



Recent progress in nano-oxides and CNTs based corrosion resistant superhydrophobic coatings: A critical review



Vipul Sharma^a, Vipul Sharma^a, M.S. Goyat^{b,*}, Amrita Hooda^c, Jitendra K. Pandey^d, Adesh Kumar^c, Rajeev Gupta^b, Avani Kumar Upadhyay^a, Rajiv Prakash^e, John Baptist Kirabira^f, P. Mandal^b, Prashant Kumar Bhargav^a

^a Department of Mechanical Engineering, School of Engineering, University of Petroleum & Energy Studies, Dehradun, 248007, Uttarakhand, India

^b Department of Physics, School of Engineering Studies, University of Petroleum & Energy Studies, Dehradun, 248007, Uttarakhand, India

^c Department of Electrical & Electronics Engineering, School of Engineering Studies, University of Petroleum & Energy Studies, Dehradun, 248007, Uttarakhand, India

^d Department of Research and Development, University of Petroleum and Energy Studies, Dehradun, 248007, Uttarakhand, India

^e School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, 221005, India

^f Department of Mechanical Engineering, College of Engineering, Design, Art and Technology, Makerere University, P.O. Box 7062, Kampala, Uganda

ARTICLE INFO

Keywords:

Superhydrophobicity
Coatings
Corrosion
Protection
Nanostructures

ABSTRACT

Because of the serious consequences of structural failures due to corrosion, research on anti-corrosion coatings has traditionally been of highest importance toward the development of sustainable durable material. Anti-corrosive coatings have played a significant role for increasing the durability of material without affecting the bulk properties and to perform its duty effectively, an anti-corrosive coating must possess intrinsic durability, adequate flexibility, adhesion and toughness to withstand impacts, cracking and appearance when subjected to stress, swell, mechanical abuse, or weathering. Exposure of metals and alloys in a humid environment may create additional challenges either to inhibit or slow down the overall corrosion rate. Despite significant improvements in corrosion coating technologies problems are continue to persist in the durable protection of metals and alloys and this is an emerging thrust area toward the development of a holistic, permanent solution for the corrosion related issues. In recent years, bio-inspired concepts of superhydrophobicity at nano-level and self-cleaning has exhibited exceptional potential as anticorrosive coatings, particularly in humid environments. With the ability to retain mechanical properties at a higher temperature and contact angle (CA) of superhydrophobic range, nano-oxides and CNTs based superhydrophobic coatings (SHCs) are gaining momentum to reach an industrial scale for real-time applications. The present article is mainly aimed to review the impact of nano-material based SHCs on metal/alloys with a concise discussion of associated challenges, potential solutions and future opportunities.

Abbreviations: 17FTMS, (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) trimethoxysilane; AC-FAS, heptadecafluoro-1, 1, 2, 2-tetradecyl) trimethoxysilane (CF₃(CF₂)₇(CH₂)₂Si(OC₂H₅)₃); Al, aluminium; ASC, anhydrous sodium carbonate; BAPTS, bisphenol A,3-aminopropyltrimethoxysilane; B-TMOS, 2,2-bis(3-(trimethoxysilyl)-n-propyl-3,4-dihydro-2H-1,3-benzoxazine)-propane; C₁₂H₂₅NaO₃S, sodium laurylsulfonate; C₆H₁₄O₂, 2-butoxy ethanol; CeCl₃, cerium chloride; CTAB, cetyltrimethylammonium bromide; Cu, copper; CVD, chemical vapour deposition; DADPS, 4,4'-diaminodiphenylamine sulfate; DDA, dodecanoic acid; DFHPTMS, dodecafluoroheptyl-propyl-trimethoxysilane; DM, dodecyl mercaptan; DMB, dimethylbenzene; DMF, N, N- dimethylformamide; DTMS, dodecyl-trimethoxysilane; ECA, ethanolic stearic acid; ECD, electrochemical deposition; EDOT, 3,4-ethylenedioxythiophene; EM, electromagnetic; EPP/PDS, ethylenepropylene propylene/polydimethylsiloxane; EtOH, absolute ethanol; FAS, fluoroalkylsilane; FeCl₃, ferric chloride; FMSO, fluoro- methylhydro-silicone oil; FPMHS, fluorinated polymethylhydrosiloxane; GOPTMS, 3-glycidoxypropyltrimethoxysilane; GPS, 3-glycidoxypropyl trimethoxysilane; H₃BO₃, boric acid; ISA, icosanoic acid; LiClO₄, lithium perchlorate; LSD, Langmuir-schaefer deposition; Na₂CO₃, sodium carbonate; Na₂SiO₃·9H₂O, sodium metasilicate nonahydrate; Na₅P₂O₁₀, sodium polyphosphate; N-OTS, N-octadecyltrichlorosilane; NPTMS, N-propyl-trimethoxy-silane; ODA, octadecanoic acid; ODTS, octadecyltrichlorosilane; OTES, octyltriethoxysilane; PANI, polyaniline; PDMS, polydimethylsiloxane; PFODA, perfluorooctadecanoic acid; PFDTs, 1H,1H,2H,2H-perfluorodecyltriethoxysilane; PFOTS, 1H, 1H, 2H, 2H-perfluorooctyl-trichlorosilane; PFSA, perfluorosulfonic acid; POTS, perfluorooctyl triethoxysilane; PS-COOH, carboxyl-terminated polystyrene; PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride; SDBS, sodium dodecylbenzene sulfonate; SDS, sodium dodecylbenzene sulfonate; Si, silicon; SS, stainless steel; TCS, trichloro (1H,1H,2H,2H heptadecafluorodecyl) silane; TDA, tetradecanoic acid; TEOS, tetraethylorthosilicate; THF, tetrahydrofuran; TFE, tetrafluoro ethylene; TMPA, N-3-trimethoxysilylpropyl aniline; TMPS, trimethoxypropylsilane; TP, trisodium phosphate; TPOZ, zirconium (IV) propoxide; TSP, trisodium phosphate; TTEOS, tetraethoxysilane

* Corresponding author.

E-mail address: goyatmanjeetsingh@gmail.com (M.S. Goyat).

<https://doi.org/10.1016/j.porgcoat.2019.105512>

Received 3 July 2019; Received in revised form 28 November 2019; Accepted 17 December 2019

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1. Introduction

The idea of superhydrophobicity stems from the self-cleaning effect of the lotus plant, the leaves of the lotus plant including many other plants have specific water-repelling qualities [1]. Owing to the efficient water-repelling ability of lotus leaves, the water droplets can easily roll off their surface and keep the surface clean [2–7]. A hierarchical roughness on the lotus leaves is mainly responsible for their superhydrophobic properties. The surface features of lotus leaves can be mimicked on various metal substrates to avoid the corrosion by utilizing the concept of the superhydrophobicity. Rusting of iron is a serious concern for metal/alloy industries. The deterioration of metals/alloys due to the corrosion creates serious problems for their use in marine environments which generally have quite high salinity along with high humidity [8]. The major cause of corrosion of metals/alloys is their use in humid environments. The corrosion of metals/alloys is unavoidable but can be minimized by using organic coatings on their surfaces to retain the mechanical properties. The use of such coatings can significantly extend the service life and reduce the maintenance costs of the metals/alloys. However, the diffusion of water via such anti-corrosive (generally polymer-based) coatings is a primary cause of reducing the adhesion of the coatings on the metal surfaces which subsequently leads to delamination of the anti-corrosive coatings and thereby increasing the maintenance costs [8]. The use of SHCs is a modern solution to prevent the corrosion of metals/alloys [9]. The wetting properties of a solid surface can be portrayed by CA between the surface and the liquid droplet. A surface can be hydrophilic, hydrophobic and superhydrophobic based on the CA. For a hydrophilic surface, the $CA < 90^\circ$, for a hydrophobic surface, the $CA > 90^\circ$ and for a superhydrophobic surface the $CA > 150^\circ$ with a sliding angle (SA) usually less than 5° as shown in Fig. 1. Generally, for a surface, the superhydrophobicity relies on the surface features such as the presence of micro/nanostructures on the surface and the surface energy which can be altered by using a chemical substance. The CA of a surface is usually determined when a water drop present on that surface [10].

Self-cleaning utilizing hydrophobic property has been one of the major thrust areas of research. Inspired by nature, scientists and researchers are keen on controlling the surface wetting properties of man-made surfaces or structured surfaces that have potential applications [13]. To unveil the underlying mechanism of non-wettability or how dewdrops or rainwater drops smoothly roll off the leaves (lotus leave for example) without any pinning, Barthlott and Neinhuis studied scanning electron microscopy of lotus leave, the appealing hydrophobic system. They revealed that there are many epidermal cells of the order of micrometer covered with natural wax of the order of nanometer are available on the leaves. Other researchers also revealed the same features on the lotus leaves (Fig. 2) [14]. The gap between two grooves is much lesser than the size of a water droplet so that the water droplet cannot get inside the grooves and water droplet on it become spherical

and shows the repelling tendency. When the water droplet passing through such surfaces, the dirt contamination can easily stick with the droplet and can roll off easily from the surface and exhibits the self-cleaning property.

Similarly, many animal species like a water strider, butterfly wings exhibit excellent repellent tendency [15–19]. The reason behind it is the special hierarchical structure on water strider legs, which includes large amounts of oriented tiny hairs called micro-setae, fine nano-grooves and a covering of secreted cuticle wax. The atmospheric air gets trapped in the spaces between the microsetae and nano-grooves thus forming a cushion at the leg-water interface and water strider can easily walk, stay on the water surface. Butterfly wings exhibit anisotropic on the one-dimensional level and composed of overlapping layers of scales, structural colour, fluorescence emission functions due to the multi-scale structures, self-cleaning and chemical sensing capability.

Over the past few decades, nano-oxides [20–24] and CNTs [25–31] are among the most studied materials because of their unique advantageous properties. Significant research has been performed on the development of nano-oxides and CNTs incorporated SHCs for numerous potential applications including anti-corrosive coatings [32–36], anti-dust [37,38], anti-ice [39–43], anti-mud deposition [44–47], anti-fouling [48], etc.

This review is focused on the recent developments in the field of corrosion resistant SHCs for metal/alloy industry including the routes followed to develop such coatings. This review is also addressing the challenges of fabrication of stable SHCs and limitations of corrosion resistant coatings those still need to be described to develop durable long-lasting SHCs for metal/alloy industry. The review has five main sections: the first section is dedicated to the concept of superhydrophobicity. The second section describes the role of oxide nanoparticles and CNTs in developing corrosion-resistant SHCs. The third section covers the progress in the development of corrosion resistant SHCs on various metals/alloys. The fourth section describes the challenges in the fabrication of the corrosion resistant coatings and finally, the fifth section outlines the future trends followed by concluding remarks.

2. The basis of superhydrophobic surfaces

The wettability of water droplet on a surface depends on surface energy and surface roughness. Numerous conceivable outcomes can be visualized to change the surface structure of substrates to enhance the repellency nature. Watchful investigations of natural surfaces by Zisman and associates revealed that the surface energy is resolved primarily by the chemical structure at the surface and they built up that the surface energy diminishes with increasing fluorine. Further, all the fluoro-containing surfaces show the less value of the surface free energy [1,49] and its value can be enhanced by replacing fluorine, H and C, in the order. The closest hexagonal packing of CF_3 — groups makes the

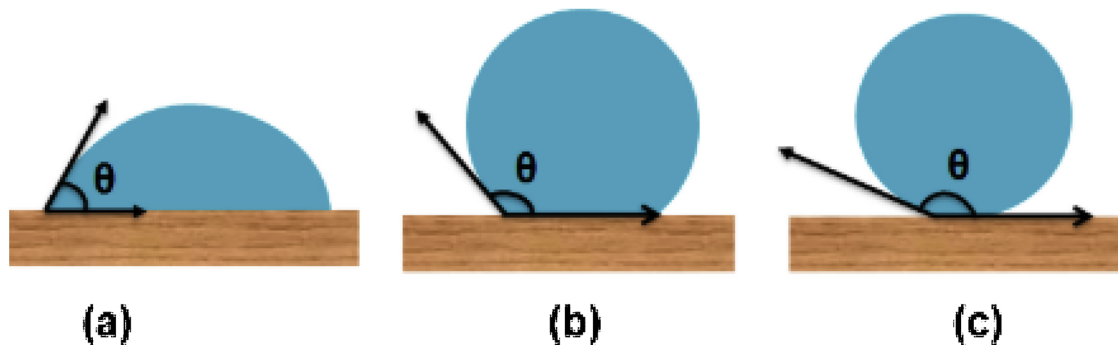


Fig. 1. A graphic demonstration of a water drop on various types of surfaces such as (a) hydrophilic, (b) hydrophobic, and (c) superhydrophobic [11,12].

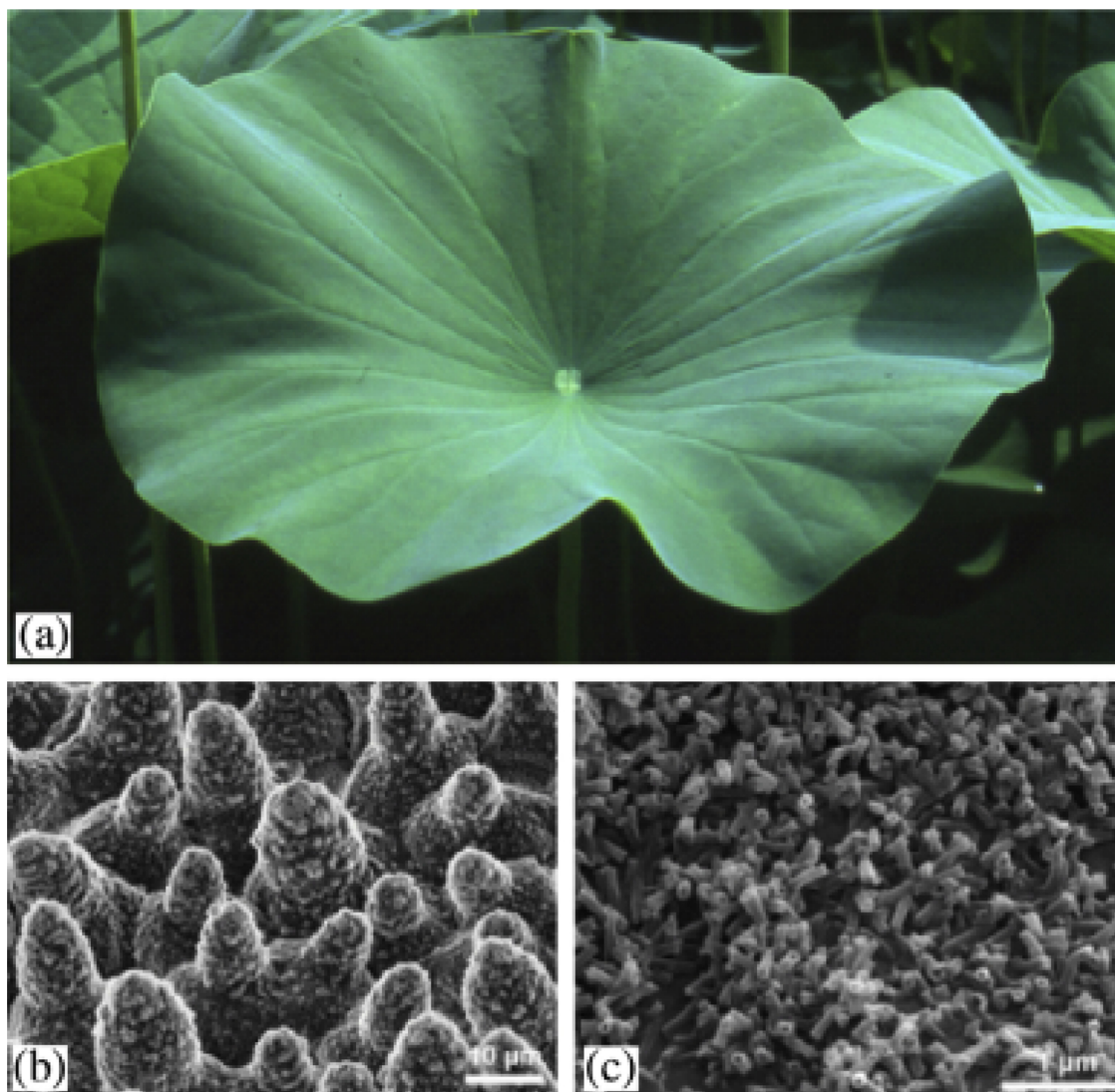


Fig. 2. (a) Lotus leaves which shows the repellent behaviour (b) Scanning Electron Microscope (SEM) image of the upper leaf side shows the epidermal cells of the order of micrometers size between two grooves are very small (c) Wax tubules of the order of nanometers on the upper leaf side [14].

surface of lowest energy and shows the excellent hydrophobic surface sticking together the substrate and fluorine-based hydrophobic coating via very weak van der Waals force.

Many research groups detailed the blend of the fluorinated atoms and all the more especially they endeavoured to functionalize the surfaces with a most extreme of CF_3 groups, despite that the highest CA can't surpass 120° [50,51].

2.1. Young's equation

The physics of wetting is concerned with the interaction of the molecules of liquid and solids surface and based on their interaction, the surface behaves differently i.e. will show the different CA of the liquid on the solid surface. The degree of wettability can be characterized by the CA which can be defined as the angle between the two interfaces, liquid-solid, and liquid-air. For the smooth surfaces, the CA is defined by the by Young's equation, Eq. (1).

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

Here γ_{SV} is the interfacial energy between solid and vapor, γ_{SL} is the interfacial energy between solid and liquid and γ_{LV} is the interfacial energy between liquid and vapor state [52]. Here, $\cos\theta_Y$ is the Young's

CA for the smooth surface and its value depends on the surface composition /surface chemistry. The smooth surfaces can give the CA up to 120° . Further, the value of the CA can be enhanced by introducing the additional feature known as surface roughness.

2.2. Wenzel's equation

A large portion of surfaces has deformities and defects that add to surface roughness. It is interesting to note that the micro and nano structures on the surface can modify the wetting property of the solid surface. The impact of surface roughness on CA was summarized by Wenzel and Cassie-Baxter model. The Wenzel model predicts that the water penetrates the grooves on the surface and therefore the contact area between water and solid surface increases with roughness [53]. Wenzel presented a roughness factor r , which is greater than or equivalent to 1. In this context, the CA on the rough surface is given by Eq. (2).

$$\cos\theta_w = r \cos\theta_Y = r \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2)$$

This equation is called Wenzel's equation. Here, θ_w is the modified CA after introducing the surface roughness and called the Wenzel's CA. This r represents the roughness of the surface and known as the

roughness factor.

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

For a rough surface, $r > 1$ and for an ideally planar surface $r = 1$. There are several methods available to introduce or enhance the roughness. The homogenous wetting demonstrates that a hydrophobic surface ($\theta > 90^\circ$) will turn out to be more hydrophobic by increasing its roughness, while a hydrophilic surface ($\theta < 90^\circ$) will turn out to be more hydrophilic if a similar kind of roughness is incorporated. The relation between surface roughness and CA is shown in Fig. 3. However, when $\theta > 90^\circ$, under some roughness circumstances, air pockets might be caught in the rough grooves, for such situations the wetting behaviour was portrayed by Cassie and Baxter [54].

2.3. Cassie-Baxter's equation

Wenzel equation is true for the homogeneous interface and if we have the heterogeneous surface, another model was proposed by Cassie and Baxter [54]. A new concept area fraction (f) was introduced. Area fraction is a proportion of the contact area of an individual component in a general contact area. If a composite surface has two dissimilar components and intrinsic CAs of θ_1 and θ_2 , respectively, with area fraction of each components are f_1 , f_2 . Then $f_1 + f_2 = 1$. Therefore, the CA can be obtained by Cassie-Baxter Eq. (4).

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

When air trapped in grooves of a rough surface, the water droplet cannot pierce the grooves, which lead a surface with two phases such as solid and air. So, the authentic contact area of a water droplet is the contact area between the droplet and solid surface including the contact area between droplet and air. If the CA between a solid surface and air, $\theta_2 = 180^\circ$. The apparent CA can be determined using Eq. (5).

$$\cos\theta = f_{SL} \cos\theta_0 + f_{SL} - 1 \quad (5)$$

The increasing roughness factor also increases the hydrophobicity, the water droplet can easily rest on the rough surface as in Cassie mode. However, in Cassie and Baxter case, the superhydrophobic state with CA $> 150^\circ$ can be achieved by modifying the surface morphology at a microscopic level or decreasing the solid-liquid contact interface. Additionally, the sliding or roll-off angle of droplet becomes smaller, which enhance the self-cleaning ability of the surface. The detailed description of theories of Young's state, Wenzel's state, Cassie-Baxter's state, the intermediate state of Cassie-Baxter and with the help of schematic diagram is shown in Fig. 4.

3. SHCs for metals/alloys

3.1. Synthetic coatings

Significant research is going on the development of SHCs for various industrial applications such as anti-corrosive coatings, anti-dust, anti-ice, anti-mud deposition, anti-fouling, drag reduction coatings, etc. Worldwide, researchers obtain the idea of superhydrophobicity from natural lotus plant leaves and water striders, etc. and they are working on mimicking the surface features of lotus leaves on various substrates to achieve new unique wetting properties. Plenty of laboratory scale research has been carried out to develop the SHCs for various substrates. Such type of developed synthetic coatings can prove their potential at the industry level. For instance, Mo et al. [35] described a novel route for the fabrication of superhydrophobic nanocomposite coatings on a steel substrate. Modified nano titanium oxide particles were added to fluoromethylhydrosilicone oil, which was obtained by a dehydrogenation coupling reaction of amidmethylhydrosilicone oil and dodecafluoroheptylpropyl-trimethoxysilane. Later on, the nanocomposite SHCs were obtained by the deposition of resulting solution on a

steel substrate via dip coating method followed by heating as illustrated in Fig. 5(a). The developed composite coating showed the water CA of 151.5° (Fig. 5b) and also demonstrated good corrosion inhibition ability.

3.2. Nano-silica based coatings

Till date the most preferred nanomaterial for the preparation of SHCs is nano-silica [39,56–62] because of its low cost, wide availability, high transparency and it can be easily functionalized via various types of functionalizing agents [8]. Zhang et al. [63] reported the preparation of a mechanically durable SHCs by dual-layer route for self-cleaning and anti-corrosion application. Initially, silicon dioxide nanoparticles (10–20 nm) were functionalized using trichloro (1H,1H,2H,2H-perfluorooctyl) silane and then the functionalized particles were added in a poly-dimethylsiloxane (PDMS) resin followed by the addition of a curing agent. Then the resulting material was coated on the glass and copper substrates using spray coating followed by another layer deposition on that coating by spraying fluorinated silica to achieve the desired functionality. In the final step, the coating was dried at 120°C for 1 h to provide mechanical durability. Fig. 6(a) shows a dual layer method to produce a SHC. The PDMS provides better adhesion with the substrate, so a tightly coated coating on the glass and metal substrate is illustrated in Fig. 6(b). The modified wettability of coated glass and metal after the spray coating is shown in Fig. 6(c).

In another study, Liu et al. [64] reported a facile and new route to produce a SHC based on raspberry-like silica nanoparticles for self-cleaning application. The silica nanoparticles were functionalized by fluoroalkoxysilane through their condensation in ethanol at ambient conditions. The sol-gel method was employed to introduce functionalized nanoparticles in a silica matrix and later on deposited on a glass substrate. Water CA of 152° with a SA of less than 10° was obtained. The self-cleaning properties were studied by spreading dust on the developed coating and then it's cleaning. The low SA helped in removing the deposited dirt particles from the surface of the SHC. The stability of the prepared coating via a scratch resistance test and water stream or water jet impact test was evaluated. The developed coatings tolerated the scratch test with an applied force of 150 mN. Such kind of developed coatings can provide better results, especially on etched metal substrates.

Wang et al. [65] prepared SHCs using polytetrafluoroethylene (PTFE) and nano-silica on the carbon steel surface via a spray deposition method. The superhydrophobic PTFE emulsion mixtures were blended by a physical method. For the comparison, both the inorganic SiO_2 as well as organic PTFE nanoparticles were used. The surface

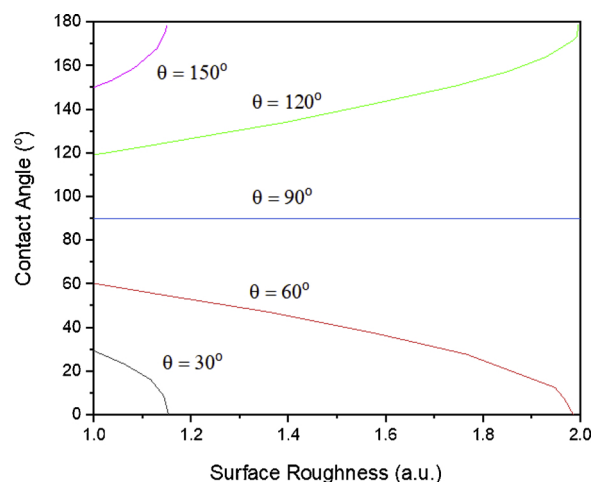


Fig. 3. The variation of the CA with surface roughness on hydrophilic and hydrophobic surfaces [55].

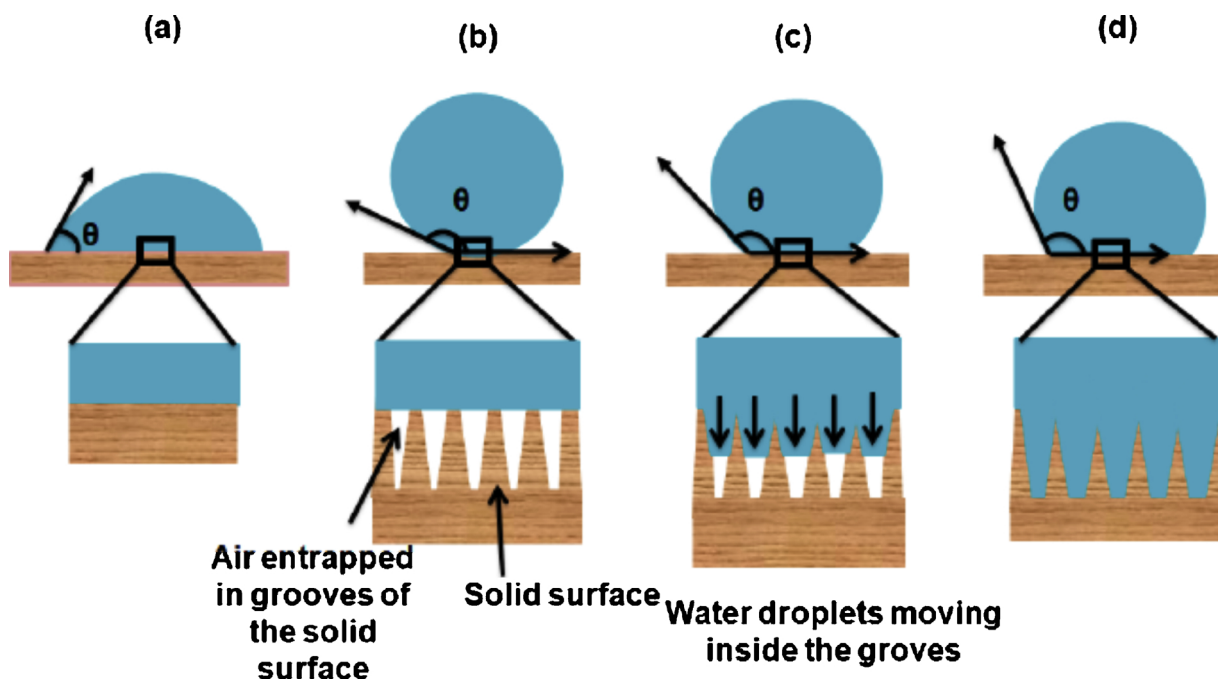


Fig. 4. (a) Young's state: water droplet on the smooth surface; low CA, (b) Cassie-Baxter state: water droplet partially sits on solid surface and air trapped in the air pocket, (c) Intermediate state of Cassie-Baxter and Wenzel state, water droplet trying to get the position inside the grooves, (d) Wenzel state: water droplet getting the position in the grooves [11].

modification of SiO₂ nanoparticles was performed with a silane agent KH-570. Both the inorganic and organic nanoparticles were dispersed in coating emulsions by magnetic and ultrasonic stirring followed by the spraying of the coating emulsions to ensure the uniformity of dispersion during the deposition of the coating on the metal substrate. A cauliflower-like hierarchical superhydrophobic surface with CA more than 150° using both the nanoparticles was obtained. The thermal stability of the developed coatings was tested by treating them up to a temperature of 550 °C. The PTFE nanoparticle filled coatings found superior to the silica filled coatings in respect of excellent water repellency and acid resistance.

Mahadik et al. [66] reported the preparation of multifunctional SHCs on various substrates like steel, germanium, brass, and copper via a simple sol-gel and spray coating route. A facile, less-time consuming, economical, eco-friendly and adaptable to domestic and industrial scale approach was proposed. SHC was prepared via a sol-gel spray coating method. The anti-corrosion performance of the coatings was tested by exposing them against a corrosive salt solution for six months at ambient conditions, which revealed an excellent corrosion resistant performance. The exceptional long-lasting durability, anti-corrosion resistance, mechanical and thermal stability of the developed SHC was realized. SEM images of the SHCs onto various metal substrates revealed different hierarchical textures like marigold flower forms with nano-scale bumps on a germanium substrate, similarly, the uneven grains with porous residues on the brass, steel, and copper coated substrates. Different water CA almost more than 150° with SA less than 10° were obtained on the various coating substrates such as germanium (CA = 163 ± 2°), brass (CA = 170 ± 1°), steel (CA = 161 ± 2°) and copper (CA = 170 ± 1°). The corrosion tests for the coated substrates were performed in a corrosive salt solution consisting of a specific ratio of NaCl, CaCl₂, and Na₂SO₄. The specimens (area of 1 × 5 cm²) were perpendicularly hanged in the salt solution for 6 months at ambient conditions. The corrosion test results indicated that the corrosion on the coated substrates decreased by 4 % compared to the uncoated substrates. Under the corrosive environment, the substrates revealed a minor corrosive effect on the CA and SA of the superhydrophobic substrates.

In a recent study, Wanget et al. [67] reported the preparation of SHC based on a composite consisting of fluorosilicone (a resin) as a base matrix and silica nanoparticles as fillers. The SHC that can be cured easily at room temperature was obtained by the dispersion of 1H, 1H, 2H, 2H perfluorooctyltriethoxysilane modified silica nanoparticles in fluorosilicone resin. The effect of the silica concentration and dispersion time in the resin was studied for the wetting properties. The mechanism of formation of superhydrophobic nanocomposite based coating on a glass substrate is shown in Fig. 7.

The SEM images with optical images of the water CA of the superhydrophobic composite coatings with different dispersion times such as 15, 60 and 120 min are shown in Fig. 8. The images revealed the roughness variation due to the difference in the dispersion time of the nanoparticles in the resin.

3.3. Nano-titania based coatings

Several researchers have preferred TiO₂ nanoparticles to develop SHCs owing to their manageable structure, required stability, photocatalytic activity and biocompatibility [8,68–71]. Qing et al. [72] reported a simplistic, low cost and environment friendly technique for preparation of a hybrid superhydrophobic fluorinated polymethylhydrosiloxane/TiO₂ nanocomposite coating via a spray-coating method on steel substrates. They introduced hydrophobic groups such as CH₃ and CH₂ onto the surface of TiO₂ nanoparticles to achieve hydrophobicity. For an optimized weight ratio of the surface modified TiO₂ nanoparticles to fluorinated polymethylhydrosiloxane (7:3), static water CA of 161° with a SA of 5° was obtained due to low surface free energy and micro/nano binary structure of the coating. The durability of the developed coatings was tested against pH and corrosion-resistant performance of the SHC was measured on a steel substrate by immersing in 3.5 wt% NaCl aqueous solution. The SHCs revealed almost same wetting properties after their exposure to air at ambient conditions or their immersion in a corrosive salt solution, demonstrating the tremendous durability and exceptional superhydrophobicity of the developed coating on the steel substrates. Such developed coatings can prove their potential in various research and industrial sectors. A

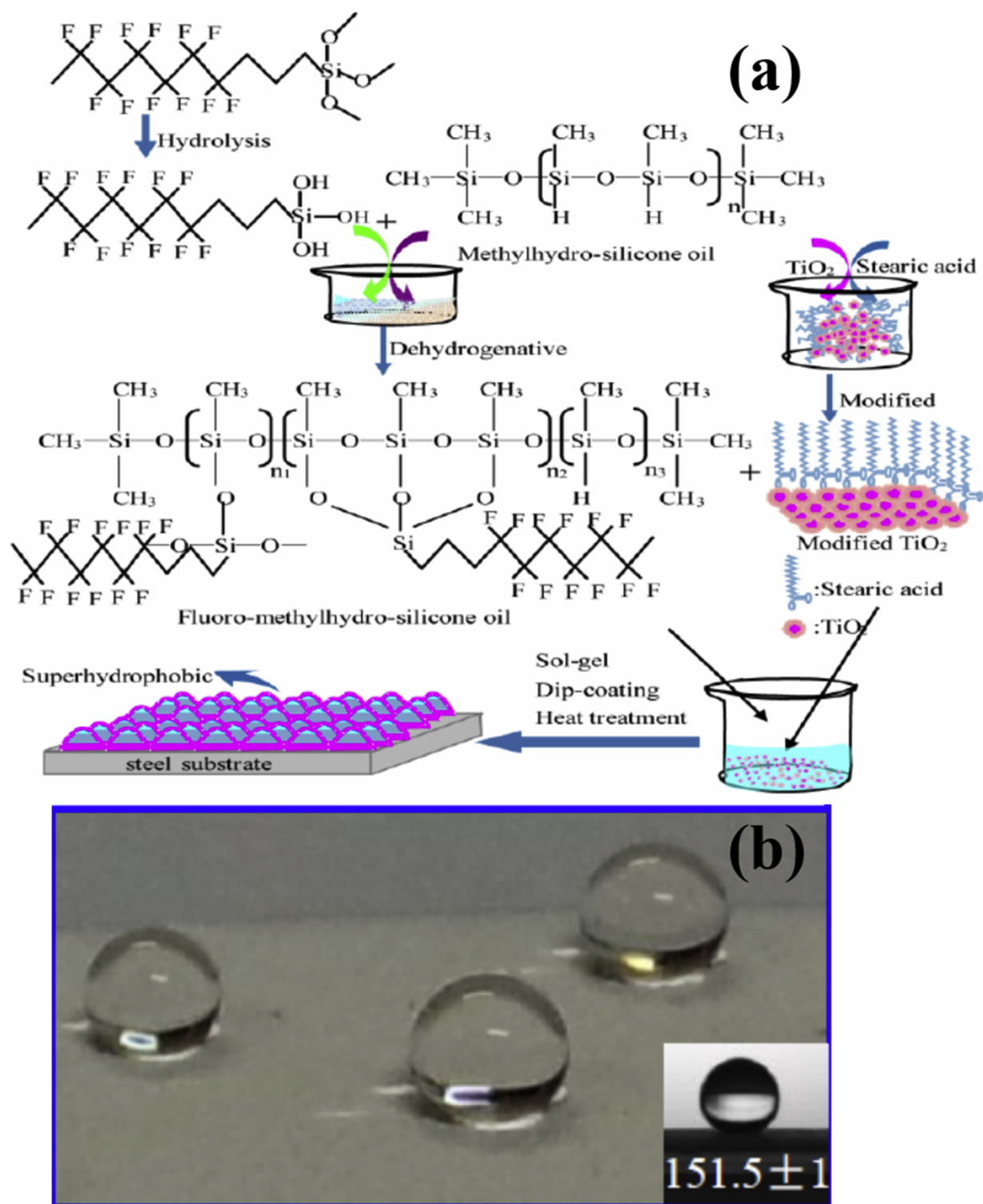


Fig. 5. (a) Schematic representation of the synthesis of a superhydrophobic nanocomposite coating on a steel substrate and (b) the optical image of the water droplets on the coated steel substrate [35].

schematic diagram of the formation of a hybrid superhydrophobic fluorinated polymethyl-hydrosiloxane/TiO₂ coating on a steel substrate and optical images showing superhydrophobicity of the modified nanoparticles and the developed coating is shown in Fig. 9.

Huang et al. [73] reported the fabrication of superhydrophobic TiO₂-nanotube coatings for the reduction in platelet adhesion and better corrosion resistance of 316 L stainless steel. The vertically aligned superhydrophobic TiO₂ nanotube (TNT) arrays were prepared

on the steel substrate by electrochemical anodization of Ti films deposition followed by calcination and fluorosilanization. Initially, 316 L stainless steel sheets were de-greased by successive washings in acetone, ethanol and deionized water using an ultrasonic bath and dried at ambient conditions. Ti films were deposited on metal substrates by DC sputtering. TNTs were synthesized by electrochemical anodization with a neutral electrolyte consisting, 2 wt.% NH₄F in glycerol with 2.5–3.5 vol.% of deionized water. Then the synthesized amorphous

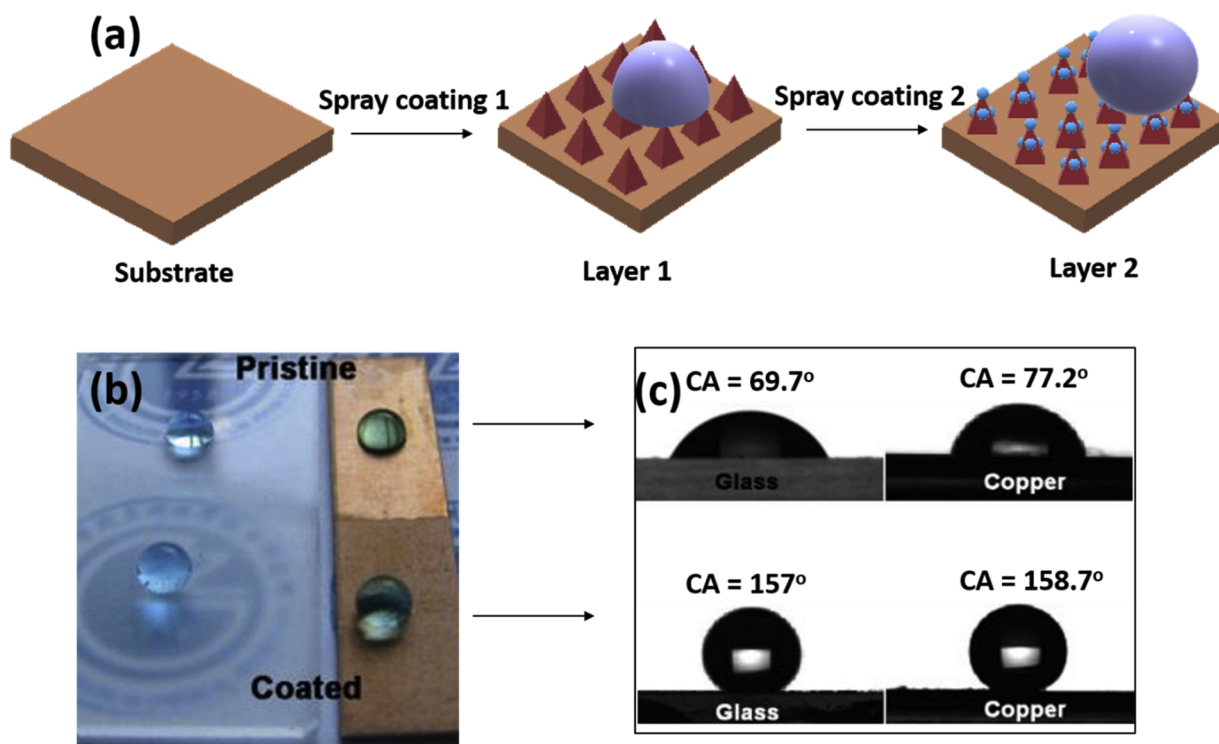


Fig. 6. (a). Schematic diagram of the preparation of a SHC, (b) the optical description of water drops residing on the glass and copper substrate, and (c) the CAs of glass and copper substrates [63].

nanotubes were crystallized via annealing at 450 °C for 2 h followed by treatment with a methanol solution of hydrolyzed 1 wt.% 1H,1H,2H,2H-perfluorooctyl-triethoxysilane for 1 h and later heated at 140 °C for 1 h to achieve the superhydrophobic surfaces. For the developed coatings, the maximum water CA of 152.2° ± 0.8° was achieved. The corrosion-resistant performance of the coatings was tested and revealed improved performance and it was realized that coatings also strongly affect platelet bonding and fibrin formation in

contact with platelet-rich-rabbit-plasma. The developed coatings improved both the corrosion resistance and blood compatibility, exhibiting their potential use in blood contacting corrosion resistant biomedical devices.

Roy et al. [74] reported a solution treated scalable functionalized discrete TiO₂ nanotubes based SHCs on stainless steel substrates. The self-assembled monolayers (SAMs) of octadecylphosphonic acid (ODPA) were grown for thorough passivation on discrete titania-

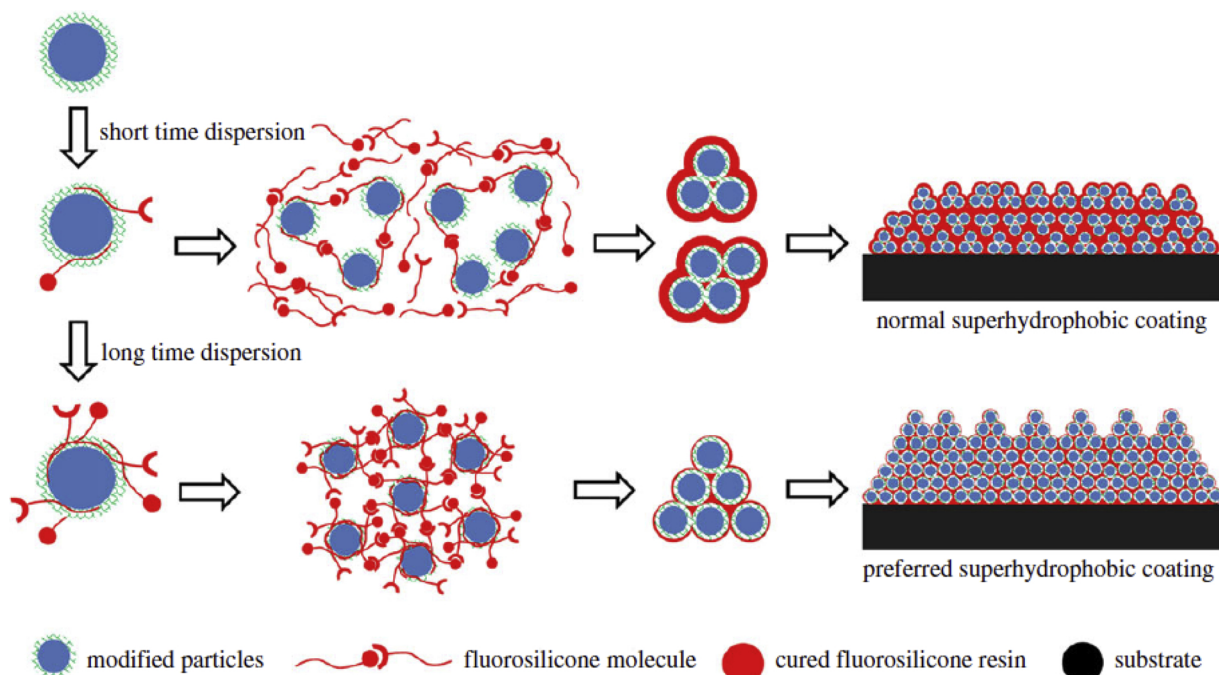


Fig. 7. Mechanism of synthesis of superhydrophobic nanocomposite based coating on a glass substrate [67].

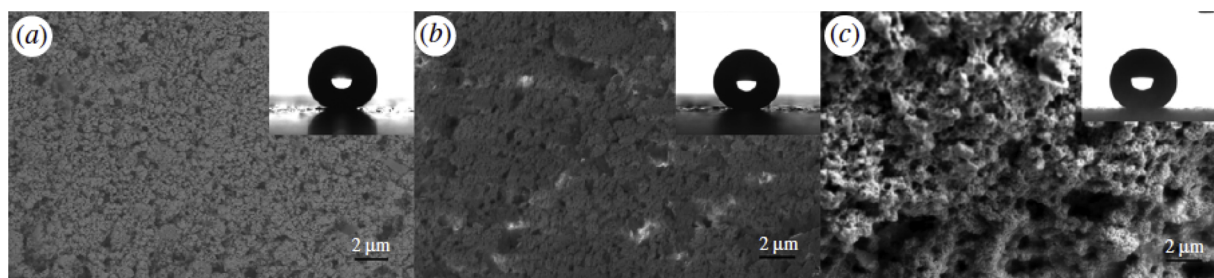


Fig. 8. SEM and optical images of the water CA of the superhydrophobic composite coatings with different dispersion times (a) 15 min, (b) 60 min and (c) 120 min, respectively [67].

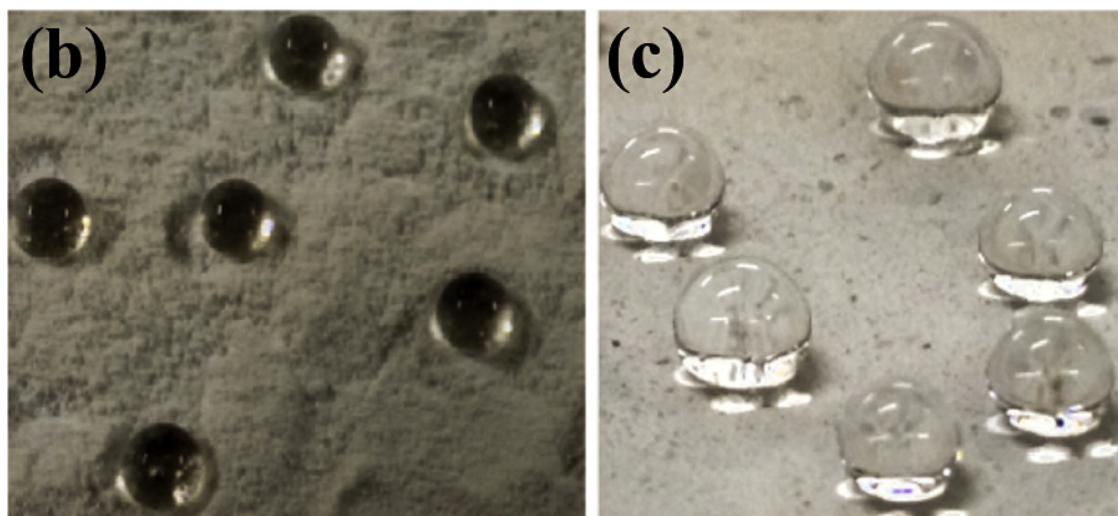
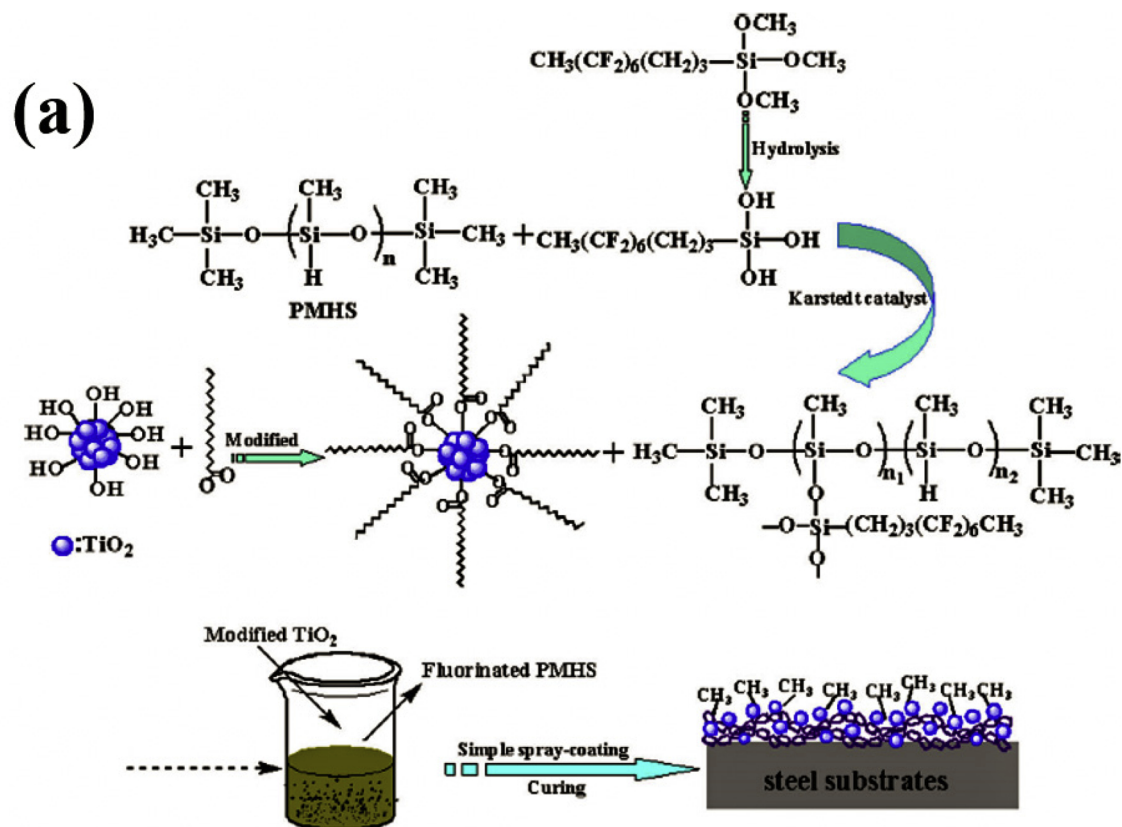


Fig. 9. (a) Schematic diagram of the formation of a hybrid superhydrophobic fluorinated polymethyl-hydrosiloxane (PMHS)/ TiO_2 coating on a steel substrate and optical images of water droplets on (b) the modified nanoparticles and (c) the developed coating [72].

nanotube (d-TNT) coated stainless steel substrates. Initially, 0.5 mm T-304 stainless steel substrates were cleaned by successive solvents such as methanol (99.8 %), n-hexane (99 %) and isopropylalcohol (99.8 %) for 15 min in each case using an ultrasonic bath. Later on, the washed substrates were kept under O_2 plasma for 10 min to remove carbon impurities followed by drop coating of a d-TNT solution on the plasma treated substrate and dried overnight. Then the coated substrate was immersed in a 1 mM octadecylphosphonic acid (ODPA) in 4:1 methanol and water ratio at ambient conditions for 20 h. Similarly, 1H,1H,2H,2H-perfluorodecylphosphonic acid (PFDDPA) was employed to ODPA to make samples for mechanical testing. Finally, the modified and passivated substrate surface was cleaned with methanol and dried under N_2 atmosphere to remove physisorbed molecules. They prepared the d-TNTs by choosing Titanium (Ti) foils of 0.79 mm thickness. The Ti foils were cleaned in an ultrasonic bath using methanol and deionized water and then dried under N_2 atmosphere. A two-electrode system of the electrochemical cell was employed for anodic production of TNTs using 2 % HF and dimethylsulfoxide (DMSO) as an electrolyte and keeping the anodizing voltage of 60 V for 3 days. Annealing of DMSO-prepared TNTs was performed in air at 500 °C for 2 h. After annealing, the TNTs were isolated from the titanium foil using a blade and transferred into 1 mL methanol consisting of small vials and finally discretized using a tip sonicator. The schematic representation of the passivation process of the stainless steel substrate with the anticipated superhydrophobic behaviour is shown in Fig. 10. A new approach was presented to produce corrosion-resistant superhydrophobic stainless steel surface by a facile, scalable and cost-effective solution processing. The industrial importance of this approach was highlighted by achieving a water CA of $166 \pm 8^\circ$ on the steel substrate passivated by d-

TNTs and ODPA SAM, inferring extreme water repellent performance and significant corrosion resistance. Such a coating can be easily extended to other types of substrates [74].

Hua et al. [75] reported the fabrication of corrosion and intense cavitation resistant superhydrophobic octadecylphosphonic acid (ODPA) or 1H, 1H', 2H, 2H'-perfluorodecyl phosphonic acid (PFDDPA) functionalized TiO_2 nanotubes arrays (TNTAs). The superhydrophobic TNTAs were tested under harsh conditions including abrasion, corrosion in saline water, intense ultra-sonication and water-jet impact. The self-assembled monolayers were developed on the TNTA surfaces to fabricate superhydrophobic PFDDPA-TNTA or ODPA-TNTA surfaces. For superhydrophobic ODPA-TNTA, the CA of $156^\circ \pm 1.5^\circ$ with a SA of 3° while for the superhydrophobic PFDDPA-TNTA, the CA of $168^\circ \pm 1.5^\circ$ with a SA of 0.8° was obtained respectively. The mechanism of preparation of corrosion and intense cavitation resistant superhydrophobic octadecylphosphonic acid (ODPA) or 1H, 1H', 2H, 2H'-perfluorodecyl phosphonic acid (PFDDPA) functionalized TiO_2 nanotubes arrays (TNTAs) is shown in Fig. 11. Both the PFDDPA-TNTA and ODPA-TNTA showed great resistant to intense cavitation, abrasion and water-jet impact without any damage to TNTAs or any delamination of the self-assembled monolayer. Such results are quite interesting for practical applications of the superhydrophobic surface-modified TNTAs.

Li et al. [76] reported the fabrication of a TiO_2 /polysiloxane resin composite based full-thickness SHC. The rutile TiO_2 nanoparticles were functionalized via triethoxyoctylsilane to obtain excellent superhydrophobicity and thermal stability of the coating. A durable and tough superhydrophobic TiO_2 /polysiloxane resin composite coating was synthesized through the mixing of a polysiloxane resin and functionalized TiO_2 nanoparticles. The 1:2 wt ratio of polysiloxane resin and

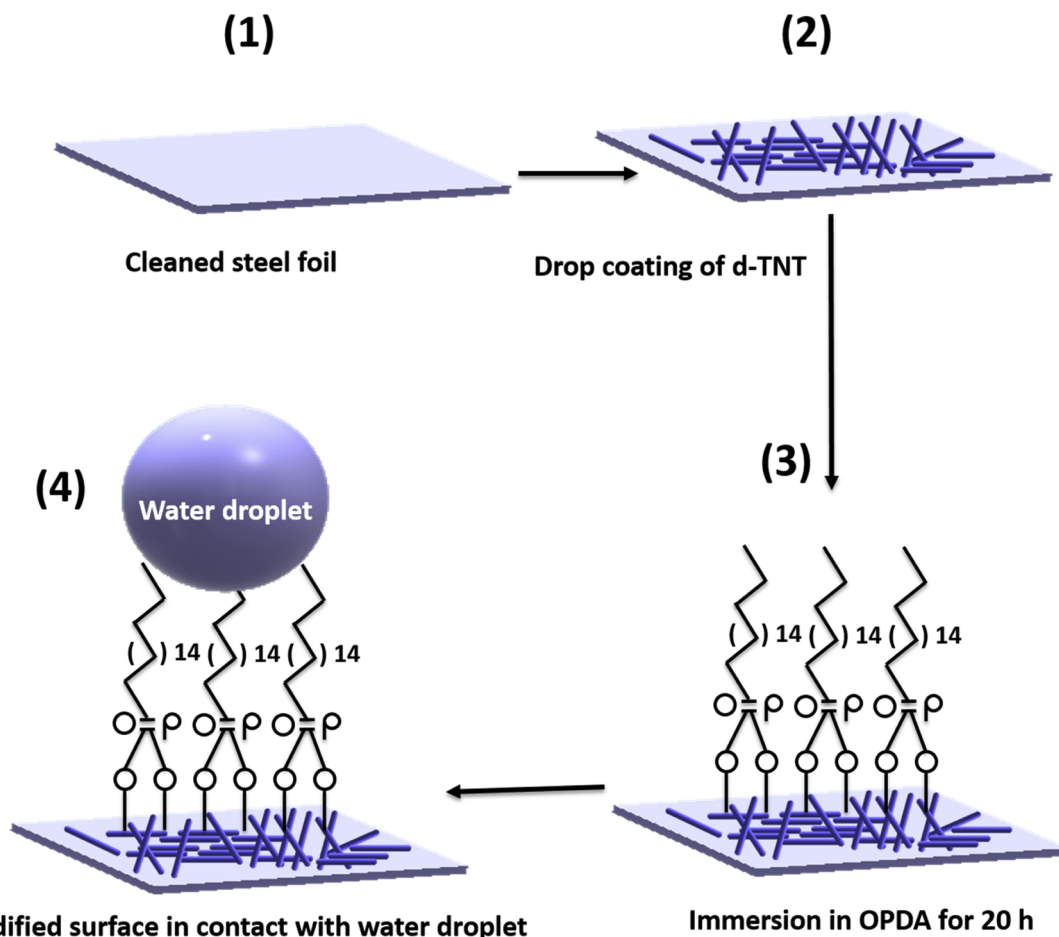


Fig. 10. Stepwise schematic diagram of the passivation process of a stainless steel substrate with the anticipated superhydrophobic behaviour [74].

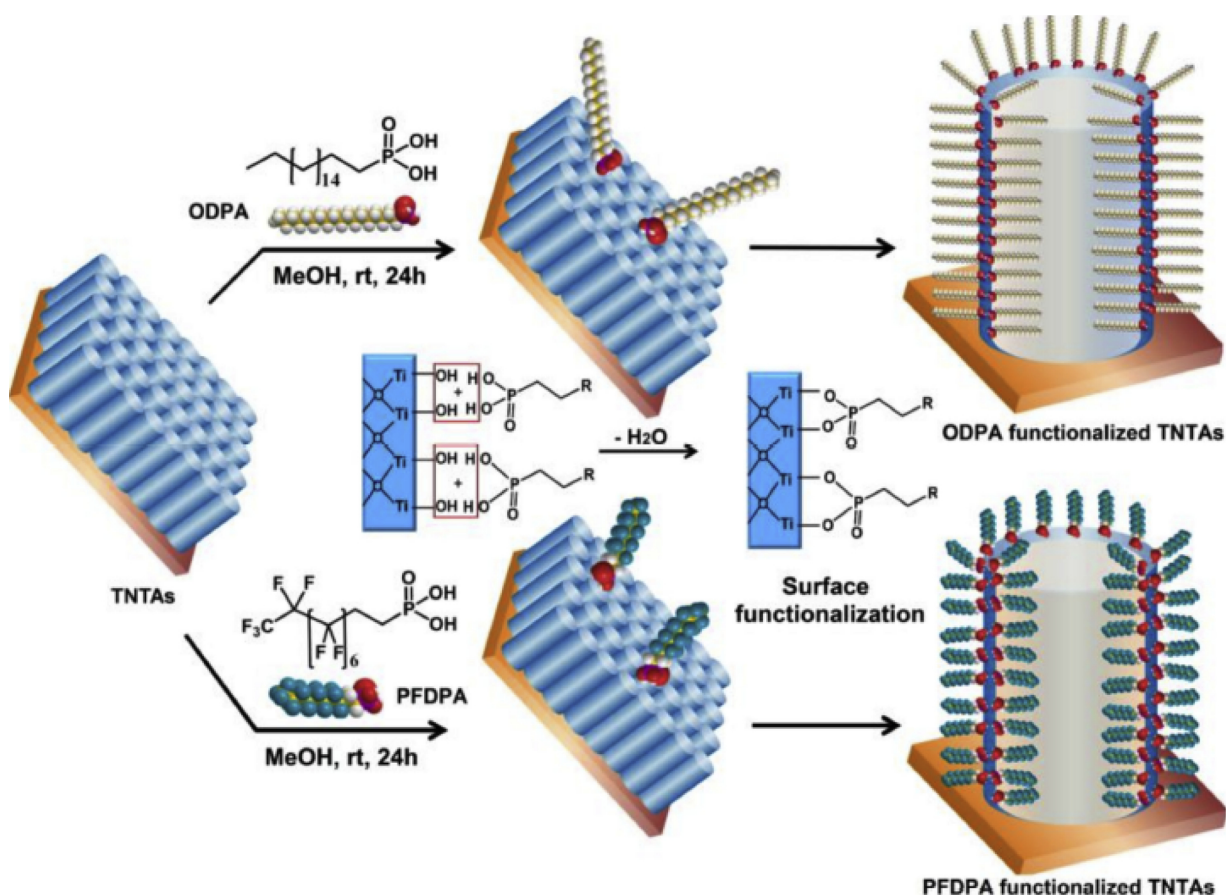


Fig. 11. Schematic diagram of the mechanism of formation of superhydrophobic functionalized TiO_2 nanotube arrays (TNTAs) [75].

functionalized titania nanoparticles coating on carbon steel substrate revealed superhydrophobicity with a water CA of 151° and SA $\sim 0^\circ$. Fig. 12 shows the schematic illustration of the modified TiO_2 /poly-siloxane resin composite coating structure and the water droplet bouncing process on the composite coating. The resulting superhydrophobic composite coating also showed good thermal stability up to a temperature of 160°C . The abrasion test results indicated the wetting properties were hardly affected by the worn surface of the SHC confirming the full-thickness superhydrophobicity of the developed coatings. However, the composite coating after its immersion in 3.5 wt % NaCl solution for about 16 days illustrated good corrosion resistance but the topmost layer of the composite coating lost its superhydrophobicity.

3.4. Nano-zinc oxide based coatings

Zinc oxide (ZnO) nanoparticles are one of the most widely studied material because of low cost, abundance, ease in tuning its morphology, wide bandgap semiconductor, chemically, mechanically and thermally stable properties and eco-friendly nature etc. [77–81]. Many researchers tuned the hydrophilic character of ZnO nanoparticles [82] to superhydrophobic [83–85]. In a recent study, Rezaei and Entezari [86] reported the synthesis of a robust superhydrophobic aluminium surface via etching and the deposition of ZnO nanoparticles. They deposited the ZnO nanoparticles on the Al surface via facile methods such as immersion and ultrasound. The surface energy of the Al substrate was abridged by stearic acid (STA) ethanol solution. The ultrasound method (STA–ZnO–Al–U) was found superior to the immersion method (STA–ZnO–Al–I) in order to provide stable superhydrophobic Al surfaces. A schematic diagram of the stepwise process of fabrication of

corrosion resistant SHCs on Al surface with or without etching is shown in Fig. 13.

The potentiodynamic measurements exhibited that etching of the surface in HCl solution under ultrasound results in the superhydrophobic surface (STA–ZnO–Al(E)–U). Such sample showed the outstanding decline in corrosion current density as well as and long-lasting stability enhancement versus immersion in corrosive 3.5 wt.% NaCl solution compared to the sample without etching (STA–ZnO–Al–U) due to the generation of a hierarchical structure in the first case. The optical images of water droplets on STA–ZnO–Al(E)–U and STA–ZnO–Al–U before and after corrosion test are shown in Fig. 14.

Recently Radwan et al. [87] reported the fabrication of a corrosion resistant SHC based on polyvinylidene fluoride (PVDF) and ZnO nanoparticles via one-step electro-spinning route for aluminium (Al) substrate. They obtained the water CA of $155 \pm 2^\circ$ with CA hysteresis of $4.5 \pm 2^\circ$. They claimed that the concentration of ZnO nanoparticles was $1/6^{\text{th}}$ in case of the electrospun coating compared to the spray coating of the same material to achieve the superhydrophobicity of the surface. The electrospun coating revealed a better distribution of pristine nanoparticles without any functionalizing agent. The corrosion test results showed that the introduction of ZnO nanoparticles in PVDF made it much better performer material against corrosion on Al substrate compared to the PVDF alone. The main function of the ZnO nanoparticle in improving the hydrophobicity of the PVDF–ZnO composite coatings is associated with the shrinking the pore size of the coating and enhancing the air trapping within the structure of the surface. The developed nanocomposite coating on Al substrate exhibited 35 times higher corrosion resistance than the uncoated or bare Al substrate. A significant difference in the water CAs on coated and uncoated substrates is shown in Fig. 15.

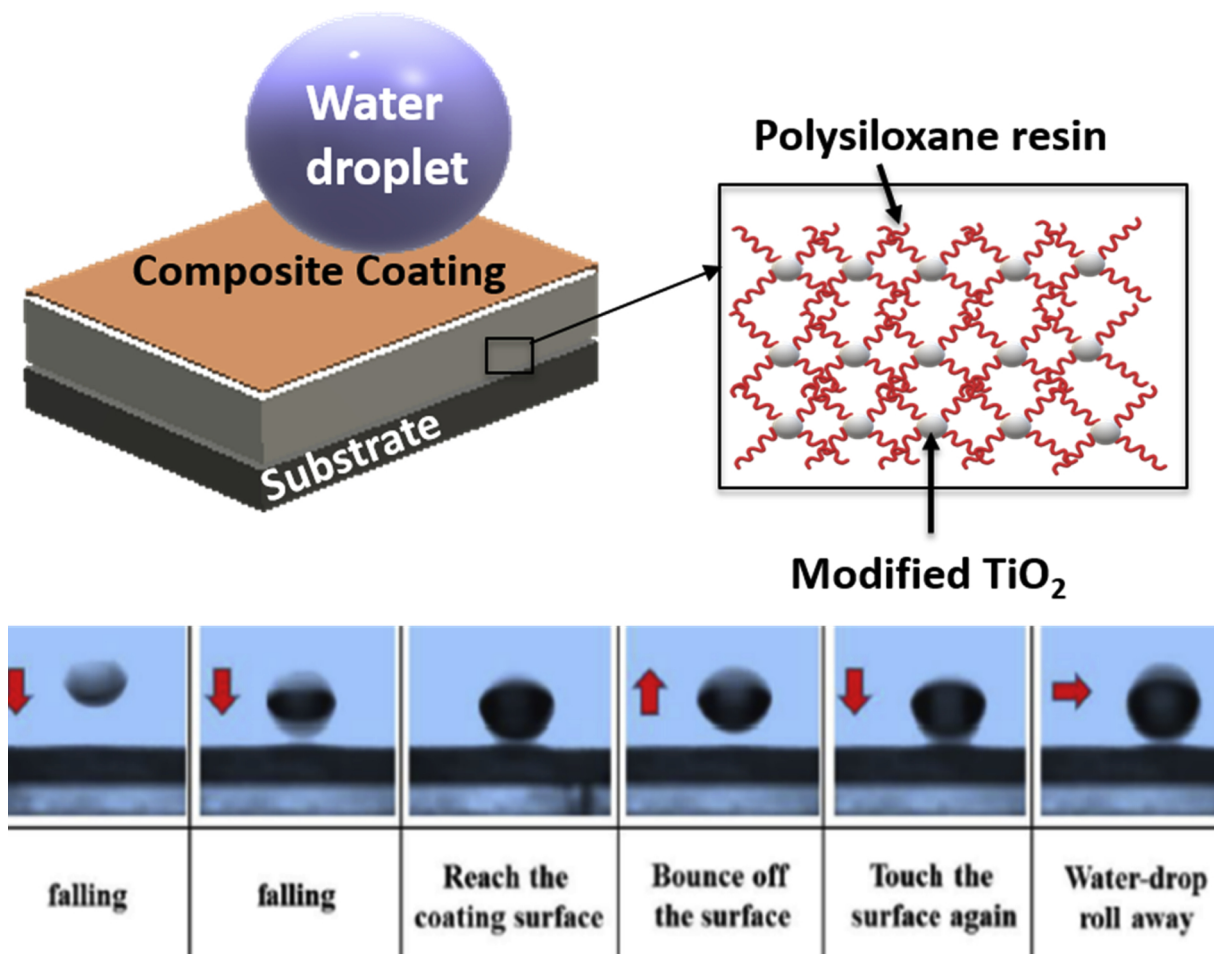


Fig. 12. Schematic illustration of the modified TiO₂/polysiloxane resin composite coating structure and the water droplet bouncing process on the composite coating [76].

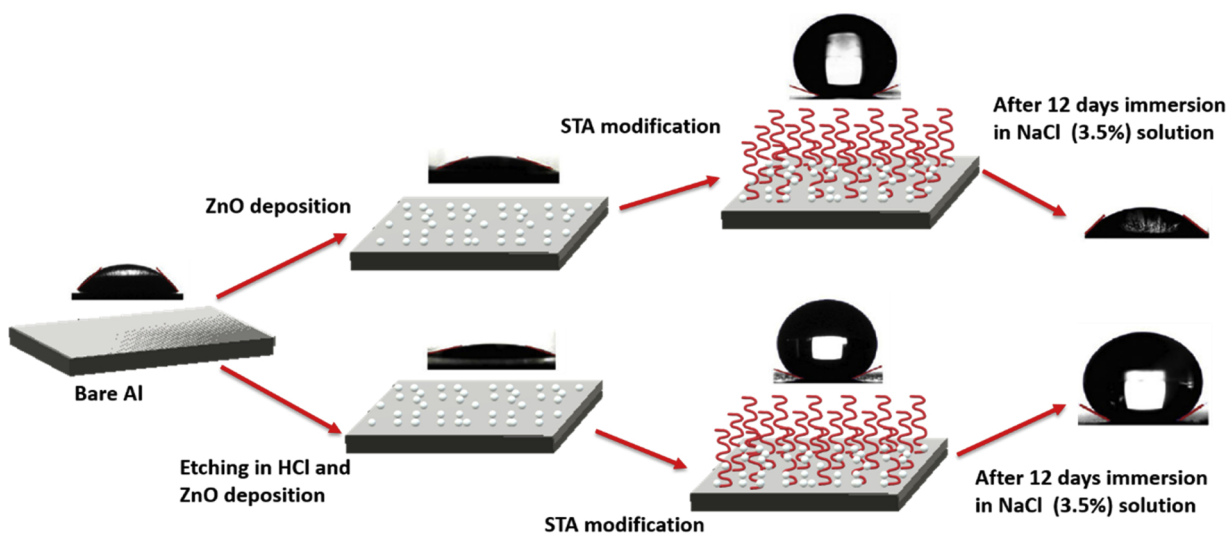


Fig. 13. Schematic diagram of the stepwise process of fabrication of corrosion resistant SHCs on Al surface with or without etching [86].

3.5. Carbon nanotubes (CNTs) based coatings

Since its discovery in 1991, carbon nanotubes have created awesome enthusiasm for established researchers and extremely extraordinary interdisciplinary research is directed all around [88]. In fact, the carbon nanotubes have been generally utilized as a part of

numerous applications from the past decade in light of their electrical, mechanical, optical and thermal uniqueness. Some researchers reported the synthesis of carbon nanotube-based SHCs for the protection of metals against corrosion.

Nicola et al. [89] reported the development of superhydrophobic multi-walled carbon nanotube (MWCNT) based coatings for stainless

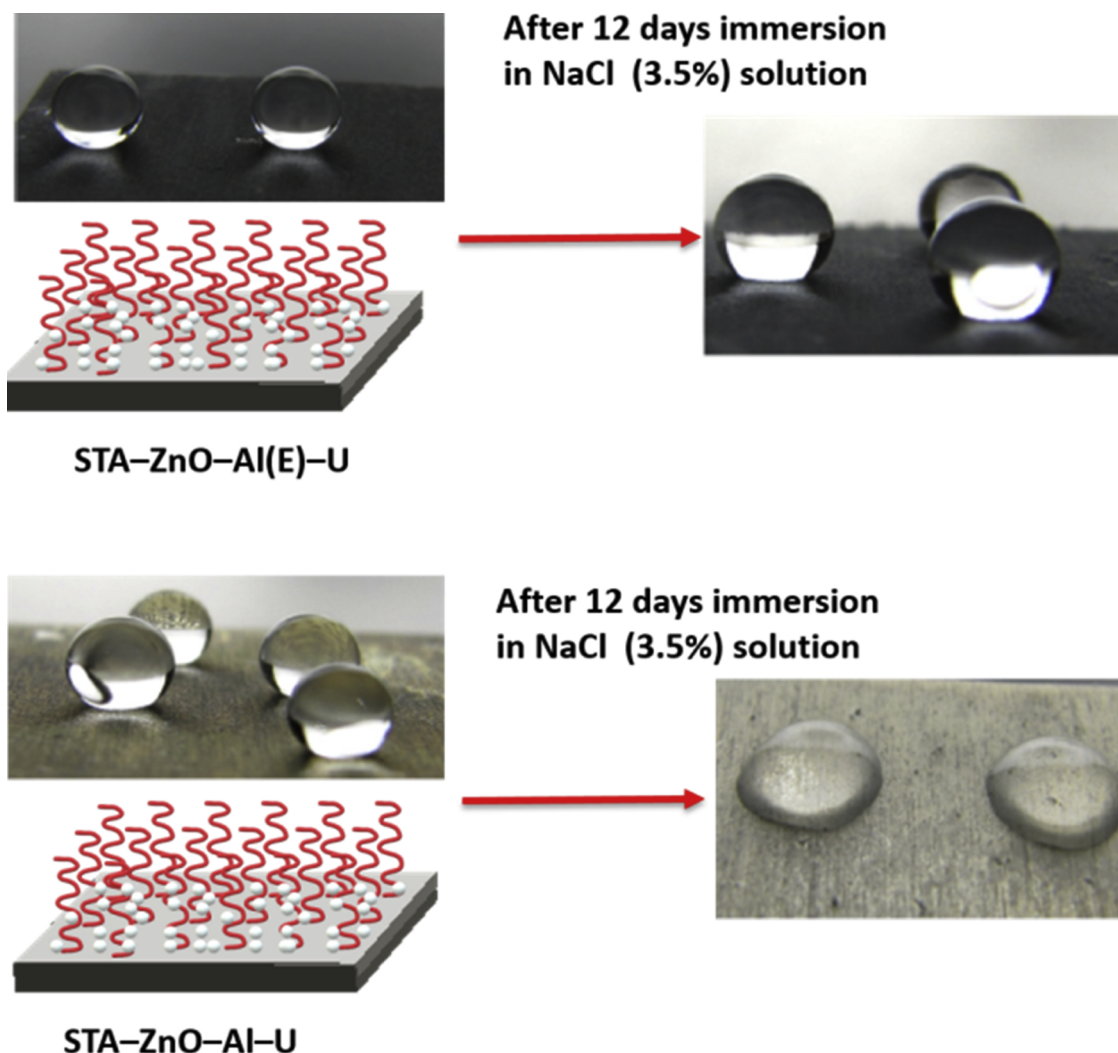


Fig. 14. Optical images of water droplets on STA-ZnO-Al(E)-U and STA-ZnO-Al-U before and after immersion in 3.5 wt.% NaCl solution for 12 days [86].

steel substrate. The intrinsic surface roughness and iron content of stainless steel (AISI 316) were utilized to produce random networks of MWCNT by chemical vapour deposition method at a temperature less than 1000 °C deprived of any outside catalysts or additional pre-treatment. The developed superhydrophobic MWCNT films on the stainless

steel substrate exhibited a high CA of 154° with high CA hysteresis (Fig. 16). The SHC was found stationary for conductive steel substrate and can be used to prevent corrosion and fouling.

A facile synthesis technique is reported for the fabrication of MWCNT and silicone rubber based stable superhydrophobic composite

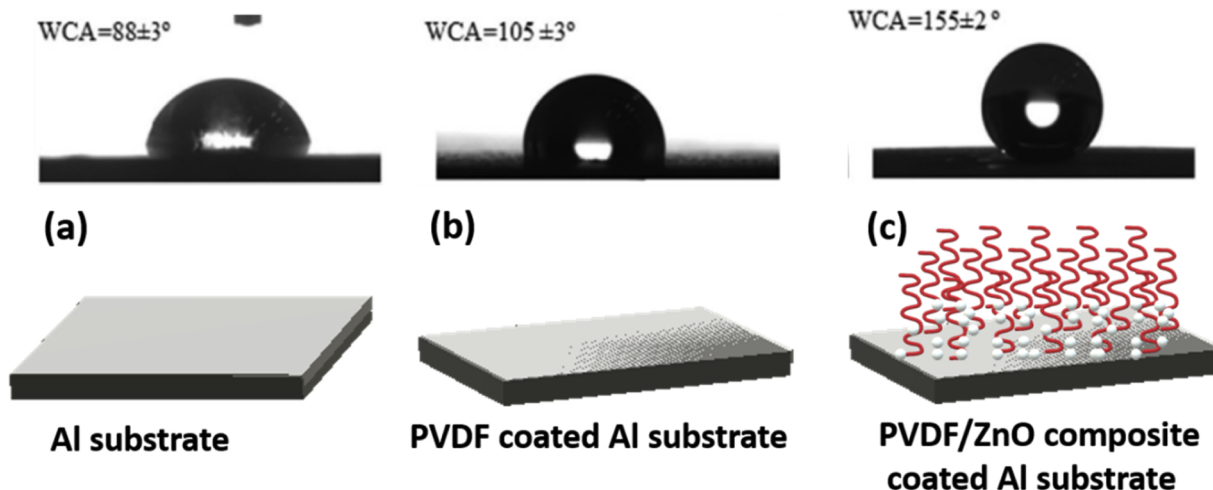


Fig. 15. Schematic diagrams and optical images of the CAs on (a) Al substrate, (b) PVDF coated and (c) PVDF-ZnO composite coated Al substrates [87].

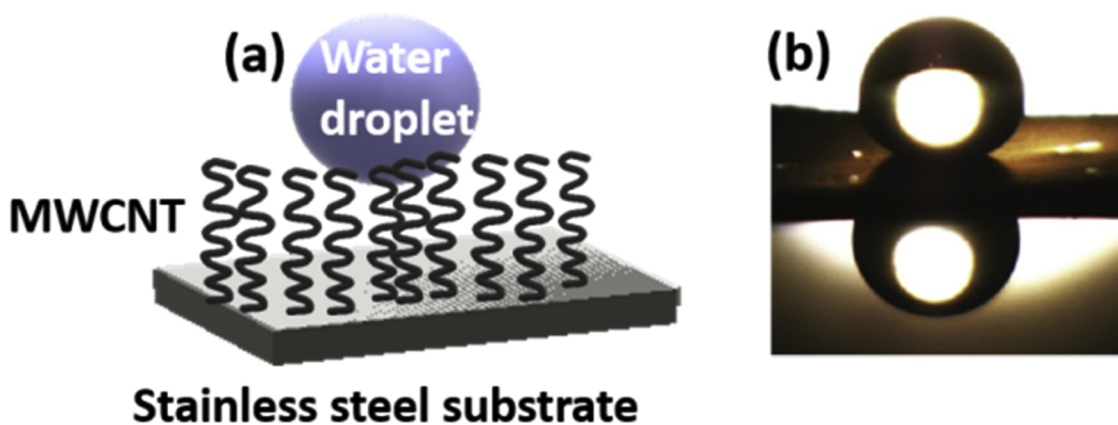


Fig. 16. (a) Schematic diagram and (b) the optical image of the water CA of $154^\circ \pm 4^\circ$ measured on the MWCNT coating on stainless steel substrate [89].

by Mokarian et al. [90]. Water CA of 159° with very low roll-off angle was achieved using de-ionized water as shown in Fig. 17. The measured surface free energy of the developed coating was about 26 mJ/m^2 . The developed coating revealed good stability under ultraviolet exposure, pencil hardness test, heating, different pH values as well as ionic-strength solutions. Additionally, the stability of the coating under condensed hydrochloric acid, tape test, boiling water and 5 wt.% NaCl aqueous solution was good.

Yang et al. [91] reported the synthesis of superhydrophobic epoxy based coating amended by fluorographene for self-cleaning and anti-corrosion applications. Copper was used as a substrate to develop organic superhydrophobic surface. A rough epoxy resin coating with random micro/nanostructures was prepared by a low-surface-energy material such as liquid-phase exfoliated fluorographene nanosheets of different sizes and shapes. The superior protection performances were realized for the developed coating owing to the mechanical abrasion resistance, self-cleaning function, and chemical stability in acidic as well as alkaline aqueous solutions. A novel and operative approach was provided to guard materials by combining the shielding function of both the organic coating and SHC which is very useful for commercial-scale production of superhydrophobic organic coatings.

Zhu et al. [92] reported MWCNTs improved superhydrophobic MWCNTs-Co/a-C:H carbon-based coating for outstanding self-cleaning and corrosion resistance application. A robust and safe technology named as electrochemical deposition was used for the fabrication of the SHC. A micro-nanoscale hierarchical surface was tailored using MWCNTs and Co nanoparticles having nanocrystallite/amorphous microstructure. A high water CA of $\sim 158^\circ$ with a very small SA of $\sim 3^\circ$ was achieved, which is having complete water repellency. The developed coating may be an excellent option for anti-corrosion and self-cleaning purposes. The superhydrophobicity of the developed coating was maintained even after the tape adhesion test and sandpaper abrasion test, which revealed its stability due to the strong bonding of the MWCNTs and Co nanoparticles with the coating. It was realized that MWCNTs-Co/a-C:H film demonstrated excellent self-cleaning effect compare to the pure diamond-like carbon film. Further, Zhou et al. [93] reported the development of excellent superhydrophobic and corrosion resistance carbon-based coatings consisting of MWCNTs and nickel nanoparticles. The nickel nanoparticles and MWCNTs were doped into diamond-like carbon films and nanocomposite MWCNTs-Ni/a-C:H film was fabricated using one-step electrochemical deposition technique. High water CA $\sim 159^\circ$ with a very small SA $\sim 2^\circ$ was obtained, which led the micro-nanoscale hierarchical roughness to the film. Additionally, the superhydrophobic thin film revealed good mechanical stability, excellent corrosion resistance, and exceptional self-cleaning behaviour.

4. Progress in developing the corrosion resistant SHCs on various metals/alloys

Table 1 is summarizing the development of corrosion resistant SHCs on various metal/alloy substrates via different techniques.

5. Challenges in the fabrication of stable SHCs

The stability of SHCs/films/surfaces is a crucial parameter for their espousal in various industries. The tremendous applications of SHCs make them potential candidates; therefore, the worldwide research is going on the development of stable SHCs. Generally, the SHCs are fragile in nature, and such coatings can easily lose their superhydrophobicity when they encounter any external surface. Therefore, high mechanical stability is a key pre-requisite for industrial applications of such coatings. The increasing demand for mechanical stability of these coatings boosted the research in this field. Mechanical stability can be determined using numerous approaches. Some of the current approaches including the developments in improving the mechanical stability of the coatings are covered in this section.

Hitherto significant research has been performed on the enhancement of mechanical stability of the SHCs. An exciting way to enhance the mechanical stability of the SHCs is to develop dual scale surface roughness [139], which can easily bear the mechanical loads without significantly sacrificing the superhydrophobic properties. The development of self-repair coatings is another way to improve mechanical stability. Such coatings have the potential of repairing the damaged

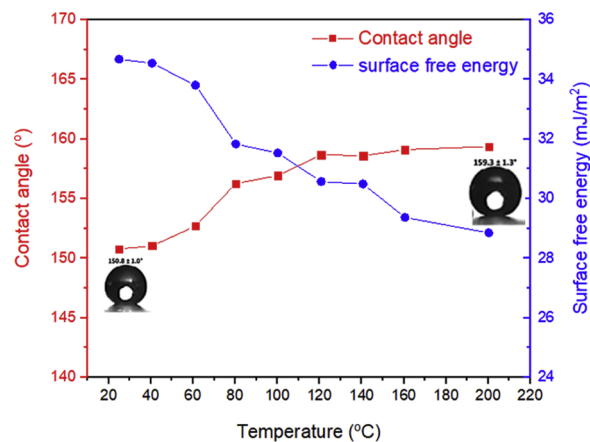


Fig. 17. (a) Water CA and surface free energy vs. heating temperature of SHC including optical images of the water droplet on the coating before and after heating up to 200°C [90].

Table 1
Corrosion resistant SHCs on various metal substrates via different techniques done so far.

Processing Technique	Nanostructure Type	Substrate	Chemical agents		CA (°)	SA (°)	Applications	Ref.
			Main Agent	Accompanying Agents				
Sol-gel Process	SiO ₂	Glass plate	17FTMS	TEOS, ethanol & nitric acid (69 %)	152	10	Self-cleaning	[64]
Air spraying technique	PANI, CNT, SiO ₂	Al plate	Ethyl acetate	Ethyl, TPE powder and POTS	167	< 1	Anti-erosive, anti-abrasive coating	[94]
LSD and spin coating	SiO ₂	Float glass plate	ODTS, Toluene	Water, Chloroform	> 170	< 1	Superhydrophobic coating, photovoltaics	[12]
Spray coating	TiO ₂	Steel plate	PFMHS	Compressed Nitrogen	161	5	Anti-corrosive superhydrophobic coating	[72]
Solvothermal	CO ₃ O ₄	Glass plate	NA	NA	169.2	< 3	Superhydrophobic, anti-icing	[95]
Sol-gel	TiO ₂	Steel plate	FMSO	Silane	151.5	6	Anti-corrosion	[35]
Suspension flame spraying	Al ₂ O ₃	SS plate (316L)	Polyurethane	Al Arc spray (diameter 2 mm)	151	6.5	Anti-corrosion coatings for marine	[96]
Spin coating	Al ₂ O ₃	Al 6061	Silicon rubber solution	Acetone	> 160	< 5	Anti-corrosive, ice-phobic coatings	[59]
Hierarchical structure development	NA	Steel plate (1045)	H ₂ O ₂ and acid (HCl/HNO ₃)	Hexane	160	6	Anti-icing, anti-corrosive, UV-resistant	[97]
Sol-gel	SiO ₂	Fiber glass	NH ₃ ·H ₂ O	TEOS	154	5	Superhydrophobicity, oil-water separation	[98]
Hydrothermal	NA	AZ31 Mg alloy plate	NaOH	ASC, TP, SDS, Na ₂ CO ₃ , TSP and SDBS	166	< 5	Anti-corrosive	[99]
Nanosecond laser treatment	NA	AMG Al-alloy, AlMg ₃ alloy	1 % solution of MAF	NA	173.1	2.1	Automotive, aerospace, medical, etc.	[63]
Electro-deposition	Zn	Steel plate	ZnCl ₂ / Zn(NO ₃) ₂	Silicon polymer in toluene	155	NA	Anti-icing, anti-corrosive	[100]
Sol-gel	SiO ₂	Glass plate	(17FTMS)/ (TEOS)	Ethanol/ Nitric acid	152	10	Transparent self-cleaning for windshields	[64]
Micro-working Robot	NA	Al foil	Polypropylene	NA	> 150	< 5	Mechanically durable hydrophobic coatings	[101]
Immersion	NA	AZ31 Mg alloy	(FeCl ₃ ·6H ₂ O)	TDA and ethanol	165	NA	Anti-corrosive, anti-fouling SHCs	[102]
Chemical etching	NA	S ₄₅ C steel substrate	HF	H ₂ O ₂ /Nital	158 ± 2°	3 ± 1°	Anti-corrosion, anti-wear	[34]
EGD and CVD	NA	ITO glass	EDOT	(LiClO ₄), methanol	> 156	< 10	Anti-corrosion, EM shielding	[103]
Gelation	Carbon	Cu Plates	Cerium chloride	Myristic acid	161		Hydrophobic coating	[104]
Chemical etching	NA	Glass Plate	PVDF, DMF,	Methanol, Ethanol	172	2	Oleophilic, hydrophobic	[105]
Electro-deposition	Zn	AA 6061 Al alloy	NaOH	0.01 M ECA	> 150	NA	Hydrophobic, anti-corrosion	[106]
		Steel, Al and Cu	ZnSO ₄	KCl, Dopamine	167.6	< 1	self-cleaning, anti-corrosion, anti-abrasion	[107]
Electro-deposition	Ni	Cu plate	NiSO ₄ ·6H ₂ O/ NiCl ₂ ·6H ₂ O/ PTFE Particles	CTAB	152	NA	Superhydrophobic	[108]
Thermal oxidation and self-assembly	TiO ₂	Titanium plate	N-OTS	n-Hexane	166	2	Chemically and mechanically durable coating	[109]
Chemical etching	Ag	Magnesium alloy AZ91	AgNO ₃	DM	154	5	Superhydrophobic, anti-corrosion	[110]
Air spraying	SiO ₂	Al plate	Fluorinated EPP/PDS	Anhydrous ethanol	173 ± 2	1	Durable anti-corrosion, superhydrophobic, amphiphobic	[111]
Thermal spray deposition	Al, Cu, NiCrBSi	Ceramic tiles, Cu, glass, 316SS, titanium alloy	Al wire/ Cu powder/ NiCrBSi powder	PTFE	155	3.5	Superhydrophobic	[112]
Electro-deposition	Zn	Cu plate	ZnCl ₂ / polypropylene	Chlonie chloride), Thiourea, DMB	170		Superhydrophobic, anti-corrosion	[113]
Air spraying	SiO ₂	Glass plate	TMPS	HCl	158.5	3.9	Transparent, superhydrophobic, self-cleaning coating	[114]
Electro-deposition	Ni	SS	HCl	Na ₂ CO ₃ , Na ₃ PO ₄	160	< 1	Self-cleaning, rust protection coating	[115]
Hydrothermal treatment	NA	AZ31 Mg alloy	Mg(OH) ₂	Stearic acid (0.01 M)	157.6	NA	Superhydrophobic, anti-corrosion	[116]
Oxidation, Heat treatment, Grafting	CuO	Cu plate	Stearic Acid (STA)	NaOH, (NH ₄) ₂ S ₂ O ₈	157.3	5	Superhydrophobic, anti-corrosion, self-cleaning, anti-icing, anti-frosting	[117]
Anodization	TiO ₂	Ti plate	Stearic Acid (STA)	NH ₄ F and C ₂ H ₂ O ₄	161.4	~ 0	Self-cleaning, robust, SHC	[118]
Dip coating	SiO ₂	Metals, cement, wood, plastic	Aniline monomer, TTEOS	Aqueous sol. of oxidative initiator	160	5-7	Transparent, long-life water-proof coatings	[119]
Electro-deposition	NA	Mg-Mn-Ce magnesium alloy	Cerium nitrate hexahydrate (0.05 M)	Myristic acid (0.2 M)	159.8	2	Durable, stable superhydrophobic coating	[120]
Dip-coating	Na ₂ Al ₂ Si ₃ O ₁₀	Aluminium 6061	NPTMS	Ethanol and acetic acid	125-140	NA	Highly Hydrophobic, anti-corrosion	[121]
Electro-deposition	NiO	Copper	NiCl ₂ ·6H ₂ O	H ₃ BO ₃ , C ₂ H ₁₀ C ₁₂ N ₂	155.7	NA	Anti-corrosive, anti-contamination Materials	[122]

(continued on next page)

Table 1 (continued)

Processing Technique	Nanostructure Type	Substrate	Chemical agents		CA (°)	SA (°)	Applications	Ref.
			Main Agent	Accompanying Agents				
Electro-polishing/ Chemical grafting	Al ₂ O ₃	Aluminium	PFODA	PFSA, PTFE copolymer (Nafion), DDA, TDA, ODA and ISA	161.5	NA	Anti-corrosive, superhydrophobic coatings	[123]
Spraying/ Brush painting/ Dip coating	Graphene, TiO ₂	metal, glass, and paper	PDMS, THF, N ₂ H ₄ , KMnO ₄	H ₂ SO ₄ , H ₃ PO ₄ , H ₂ O ₂ , HCl, Ethanol, PDMS	170	NA	Transparent deicing, self-cleaning, anti-bacterial, anti-biofouling coatings	[124]
Spray coating	ZnO	Steel	Fluorinated Polysiloxane	DFHPTMS	166	4	Anti-corrosion, self-cleaning microfluidics	[125]
Electro-deposition	Ni	Copper	Nickel sulfate	NiCl ₂ ·6H ₂ O, H ₃ BO ₃ , AC-FAS	162	3	Self-cleaning, anti-abrasion, anti-corrosion	[126]
Hydrothermal/ Dip coating	ZnO	Bamboo	Zinc acetate dihydrate, zinc nitrate hexahydrate	Monoethanolamine, Methanol (0.75 M), SDS, FAS	> 150	< 15	Multifunctional super-amphiphobic coating	[127]
Spray coating	CuSA ₂	Stainless steel	Sodium Stearate	Cupric acetate, iron (III) Chloride Hexahydrate, Zinc chloride	> 162	< 5	Superhydrophobic anti-corrosion coatings	[128]
Spray coating	SiO ₂	Copper	Toluene, PFOTS	Acetone	158	3.7	Anti-corrosion, anti-contaminant coatings	[129]
Electro-chemical anodization	Al ₂ O ₃	Aluminium alloy	Myristic Acid	HNO ₃ , NaOH, H ₂ SO ₄ , NaCl, Absolute Ethanol	155.6 ± 1.0	5.7 ± 0.2	Superhydrophobic, anti-corrosion coating	[130]
Chemical etching/ Post surface modification	Al ₂ O ₃	Aluminium	DMF	HCl, Stearic Acid	167.3	1.5	Superhydrophobic, anti-corrosion coatings	[131]
Micro-arc oxidation/ Hydrophobic treatment	TiO ₂	Titanium alloy (Ti 6Al-4V)	PFOTS	Sodium Phosphate	153.39	NA	Hard tissue repair, replacement implants, blood coating implants	[132]
Spray coating	SiO ₂	38Cr-Mo-Al carbon steel sheets	Iso-propyl alcohol	N-methyl-2-pyrrolidone	163.1	< 2	Transparent, self-cleaning, anti-fogging, anti-corrosion coatings	[65]
Chemical etching/ Post-surface modification	SiO ₂	6061 aluminium alloy	TCS	Ethanol, KMnO ₄	155.7	2.7	Shipbuilding, aerospace, machine manufacturing, etc.	[133]
Hydrothermal oxidation	ZnO	Zinc	DFHPTMS	NaCl, ethanol, Actyflon-G502	156	3	Anti-corrosion, superhydrophobic	[134]
Electro-deposition/ Dip coating	SiO ₂	Mild steel	TEOS, DTMS, TTEOS, DTMS	Na ₂ CO ₃ , Na ₂ SiO ₃ ·9H ₂ O, Na ₂ P ₂ O ₁₀ , C ₁₂ H ₂₅ NaO ₅ S, Triton X-100	155	NA	Mechanical abrasion resistance, thermal stability	[135]
Chemical etching, Anodization, Dip coating	Al ₂ O ₃	Aluminium (GB 1A99)	PFDTs	Alcohol, NaOH, 2 M H ₂ SO ₄	170	1	Superhydrophobic, Anti-corrosion, Mechanically durable coatings	[136]
Spray coating	SiO ₂	Glass	PFDTs	TEOS, NH ₃ , absolute ethanol (EtOH), and acetone	165.6 ± 0.9	3.5 ± 0.4	Self-cleaning, anti-corrosion metals and microfluidic systems	[137]
Chemical etching/ Post surface modification	Al ₂ O ₃	Aluminium (Al6063)	PS-COOH, GPS	Acetone, ethanol and toluene	153.6	3	Self-cleaning, anti-icing, anti-corrosion, drag-reduction and anti-bio adhesion	[138]

surfaces and can preserve the superhydrophobicity [140].

6. Potential solutions for the fabrication of stable SHCs

6.1. Mechanical durability by the abrasion test

Gao and Guo [141] developed a mechanically stable, corrosion resistant superhydrophobic steel with a slippery surface and repairable stability. Superhydrophobic steel surface was fabricated using chemical etching and surface modification method via controlling the concentration of an acid solution and an acid/H₂O₂ ratio. Water CA of 163.5° with a SA of about 0° was achieved. The mechanical stability of the superhydrophobic steel substrate was evaluated using sandpaper meshes of size 400 # and 1000 # under loadings of 100 g and 200 g. The superhydrophobicity of the steel surface remains even after the mechanical abrasion tests. Additionally, the superhydrophobic steel showed good corrosion resistant against 3.5 wt% NaCl, KBrO₃, K₂SO₄, and NaNO₃ aqueous solutions. Even if the superhydrophobicity and slippery characteristics have vanished during the soaking in salt solutions, both the properties could be regained by 1H,1H,2H,2H-perfluoroalkyltriethoxysilane-treatment and by the re-infusing lubricant.

Hua et al. [75] reported the synthesis of corrosion and intense cavitation resistant superhydrophobic octadecylphosphonic acid (ODPA) or 1H, 1H', 2H, 2H'-perfluorodecyl phosphonic acid (PFDDPA) functionalized TiO₂ nanotubes arrays (TNTAs). The superhydrophobic TNTAs were tested against abrasion. The abrasion testing was performed using a 50 g weight on both the ODPA-TNTA and PFDDPA-TNTA materials up to a distance of 5 cm on 320-grit sandpaper. The response of water CA vs. abrasion cycles of the superhydrophobic ODPA-TNTA and PFDDPA-TNTA materials is shown in Fig. 18. The abrasion tests revealed that there is no significant effect on the CAs of both the systems. This indicates the robustness of self-assembled monolayer bonding with the TiO₂ nanotubes and the mechanical durability of the TNTA system.

6.2. Mechanical durability: knife-scratch test and sandpaper abrasion test

Wang et al. [67] developed a durable superhydrophobic nanocomposite coating based on fluorosilicone resin and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane functionalized SiO₂ nanoparticles. Cross-cut knife-scratch tests were performed on the superhydrophobic nanocomposite coating (Fig. 19a). The scratch tests generated deep vertical cross-scratches on the nanocomposite coating (Fig. 19b). The cross-cut test results revealed no marks of water drops when they rolled off the nanocomposite coating, indicating good mechanical stability of the coating.

The wear resistance of the coatings was investigated by sandpaper abrasion tests using SiC sandpaper (1000 grit) with a weight of 200 g and pressure of 8 kPa (Fig. 19c). The abrasion test results indicated that the superhydrophobic surfaces maintained the CA > 150° with a SA < 10° even after 20 abrasion cycles (Fig. 19d). The CA reduced to 150°, while the SA abruptly increased to 49.5° after 40 abrasion cycles (Fig. 19e). The SEM results revealed a coarse surface with many bulges before the abrasion test of the coating (Fig. 19f) and flat surface with exposed nanoparticles after the abrasion test (Fig. 19g). That might be responsible for an abrupt increase in the SA and a slight reduction in the CA of the developed coating. The knife-scratch test and abrasion tests clearly indicated the good mechanical durability of the developed SHCs.

6.3. Long-term durability in air, thermal stability, durability in water and adhesive tape peeling

Li et al. [142] reported a facile and cost-effective process to synthesize a SHC based on Zn using the electrodeposition method followed by a hydrothermal process for in-situ generation of ZnO nanosheets. The SHC was obtained after surface functionalization of the substrate

using a low-energy pentadecafluorooctanoic acid. For the SHC, high water CA ~ 158° was obtained with a SA of 6°. The mechanical stability of the developed SHC was tested using various tests such as long-term durability, thermal stability, durability in water and adhesive tape peeling durability. The CA of the SHC slightly changed and still greater than 150° even after storing of the coating in air medium for six months. It reveals the coating has noteworthy long-lasting stability. The SHC was tested at a high temperature of 200 °C for 7 h and it was realized that the CA not changed significantly and remained more than 150° indicating the good thermal stability. The SHC was tested by immersing it in water for 4.5 h, the immersion of the coating in water showed a negligible effect on the CA till 4.5 h. The water CA of the coating even after the immersion test was more than 150° indicating good water immersion stability of the coating. The adhesive peel test of superhydrophobic Zn coating consisting ZnO nanosheets on steel surface did not change the water CA much. After the peeling test (7 times peeling), the CA of the coating was realized more than 150° indicating the excellent mechanical stability of the coating.

Qian et al. [143] prepared a corrosion resistant micro and nanosilica-based SHCs on Mg alloy (AZ31B) using the spraying technique. 1H,1H,2H,2H-Perfluorooctyltriethoxysilane was used as a surface modifying agent. More than three times low corrosion was reported for the coated alloy compared to the uncoated alloy due to the increase in water CA from 32° to over 155°. Additionally, for the SHCs, the mechanical, chemical and environmental stability using abrasion test, immersion test, and salt spray test were performed respectively. The mechanical stability of the developed SHCs was estimated by sandpaper abrasion test, consisting a weight of 100 g with 1200 grit sand paper. Even after the 10 cycles of the abrasion test, the CA was greater than 155° with SA less than 3°, indicating good mechanical stability of the coating.

The chemical and environmental stability of SHCs was examined by determining the variation of water CA and SA with respect to the exposure of the coating to air for about 60 days or immersing the coating in 3.5 wt% NaCl solution for about 168 h. The results showed that the water CA and SA of the SHC have negligible change after exposure to air or immersion in the solution indicating the good chemical and environmental stability.

7. Future trends and concluding remarks

Present literature clearly indicates that unique properties of nano-oxide and CNT can be successfully employed for the development of SHCs for protecting the metal surfaces in challenging environments. Tailored processability, mechanical, thermal and chemical resistance with the flexibility to customize the surface roughness through various functionalization of nano-oxide and CNT based coatings have been a promising coating material for achieving the complete repellency. Although superior anti-corrosive properties were attributed to the development of air barrier film, inhibiting penetration and reaction of

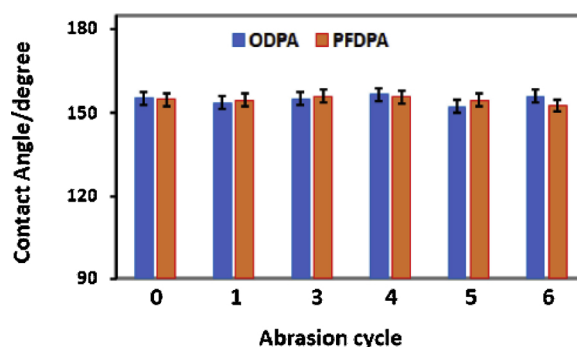


Fig. 18. Water CA vs. abrasion cycles of the superhydrophobic ODPA-TNTA and PFDDPA-TNTA materials [75].

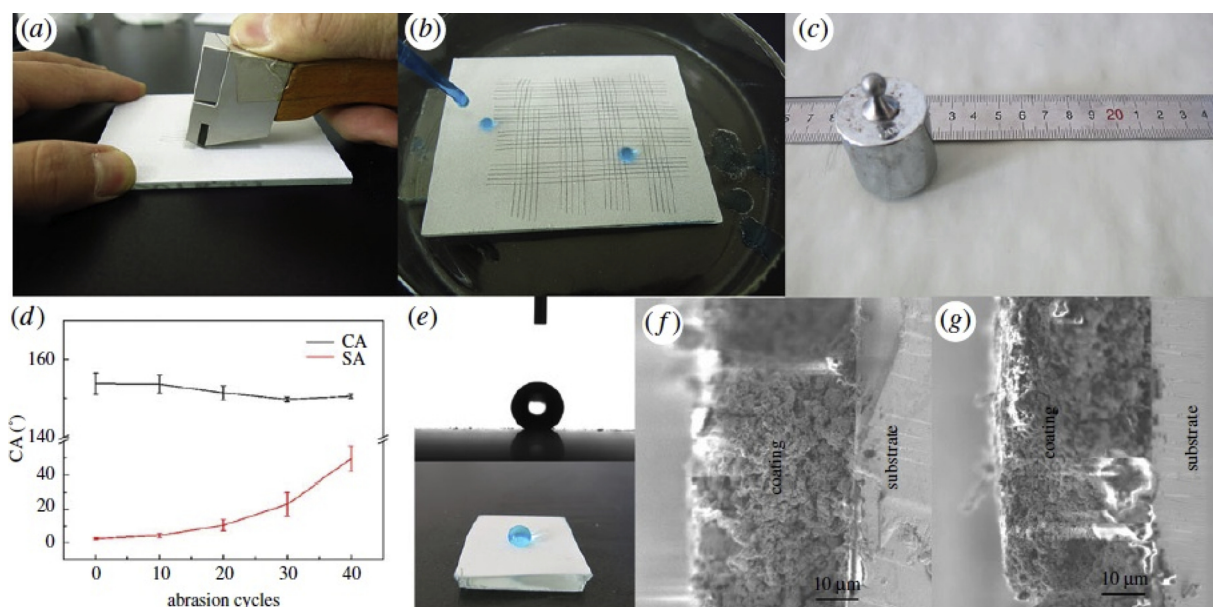


Fig. 19. (a). An illustration of a knife-scratch test of the superhydrophobic nanocomposite coating, (b) rolling of water droplet from the knife-scratched coating, (c) Photograph of abrasion test, (d) The variation of CA and SA vs. abrasion cycles, (e) optical images of the CA of abraded coating and the SEM images of the coating (f) before and (g) after the abrasion tests [67].

corrosive species, still a clearly defined mechanism may require more research at the interfaces of SHCs and metals. Costly precursors, complex experimental processes, sustainability at large scale, toxicity and effect of inherent characteristics of metals remains a little explored area of research. Additionally, the synthesis of a SHC with exceptional water repellency, excellent adhesion performance, prolonged service life for industry scale need to be achieved. Spray coatings, Nanosecond laser treatment based coatings; electro-deposition and chemical etching have shown the promises for the future. Such techniques need a precise control over all the processing parameters, which is highly required in order to develop commercial scale products. Self-healing nanocomposite based corrosion resistant SHCs can open up new window for the research in this field. Such coatings are capable of self-repairing the damaged site and do not lose the superhydrophobicity for the extended time when exposed to harsh environmental conditions. Although superhydrophobic surfaces have been subjected to intensive investigations, it is apparent that further investigations are still necessary for both fundamental and applied aspects.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.porgcoat.2019.105512>.

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