity is governed by two prime factors as described earlier by Wenzel [22] and Cassie Baxter [23]. The intrinsic hydrophobic material presents at the extreme surface and the micro and nano-scale roughness on the topography. Scientists and researchers have utilized several techniques to fabricated biomimetic SH surfaces. The details of the various approaches are summarized in the subsequent section.

2. Fabrications Techniques

This section addresses the most used fabrication techniques for SH surfaces. Techniques such as spraying [24–25], chemical etching [26–28], lithography [29–30], electrospinning [31–32], surface wrinkling [33–34], chemical vapor deposition (CVD) [35–37], layer-by-layer coating [38–39], and photolithography laser surface treatment [40,41] are the numerous approaches for reported in recent years.

Spray coating is one of the most used techniques which is carried out by using a spray gun. A micron-level thickness with/without multi-layer coatings can be easily done in this technique. Zhang et al. [42] have fabricated a robust fluorine-free SH surface with a self-clean effect by first coating epoxy resin on a surface and then spraying silica nanoparticles and dodecyltrimethoxysilane to induce roughness and thereby reduce the surface energy. The coated surface demonstrated a water contact angle of >153°, which also can be used for oil-water separation applications. In the same line, Polizos et al. [43] reported a scalable technique for developing anti-soiling coatings based on SH surfaces by using the spray coating method. The authors have used polymer binders and silica nanoparticles and obtained a WCA of > 166°. Hence, this unique fabrication technique is a promising technique for producing SH surfaces for outdoor and indoor applications.

Chemical etching is another approach to designing SH surfaces; wherein etchant chemicals are used to produce corrugated surfaces. Varshney et al. [44] have prepared SH brass surfaces using a two-step process. In the first step, they have used a chemical etching method with a mixture of hydrochloric and nitric acids and then treatment with lauric acid. With the help of this etching technique, they obtained an adequate rough surface that demonstrated a WCA of > 173°. The authors also proposed its wide application in self-cleaning and anti-fogging applications.

Lithography is a non-complicated and dynamic approach that was developed to prepare different grades of nano/micro-structured surfaces over large areas. Jinpeng et al. [45] have used an ultrafast laser to develop nano/micro hierarchical structures on a metal surface with tunable micro-cones. Such a SH surface can withstand 70 abrasion cycles, 28 minutes of solid particles impact, or 500 peeling tape cycles and still can show a WCA of > 150°. This article explains the promising possibility of accomplishing excellent durability for real-time applications. Feng et al. [46] have reported a novel, versatile and efficient method for the fabrication of microscopic hierarchical SH surfaces with the presence of both micro and nano-scale textures using the electron-beam lithography technique.

SH coatings can also be prepared by using the electrospraying process. Radwan et al. [47] successfully fabricated PVDF/ZnO-based SH coating using this technique, which demonstrates a contact angle of 155° and contact angle hysteresis (CAH) of 4.5°. Though there were a number of literature reporting different coating techniques to design PVDF/ZnO based SH coating with excellent phobic nature but the significance of the study reported by Radwan and co-workers [47] are: (i) the authors have used a very low ZnO concentration without compromising with its phobic nature, (ii) an excellent dispersion was attained without any usage of dispersing agent, (iii) the ZnO filler doesn’t phase out with time, (iv) the entire fabrication is a one-step process and (v) the formulated coating material demonstrates excellent corrosion protection nature.

Surface wrinkling is a spontaneous process of generating a rough surface. Scientists use this mechanism to fabricate corrugated surface-based SH surfaces. This phenomenon occurs due to the mismatch in elasticity among the underneath shrinkable substrate and the top rigid coated layer. Upon allowing the substrate to shrink, the first waves appear in the top layer and as more stress is applied, they turn into wrinkles and finally into folds [48–51]. Using this approach, Scarratt et al. [52] reported the fabrication of both single scale and hierarchical SH surfaces prepared by exploiting the spontaneous wrinkling of rigid Teflon film on two types of shrinkable plastic substrates. The hierarchical wrinkled SH surface exhibits an excellent WCA of ~172° with a very low CAH of 2°. The authors suggested that such an approach can be tuned to obtain micro-to-nano scale wrinkled surfaces in one step.
Chemical vapor deposition (CVD) is another versatile approach to preparing a SH surface by reducing the surface free energy. Rezaei et al. [53] have prepared a bio-inspired SH coating by using vinyltrimethoxysilane and triethyl orthosilicate as surface-modifying molecules and ammonia. This material showed a WCA of >160° and a low sliding angle of <5°. The major advantages of this article were, (i) the authors have explored an all gas-phase and simultaneous deposition and modification of silane coating to avoid HCl production and post-treatment of silica nanoparticles. With the help of ammonia, they were able to lower the working temperature, which suggests that such technology can also be used for temperature-sensitive materials. There are several types of CVD processes, such as atmospheric pressure chemical vapor deposition (APCVD), aerosol-assisted chemical vapor deposition (AACVD), and plasma enhanced chemical vapor deposition (PECVD), used for fabricating SH surfaces. A comprehensive study can be found elsewhere [54]. The fundamental behind such different approaches to developing SH surfaces are like to reduce the surface free energy either by using low surface energy treatment or by designing corrugated surfaces.

2.1 Treatment with Low Surface Energy Polymers

Irrespective of the substrate used, the surface energy treatment relies on silane and fluorine chemistry. The silane treatment is generally preferred over fluorine treatment considering the toxicity impact on the environment. Researchers employ poly(vinylidene fluoride) (PVDF) [55,56], per(fluoro octane) (PFO) [57,58], fluoroalkyl silane (FAS-17) [59-61], and poly(tetrafluoroethylene) (PTFE) [62] etc., for fluoro treatment while making the desired surface SH. For silane treatment researchers use (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane [63], tetraethyl orthosilicate (TEOS) [64-66] and heptadecafluoro-1,1,2,2-tetrahydrodecyltriethoxysilane [67].

2.2 Designing of Hierarchical Surface Texture

Besides low surface energy treatment, the construction of micro or nanoscale rough surfaces is also an important technique to reduce the water attachment to the surface [1]. Achieving a WCA of > 120° is not feasible only by surface treatment with low-energy polymers. Hence, combining low surface energy with surface roughness is obligatory to obtain a SH surface with an excellent WCA of >150° and a very low CAH of <5°. There are several ways to prepare micro/nano-scaled rough surfaces with enhanced contact angles, a few of them have already been discussed earlier in the manuscript in section 2. It can be considered that keeping the material same if the contact angle on a flat surface is around 100°-120°. Then it can be turned into 150°-160° only by adding roughness to it [68]. Two different models have been developed earlier to explain this effect, as depicted in Figure 2. When the rough pillars allow sufficient water molecules to impregnate the grooves, then a maximum wetting condition can be obtained, which is known as the Wenzel model [69]. When the rough pillars prevent the water molecules from entering inside it, thusly the water remains in a completely spherical shape and sits above the pillars then; it is considered as Cassie-Baxter model [23]. In this case the rolling angle is also very low.

![Figure 1. Various fabrication techniques used for SH coating materials.](image-url)
3. Application of Molecular Dynamics (MD) Simulation in SH Coatings

MD simulations have long been served as a fundamental tool to gain understanding in different sectors of research, such as estimation of interaction energy among various polymers/fillers \(^{[70-73]}\), the surface energy of polymers/metals \(^{[74]}\), interfacial shear strength \(^{[75]}\), and wetting characteristics \(^{[76]}\), etc. Computational scientists use different water models such as SPCE, SPC, TIP3P, and TIP4P \(^{[77]}\), etc. to replicate the water droplets in MD simulations and then predict the SH nature of the desired surface \(^{[76]}\). To predict the simulated contact angle a number of methods have been developed, like microscopic wetting phenomena \(^{[78]}\), float method \(^{[79]}\), and quick-hull recursive method \(^{[80]}\), etc. The details of each computational technique can be found elsewhere \(^{[76]}\).

In this line, Sethi et al. \(^{[81]}\) have first predicted the blend compatibility among poly(dimethylsiloxane) (PDMS) and poly(vinyl acetate) (PVAc) using MD simulations. Later on, the authors have predicted the easy-clean behavior of the PVAc-PDMS blend \(^{[82]}\) and obtained a contact angle of 97 ± 1° for a 20:80 ratio of PVAc to PDMS. Owing to the incompatibility among polar PVAc and nonpolar PDMS, the authors have then grafted PVAc over PDMS, considering the same 20:80 concentration of PVAc to PDMS \(^{[83]}\). Subsequently, they have incorporated CNT \(^{[84]}\) and ZnO QDs \(^{[74]}\) in PVAc-g-PDMS and computed the WCAs, and found 109±2° (4 wt.% of ZnO QDs) and 117 ± 2° (3 wt.% of CNT). In another work, Sethi et al. \(^{[85]}\) have computed the impact of roughness on wettability. They have modelled different surfaces with varying grooves and studied how it affects the surface wettability. In the same line, Xu et al. \(^{[86]}\) have investigated the variation in wetting characteristics with varying defect % in graphene oxide. They found that the WCA increased from 70° to 82°, when the defective concentration increased from 0 to 10% (as shown in Figure 3). Similarly, researchers have computed the SH nature of graphene \(^{[86,87]}\), poly(vinylidene fluoride) (PVDF) \(^{[55]}\), poly(ethylene terephthalate) (PET) \(^{[88]}\) and sphalerite \(^{[89]}\), etc. using MD simulations.

![Figure 2. Schematic representation of WCA on (a) flat surface, (b) Wenzel model, and (c) Cassie-Baxter model.](image)

![Figure 3. Illustration of water contact angle profile of graphene oxide with varying defect %. (a) 0%, (b) 2%, (c) 5%, and (d) 10% defects in graphene oxide. Reprinted with permission from \(^{[86]}\).](image)
4. Limitations to the Development of SH Coatings

Although there is a wide range of applications for SH surfaces, still not many commercial products have been developed with these functionalities. Some of the major limitations have been listed and discussed below.

4.1 Cost of Materials

A few of the fabrication techniques discussed above are very costly. Sometimes the fabrication process may also require costly materials. Techniques such as lithography and templates cannot be used on very large areas. Hence, designing small part surfaces and stitching them together to make a larger one may sometimes also increase the overall product’s cost \([29,30,46]\).

4.2 Technique to Fabricate SH Material

Out of all possible techniques, a few of them have limitations to their usage. Like template technique cannot be used for all materials, the attainable geometry is also limited \([90]\).

4.3 Durability of Coating Material

Any SH surface requires either a dual-scale or nano-scale roughness. Most of the time, such roughness is not durable enough to withstand the abrasion caused during their daily usage; thereby, it loses its SH nature \([91]\). Especially in the case of polymers, it is not very easy to maintain the corrugated textured surface for a long duration. Also, there is a standoff among its SH nature and its durability, as it is not very easy to bond any SH nanoparticle without degrading or affecting its SH nature \([92]\).

4.4 Precipitation/Condensation Issue

Since the SH surfaces are designed to repel water hence at below certain dew points when water condenses, it may not get repelled by the developed surface. Hence the surface can substantially be wetted when the temperature of the environment changes \([93,94]\).

4.5 Health and Environmental Effects

The most developed SH surfaces are derived from fluoro-based polymers. Though a little concentration may not have that much impact on health or the environment but a higher concentration may cause serious health issues during product manufacturing, usage, or disposal. It may cause fever, teeth and bone decay, harm to kidney nerves and muscles, and eye and nose irritations \([95,96]\). Besides, most of the silanes are poisonous.

5. Summary and Conclusions

In this review article, the latest achievements in the field of SH surface generation have been presented. The basic idea to create a SH surface is by surface treatment with low surface energy and construction of a rough-textured surface to enhance the water repellence nature. Properties like self-cleaning, anti-corrosion, and anti-sticking have been identified for such SH surfaces and have a broad potential application. Here, several fabrication techniques along with computational techniques to gain some fundamental insight into wetting behavior were reviewed and discussed. Several manufacturing processes have certain limitations; those are also briefly discussed. Limitations such as cost, technique, durability, and environmental impact are of great challenge for researchers. Designing fluorine-free eco-friendly self-clean coating materials are receiving overwhelming attention owing to its non-health hazardous effect. The importance of industrial SH surfaces requires enhanced durability, for which scientists have developed robust self-clean surfaces with highly stable and durable surface characteristics. Simultaneously, the durable SH surfaces may be merged with some additional functionalities to develop multi-functional surfaces/coating materials that can be further strengthened to be developed in future work in this field.

Author Contributions

Sushanta K. Sethi: Writing, reviewing, editing, and conceptualization.

Conflict of Interest

The author declares there is no conflict of interest.

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