

REVIEW

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Corrosion behavior of superhydrophobic surfaces: A review



Adel M.A. Mohamed ^{a,b}, Aboubakr M. Abdullah ^{a,c,*}, Nathalie A. Younan ^a

 ^a Center for Advanced Materials, Qatar University, Doha 2713, Qatar
^b Department of Metallurgical and Materials Engineering, Faculty of Petroleum and Mining Engineering, Suez University, Box 43721, Suez, Egypt
^c Chemistry Department, Faculty of Science, Cairo University, Giza 12613, Egypt

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KEYWORDS

Superhydrophobic; Materials; Surfaces; Corrosion; Protection **Abstract** Superhydrophobic surfaces have evoked great interest in researchers for both purely academic pursuits and industrial applications. Metal corrosion is a serious problem, both economically and operationally, for engineering systems such as aircraft, automobiles, pipelines, and naval vessels. Due to the broad range of potential applications of superhydrophobic surfaces, there is a need for a deeper understanding of not only how to fabricate such surfaces using simple methods, but also how specific surface properties, such as morphology, roughness, and surface chemistry, affect surface wetting and stability. In this article, a comprehensive review is presented on the researches and developments related to superhydrophobicity phenomena, fabrication of superhydrophobic surface and applications. A significant attention is paid to state of the art on corrosion performance of superhydrophobic coatings.

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* Corresponding author at: Chemistry Department, Faculty of Science, Cairo University, Giza 12613, Egypt. Tel.: +20 974 4403 5672; fax: +20 974 4403 3889.

E-mail addresses: abubakr_2@yahoo.com, bakr@qu.edu.qa (A.M. Abdullah).

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1. Introduction

Superhydrophobic surfaces have evoked great interest in researchers for both purely academic pursuits and industrial applications. Many review articles covering different aspects of superhydrophobicity have been published (Bhushan and Jung, 2011; Ma and Hill, 2006; Nakajima et al., 2001; Quere, 2005; Roach et al., 2008; Xue et al., 2010). Superhydrophobic surfaces (SHS) exhibit extremely high water repellency, where water drops bead up on the surface, rolling with a slight applied force, and bouncing if dropped on the surface from a height.

It is well known that the degree to which a solid repels a liquid depends upon two factors: surface energy and surface morphology. When surface energy is lowered, hydrophobicity is enhanced. Chemical compositions determine the surface free energy and thus have a great influence on wettability (Woodward et al., 2000). However, certain limitations are encountered and superhydrophobic surfaces cannot be obtained only by lowering the surface energy. For example, the $-CF_3$ - terminated surface was reported to possess the lowest free energy and the best hydrophobicity, but the maximum contact angle on flat surfaces could only reach 120° (Nishino et al., 1999).

In superhydrophobic surface, the surface morphology plays a crucial role effecting wettability. Roughening a surface can not only enhance its hydrophobicity due to the increase in the solid–liquid interface (Wenzel, 1936, 1949) but also when air can be trapped on a rough surface between the surface and the liquid droplet. Since air is an absolutely hydrophobic material with a contact angle of 180°, this air trapping will amplify surface hydrophobicity (Ogihara et al., 2013; Sun et al., 2005). Hierarchical micro- and nanostructuring of the surface is thus responsible for superhydrophobicity.

Surface wetting behavior can generally be broken into 4 different regimes, based on the value of water contact angle (WCA). The two most conventional regimes are the hydrophilic and hydrophobic regimes, defined as WCAs in the range of $10^{\circ} < \theta < 90^{\circ}$ and $90^{\circ} < \theta < 150^{\circ}$, respectively. The hydrophobic coatings are intensively used in plenty of engineering applications, however; the hydrophilic coatings are widely used in paint and varnish industries. Although the applications of hydrophobic and hydrophilic regimes, the other superhydrophobic and superhydropholic regimes, which describe the extremes of surface wetting behavior, are wholly more interesting. Superhydrophilicity, which is characterized by WCAs in the range of $\theta < 10^\circ$, within 1 s of the initial wetting, describes nearly perfect wetting. In contrast, superhydrophobicity, described by WCAs of $\theta > 150^{\circ}$, describes a state of nearly perfect non-wetting (Fig. 1).

In addition to high contact angles, superhydrophobic surfaces exhibit very low water contact angle hysteresis CAH ($<10^\circ$). Contact angle hysteresis is the difference between advancing and receding contact angle. This leads to the rolling and bouncing of the water droplets, which will entrain particle contaminants from the surface leading to a self-cleaning property of superhydrophobic surfaces. The physical reason of self-

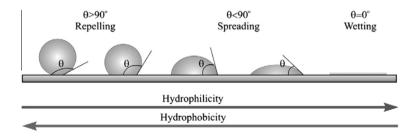


Figure 1 Schematic of contact angle (CA) for a water drop placed on surfaces of different hydrophobicities (Krasowska et al., 2009).

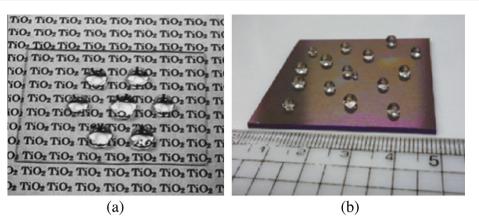


Figure 2 (a) Transparent super-hydrophobic thin film with TiO_2 photocatalyst (Nakajima et al., 2001). (b) Colored superhydrophobic magnesium alloy (Ishizaki and Sakamoto, 2011).

cleaning is the joint action of small adhesion of dust particles to the surface and high capillary force acting on the dust particles at water drop-air interface. These properties arise from the combination of the low interfacial energy and their rough surfaces (Barkhudarov et al., 2008). This combination leads to apparent water contact angles (WCAs) larger than 150° with low sliding angles and the self-cleaning effect.

Besides water repellency and self-cleaning, other properties have also been incorporated in superhydrophobic surfaces such as transparency and color (Fig. 2), anisotropy, reversibility, flexibility and breathability (moisture vapor transfer) (Ma and Hill, 2006).

2. Superhydrophobicity phenomena in nature

The amazing water-repellency, superhydrophobicity, of some plants has received a great deal of interest. The leaves of several plants such as *Nelumbo nucifera* (Lotus), illustrated in Fig. 3, *Brassica oleracea, Colocasia esculenta*, and many others, as well as the wings of butterflies (Goodwyn et al., 2009) and the legs of water striders (Gao and Jiang, 2004) are all superhydrophobic surfaces.

Gao et al. (2004) showed that the unique hierarchical structure of the water striders' legs, which are covered by large numbers of oriented tiny hairs (microsetae) with fine nanogrooves, is

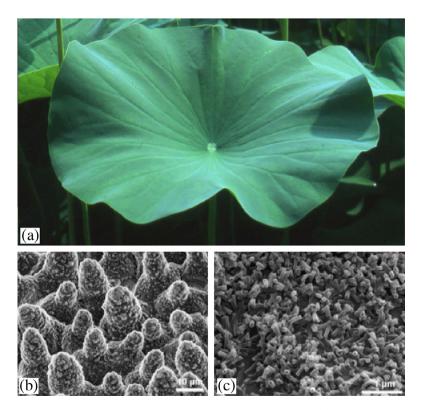


Figure 3 (a) Lotus leaves, which exhibit extraordinary water repellency on their upper side. (b) Scanning Electron Microscope (SEM) image of the upper leaf side prepared by 'glycerol substitution' shows the hierarchical surface structure consisting of papillae, wax clusters and wax tubules. (c) Wax tubules on the upper leaf side (Ensikat et al., 2011).

responsible for their water resistance. The air trapped in spaces between the microsetae and nanogrooves leads to the superhydrophobic property of the legs, with a contact angle found to be around 167°. This allows water striders to survive on water.

Bechert et al. (2000) showed that the shark skin is covered by very small individual tooth-like scales called dermal denticles (little skin teeth), ribbed with longitudinal grooves (aligned parallel to the local flow direction of the water). These grooved scales reduce the formation of vortices present on a smooth surface, resulting in water moving efficiently over their surface.

Neinhuis and Barthlott (1997) reported the water contact angles of more than 200 plant species and investigated their surface morphologies. There are two different types of waterrepellent plant leaves: the first type is hair covered leaves such as Lady's Mantle, and the second type is macroscopically smooth leaves such as Lotus (Otten and Herminghaus, 2004). Water droplets completely run off both plants' leaves and their surfaces remain dry even after heavy rains.

Although many plants have exhibited similar contact angles (around 160°), the lotus leaves have shown better stability and perfection as water repellent. These observations have led to the concept of the "Lotus effect" and made out of the Lotus plant an archetype and an ideal model for superhydrophobicity. Some works made it obvious that the contact angle alone is not sufficient to compare the efficiency of superhydrophobic samples (Bechert et al., 2000; Ensikat et al., 2011; Neinhuis and Barthlott, 1997). Many other factors interfere, such as the morphology of the epidermal structure (papillose or non-papillose surface), the nanoscopic epicuticular wax crystals of the leaves and the stability of the superhydrophobicity un-

Table 1	Surface tension of common materials at 20 °C (http://
www.afc	ona.com.my/

Slip and Leveling agent mar 2010.pdf).

Material	$\gamma (mN/m)$
Water	72.8
Ethanol	22.4
Toluene	28.5
Polyethylene PE	33.2
Polypropylene PP	28.0
Polyvinyl chloride PVC	39.8
Teflon (polytetrafluoroethylene PTFE)	19
Silicone (polydimethylsiloxane PDMS)	19
Fluorosilicone	14.7
Glass	70.0
Steel, pre-treated	45.0

der moisture condensation conditions. Only the Lotus plant showed no significant loss of the water repellency property under these conditions.

All in all, the unique shape of its papillae, the unique properties of its epicuticular wax and its stable superhydrophobicity have made out of the Lotus leaf an outstanding model for the development of many superhydrophobic structures.

3. The theory of superhydrophobic surfaces

In this section, the theory and fundamentals of wetting of a rough surface and the equations that govern the contact angle of a liquid are presented and discussed.

3.1. Contact angle and the Young equation

Atoms or molecules at the surface of solids or liquids possess fewer bonds with neighboring atoms than those in the interior, and thus, have higher energy. This surface energy or surface tension, γ , is equal to the work required to create a unit area of the surface at constant pressure and temperature, and is measured in N/m. The values of surface tension of some materials at 20 °C, found in the literature, are listed in Table 1.

As illustrated in Fig. 4a, when a liquid drop is placed in contact with a solid, the equilibrium of the solid and liquid surfaces will be established at a certain angle called the static contact angle CA, θ_0 , given by the Young equation:

$$\cos\theta_0 = \frac{\gamma_{\rm SA} - \gamma_{\rm SL}}{\gamma_{\rm LA}} \tag{1}$$

where γ_{SA} , γ_{SL} and γ_{LA} are the surface energies of the solid against air, solid against liquid and liquid against air, respectively. The analysis does not change in the case of another gas, other than air. In another way, the contact angle can be defined as the angle between liquid/gas interface and liquidsolid interface when a liquid droplet is placed on a solid surface.

This equation is applicable only to flat and smooth surfaces and not to rough ones. It agrees with the fact that the WCA increases with decreasing difference between solid–vapor and solid–liquid surface energies, taking into consideration the sign of this difference.

Hydrophobicity is usually determined by measuring the CA of water droplets on a surface. The contact angle hysteresis, CAH, the difference between the advancing CA, θ_{adv} , and the receding CA, θ_{rec} , as shown in Fig. 4b, are an important parameter to characterize the wetting phenomena on any surface. A superhydrophobic surface should have a low CAH

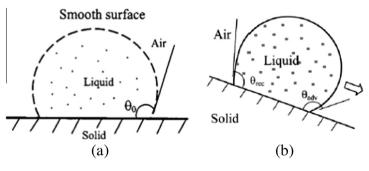


Figure 4 Schematics of a liquid drop on a (a) smooth solid surface (Bhushan and Jung, 2011) and (b) tilted surface showing advancing and receding CAs (Nosonovsky and Bhushan, 2009).

 $(<10^\circ)$ in addition to high CA $(>150^\circ)$. As mentioned in the previous sections, a low CAH allows water to roll-off easily along the surface. Occurrence of contact angle hysteresis is associated with the surface defects, which could be from the surface roughness, chemical heterogeneity, or wetting state. According to the difference of contact angle hysteresis, surfaces can perform as slippery or sticky surfaces. The pinning phenomenon during the evaporation of a droplet is an example of the contact angle hysteresis.

The Young equation was based on the concept of an idealized, atomically smooth solid surface. However, all surfaces have defects and imperfections that contribute to surface roughness, and this roughness will contribute to the surface wetting behavior (Patankar, 2004). In view of this roughness-induced wettability modification, two well-established models have been developed to account for these effects: the Wenzel model (1936) and the Cassie-Baxter model (1944).

3.2. Rough surfaces and the Wenzel and Cassie-Baxter models

On rough surfaces, the Young equation no longer applies. Wenzel (1936, 1949) proposed a model to describe the contact angle, θ , with a rough surface, by relating it to that with a flat surface θ_0 . He modified the Young equation as follows:

$$\cos\theta = r \left(\frac{\gamma_{\rm SA} - \gamma_{\rm SL}}{\gamma_{\rm LA}}\right) = r \cos\theta_0 \tag{2}$$

This is called the Wenzel equation, where r is the nondimensional surface roughness factor, defined by the ratio of the actual area of a rough surface, A_{SL} , to its flat projected area, A_{F} :

$$r = \frac{A_{\rm SL}}{A_{\rm F}} \tag{3}$$

Since r > 1, roughness on a hydrophobic surface $(\theta_0 > 90^\circ)$ increases the contact angle and renders the surface more hydrophobic, whereas on a hydrophilic surface $(\theta_0 < 90^\circ)$, roughness has the opposite effect, decreasing θ toward 0° and yielding a more hydrophilic surface.

The Wenzel equation is only valid for the homogeneous solid–liquid interface shown in Fig. 5a. It no longer applies for heterogeneous surfaces.

Therefore, Cassie and Baxter (1944) proposed another model for heterogeneous surfaces composed of two fractions, one with a fractional area f_1 and contact angle θ_1 and the other with f_2 and θ_2 , with $f_1 + f_2 = 1$. The contact angle is thus given by:

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{4}$$

For the case of a composite interface, shown in Fig. 5b, the first fraction corresponds to the solid–liquid interface $(f_1 = f_{SL}; \theta_1 = \theta_0)$ and the second fraction to the liquid–air interface $(f_2 = f_{SL} = 1 - f_{SL}; \theta_2 = 180^\circ)$.

Combining Eqs. (2) and (4) gives rise to the Cassie & Baxter equation:

$$\cos\theta = rf_{\rm SL}\cos\theta_0 - 1 + f_{\rm SL} \tag{5}$$

or

$$\cos\theta = r\cos\theta_0 - f_{\rm LA}(r\cos\theta_0 + 1) \tag{6}$$

The opposite limiting case with $\theta_2 = 0^\circ$, corresponding to the water-on-water contact when the rough surface is covered by holes filled with water instead of air (Fig. 5c), yields the Cassie equation:

$$\cos\theta = 1 + f_{\rm SL}(\cos\theta_0 - 1) \tag{7}$$

According to Eq. (6), for a hydrophobic surface ($\theta_0 > 90^\circ$), the contact angle increases with an increase of f_{LA} leading thus, to a more hydrophobic surface. For a hydrophilic surface ($\theta_0 < 90^\circ$), the contact angle can also increase with f_{LA} , in certain conditions at which the surface shifts from hydrophilic to hydrophobic (Jung and Bhushan, 2006). Boinovich and Emelyanenko (2008) reviewed the theory and fundamentals of hydrophobic materials in more detail.

Unlike the Cassie state, homogenous wetting, or the Wenzel state, leads to a larger solid contact area and subsequently higher CAH that, in turn, results in greater adhesion to the surface. Theoretical calculations and molecular dynamic simulations have also confirmed the fact that CAHs in the Cassie

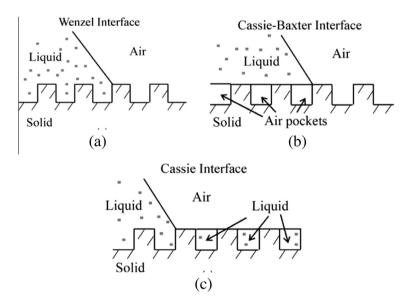


Figure 5 Configurations described by (a) Wenzel equation for homogeneous interface, (b) Cassie and Baxter for the composite interface with air pockets and (c) Cassie equation for the homogeneous interface (Nosonovsky and Bhushan, 2009).

state are weaker than those in the Wenzel state (Koishi et al., 2011; Lafuma and Quere, 2003; Dupont and Legendre, 2010; Kong and Yang, 2006). For example: Lafuma and Quere (2003) compared the CAH of water droplets in the cases of both Cassie and Wenzel states on the same microtextured surface. For the Cassie state, the water droplet was gently dispensed on the surface while, in order to maintain the Wenzel state, the water droplet was condensed onto the surface. In addition to a higher advancing CA, it was shown that the CAH was significantly lower in the case of the Cassie state. Koishi et al. (2011) used molecular dynamic simulations to elucidate the relationship between the values of the CAH and the corresponding wetting regime. They found that the CAHs, in the case of the composite Cassie state, are weaker in comparison with those in the homogenous wetting Wenzel state on the same structure.

It may be concluded that, the Cassie model is a more general model that can be used to predict entire wetting regimes from low extreme to high extreme, whereas the Wenzel model can predict only moderate homogenous wetting regimes between the two extremes. From the Cassie model, it can be noticed that a reduction in the solid fraction and an increase in the air fraction would enhance the water repellency of a surface regardless of whether the surface is hydrophobic or hydrophilic.

4. Fabrication of superhydrophobic surfaces

A variety of materials have been used to prepare superhydrophobic surfaces including both organic and inorganic materials. For polymeric materials, which are generally inherently hydrophobic, fabrication of surface roughness is the primary focus. For inorganic materials, which are generally hydrophilic, a surface hydrophobic treatment must be performed after the surface structures are fabricated. Several techniques for the preparation of superhydrophobic surfaces have been investigated and reported. However, they can simply be divided into two categories (Ma and Hill, 2006; Roach et al., 2008; Xu et al., 2011):

- i. Making a rough surface from a low surface energy material.
- ii. Modifying a rough surface with a material of low surface energy.

Various methods are used for the preparation of rough surfaces, such as mechanical stretching, sol-gel processing, layer-by-layer assembly, etching, lithography, chemical and electrochemical depositions and chemical vapor deposition. A brief description and use of some of these important techniques are presented in the following subsections.

4.1. Sol-gel process

The sol-gel process is an efficient, low-cost and lowtemperature/low pressure procedure and can produce rough surfaces on a variety of oxides. This approach is a very versatile process for the preparation of superhydrophobic films or bulk materials. The roughness of the surface obtained with this process can be easily modified simply by changing the composition of the reaction mixture and the protocol followed. Silica coatings are the most used in the sol-gel method. Sol-gel processes can produce rough surfaces on a variety of oxides such as silica, alumina, and titania (Roig et al., 2004; Tadanaga et al., 1997). This approach is a very versatile process for the preparation of superhydrophobic thin films or bulk materials. The sol-gel process can form a flat surface coating, xerogel coating or aerogel coating depending on the process conditions; both xerogel and aerogel show rough or fractal surfaces.

Barkhudarov et al. (2008) used organo-trimethoxysilanes as starting materials to make optically transparent superhydrophobic films with contact angles exceeding 155° and reaching 170°. Xiu et al. (2008) generated superhydrophobic isobutyl surface groups by incorporating isobutyltrimethoxysilane (IBTMOS) into silica layers. With a TMOS/IBTMOS ratio of 1:1, a contact angle of 165–170° was observed. As shown in Fig. 6, the obtained surface consists of globules (20–50 nm in diameter) surrounding a network of pores (submicron size), which indicates a hierarchical roughness in two scales: nanoscale and submicron scale.

Latthe et al. (2009) managed to prepare superhydrophobic silica films on glass substrates using trimethylethoxysilane as a co-precursor. The silica films obtained were transparent and stable to high temperatures (up to $275 \text{ }^{\circ}\text{C}$) and humidity, having a water contact angle of 151° and a sliding angle of 8° .

Feng et al. (2004) managed to grow superhydrophobic aligned ZnO nanorods starting from ZnO sol. Water contact angles exceeding 160° were observed. These nanorod films exhibited a reversible behavior from superhydrophobicity to superhydrophilicity by alternation of ultraviolet irradiation and dark storage: after UV illumination for 2 h, the water contact angle drops from $\sim 160^{\circ}$ to 0° and returns to the initial value after storage in the dark for 7 days. The reason for the reversible behavior is due to the generation of electron-hole pairs in the ZnO surface resulting from the UV irradiation, some of these holes can react with the lattice oxygen to form surface oxygen vacancies. At the same time, both water and oxygen may compete to dissociatively adsorb on them. The defective sites are kinetically more favorable for hydroxyl adsorption than oxygen adsorption. In the case of rough surface, water will enter and fill the grooves of the films, leaving

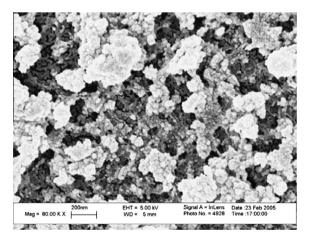


Figure 6 High resolution SEM image of a silica film with a TMOS/IBTMOS ratio of 1:1 (Xiu et al., 2008).

only the upper part of the nanorods not in contact with liquid. This effect results in a water CA of about 0° (Sun et al., 2001; Bico et al., 2001).

It should be stated that these superhydrophobic coatings synthesized using the sol-gel processing are usually stable due to the formation of covalent bonds between the coating and the substrate (Xue et al., 2010). The resulted coatings are robust and rough (Xiu et al., 2008).

4.2. Layer-by-layer self-assembly

The layer-by-layer (LBL) assembly is a simple and cheap method to construct thin-film coatings by depositing alternating layers, oppositely charged, with intermediate washing steps. It uses electrostatic interaction and covalent bonds to form multilayer grafts. The advantage of this technique is that it possesses a high degree of molecular control over the film thickness, which arises from the linear growth of films with respect to the number of bilayers. Recently, LBL method has been employed by many groups in order to fabricate superhydrophobic coatings with rough surfaces.

Isimjan et al. (2012) prepared titanium thin films on steel substrates by means of LBL deposition process. At first, the steel substrate was deposited with a precursor layer of Poly(diallyldimethylammonium) (PDDA)/Poly(sodium 4-styrenesulfonate) (PSS) by three cycles of alternate immersion of the substrate in PDDA and PSS aqueous solutions. Then, the substrate was alternatively dipped in TiO₂ P25 aqueous solution and PSS. This cycle was repeated many times in order to obtain multilayer films of $(TiO_2/PSS)*n$, where n corresponds to the number of deposition cycles. The resulting superhydrophobic coatings on steel substrate exhibited a strong repulsive force to water droplets, with contact angles greater than 165°. Fig. 7 illustrates water droplets on the three layers of TiO₂ nanoparticle coated surface and shows SEM images of one to three layers of P25 on the steel surfaces. Zhai et al. (2004) also prepared a polyelectrolyte multilayer surface by LBL assembly and then overcoated the surface with silica nanoparticles to mimic the hierarchical scale present on lotus leaf surfaces. Superhydrophobicity was achieved after surface fluorination with a fluoroalkyl silane.

Amigoni et al. (2009) constructed hybrid organic/inorganic surfaces by alternating different layers of amino-functionalized silica nanoparticles and epoxy-functionalized smaller silica nanoparticles. They found out that the hydrophobicity increases with the number of layers and obtained a water contact angle around 150° with the alternation of nine layers.

LBL assembly could be combined as well with electrodeposition to make superhydrophobic coatings as described by Zhao et al. (2005).

4.3. Etching

Etching is another simple and efficient method to produce superhydrophobic coatings with rough surfaces. Different etching techniques, such as chemical, plasma and laser etching have been recently used (Dong et al., 2011).

Li et al. (2012) used hydrochloric acid as chemical etching solution to prepare superhydrophobic surface on aluminum alloy AA2024. It has been shown that the roughness depended

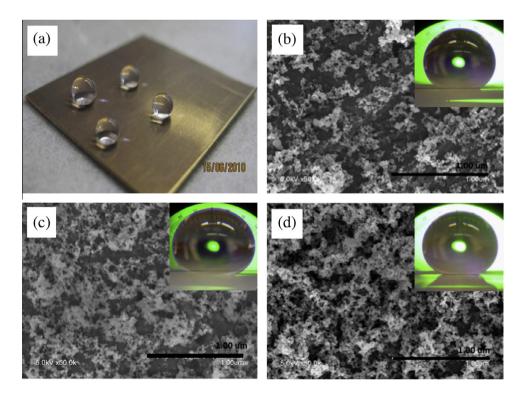


Figure 7 SEM images of different layers of TiO_2 nanoparticles in steel surface: (a) Water droplets on the treated steel surface. (b) TiO_2 one layer (TiO_2)*1. (c) TiO_2 two layers (TiO_2)*2 and (d) TiO_2 three layers (TiO_2)*3 (Isimjan et al., 2012).

on the chemical etching time. A contact angle larger than 150° was achieved at an etching time of more than 3 min.

Pan et al. (2010) established a simple cetyltrimethylammonium bromide (CTAB) and ultrasonication assisted nitric acid HNO₃ etching technique to fabricate a rough surface on the copper substrate. A superhydrophobic coating was obtained with a contact angle around 155° .

Gao et al. (2012) fabricated a rough surface on the zinc substrate using a glow discharge electrolysis plasma (GDEP) reactor to etching. This apparatus consists of a high voltage supply unit and two electrodes submerged in an electrochemical cell separated by a dielectric wall with a diaphragm.

Shiu et al. (2005) developed an approach for making tunable superhydrophobic surfaces using oxygen plasma etching. Water contact angles up to 170° were obtained.

4.4. Chemical and electrochemical deposition

Chemical and electrochemical deposition techniques have been intensively employed to prepare superhydrophobic surfaces. Darmanin et al. (2013) reviewed the most published researches showing the details of electrochemical oxidation processes, such as oxidation of metals in solution, anodization of metals or electrodeposition of conducting polymers, and reduction processes, e.g., the electrodeposition of metals and galvanic deposition.

Ou et al. (2012) investigated the corrosion behavior in NaCl solution of superhydrophobic surfaces prepared by 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS) chemically adsorbed onto the etched titanium substrate. It has been shown that the strong chemical interfacial bonding between PFOTS and Ti leads to a higher stability and corrosion inhibition efficiency. Yin et al. (2008) also prepared a stable superhydrophobic film by mystic acid chemically adsorbed onto anodized aluminum substrate. The contact angle was in the order of 154°, and corrosion in seawater was significantly decreased.

Huang et al. (2013) demonstrated that the copper surface covered with copper stearate, which was formed by an electrochemical reaction with a DC voltage of 30 V in stearic acid solution, showed superhydrophobic properties. Shirtcliffe et al. (2004) electrodeposited copper from acidic copper sulfate solution onto flat copper substrates to obtain superhydrophobic surfaces of varying levels of roughness, depending on the current density during deposition.

4.5. Other techniques used

Other approaches to the fabrication of superhydrophobic surfaces have been developed and used, these include spraying nanoparticle suspensions onto substrates (Ogihara et al., 2013), chemical vapor deposition (Ishizaki et al., 2010), electrospinning (Acatay et al., 2004; Ma et al., 2005), sublimation (Nakajima et al., 1999), hydrothermal synthesis (Shi et al., 2005), and wax solidification (Onda et al., 1996).

Spraying is a one-step, time-saving, low-cost and repairable method for preparation of superhydrophobic surfaces. Xu et al. (2011) fabricated superhydrophobic copper meshes by evenly spraying an emulsion of n-octadecanethiol and silver nitrate in ethanol onto the copper mesh with nitrogen gas by a spray gun. Alkanethiols contain long-chain alkyl groups that have low surface free energy. One advantage of this method is that in the case of mechanical damage of the surface, it can simply be repaired by partial spraying. In a similar way, Ogihara et al. (2013) prepared superhydrophobic paper using mixtures containing nanoparticles and ethanol, manually sprayed over paper from 20 cm away with a vaporizer. In this case, the surface energy and the roughness structure could be controlled by the spray-coating conditions, such as the type of nanoparticles and their size.

Electrospinning is another powerful, simple and practical one-step method to generate continuous ultrathin fibers with micrometer and sub-micrometer diameters from a variety of polymeric materials. Electrospun fibers intrinsically provide at least one length scale of roughness for superhydrophobicity because of the small fiber size. The fiber mats composed solely of uniform fibers could be obtained by electrospinning a hydrophobic material (i.e., poly(styrene-block-dimethylsiloxane) block copolymer) blended with homopolymer polystyrene (PS) (Ma et al., 2005). Table 2 shows the most important parameters controlling the electrospinning process.

Acatay et al. (2004) electrospun a thermoset fluorinated polymer onto an aluminum foil substrate, by applying an electrical bias from the tip of the polymer solution-filled syringe to a grounded collection plate. The formed electrospun film consisted of a continuous web or mat of randomly aligned fibers.

After the roughening of the surfaces, most substrates still do not show superhydrophobicity. Consequently, the surface energy of such coatings should be lowered using low surface energy materials. The most common ones are fluorocarbons, silicones, and some organic materials (polyethene, polystyrene, ...). Although, inorganic materials such as ZnO and TiO₂ have high surface energy, the nanoparticles from these materials are easily covered by airborne organic contaminations. Due to such contaminations the surfaces modified with such nanoparticle layers may demonstrate superhydrophobic behavior. For instance, fluoroalkylsilane (FAS) molecules were intensively used by several groups in order to modify the surface and enhance superhydrophobicity due to their extremely low surface free energy and the simple reaction of the silane groups with

Table 2 Most important electrospinning parameters (Sas et al., 2012).								
Materials properties	Process parameters	Equipment design	Ambient conditions					
Viscosity	Electrical field strength	Needle design	Relative humidity					
Conductivity	Solution charge polarity	Solution charge polarity Collector geometry						
Solvent volatility	Electrical signal type	Electrical signal type						
Surface tension	Tip to collector distance	Tip to collector distance						
Polymer MW	Flow rate	Flow rate						
Polymer type	Collector take-up velocity							

the hydroxyl groups on coatings (Hu et al., 2012; Ishizaki et al., 2011; Liang et al., 2013; Song et al., 2012).

5. Applications of superhydrophobic surfaces

The impetus for the development of materials with superhydrophobic properties is for use in practical applications. Superhydrophobic surfaces have attracted growing interest in the past two decades because of their unique water repellency, self-cleaning property and their importance in various applications. including self-cleaning windows, roof tiles, textiles, solar panels and applications requiring anti-biofouling and reduction of drag in fluid (micro/nanochannels) (Bhushan and Jung, 2011). Some agricultural applications were also discussed, such as biomedical applications (Xiu et al., 2007), stain resistant textiles (Satoh and Nakazumi, 2003), ant-sticking of snow for antennas and windows (Kako et al., 2004) and many others. One of the most important applications for superhydrophobic surface is corrosion resistance for metals and alloys, and remains the most significant goal in this review. The following section includes how superhydrophobic coatings are used to improve the performance of some applications by surface modification.

5.1. Anti-adhesion and self-cleaning

As previously mentioned, the high water contact angle (above 150°) and the low contact angle hysteresis of superhydrophobic surfaces characterize them with low adhesion and selfcleaning properties that are extremely useful for practical applications such as self-cleaning window glasses.

In a natural environment, surfaces get contaminated very easily and frequently. Cleaning them requires effort, time and money. Thus, the creation of substrates that are self-cleaning and that have low-adhesion to contaminants has been a hot topic of research for several decades. As illustrated in Fig. 8, when a water droplet rolls off a superhydrophobic surface, it entrains the dust and contaminants with it. This is not the case for normal surfaces, where the dust remains.

Nimittrakoolchai and Supothina (2008) studied the antiadhesion and self-cleaning properties of a superhydrophobic film by applying red powder and dust onto it. The superhydrophobic coating was prepared by the deposition of a polyelectrolyte film on a glass substrate, followed by etching in HCl solution to roughen the surface, and by the deposition of SiO_2 nanoparticles onto the etched film. They showed that much of the red powder was still spread on the uncoated surface after cleaning with water droplets as compared to the superhydrophobic surface, which was much cleaner. Moreover, dust particles were heavily sprinkled on the coated surface and were simply removed by flipping it, showing the anti-adhesion property for contaminants of such films.

Superhydrophobic surfaces with self-cleaning property also have many applications in the textile industry. For example, self-cleaning textile shirts, blouses, skirts and trousers, which are stain-proof, have already been synthesized (Xue et al., 2010). Furthermore, the self-cleaning effect is used in optical applications, such as solar panels, lenses and mirrors that have to stay clean (Nosonovsky and Bhushan, 2009).

5.2. Anti-biofouling applications

Biofouling of underwater structures and ships' hulls, in particular, increases operational and maintenance costs (Gudipati et al., 2005; Townsin, 2003). It can be reduced through underwater superhydrophobicity, i.e., forming a hydrophobic rough surface that supports an air film between itself and the water (Marmur, 2006). The reduction of the wetted area minimizes the probability that biological organisms encounter a solid surface. The design of such surfaces should involve optimization between mechanical stability and minimal wetted area. The anti-biofouling properties of superhydrophobic coatings have been investigated (Zhang et al., 2005). Compared to normal substrates, which fouled within a day, almost no micro-organisms attached to the superhydrophobic surfaces in the first week after immersion.

5.3. Corrosion inhibition

The concept of preparing surfaces that repel water creates huge opportunities in the area of corrosion inhibition for metals and alloys. Given their water repellency, superhydrophobic coatings form an important and successful method to slow down the breaking of the oxide layer of metals and thus prevent the metal surface underneath from further corrosion.

Several works have been carried out in order to study the corrosion resistance of metals coated with superhydrophobic surfaces. Some of the results obtained will be overlaid and discussed in the next section.

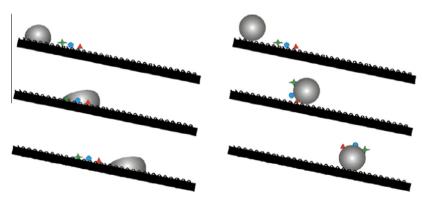


Figure 8 Water droplets rolling off substrates with a normal hydrophobic surface (left) and a self-cleaning superhydrophobic surface (right) through dust particles (Xue et al., 2010).

5.4. Drag reduction

Turbulent flows of a liquid along a surface experience frictional drag, a macroscopic phenomenon that affects the speed and efficiency of marine vessels, the cost of pumping oil through a pipeline, and countless other engineering parameters. The drag arises from shear stress, the rate per unit area of momentum transfer from the flow to the surface. Superhydrophobic surfaces can be fabricated in order to reduce the drag based on its highly water repellent property and capable of forming a thin air film over an underwater surface which stops the surface from becoming wet. The air film formed over the surface has the property of being able to take in air supplied from outside because of the surface tension of water. The superhydrophobic surfaces to reduce frictional drag have been used in ships. When air is supplied from the bow section to a ship's hull with superhydrophobic coatings, it becomes attached to the superhydrophobic surface and forms an air film on it. The frictional drag can thus be reduced by an air lubricant effect.

6. State-of-the-art studies on corrosion resistant coatings using superhydrophobic coatings

Corrosion is the decaying or destruction of a material due to chemical reactions with its surroundings. In other words, corrosion is the wearing away of metals due to a chemical reaction. Superhydrophobic coatings on metallic substrates have shown, during the past two decades, remarkable corrosion resistance in highly aggressive media. Many techniques of preparing such surfaces, as well as various methods of characterization and analysis were applied, but the conclusion was the same and it states that superhydrophobic coatings prevent metallic substrates from corrosion. The air retained on such superhydrophobic surface can prevent corrosive processes, e.g., chloride ions in seawater from attacking the metal surface, offering a new efficient mechanism for anti-corrosion (Fig. 9) (Jeong, 2013; Liu et al., 2007; Yin et al., 2008; Zhang et al., 2008). Table 3 summarizes the current state-of-the-art studies on anti-corrosion using superhydrophobic coatings. Although the idea of using the air retained on the superhydrophobic surface as a passivation layer is promising as a new efficient anti-corrosion scheme, potentially superior to the other conventional methods, it should be noted that all the superhydrophobic surfaces tested thus far were based on irregular coatings resulting in a random surface roughness in micron scale. Such microscale surface roughness with poor controllability of the structural dimensions and shapes has been a critical drawback, precluding the systematic understanding of the effect of superhydrophobic surface parameters on the corrosion resistance as well as the practical applications in a controllable way.

Ning et al. (2011) managed to form a stable superhydrophobic surface on zinc substrates by means of one-step platinum replacement deposition process without any further modification, simply by immersing the zinc in PtCl₄ solution. The structure of the surface exhibited high roughness and porosity which led to high corrosion resistance with contact angles $>150^{\circ}$, in different corrosive media, as compared to unprotected zinc plates. The effect of the superhydrophobic film on the corrosion behavior of zinc was investigated using linear sweep voltammetry (LSV). The results showed that, in the presence of the superhydrophobic surface, the anodic corrosion potential is shifted toward more noble values and the anodic and cathodic corrosion currents are significantly reduced. Furthermore, the prepared surface was proven to be stable in sodium hydroxide solution, hydrochloric acid solution and toluene solvent, maintaining all its superhydrophobic characteristics.

Similar results have been obtained by Yuan et al. (2011) who investigated the corrosion behavior of fluoropolymer films on copper substrates, in NaCl solution, by the measurements of Tafel polarization curves and electrochemical impedance spectroscopy (EIS) spectra. They also found that the corrosion potential undergoes a positive shift toward more noble values. Furthermore, the magnitude of the corrosion current was lower by about 12-fold as compared to the bare copper, after 21 days of exposure in the NaCl (3.5%) solution.

Yin et al. (2008) studied the corrosion inhibition, in seawater, of superhydrophobic films prepared by chemical adsorption of myristic acid onto anodized aluminum substrate. The polarization curves showed the same results concerning the corrosion potential and corrosion currents. The corrosion inhibition efficiency was also calculated and yielded an increase from 61% to 96%, for the uncoated and coated anodized aluminum surfaces, respectively.

Scanning electron microscope (SEM) and measurements of the water contact angles can also be useful to predict the anticorrosion ability of superhydrophobic coatings. Kang et al. (2011) investigated the corrosion resistance of porous polyvinyl chloride (PVC) surfaces on glass substrates, in acid and alkali corrosive media. The SEM confirmed that the surface topography was not damaged by the exposure in the aggressive solutions. In addition, the contact angles measured were similar to those obtained before exposing the films to corrosive media (>150°).

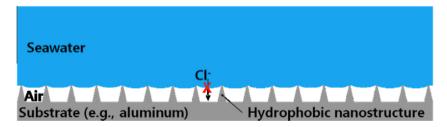


Figure 9 Basic concept of anti-corrosion using a superhydrophobic surface. The micro- or nano-structured superhydrophobic surface creates a composite interface with water by retaining air on the surface. The composite interface minimizes the water contact area to the metal surface, preventing chloride ions, which is a major corrosive constituent in seawater, from invading the metal surface (Jeong, 2013).

Table 3 State-of-the-art	studies on anti-corros	Table 3 State-of-the-art studies on anti-corrosion using superhydrophobic coatings.	coatings.		
References	Substrate materials	Surface treatment	Test solution Test method	Test method	Main results and issues
Shchukin et al. (2006)	Aluminum alloy	Layer-by-layer (LbL)	5% NaCl	Electrochemical impedance spectroscopy (EIS)	The nanoreservoirs increase long-term corrosion protection of the substrate and provide effective inhibitor storage and its prolonged release on demand
Liu et al. (2007)	Copper	Myristic acid	Sea water	Polarization, EIS	The corrosion resistance of the material was improved remarkably
Yin et al. (2008)	Aluminum	Myristic acid	Sea water	Polarization, EIS	Film stability should be improved further
Barkhudarov et al. (2008)	Aluminum	Organosilica aerogel coating	5% NaCl	Neutron Reflectivity	The surface prevents infiltration of water into the superhydrophobic porous film and limits the exposure of corrosive elements to the metal surface
Zhang et al. (2008)	Aluminum	Hydroxide films	3.5% NaCl	Open-Circuit Potential Polarization	Good film adhesion and mechanical stability
Liu et al. (2007)	Zinc	PFTS	3% NaCl	Polarization	Higher corrosion resistance properties
Ishizaki et al. (2011)	Magnesium alloy	FAS	5% NaCl	Polarization, EIS	Superhydrophobic surface would be an effective strategy for improving the anticorrosion peer performance of various engineering materials
de Leon et al. (2012)	Steel	Polythiophene	3.5% NaCl	Polarization	Fabrication of the dual properties of superhydrophobic anticorrosion nanostructured conducting polymer coating follows a two-step coating procedure that is very simple and can be used to coat any metallic surface

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As defined by Piron (1991), in his book entitled "The electrochemistry of corrosion", corrosion is the destruction of a metal by chemical or electrochemical reactions between the metal and its environment. This definition includes electrochemical corrosion in aqueous media, molten salts, or in other environments where two simultaneous reactions involve electron transfers. Oxidation of the metal liberates electrons, which are accepted by the reduction of another substance such as hydrogen ions or oxygen. This definition also includes the destruction of metals by oxidation at high temperatures in a solid–gas reaction, which is considered to be a chemical reaction.

All active metals such as aluminum, zinc, iron, ..., and their alloys are prone to corrosion in contact with water, especially in aggressive and corrosive environments such as in alkaline or acidic media, or in strongly saline aqueous solutions. Therefore, it is necessary to enhance their corrosion resistance property in corrosive environment which will greatly extend their industrial applications (Yu et al., 2013).

In dry environments, metals and alloys usually develop a thin oxide layer onto their surface. This oxide layer protects the metal from further corrosion. However, in aqueous, salty and other aggressive environments, the oxide layer is penetrated and can no longer inhibit further corrosion. Given the properties mentioned above, especially the water repellency, superhydrophobic coatings form an important and successful method to slow down the breaking of the oxide layer and thus prevent the metal surface underneath from further corrosion.

Zhang et al. (2011) explained the mechanism of anticorrosion of superhydrophobic coated titania/titanium surface by suggesting that the film is sufficiently densely packed to prevent the diffusion of oxygen to the substrate. They attributed the excellent anti-corrosion property of the film to the air trapped in the nanopores, which prevents infiltration of water into the substrate and limits the concentration of corrosive species in the titania/titanium holes.

Yu et al. (2013) studied the corrosion behavior of Ni-P, TiO_2 and octadecyltrimethoxysilane (ODS) superhydrophobic composite coating on carbon steel. They reported that the three-layer composite coating on C-steel improves the corrosion resistant in sterilized seawater, as seen in Fig. 10.

The corrosion resistance mechanism of superhydrophobic surfaces proceeds as follows: when exposed to a corrosive medium, superhydrophobic coatings, made of hierarchical rough structures can easily trap a large amount of air within the valleys between the rough structures (Xu et al., 2011). These "air valleys" prevent the infiltration of corrosive ions, such as Cl⁻, as illustrated in the simulated model in Fig. 11.

Another important reason why the modified surface can improve the anticorrosion of metals is 'capillarity', which was introduced by Liu et al. (2007). They showed that, for contact angles higher than 150°, the water transport against gravity is easy in the porous structure of the superhydrophobic surfaces. As a result, the seawater can be pushed out from the pores by the Laplace pressure and thus, the substrate could be perfectly protected from corrosion in the seawater.

7. The stability of the superhydrophobic surfaces

For engineering applications of superhydrophobic surfaces, the stable behavior under various conditions needs to be investigated. Stability issues in solvents including organic

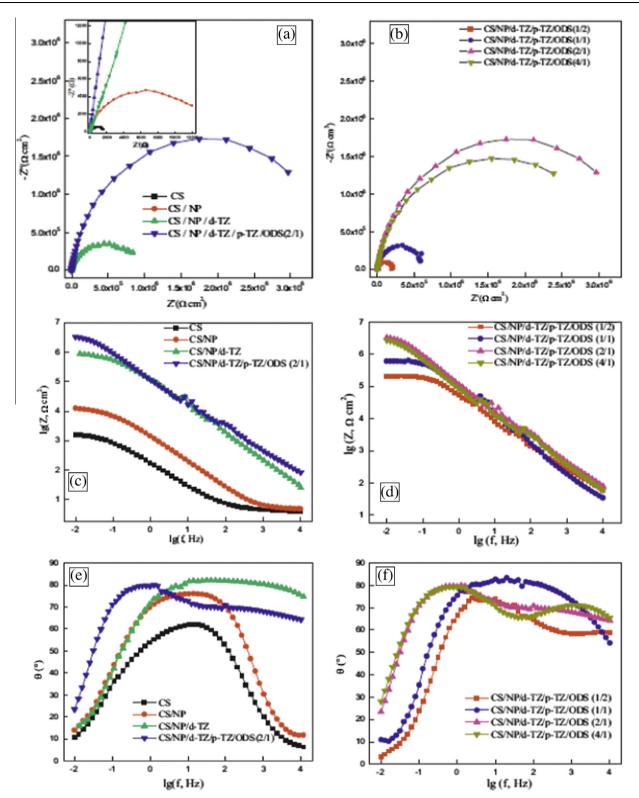


Figure 10 Nyquist (a–b) and bode (c–F) plots of the composite coatings from the electrochemical impedance spectroscopy (EIS) (Yu et al., 2013) where, CS: carbon steel; NP: Ni-P; TZ: TiO_2/ZnO ; ODS: octadecyltrimethoxysilane.

and aqueous, basic and acidic solutions, thermal stability, as well as the influence of humidity and UV radiation will be discussed in this section. In general, high chloride concentration, high temperature and low pH represent the main reasons responsible for damaging the surfaces.

7.1. Solvent stability

Many works have been carried out in order to study the stability and durability of superhydrophobic coatings on different metallic substrates, in water and various organic solvents.

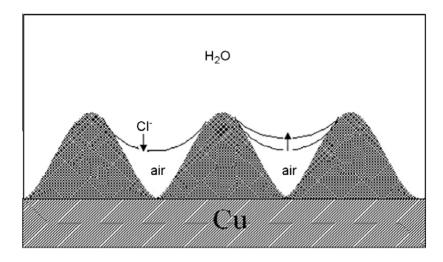


Figure 11 Model of the interface between superhydrophobic surface and corrosive seawater. The Cl^- ions can barely reach the bare surface because of the 'air valleys' (Liu et al., 2007).

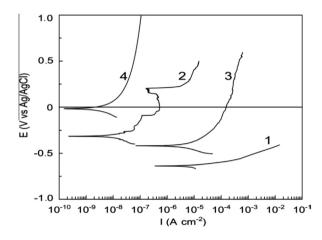


Figure 12 Polarization curves in 0.5 M NaCl aqueous solution for low-carbon steel samples with different surface layers: (1) Native oxide; (2) MC-1 + NSC (MC-1: Magnetite coatings formed at 98 °C and at high stirring, NSC: nanocomposite superhydrophobic coatings); (3) MC-2 + NSC (MC-2: Magnetite coatings formed at 92 °C); (4) PEO + NSC (Boinovich et al., 2012).

For instance, Isimjan et al. (2012) investigated the effect of water, chloroform and decane on the contact angles of TiO_2/SiO_2 coated steel substrates measured after every 24 h for a period of eight days. It was shown that the contact angles remained constant and the surfaces were stable even after 8 days. In another work, coated zinc substrates were immersed in toluene for 24 h at room temperature (Ning et al., 2011).

The resulting contact angles had no variation, suggesting a good stability of the surface.

The stability of superhydrophobic surfaces on different substrates in seawater was also intensively studied and revealed the conservation of superhydrophobicity even after a long duration exposure (He et al., 2009; Liu et al., 2007, 2008; Yin et al., 2008; Yu et al., 2013). Zhu and Jin (2007) created a superhydrophobic film by using electroless Ni-P composite coating on carbon steels. The superhydrophobic film has good stability in the air at room temperature and good corrosion resistance in 5 wt% NaCl solution, neutral salt spray test and water erosion test. Boinovich et al. (2012) also studied the corrosion behavior of highly hydrophobic and superhydrophobic coatings for low C-steel steel under atmospheric conditions and aggressive media. Their results showed that the most durable protection against corrosion is obtained by the formation of multilayer coatings which contain the nanocomposite superhydrophobic layer in combination with oxide layer. The potentiodynamic polarization curves in 0.5 M NaCl aqueous solution for low-carbon steel samples with different surface layers are shown in Fig. 12.

Boinovich et al. (2013) also investigated the effect of different corrosive active media on the Mg–Mn–Ce alloy coated by nanocomposite syperhydrophobic materials. They indicated that the preliminary plasma electrolytic oxidation of alloy improves the adhesion and water repelling properties of the coatings and consequently increases the corrosion resistance of Mg alloy. Xu et al. (2011) fabricated the superhydrophobic coating for Mg alloy using a facile electrochemical machining process. Their results showed that the superhydrophobic Mg alloy surface has excellent corrosion resistance in acidic, alkaline and salt solutions. Table 4 presents the corrosion potential (E_{corr})

Table 4	$E_{\rm corr}$ and $I_{\rm corr}$ of the untreated	and superhydrophobic Mg alloy surfaces in	n different corrosive solutions (Xu et al., 2011).
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Sample	NaCl sol	ution	Na ₂ SO ₄		NaClO ₃		NaNO ₃	
	E _{corr}	Icorr	Ecorr	I _{corr}	E _{corr}	Icorr	E _{corr}	Icorr
Untreated Mg alloy Surface	-1.585	9.96×10^{-5}	-1.616	4.71×10^{-7}	-1.525	8.58×10^{-7}	-1.403	1.15×10^{-7}
Superhydrophobic Mg alloy surface	-1.422	9.68×10^{-8}	-1.510	7.62×10^{-8}	-1.530	7.37×10^{-10}	-1.285	3.51×10^{-9}

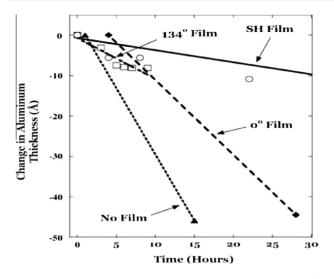


Figure 13 The change in aluminum thickness versus time for samples protected by films of varying contact angle and a sample with only native Al_2O_3 layer. The superhydrophobic films improved corrosion resistance by a factor of six compared to unprotected aluminum surface (Barkhudarov et al., 2008).

and corrosion current density (I_{corr}) of untreated and superhydrophobic Mg alloy in different corrosive media.

Barkhudarov et al. (2008) investigated the behavior of superhydrophobic coatings as corrosion inhibitors. They concluded that the extreme case of a superhydrophobic coating with a contact angle of $> 160^{\circ}$ decreases the rate of corrosion roughly tenfold compared to the unprotected aluminum. Fig. 13 shows the changes in aluminum thickness after the test with different surface conditions.

Liu et al. (2009) successfully created a superhydrophobic surface on aluminum surface by an anodization process and chemical modification using myristic acid. Their results showed that, the superhydrophobic surface significantly improves the corrosion resistance of aluminum in sterile seawater. The superhydrophobic surface affects mainly the aluminum anodic reaction, whose currents (I_{corr}) are reduced by about three orders of magnitude, the corrosion potential $(E_{\rm corr})$ shifts positively by 0.2 V when the anodized aluminum is covered with the myristic acid. The significant point of this research is the possibility of applying this method to a large scale production of superhydrophobic engineering materials for ocean industrial applications. In another research, Liu et al. (2009) studied the use of superhydrophobic surfaces on aluminum as a method for inhibition of microbially influenced corrosion. Their study showed that the superhydrophobic film does not only decrease the corrosion current densities, but also microbially influencing corrosion acceleration inhibition due to preventing colonization of microorganisms.

7.2. pH stability

The stability of superhydrophobic surfaces over a wide pHrange is crucial for their use as engineering materials in several industrial applications. Guo et al. (2005) investigated the stability of coated aluminum alloy, over the pH range from 1 to 14. All the measured contact angles were around 160° to 162°, showing that the pH of the aqueous solution had little or no effect.

Similar results were obtained by Ishizaki et al. (2011) where the chemical stability of the color-tuned superhydrophobic magnesium alloy surface and untreated magnesium alloy surface was examined, in the pH range from 1 to 14. The results showed static water contact angles (>145°) for the coated substrates for all pH solutions. On the other hand, all the untreated substrates showed hydrophilic behavior (contact angles <40°) and thus, evidence of corrosion.

7.3. Thermal and humidity stability

High temperatures usually reduce the durability of superhydrophobic coatings and lead to an irreversible change of the hydrophobic character to a hydrophilic character. However, some surfaces exhibit resistance toward heat up to a certain temperature.

Xiu et al. (2008) generated porous inorganic silica films on glass substrates, by the sol-gel process, using tetramethoxysilane and isobutyltrimethoxysilane as precursors. At elevated temperatures (> 200 °C), the hydrophobic isobutyl group in the silica surface decomposes and leads to the loss of superhydrophobicity. The contact angle decreased with increasing temperature and the contact angle hysteresis increased. However, when the as-prepared silica films were modified with fluoroalkyl silanes, the thermal stability was significantly improved: at a temperature of 400 °C, the surface remained stable. Further heating resulted in a decrease of contact angle and when the temperature reached 500 °C, the film was no longer hydrophobic (contact angle almost became 0°).

Latthe et al. (2009) studied the influence of temperature on silica coatings by putting the samples in a furnace for 5 h. It was found that the films retained their superhydrophic property up to a temperature of 275 °C. Above this value, the films became superhydrophilic with contact angles smaller than 5° .

Furthermore, the influence of humidity was also investigated. The silica films were exposed to a relative humidity of 85%, at 30 °C for a duration of 60 days. The results showed a strong stability and durability against humidity.

Similar results were obtained by Rao et al. (2011) who investigated the effect of humidity on the wetting properties of silica films on copper substrate. The experiment was carried out at a relative humidity of 95% at 35 °C for a period of 90 days. No significant change in the superhydrophobicity of the films was observed, showing the durability and resistance of such surfaces against humidity.

7.4. UV stability

The stability of superhydrophobic films against UV irradiation is extremely important, especially for outdoor surfaces that are exposed to UV light. Feng et al. (2004) obtained superhydrophobic ZnO nanorod films that lost their superhydrophobicity under UV illumination for 2 h: the water contact angle dropped from 160° to 0° .

On the other hand, the results obtained by Isimjan et al. (2012) revealed that the TiO_2/SiO_2 coated steel surfaces strongly resist against UV radiation: the contact angles remain constant even after a period of 5 h UV exposure. This was explained by the fact that in the presence of SiO₂ nanoparticles,

the high energy electrons generated by TiO_2 under UV cannot diffuse to the surface and thus, no hydroxyl radicals can be formed and no oxidation will occur.

Xiu et al. (2008) managed to fabricate one of the most stable superhydrophobic silica surfaces treated with fluoroalkyl silanes, which showed resistance after 5500 h UV irradiation without degradation of either contact angle or contact angle hysteresis. The fact that the C—F bonds are much stronger than the C—H bonds was the reason of this improved UV stability.

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