

Review

Mechanical Durability of Engineered Superhydrophobic Surfaces for Anti-Corrosion

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Abstract: Engineered superhydrophobic coating for anti-corrosion applications is a subject of great significance at present. However, the use of superhydrophobic coatings for anti-corrosion applications is hindered by the mechanical durability in many cases. There is a need for an understanding not only of how to fabricate such surfaces, but also of the corrosion resistance and mechanical durability of those coatings. This review discusses recent developments in the mechanical durability of superhydrophobic coatings primarily used for anti-corrosion. First, superhydrophobicity is introduced with an emphasis on different wetting models. After that, this review classifies the nanofabrication methods based on the material and methods of surface functionalization. Furthermore, the testing procedures used for the measurement of corrosion and mechanical durability are presented. Finally, the mechanical durability and anti-corrosion performance of the developed superhydrophobic coatings are discussed.

Keywords: anti-corrosion; superhydrophobic coatings; mechanical durability

1. Introduction

It is an observed natural phenomenon that pure metals and their alloys interact with a corrosive environment, chemically or electrochemically, to form stable compounds [1–5]. During this conversion process, loss of metal is inevitable but not desirable. During the corrosion process, a chain of simultaneous electrochemical processes takes place that involves the dissolution of metal ions into the electrolytic solution at the anode, which is, comparatively, a more active site during the corrosion process. Electrons are then transferred from the metal under consideration, through an ionic current in the solution and an electric current through the metal [6], to a comparatively less active site called a cathode. It should be noted that this process requires an electron acceptor such as oxygen, another oxidizing agent, or hydrogen ions. By analyzing these processes involved in corrosion, it can be inferred that corrosion can be partially or completely arrested by controlling or completely preventing anodic reactions, cathodic reactions, or both for the best outcome.

Since ancient times, different techniques have been used to control metal corrosion, by controlling either anodic or cathodic reactions [7]. However, another way to effectively control corrosion is to isolate the surface completely from corrosive media by applying protective coatings such as paints or other appropriate metals [8–15]. Though there are different coating methods available for corrosion protection that differ based on the corresponding metals to be protected or the nature of the corrosive environment to which the metal is exposed, superhydrophobic coatings are favored due to their inherently water-repellent nature [16–19]. For all types of anti-corrosion coatings, the mechanical durability of the coating is significant irrespective of the material and environment.

In similar literature reviews focused on the applications of special function coatings for corrosion protection, there was a limited emphasis on equally important properties—for example, mechanical robustness, which is significant for determining the applicability of developed coatings. Though there is a discussion on the principal working theories, procedures for preparation, performance investigations, and applications [20–25], a comparative review that accounts for all factors, including durability and other mechanical properties, is essential for understanding the applicability of an advanced coating at a practical level.

In this particular review, we focus on different coating preparation techniques and their resulting properties, such as mechanical durability and corrosion resistance. Since corrosion resistance and durability are the highlighted requirements, it also summarizes various methods that are in practice for measuring these factors. Finally, this review offers a qualitative comparison, based on the mechanical durability and corrosion resistance achieved, of the different fabrication methods reviewed in this article.

2. Superhydrophobic Corrosion-Resistant Coatings

The wetting behavior of solid surfaces is of great interest in the scientific community owing to potential applications in various industrial fields. Recent trends in corrosion protection methods incline towards the use of superhydrophobic coatings to a great extent, and numerous research groups are scrutinizing the capability of these coatings as potential barriers against corrosion. With an emphasis on the durability of the resulting coatings, this work discusses recent advancements in the types of superhydrophobic coatings developed for metal surfaces and their effectiveness in controlling corrosion problems. In order to better understand superhydrophobic behavior as a physical phenomenon, the fundamental principles are also discussed, as are the theoretical models used to explain the wetting behavior of a rough surface and several approaches used for fabricating superhydrophobic coatings.

For the past few decades, the scientific community has been concerned with the study and development of superhydrophobic surfaces, and nature has inspired this work [26–28]. Many entities of natural origin (lotus leaves, rose petals) exhibit superhydrophobic behavior, which can be considered among their characteristic features and serve specific purposes [29,30]. Quantitatively, superhydrophobic surfaces can be defined as those surfaces possessing a water contact angle above 150°. Due to their highly repellent nature towards water, superhydrophobic surfaces have attracted numerous research teams to exploit this capability in various applications such as corrosion resistance [31–33], self-cleaning [34–37], anti-biofouling [38–42], drag reduction [43–46], etc. Over the past few years, introducing a mechanically stable superhydrophobic coating on the surface of metallic materials has become a popular research area owing to the scope for further improvement and adaptable fabrication methods [47].

3. Theory of Superhydrophobic Behavior

The degree of water repellency possessed by a surface depends on its surface morphology and the surface free energy [48,49]. Alteration of surface chemistry alone may impart a considerable increase in the hydrophobicity, but to attain superhydrophobic behavior the altered surface chemistry should be accompanied by high surface roughness. Many studies reveal that roughness plays an important role in the hydrophobicity of surfaces [50–52].

The degree of hydrophobicity of a flat surface is quantified by the contact angle θ made by a water droplet on the surface. Mathematically, the contact angle is calculated by Young's equation as:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

where γ_{SV} , γ_{SL} , γ_{LV} stand for the interfacial surface tensions, with the solid represented by S, liquid by L, and gas by V [53].

Young's equation is applicable to perfectly smooth, chemically uniform solid surfaces, which is ideal; however, most surfaces bear defects that yield to surface roughness. The surface could be heterogeneous instead of homogeneous, which is an essential condition to apply Young's equation. Due to these deviations, the study of the wetting behavior of a rough surface is more complicated. Cassie, Baxter, and Wenzel studied and modeled the implications of roughness on contact angle and thus the wetting nature of surface for the first time [54,55].

In the Cassie–Baxter model, the liquid is suspended on the surface asperities and does not penetrate into the air pockets present in the gaps between asperities, as shown in Figure 1. Cassie and Baxter subdivided the overall solid–liquid interface into two different surfaces with surface fractions of f_1 and f_2 . The contact angle made by a liquid droplet on such a surface can be expressed in terms of contact angles θ_1 and θ_2 for homogeneous surface 1 and surface 2, respectively.

$$\cos \theta_C = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2)$$

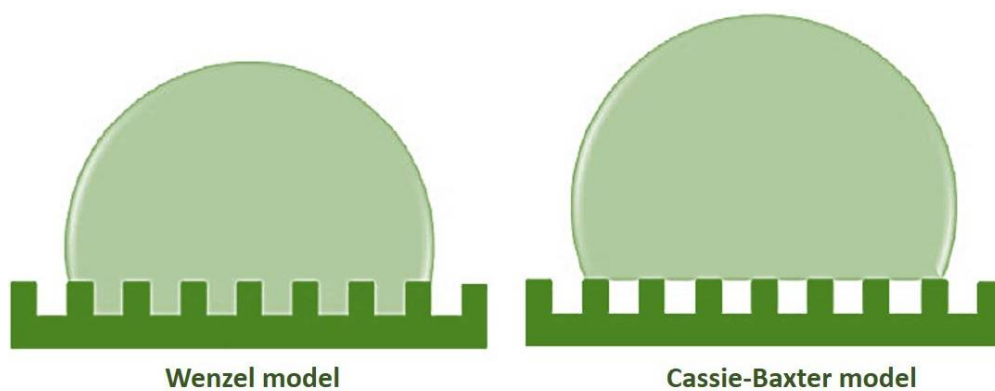


Figure 1. Wenzel model and Cassie–Baxter model of wetting regimes.

When the types of protrusions present are identical, the fraction of solid surface, which is the fraction of asperities, can be defined by f and the air fraction as $1 - f$. In this case, the contact angle can be expressed as follows:

$$\cos \theta_C = f(1 + \cos \theta) - 1 \quad (3)$$

The value of surface fraction f lies between 0 and 1. If $f = 1$, then the surface is completely wetted as similar to the situation on a flat surface. When $f = 0$, there is no actual contact between the liquid medium and the solid surface. In the Cassie–Baxter model, surfaces are considered to be slippery when they are wetted by a liquid medium.

In the Wenzel model, a water droplet is assumed to have completely penetrated into the gaps between the surface asperities, constituting the roughness shown in Figure 1. The roughness factor r introduced by Wenzel has a value either greater than or equal to 1. The contact angle on a rough surface according to Wenzel model can be expressed as follows:

$$\cos \theta_W = r \cos \theta = \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right) \quad (4)$$

The Wenzel model introduces a homogeneous wetting regime and implies that a hydrophobic surface will become more hydrophobic as the roughness increases, whereas a hydrophilic surface becomes further hydrophilic in nature as the roughness increases, provided the introduced roughness is qualitatively identical to the existing roughness domain. Unlike in the Cassie–Baxter model, the surfaces are considered to be sticky once they are wetted by a liquid medium. Upon comparing the interaction between the liquid medium and the solid surface in view of the susceptibility towards corrosion, it may be inferred that a higher degree of corrosion restriction is achieved when the wetting

regime follows the Cassie–Baxter model as the overall interfacial contact between the metal and corrosive medium is much lower, and the air pockets act as a hindrance against chemical interactions.

4. Necessity for Mechanical Durability for Superhydrophobic Coatings

Improved superhydrophobic behavior of a metal surface often reduces the corrosion occurring on the metal surface by restricting the interaction between the metal surface and corrosive media. To ensure sustained protection against corrosion, it is extremely essential that the superhydrophobic behavior remains intact without getting disturbed. Any damage to the engineered structures will lead to the partial elimination of air pockets that are responsible for the superhydrophobic behavior and result in significant deviation in the water-repelling capability of the coating; thus, the corrosion protection capability will also be affected. Hence, maintaining the mechanical durability of the developed structures is as important as attaining a higher degree of superhydrophobicity. In addition, it has been reported that the cohesive force between these engineered structures and surfaces is weak [27]. The overall capability of a superhydrophobic coating to remain durable and mechanically stable is determined mostly by factors such as the degree of adherence to the substrate [56], the ability of the coating to resist tangential abrasive forces [57], and the ability to withstand dynamic impact [58]. The native durability and stability of the superhydrophobic coating may be a function of the type of fabrication method [27]; thus, it is necessary to understand the various fabrication methods in the following sections.

5. Various Superhydrophobic Coatings for Corrosion Prevention of Metal Substrates

Various methods are available for the nanofabrication of superhydrophobic coatings, depending on the type of functionalization and morphological modifications performed. The superhydrophobic coatings that are relatively more common and have current significance are silane-modified superhydrophobic coatings, polymer-based coatings, coatings developed by soft lithography method, titanium oxide-based superhydrophobic coatings, and nanoparticle-based coatings that are repellent to numerous fluids. These methods are discussed in detail in subsequent sections, with an emphasis on the mechanical stability and durability corresponding to each method.

5.1. Silane-Modified Superhydrophobic Coatings

One of the most popular methods for preparing superhydrophobic surfaces is altering the surface chemistry of the metal surface. This is achieved through modification with silane containing nanocomposites and then introducing hydrophobicity by combining the effect of surface roughness and low surface energy silanes. Wu et al. prepared an effective superhydrophobic coating for mild steel that has considerably good corrosion arresting capability [59]. In their work, superhydrophobic silica films of nanoscale thickness were deposited onto mild steel substrate for the purpose of corrosion protection through a one-step electrodeposition of inorganic/organic hybrid sol–gel films, from tetraethoxysilane and dodecyltriethoxysilane mixed sol–gel precursors. Silane, when disbursed in a solvent or other solution mixture, improves the characteristic features of the coating, depending on the type of solution and the method of coating deposition. Calabrese et al. studied the adhesive properties of anti-corrosion silane–zeolite coatings on aluminum substrates [60]. The coatings were developed by dip-coating in a sol–gel solution. The effects of varying concentrations of zeolite in the solution were studied by changing the concentration of the same between 60% and 90%. It was observed that the most promising results were obtained for lower concentrations of zeolite. Li et al. also developed a low-cost method for preparing a superhydrophobic coating on aluminum, specifically for 6061 aluminum alloy [61]. Jeevajothi et al. developed a non-traditional superhydrophobic coating by doping praseodymium oxide on zinc oxide nanocomposites (Pr_6O_{11} -ZnO) loaded in a hybrid sol–gel layer for the effective protection of steel substrates [62]. The praseodymium oxide–zinc oxide composite exhibits superior anti-corrosion properties compared to its traditional counterparts. The praseodymium oxide–zinc oxide composite also possesses considerable durability as is evident

in Figure 2, where certain loading was stable and durable even after 600 h of immersion in a 3.5 wt % NaCl solution. Though the methods offer a good deal of corrosion resistant characteristics, they differ with respect to the mechanical stability and durability associated with fabricated coatings. Cho et al. improved the superhydrophobicity of transparent siloxane-based nanocomposites through chemical modification with fluorosilane. The as-prepared superhydrophobic coating shows excellent anticorrosion properties along with retaining its extreme water repellency without much deviation in the water contact angle after durability testing for 90 days [63]. Gao and Guo took advantage of 1H,1H,2H,2H-perfluoroalkyltriethoxysilane (FAS-13) for modifying steel substrates etched with sulfuric acid and hydrogen peroxide. The prepared sample exhibits excellent anticorrosion behavior via more positive corrosion potentials and lower corrosion current densities. The developed surface also maintained superhydrophobicity after moving 100 cm on 1000 grit sand paper under 100 g loading via an abrasion test [64].

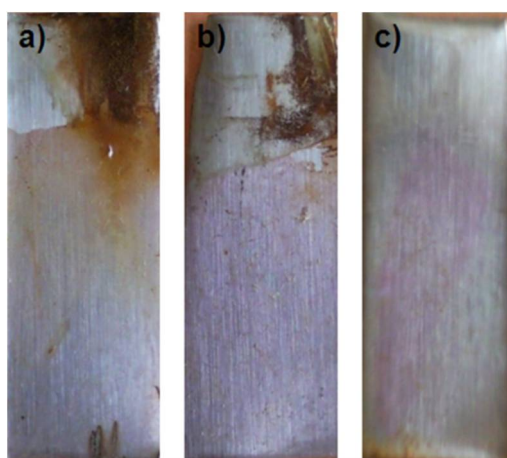


Figure 2. Durability tested samples after 600 h of immersion in 3.5 wt % of NaCl solutions. Coatings are prepared by doping praseodymium oxide on zinc-oxide nanocomposites (Pr_6O_{11} -ZnO) loaded in a hybrid sol-gel layer for the effective protection of steel substrate (a) GPZ, (b) GPZ-Pr and (c) GPZ-Pr-Zn. Reprinted from [62] with permission; Copyright Elsevier 2014.

5.2. Polymer-Based Superhydrophobic Coatings

Practical applications demand optimized methods and materials for the purpose of a one-step fabrication of superhydrophobic coatings having sufficient mechanical stability for large surface areas at considerable costs. A composite composed of a polymer base and embedded nanoparticles that are functionalized can provide the required superhydrophobicity for effecting anti-corrosion behavior along with maintaining considerable mechanical stability. Chang et al. used a nanocasting method to prepare a composite of epoxy and graphene that could act as a corrosion inhibitor [65]. The corrosion protection for steel was achieved with the cumulative effect of epoxy to act as a physical barrier against corrosion. The hydrophobic behavior of the developed surface repels water; therefore, the contact with corrosive media is restricted and well distributed, with the use of graphene nanosheets that improve the oxygen-barrier property. Glover et al. also used graphene nanoplatelets that were dispersed in polyvinylbutyral for the protection of iron-based substrates. The durability and associated mechanical stability were found to be appreciable [66]. An advantage associated with the use of polymer-based coatings is that in most cases it is a relatively simple method in terms of functionalization and coating application. Additionally, the mechanical stability of these types of coatings is proven to be in the desired range. One of the most prominent coating application methods is the spraying method. Wang et al. developed a spraying method to fabricate a robust amphiphobic poly(phenylene sulfide) (PPS)/fluorinated ethylene propylene (FEP)/poly(dimethyl siloxane) composite coating that possesses high corrosion resistance, wear resistance, and durability by having hierarchical nanoscale roughness

and fluorination using materials with low surface energy [67]. The composite coating simultaneously showed superhydrophobic and highly oleophobic properties. The robust, highly amphiphobic coating also showed remarkable durability against strong acids and strong alkali in the pH range from 1 to 14, which substantiate its chemical stability. The high durability of the fabricated coating can be justified by the results of a friction test performed on the surfaces (Figure 3). Zhang et al. also developed a spray-coating method that has excellent anti-corrosion and self-cleaning properties, and is durable as well [68]. Another distinguishable feature about the polymer-based spray coating method is that it can be applied on various substrates provided the solution used has considerable bonding capability with each substrate. Superhydrophobic polymer-based coatings that are electroactive in nature are also of great interest since the passive metal oxide layers impart good corrosion restricting properties [69]. Furthermore, these types of coatings can be effectively employed after considering the associated mechanical stability and durability.

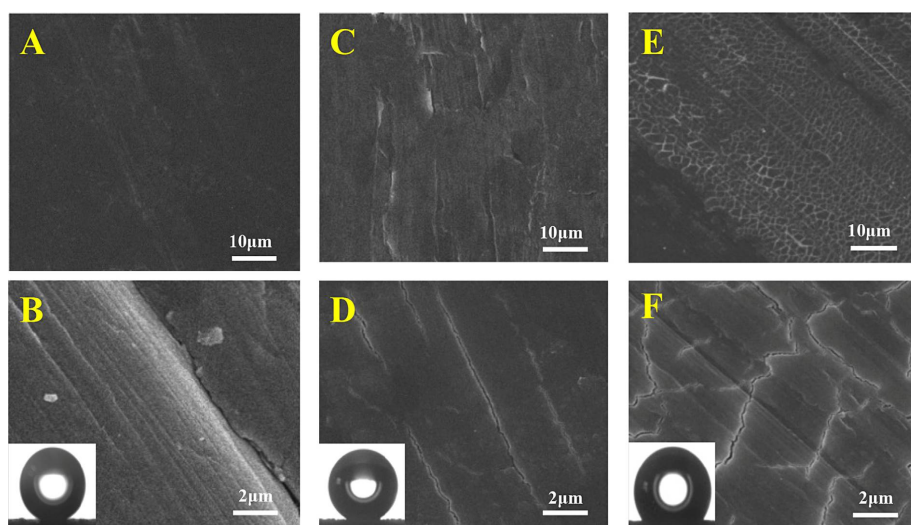


Figure 3. SEM micrographs of corrosion resistant superhydrophobic samples after being loaded for (A,B) 20,000 friction tests, (C,D) 100,000 friction tests and (E,F) 1,800,000 friction tests. Reprinted from [67] with permission; Copyright Elsevier 2015.

5.3. Soft Lithography Method

Soft lithography techniques are widely used for the purpose of templating hierarchical structures, thereby introducing the necessary roughness on the surface for attaining superhydrophobicity after appropriate functionalization. An added advantage with soft lithography-based techniques is that, since the morphological features are derived from the material bulk itself, it improves its wear resistance and also retains the chemical properties even after numerous cycles of abrasion or other environmental disturbances [70]. Biomimetic structures are fabricated using a lithography technique and are functionalized simultaneously or at a later stage to attain superhydrophobicity [71]. A nanocasting technique is used for replicating the structures on materials of interest. Control over the morphology of a surface is of very high degree in this method. Morphological features present on a naturally occurring entity, such as a lotus leaf, are often used as a pattern for making the template to be used [72,73]. It is interesting to note that this technique is capable of precise replication of overhanging hierarchical structures through atomic layer deposition. Hoshian et al. replicated overhanging nanostructures from an aluminum tube template to polydimethylsiloxane and titania using atomic layer deposition sacrificial etching [74]. Atomic layer deposition of ceramics such as titania improves the mechanical durability of developed coatings considerably. These nanoscale structures developed are durable in terms of adhesion behavior as well as response to external wear. Figure 4b shows the fabricated surface coated with superhydrophobic polyaniline after an adhesion test.

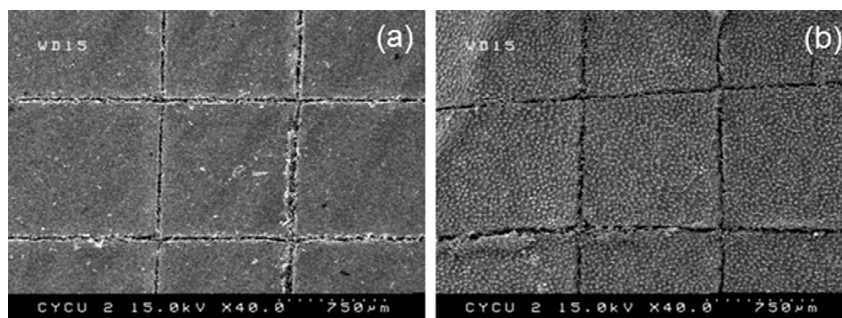


Figure 4. SEM images of (a) F-PANI coated on CRS and (b) SH-PANI coated on CRS after testing for adhesion. Reprinted from [73] with permission; Copyright Elsevier 2013.

5.4. Titanium Oxide-Based Superhydrophobic Coatings

Titanium oxide-based composite films of nanoscale thickness are of great interest in developing superhydrophobic coatings, especially due to features such as photocatalytic activity [75,76]. Titanium oxide-based coatings are very effective for developing mechanically stable and durable coatings that can also serve as a corrosion barrier. Zhang et al. developed a simple dipping process for the preparation of superhydrophobic coatings based on titanium dioxide nanowires [77]. An interesting fact to be noted is that due to the photocatalytic activity of titanium dioxide, the superhydrophobic surface transforms to a hydrophilic surface after exposure to ultraviolet irradiation. Another advantage of this particular coating is that it is easily repairable as shown in Figure 5 [77], which recommends this coating for applications where durability is significant. The superhydrophobic property could be restored by regeneration processes such as reabsorption of low surface energy molecules [78] or UV exposure in which electron–hole pairs are produced and manipulated the free monomers to recover the superhydrophobic surface [79].

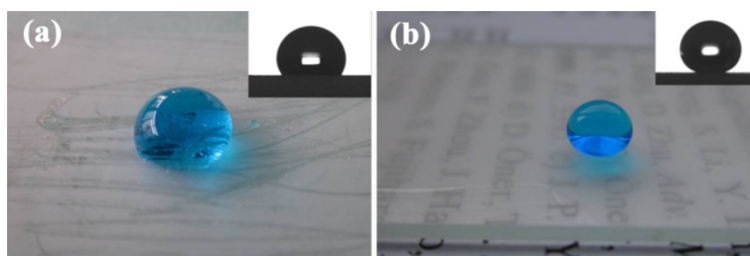


Figure 5. Photographs of a water droplet on the surface partly destroyed by mechanical scratching (a) and on the regenerated surface by immersion in TiO_2 nanowire suspension and drying again (b). Insets in (a,b) are the profiles of a water droplet with CA value $118^\circ \pm 1^\circ$ and $155^\circ \pm 1^\circ$. Reprinted from [77] with permission; Copyright Elsevier 2013.

5.5. Nanoparticle-Based Superhydrophobic Coatings

Use of nanoparticles in a dispersed manner or as reinforcing structures in composite coatings has a great advantage of imparting stable and durable superhydrophobic coatings [80,81]. Zhang et al. developed a superhydrophobic coating with mechanical stability and corrosion resistance using a spray-coating method [68]. Roughness was introduced with the aid of nanoparticles present in the spray solution, creating a durable superhydrophobic coating. The mechanical stability and corrosion resistance obtained was at appreciable levels. The developed coating was found to be effectively resistant to abrasion and varying pH levels. It was also stable against ultrasonication (Figure 6). Chen et al. also developed a spray coating with suspended alumina nanoparticles [82]. The superhydrophobicity is tunable by varying the concentration. Chen et al. developed a

superhydrophobic coating of an organic nature that has a self-repairing capability comprising modified silica nanoparticles and photocatalytic titania nanoparticles [83]. The developed coating shows self-repairing ability after mechanical damage, which is of great significance in view of the prolonged use in industrial applications. Figure 7 shows the recovery of water contact angle, sliding angle and the changes in surface morphology for the self-repairable superhydrophobic coating after weathering test. Nahum et al. developed a durable superhydrophobic coating by exploiting the covalent bonding between the photoreactive silica nanoparticles and the base polymer [84]. The rough topography was achieved by ultraviolet curing of silica nanoparticles containing photoreactive benzophenone in addition to methylated fumed silica nanoparticles, which can bind covalently to the polymer base coating on exposure to ultraviolet rays [85,86]. Covalent bonding between the dispersed nanoparticles and composite matrix improves the mechanical stability of the coating, thereby resulting in improved durability. Ammar et al. [87] and Zhang et al. [88] employed zinc oxide nanoparticles, whereas Liu et al. used nickel-based nano electro-brush plating for fabricating a superhydrophobic coating [89]. All methods exhibited variable degrees of mechanical stabilities as well.

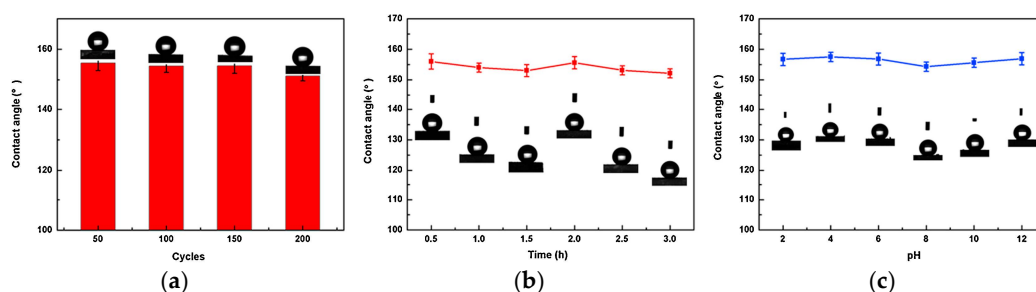


Figure 6. Stability tests of superhydrophobic coatings. (a) Mechanical stability of coatings with abrasion cycles under 250 kPa; (b) effect of ultrasonication time on the water contact angles of the coating; (c) water contact angle of the coating after immersed on aqueous solution of pH 2–12 for 12 h. Reprinted from [68] with permission; Copyright Elsevier 2016.

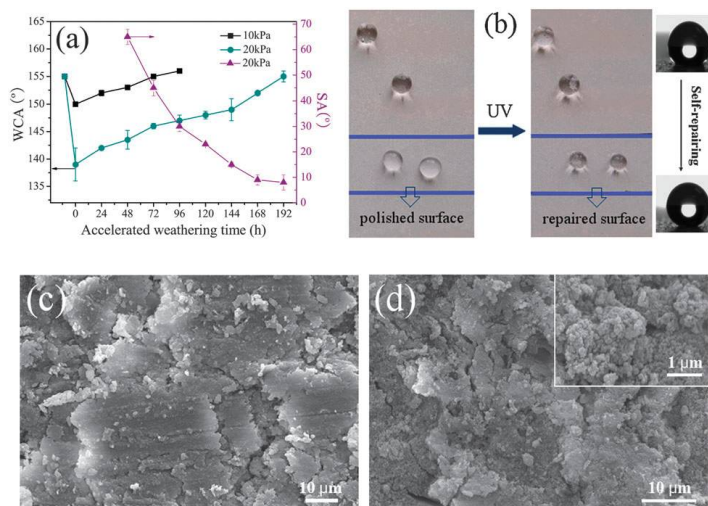


Figure 7. (a) The recovery of WCA and SA of the polished FMS/TiO₂-based superhydrophobic surfaces in an accelerated weathering tester; (b) photographs of water droplets and contact angles (139.11°–155.31°) on the polished surface and the repaired superhydrophobic surface (192 h exposure in the accelerated weathering tester); (c,d) SEM images of the polished surface after 10 cycles of abrasion under a 20 kPa pressure, and the repaired surface (192 h exposure in the accelerated weathering tester). (Composition: PMSF/PS/FMS/P25 = 17.1/40.9/36.0/6.0 wt/wt). Reprinted from [83] with permission; Copyright Royal Society of Chemistry 2014.

6. Corrosion Measurement Techniques

Corrosion monitoring is important owing to its significance in estimating the maintenance times of facilities. This section summarizes the most common corrosion measurement techniques that are adopted commercially as well as in research laboratories.

6.1. Potentiodynamic Polarization Method

Potentiodynamic polarization method is widely used for corrosion testing in laboratories [90,91]. This method is capable of providing information about corrosion rate, corrosion mechanisms, and even the susceptibility of materials to corrosion under stimulated environments [19,92]. The working mechanism of polarization method involves varying the potential of the test sample, which acts as the working electrode, and plotting the current produced as a function of either potential or time [93–95]. Though the test is less time-consuming and less complex, the results are comparable and even superior to the outputs from non-electrochemical tests that require longer time and effort. McCafferty validated the results obtained by polarization method using the Tafel extrapolation method [96]. Shi et al. studied the corrosion rate of magnesium alloys using the potentiodynamic polarization method with Tafel extrapolation to study the degree of deviation [97]. Elsener [98] and Soleymani [99] made use of the polarization method to study the corrosion behavior of steel in concrete structures.

6.2. Electrochemical Impedance Spectroscopy

Currently, the most widely used corrosion measurement technique is electrochemical impedance spectroscopy (EIS), which is very powerful and effective for the stated purpose [100,101]. A distinguishing feature of EIS over its counterparts is that it uses signals with very low amplitudes; such signals do not significantly disturb the properties under observation. Generally, EIS involves applying a low-amplitude signal to the test specimen over a range of frequencies. Once the circuit is active, the EIS system will record both the real and imaginary components of the impedance response of the system. The obtained impedance response is interpreted to get the corrosion characteristics of the test specimen [102,103]. EIS measurements are especially useful in applications that include fabricated coatings for specialized functions. Voevodin et al. used EIS to compare the corrosion characteristics of different sol-gel coatings on the same substrate [104]. Figure 8 shows a Nyquist plot of a graphene-coated aluminum alloy, which is superhydrophobic in nature, and that of bare aluminum alloy. Nyquist plots represent, on a linear scale, the real component of impedance against the imaginary one. The larger diameter curve for coated aluminum alloy in the Nyquist plot shows higher real impedance, which means the coating is more capacitive in nature and thus provides better protection against corrosion. Another popular method used in EIS for presentation is the Bode plot. A Bode plot presents impedance as a logarithm of frequency on the x -axis and impedance value and phase shift on the y -axis [105]. Figure 9 shows Bode plots for bare aluminum alloy and aluminum alloy coated with graphene.

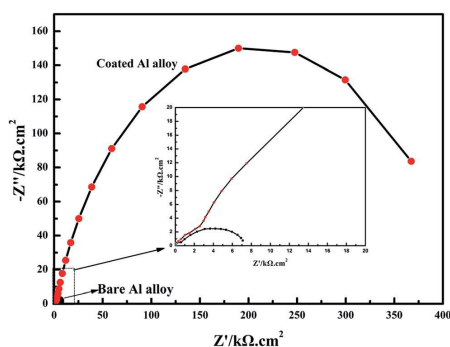


Figure 8. Nyquist plot of graphene coated Al alloy and bare Al alloy and magnification of one segment. Reprinted from [105] with permission; Copyright Royal Society of Chemistry 2014.

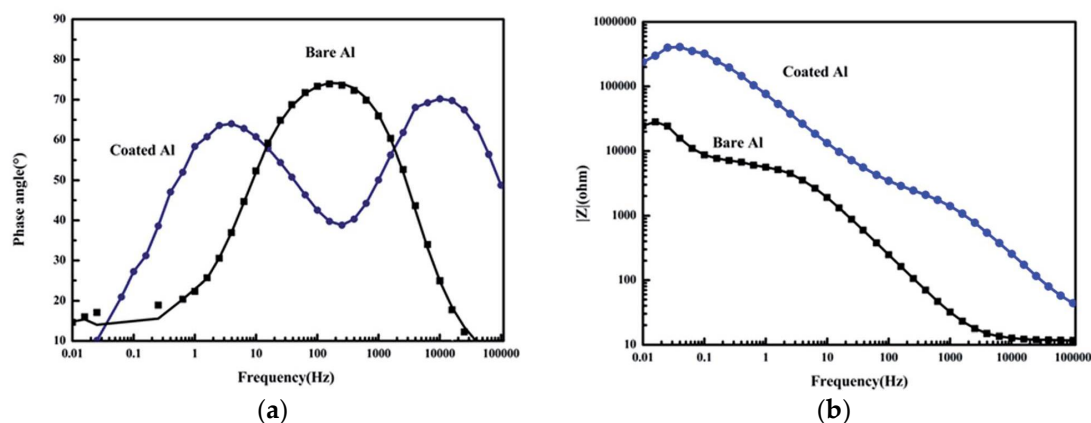


Figure 9. (a) Bode Phase angle diagrams and (b) Bode modulus diagrams of graphene coated Al alloy and bare Al alloy. Reprinted from [105] with permission; Copyright Royal Society of Chemistry 2014.

6.3. Salt Fog Test

The salt fog test, also called the salt spray test, is a standardized corrosion test method that is generally used to estimate the corrosion resistance of materials and associated coatings [106,107]. This testing method is an accelerated corrosion test in which a corrosive attack is intentionally applied to the coated samples to analyze the viability of the coating as a protectant against corrosion [108–110]. This test is carried out in a specialized apparatus that consists of a closed chamber where salt water (generally 5% NaCl) is released in the form of mist or spray that forms a corrosive environment of dense salt fog with the aid of spray nozzles along with pressurized air. Thus, the samples placed in the chamber will be subjected to severely corrosive conditions. The results of salt spray tests are generally represented in terms of testing hours without the appearance of corrosion products [109,110]. For the purpose of comparison of different surfaces, this test can be combined with EIS measurements to get a more quantitatively significant result. Figure 10 shows the visual appearance of coatings after a set time of salt fog testing. On the coating surface, large blisters and corrosion products were observed after 15 days.

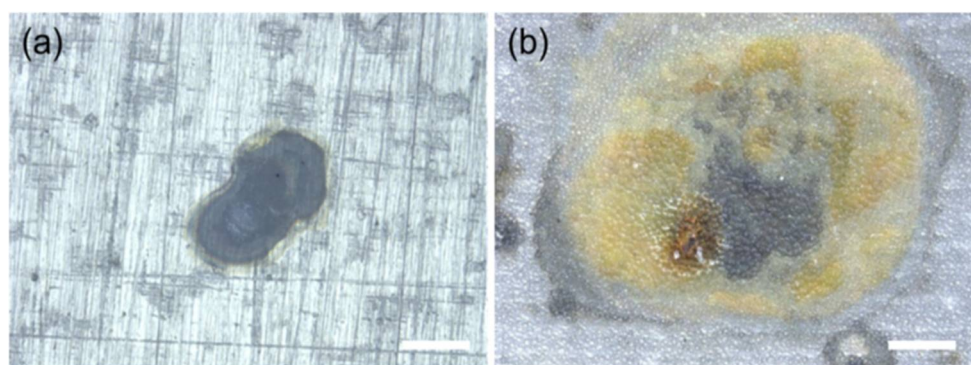


Figure 10. Coating morphologies after 15 days of salt spray tests: (a) regular coating; (b) superhydrophobic coating. The scale bar is 200 μm . Reprinted from [108] with permission; Copyright Elsevier 2016.

7. Procedures for Determining Mechanical Stability

Various standardized methods, both quantitative and qualitative, are available for the determination and comparison of mechanical stability and durability of fabricated coatings. Different tests give information, with varying degrees of accuracy, about the actual state of the coating. Following are some of the popular and simpler tests for determining the mechanical stability and durability of nanoengineered coatings.

7.1. Abrasion Tests

Prepared coatings on substrates are highly susceptible to abrasion damage during service. These tests evaluate the abrasion resistance of the coatings and offer insight about the durability and mechanical stability of the coating. The criteria selected to characterize the abrasion resistance of the coating can be the abrasion distance and amount of pressure the surface can withstand [111–113] and the number of test cycles to remove the coating or to expose the substrate underneath [114]. Primitive abrasion testing generally consists of moving the test surface against an abrasive one under applied pressure [111–113], but more advanced abrasion tests follow standardized testing methods such as ASTM D4060 [115] with the aid of automated abraders. Using the advanced tests with automated abraders, a quantitative conclusion about the wear resistance of the coating can be made in terms of weight loss per specified number of revolutions under specified load (wear index), number of cycles required to wear through a 1 mm thickness of coating (wear cycles per mm), or the number of test cycles to wear away the coating or expose the substrate (cycles to failure) [115].

7.2. AFM Measurements

The prepared coating's functionality is determined by its morphological features; hence, it is very important to study the mechanical properties of the surface at nanoscale. Quantitative nanoscale mechanical (QNM) characterization can be performed using atomic force microscopy (AFM) for mapping and differentiating between nanomechanical properties, which include adhesion properties [116], deformation, and stiffness [117] along with imaging the topography of the coating at atomic scale resolution [118]. This test measurement method is non-destructive to the sample surface. The quantitative data obtained by QNM measurement helps to analyze the materials observed on the topographic image of the coating surface being studied [118]. It is also possible to study the variation of mechanical properties across a surface using this measurement technique [117].

7.3. Sand Blasting Test

To understand the mechanical stability of coating under similar circumstances to abrasion, a sand blasting test can be performed on the coatings. The general test setup includes an abrasive gun aimed at the sample surface and placed at an appropriate distance in order to have a constantly exposed area [119]. Sand particles will blast the surface under controlled pressure for a specific duration of time. Figure 11 shows the schematic of a sand blasting set. After sand blasting, the surface is cleaned and dried for further analysis [119]. Generally, the water contact angles before and after the test are compared in order to quantify the mechanical stability [120].

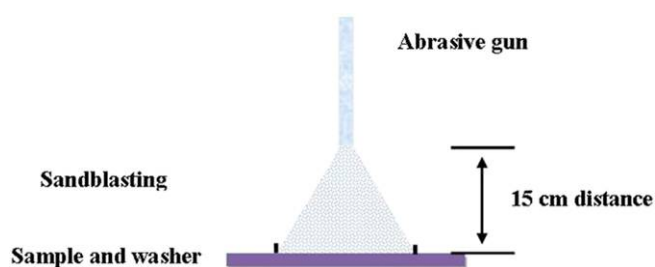


Figure 11. Schematic of micro-sand blasting test. Reprinted from [119] with permission; Copyright Elsevier 2016.

7.4. Tape Peeling Test

A tape peeling test, though simplistic in its application [121–125], is a material removal test that may provide a rough estimation of how well the developed coating has been attached or bonded to the base metal. To carry out this particular test, an adhesive tape is applied to the surface coating

to be analyzed, and the length of the tape is pressed fully and firmly after application in order to remove any air that might have been trapped between the tape and coating [126]. This removal of air also ensures proper and continuous contact between the two interacting layers. The tape is then peeled off of the surface gradually, and the underlying surface is inspected to see whether the coating has been removed from any region or whether the substrate is partially or fully visible in any region. Different grades of adhesive tapes can be used for analysis, depending upon the requirement, and the grading for adhesive tapes is considered with reference to the force of adhesion to a specified reference material [121–127].

7.5. Nano-Indentation Test

The hardness and Young's modulus of the coatings can be obtained from the load penetration curve using a nano-indentation test [128,129]. The surface of substrates could be compared before and after the surface modification on the basis of hardness and modulus. This test provides quantitative data with reference to the physical condition of engineered surfaces [36,120]. It is suggestible to compare the hardness as well as modulus of the fabricated coatings after performing accelerated weathering, corrosion or abrasion tests on the coatings. Therefore, a deeper insight into the mechanical robustness of fabricated coatings when exposed to environments could be obtained.

8. Effectiveness of Various Coatings

As observed in the previous section, different methods are available for the fabrication of superhydrophobic coatings. These methods differ from each other based on the mechanisms used for functionalizing the surface, the types of chemicals used, and potential applications for which the particular superhydrophobic coating is developed. All the coatings discussed in this section have been analyzed for their anti-corrosion properties in consideration of their mechanical stability and durability.

A silane-modified superhydrophobic coating exhibits a high contact angle and therefore exhibits favorable anti-corrosion properties, albeit with limited levels of durability and mechanical stability [55–60]. It was possible to develop effective corrosion barriers against different materials such as mild steel and aluminum; however, a matter of concern associated with silane-modified superhydrophobic coatings is their relatively limited mechanical stability and durability compared to other types of superhydrophobic coatings. The durability, mechanical stability, and wear resistance of silane-based superhydrophobic coatings are limited in terms of their extended usability in various applications [57–59]. Generally, the morphological modifications on the silane-based superhydrophobic coatings are incorporated on the parent substrate itself, so the structures are comparatively delicate and more prone to wear and similar mechanically vulnerable conditions [57–59]. Thus, it may be prudent to look at other types of superhydrophobic coatings for anti-corrosion applications involving the potential for higher wear and abrasion.

Polymer-based coatings possess considerably higher durability, mechanical stability, and wear resistance compared to silane-based superhydrophobic coatings [61–65]. A polymer-based coating with the proper binding constituents adheres to the substrate to be functionalized and forms a relatively strong bond between the coating and the substrate. Another outstanding advantage of polymer-based superhydrophobic coatings is that they can easily be applied to the surface through a spray coating method; this reduces the complexity associated with the functionalizing process. Polymer-based coatings can be recommended for anti-corrosion applications that require high wear resistance and durability.

Titanium oxide-based coatings are durable and mechanically stable superhydrophobic coatings that also possess favorable corrosion barrier properties. Titanium dioxide nanostructures can be successfully incorporated along with poly dimethyl siloxane to form a composite coating with improved mechanical properties [71]. The limiting factor that comes into play while considering titanium oxide-based superhydrophobic coatings for practical applications is its photocatalytic

activity [70]. Thus, this type of coating may not be appropriate for use in applications where the surface is susceptible to ultraviolet irradiation.

Nanoparticle-based superhydrophobic coatings differ from their counterparts in several aspects including ease of application, the domain of the substrate that can be functionalized using a particular coating solution, and tunability of the superhydrophobicity. The possibility of spray application makes this coating usable in substrates that vary widely in shape and size [72,73]. The mechanical properties and corrosion inhibition capability of nanoparticle-based coatings are comparable with those of other methods [73]. Another advantage of nanoparticle-based coatings is that various nanoparticles can be solely dispersed or combined in a polymer base [74–79].

There are studies that suggest that it is possible to develop superhydrophobic surfaces with only morphological modification (without alteration of the surface chemistry) by providing a low surface energy coating [130–133]. The superhydrophobic behavior in these cases is achieved by decreasing the liquid–solid contact fraction to a very lower magnitude by morphological modifications. Though analyses of the degree of superhydrophobicity and mechanical robustness of these surfaces show promising results, the capability of these surfaces to resist corrosion has not been well documented.

9. Conclusions

Superhydrophobic coatings remain a highly viable preventative method for controlling the corrosion of metals, and their use and development is increasing and evolving due to the introduction of new coating methods and particles. The key limiting factors that determine the usage of superhydrophobic coatings as a feasible solution for corrosion protection are their mechanical stability and durability. Therefore, it is essential to develop a deeper understanding of the mechanical stability and durability of fabricated superhydrophobic coatings. The ability of superhydrophobic coatings to partially or completely arrest the interaction between metal surfaces and corrosive media is meaningful only when that ability can be maintained for a prolonged period of time.

Among all the fabrication methods for metals discussed in this review, all methods were tested and evaluated under constraints such as mechanical stability, durability, and corrosion resistance only within the boundaries of controlled laboratory testing. The developed coating should also exhibit, in consideration of the particular application for which it is being developed, a proper balance between corrosion resistance, durability, and mechanical stability. In conclusion, it can be suggested that the selection of an appropriate superhydrophobic coating for the purpose of preventing metal corrosion could be made after having a proper understanding of the nature of the substrate, the working environment, the substances to be applied, and the required degrees of durability and mechanical stability.

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