# Durable and Regenerable Superhydrophobic Coating on Steel Surface for Corrosion Protection

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## Abstract

Corrosion limits the usage of steel and leads to the tremendous loss of the economy. Superhydrophobic coating is proven an effective way to prevent corrosion due to its excellent water repellent nature. Herein, we describe the successful preparation of superhydrophobic coating on steel surface which is synthesized by using chemical etching technique with mixture of hydrochloric and nitric acid followed by treatment with lauric acid. By optimizing the etching process parameters, super-hydrophobicity with water static contact angle of 170° and tilt angle of 5° is successfully achieved. Coated steel is found to be thermal, chemical, and mechanical stable. Besides, coating has also good regenerability. Furthermore, coating exhibits the excellent self-cleaning and anti-fogging properties. The electrochemical study is revealed the enhancement of corrosion resistance of steel after coating. This facile strategy inspires the large-scale fabrication of multifunctional steel surfaces for practical applications in self-cleaning, anti-fogging, and corrosion protection.

**Keywords** Superhydrophobic · Self-cleaning · Corrosion resistance · Anti-fogging · Water repellent

## 1 Introduction

Iron-based alloy or steel is widely used in large and small structures, like road, building, bridges, airports, railways, other infrastructure, chemical equipment, plants, home appliances, and other applications because of its high tensile strength, easy availability, and low cost [1, 2]. However, aforesaid applications are restricted due to the dirt accumulation, water vapour condensation (fogging), and corrosion; especially corrosion deteriorates the steel very fast [1–3]. This situation is worsening particularly under water. Anti-dirt, anti-fogging, and anti-corrosive coating on steel surface can solve the aforesaid problem and this can be possible by creating superhydrophobicity on steel surface. It is defined as a condition when the contact angle of water droplet on the surface is greater than 150° and the contact angle hysteresis is lower than 10° [4]. In nature, several biological surfaces, such as water striders, lotus, rose, and rice leaves, possess unique wetting properties [4]. These surfaces have diverse practical applications, including self-cleaning, anti-fogging, anti-corrosion, anti-icing, anti-scratching, anti-fouling, anti-bacterial, anti-ageing, and anti-reflective [4].

Artificially superhydrophobicity can be produced by generating unique micro/nanostructures and modifying the surface chemistry. A variety of techniques for developing superhydrophobic surfaces have been reported, such as electrochemical deposition, phase separation, emulsion, plasma method, electrospinning, solution immersion, chemical vapour deposition, wet chemical reaction, and sol–gel processing [5, 6]. These approaches are able to produce super-hydrophobic surfaces, but many of them are limited due to complicated process, time consuming, expensive equipment, restriction for substrates, not applicable for large-scale production. However, low-cost and easy methods, like immersion, dip coating, and spray coating, can facilitate the practical applications by producing large-scale superhydrophobic surfaces.

Considering the above corrosion problem, several work have been done in developing superhydrophobic anti-corrosive coatings on steel and steel-based alloy system. For instance, Motlagh et al. [7] prepared superhydrophobic and superoleophobic coating for steel surface with

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perfluorodecyltriethoxysilane and $SiO_2$ particles by using spray method and they observed good anti-corrosive property of coated steel. Wen et al. [8] modified steel surface by etching with HF followed by treating with perfluorodecyltriethoxysilane and they found good anti-corrosive and superhydrophobic nature of modified steel surface. Hao et al. [9] electrodeposited copper on steel surface and then treated with alkaline solution to make copper oxide. The copper oxide was later reacted with perfluorooctanoic acid solution and modified steel showed very good self-cleaning and anti-corrosive properties. Meena et al. [10] produced an anti-corrosive superhydrophobic coating on steel surface with polyurethane, $SiO_2$ nanoparticles, and hexadecyltrimethoxysilane by using a spin coating technique.

Li et al. [11] developed an anti-corrosive superhydrophobic coating on steel surface by producing roughness using electrodeposition and hydrothermal method and then reacting with perfluorooctanoic acid. In another work, Xia et al. [12] created a superhydrophobic coating on steel by using $TiO_2$ particles and perfluorodecyltrimethoxysilane and this coated steel also showed anti-corrosive nature. Motlagh et al. [13] synthesized a superhydrophobic and anti-corrosive coating for steel body by using a spray method using perfluorodecyltriethoxysilane and $SiO_2$ particles.

Although corrosion on the steel and steel-based alloy can easily occur and it leads to the tremendous loss of economy, but superhydrophobic coating has been proven an effective way to prevent corrosion because it can be easily precluded corrosive ions and water/moisture from contacting steel surface. In this paper, a superhydrophobic coating on steel surface was synthesized by using very simple chemical etching and immersion techniques. Surface wettability, surface morphology, and chemical composition of coated steel sample were characterized. Additionally, wetting stability of coating under harsh conditions was examined by performing various stability tests. Furthermore, self-cleaning, anti-fogging, and corrosion resistance characteristics of coated samples were also evaluated.

## 2 Experimental Details

### 2.1 Materials Used

Commercially available stainless steel alloy sheets of 2 mm thickness were used as substrates for developing the coating. Acidic etchant nitric acid ($HNO_3$, 100% concentrated) and hydrochloric acid (HCl, 35% concentrated) were acquired from Emplura, Merck Specialties, Pvt. Ltd., India. For low surface energy materials, lauric acid ($CH_3(CH_2)_{10}COOH$), obtained from Loba Chemie Laboratory Reagent and Fine Chemicals Pvt. Ltd, India was used. Other solvents, like ethanol and sodium chloride (NaCl), were procured from

Sigma-Aldrich Co., USA. In this work, Millipore water of 18.2 m$\Omega$ cm resistivity was taken throughout the experiment.

### 2.2 Development of Superhydrophobic Coatings

Prior to the experiment cleaning of the substrates is required to remove all kind of impurities present on the surface. In this, steel samples were rigrously cleaned with the tap water followed by sonication of samples in distilled water (of 18.2 m$\Omega$ cm resistivity) using an ultra-sonicator bath for 10 min. Subsequently, the samples were sonicated in acetone followed by dried at 40 °C for one hour.

In order to generate superhydrophobicity on steel surface, two steps were followed: chemical etching and treatment with fatty acid. Chemical etching was done to create surface roughness as well as for increasing adhesion strength of coating. It was done by chemical etching process in which steel substrates were immersed in an acidic mixture of $HNO_3$ and HCl (ratio 1:3) in distilled water solution. Four immersion times were taken as 15, 30, 45, and 60 min. Afterwards, etched steel were rinsed with distilled water and ethanol to remove extra etchant form the surface. Then, samples were died at 60 °C for one hour to remove cleaning water. In final step, these samples were immersed in lauric acid solution of 20 g/l concentration and left for one day. Later samples were kept in open air for one day for drying.

### 2.3 Characterization of Superhydrophobic Coatings

Wettability, surface morphology, and chemical composition of steel surface before and after coating were characterized. Wetting properties (static contact and tilt angles) of steel samples were measured using Drop Shape Analyser (25, Kruss, Germany) with water droplets of about 4–6 μL. The contact measurements were done at five different positions on each sample, and their averages along with standard deviation were calculated. Surface morphology of the steel surface before and after coating was done by scanning electron microscopy (SEM, Nova Nano SEM FEI). Elemental analysis of uncoated and coated steel was done by energy dispersive x-ray spectroscope (EDS, Nova Nano SEM FEI). As steel surface was etched before treatment of lauric acid, surface roughness is needed to measure and it was done by using stylus profilometer (Vecco Dektak 150). Functional group present on the steel surface after coating was studied by Fourier Transformation Infrared Spectroscopy (FTIR) (Thermo Fisher Nicolet iS10).

Additionally self-cleaning, anti-fogging, and anti-corrosion properties of coated samples were also studied. For self-cleaning property test, dust particles (0.5 g, chalk powder, size -4.5 μm) were sprinkled on the uncoated and coated surfaces and then water was dropped on the dust containing surfaces. Behaviour of water droplets and dust containing

surfaces was observed. Flow of the water droplets along with the chalk powder was recorded by camera (50 frames per second). In anti-fogging test, coated and uncoated steel samples were first kept in very cold environment (deep freezer, − 18 °C) for 5 h and then were exposed to the open atmosphere. While exposing to atmospheric air, the moisture present in the air started condensing over the chilled samples and images were captured by camera. Electrochemical corrosion test for uncoated and coated samples was done by using a potentiostat (7800, Amel Instruments, Italy). It was done in 3.5% (w/v) NaCl solution for 30 min. Obtained polarization curves of both uncoated and coated steel samples were plotted, and corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) for both samples were also calculated.

To make present coating applicable for industrial purposes, wetting stability of coating under harsh conditions was examined by thermal, chemical, and mechanical stability tests. Mechanical durability of steel surface after coating was assessed by adhesive tape peeling, sand paper abrasion, water jet impact, water droplet impact, and surface bending tests. To understand abrasion resistance of coating, sand paper with 20 g (0.2 N) weight was rubbed on coated surface in back and forth directions. This was repeated until coating lost its wetting property which was confirmed by measuring contact angle after regular interval of test cycle. Coating adhesiveness was checked by repeatedly gluing and peeling off an electrical insulation tape (adhesive strength—100 N/m) on the coated sample. This test was continued until loss of superhydrophobicity which was confirmed by measuring contact angle after regular interval of test cycle gluing and peeling off.

Droplet impact tests were carried out by dropping water droplets from different heights. While droplets with different velocity (kinetic energy) impacted on the surface, their response was captured by camera. In another experiment, a jet stream of water which makes an angle of about 40° and impact speed of 2.6 m/s was sprayed on the uncoated and coated steel samples. Interaction of water jet and surface was observed. Besides, uncoated and coated samples were kept on the water surface, and their sinking or floating behaviour was observed. Additionally mechanical durability was also studied by surface bending/folding tests, in which coated samples were simply folded in 90° and 180° and then unfolded. These folding and unfolding tests were repeated until sample lost its wettability which was confirmed by checking contact angle at folding area on the surface.

Annealing effect of steel sample after coating was studied by keeping one hour samples in a hot air over at elevated temperature range of 25 to 250 °C. After one hour of annealing, the samples were kept in open air to drying for 6 h and then contact angels were measured. Besides, the effect of chemical contact on the wetting stability coating was examined by immersing coated sample in sea water solution (3.5% by weight NaCl). Wetting properties of immersed samples were measured at regular interval of immersion. Further, regenerability of coating on steel surface was checked by two steps: destroying the coating by heating the sample at 300 °C for 24 h and regeneration of coating by immersing the damaged sample in lauric acid solution.

## 3 Results and Discussion

In this paper, surface modification of steel substrate was done by chemical etching technique with $HCl + HNO_3$ followed by treatment with lauric acid. Wettability, surface morphology, and chemical composition of coatings were characterized. Contact angles of samples were measured using contact angle measurement technique. It is found that cleaned steel surface before coating shows the hydrophilic in nature with water static contact angle of $72 \pm 3°$. Coating was done on cleaned steel after etching and subsequent treatment with lauric acid. Since the etching time was varied from 15 to 60 min during the synthesis process, whereas treatment time with lauric acid was kept constant; therefore, measured water static contact angles of coated steel samples were plotted against the etching time as shown in Fig. 1.

While changing the etching time, shape and size of microstructures change and so water static contact angle also changes. After 15 min etching and 24 h lauric acid treatment, water static contact angle increases from 72° of the as-received unmodified steel to about $90 \pm 5°$, i.e. by 15 min etching superhydrophobicity cannot be achieved. This enhancement of contact angle is due to lauric acid only and 15 min etching is not sufficient to create required roughness. Further increasing etching time water contact angle increases. After 30 min etching and 24 h treatment with lauric acid, it shows the water static contact angle of $130 \pm 5°$. Contact angle further increases to $163 \pm 14°$ if etching time is 45 min. This modified surface attains superhydrophobicity; however, the water static contact angle shows the high standard deviation which may be nonuniform surface roughness and coating. Additionally sliding angle for above surface is found to be more than 10°. Therefore, further etching is required.

After 60 min etching and 24 h treatment with lauric acid, steel surface successfully achieves the superhydrophobicity with water static contact angle of $170 \pm 6°$ and sliding angle of $5 \pm 0.5°$. This sample shows the good uniform superhydrophobic nature. Surface morphology of this sample was done by SEM and it is shown in Fig. 2. Morphology of uncoated steel was also examined and compared with coated one. It shows no microstructure on the uncoated surface. After etching and treatment with lauric acid, surface morphology of steel surface changes and crater-like micropatterns are formed as shown in the SEM images. The surface

**Fig. 1** Water contact angle of steel surface after chemical etching and treatment with lauric acid. Etching time was varied from 15 to 60 min, whereas treatment time with lauric acid was kept constant
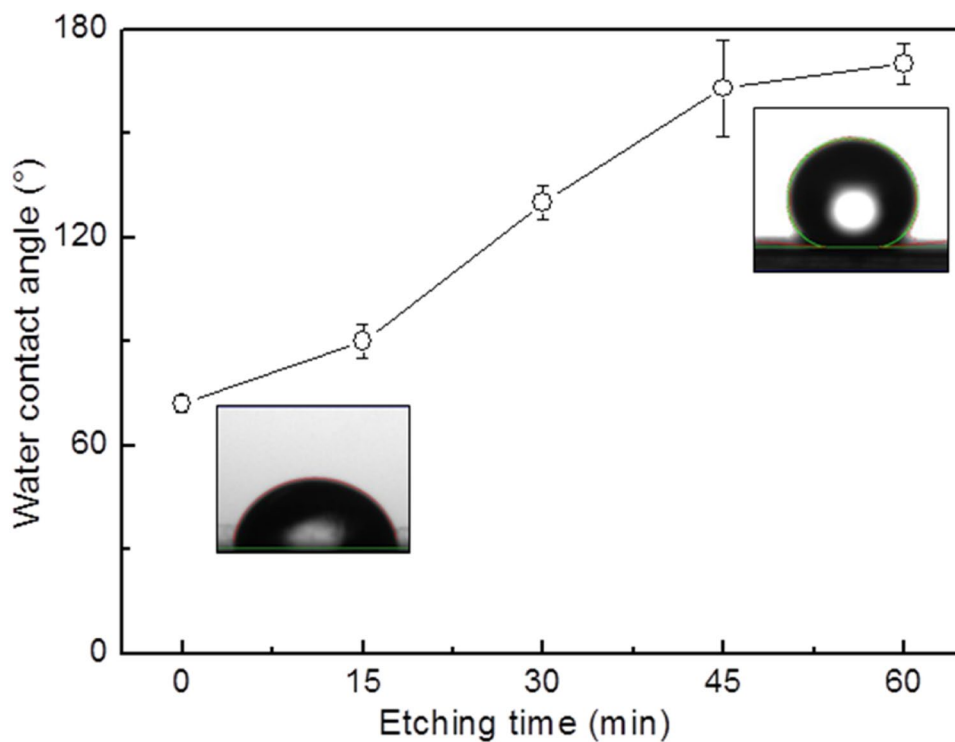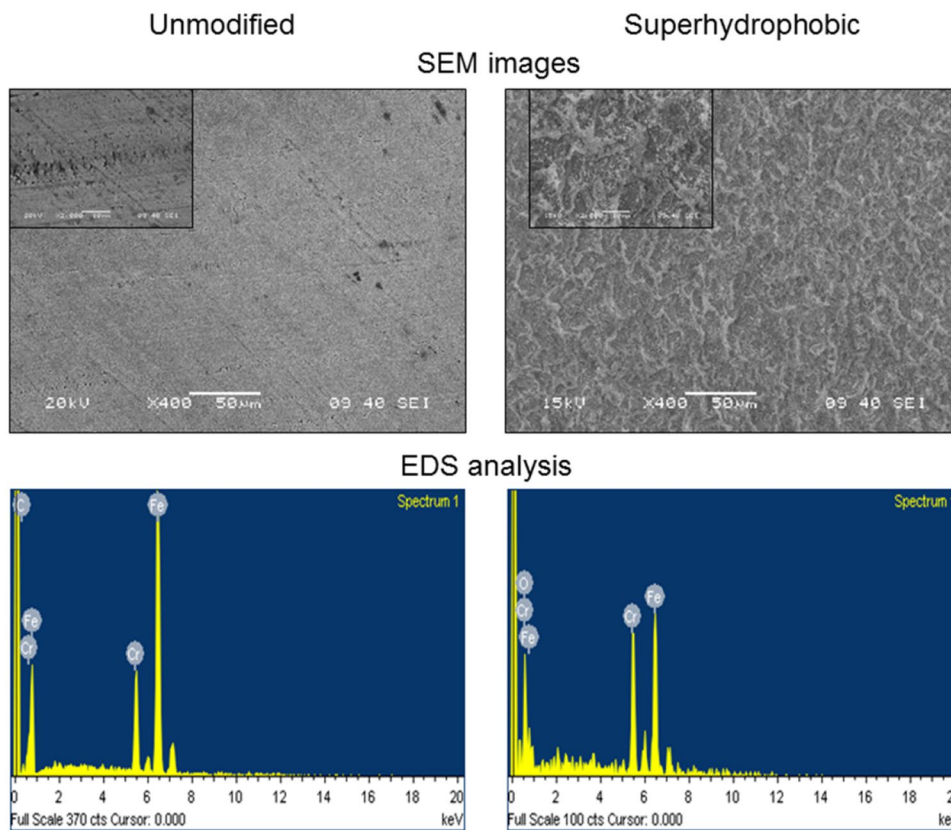


**Fig. 2** SEM images of uncoated and coated steel surfaces. Inserts show the water droplet image on corresponding steel surfaces. EDS spectrum of uncoated and coated steel surfaces



roughness of uncoated and coated samples was measured using stylus profilometer. It is found that surface roughness of coated steel surface is $0.35 \pm 0.03$ µm, whereas it is $0.085 \pm 0.044$ µm for uncoated sample.

It can be concluded that the water contact angle increases with etching time and superhydrophobicity can be achieve easily by adjusting etching time.

Creation of superhydrophobicity on steel surface after etching and treatment with lauric acid can be explained as follows. Etching with acidic solution makes the surface rough. Ions present in etchant solution attacks on steel surface and the dissolution reactions taking place are as follows:

$$Fe^{3+} + 3NO_3^- \rightarrow Fe(NO_3)_3, \tag{1}$$

$$Fe^{3+} + 3Cl^- \rightarrow FeCl_3. \tag{2}$$
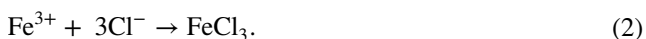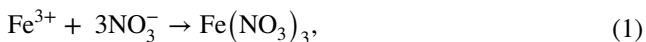
The product formed from reactions (1) and (2) are ferric (or ferrous) chloride and ferric (or ferrous) nitrate; those are pretty soluble in the etchant solution and it enables the steel surface to be etched uniformly. This process will also generate roughness on a stable native oxide layer containing steel surface. While treating etched steel with lauric acid solution, the carboxyl group (R-COO$^-$) of lauric acid is attached to the metal surface (reaction 3). In this, positive end of the lauric acid (carboxyl group) reacts with the hydroxyl or the iron atom ($Fe^{3+}$) through dehydrating process (reaction 3) and forms iron laurate ($Fe(CH_3(CH_2)_{10}COO)_3$):

$$Fe^{3+} + 3CH_3(CH_2)_{10}COO^- \rightarrow Fe(CH_3(CH_2)_{10}COO)_3. \tag{3}$$
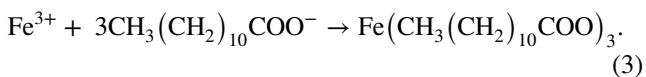
To examine the elements present in coated steel surface, EDS analysis was performed. EDS spectra in Fig. 2 shows the presence of carbon, oxygen, chromium, and iron on the steel surface after coating and it confirms the formation of iron laurate after treatment of sample with lauric acid. Additionally FTIR analysis was performed in order to examine the functional groups present on the coated steel surface. The results of FTIR are shown in Fig. 3. FTIR spectrum shows the presence of the carboxylate group at peaks of 1538 and 1575 cm$^{-1}$ and carbonyl group (C=O) at 1698 cm$^{-1}$ [14]. Besides, peaks at 2850 and 2917 cm$^{-1}$ confirm the presence of symmetric and asymmetric stretching vibration of –CH$_2$ groups, respectively [15]. Thus, the presence of the carboxylate, carbonyl, and alkyl groups confirms the formation of laurate on the steel surface after coating. Grooves on the roughed surface are formed due to the chemical etching and can easily trap air. This makes composite interface of solid–liquid–air beneath the water droplet [16]. Addition to this, attachment of laurate (hydrophobic alkyl long chains) makes surface water repellent [17, 18]. According to Cassie state [16], composite interface beneath the water drop and hydrophobic tails makes the surface superhydrophobic.

Steel or steel alloy has plenty applications in under water or water-based liquid, such as part of ship, reactors, turbines, and home appliances. But these applications are limited due to corrosion. Therefore, corrosion behaviour of steel after superhydrophobic coating was examined by using a potentiostat in a 3.5 (w/v) % NaCl solution for 30 min. This was further repeated for uncoated steel sample to compare the results of coated sample. Obtained polarization curves for both samples are plotted as shown in Fig. 4. Corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) values are obtained from the potentiodynamic polarization curves

**Fig. 3** FTIR spectrum of superhydrophobic steel surface showing the presence of carboxylate, carbonyl, and alkyl groups
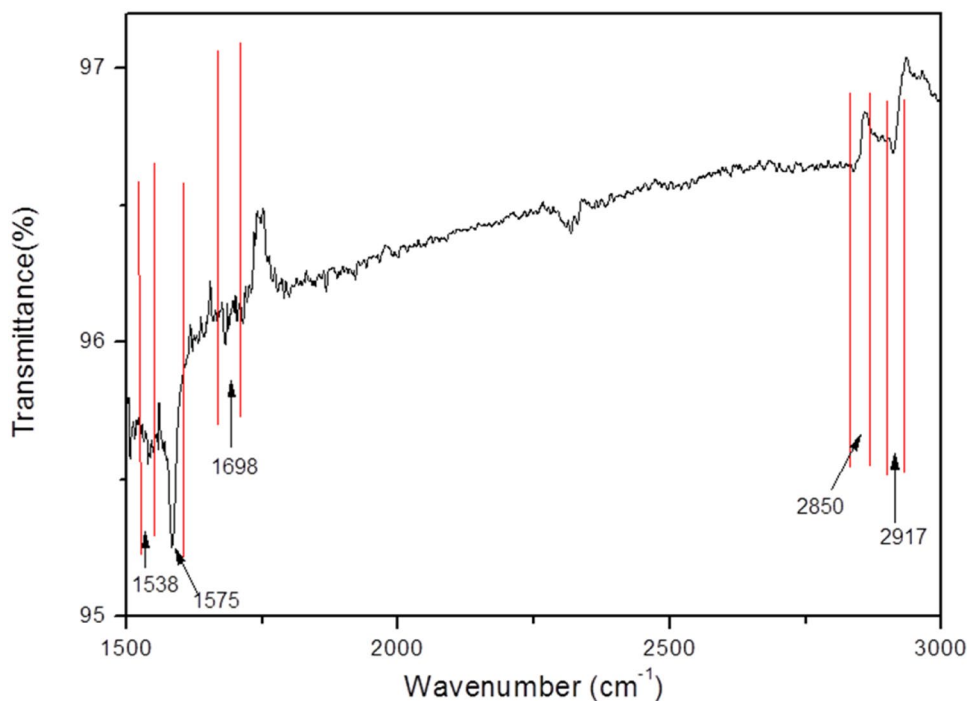
of uncoated and coated steel surfaces and listed in Table 1. $E_{corr}$ and $I_{corr}$ values for uncoated steel sample are 0.131 V and 0.008 mA/cm$^2$, respectively. After coating, $E_{corr}$ and $I_{corr}$ for superhydrophobic steel sample are found to be 0.169 V and 0.002 mA/cm$^2$, respectively. This shows that $I_{corr}$ for steel sample after coating decreases and on the contrary $E_{corr}$ increases. Ions and water molecules present in NaCl solution react immediately with uncoated steel surface due to its hydrophilic nature. In general hydrophilicity entices the ion because of polar–polar attraction. But after coating, surface becomes superhydrophobic, i.e. it makes a nonpolar barrier. Therefore, the reaction between these polar components (ions and water molecules) and surface cannot be easily happened due to polar–nonpolar repulsion. Additionally, the contact between ions present in NaCl solution and steel surface is very low due to air tapped in the groves present on the coated steel surface. Thus, corrosion resistance of the steel sample improves after present coating.

Since the prepared coated steel sample shows the static contact angle more than 150° and tilt angle less than 10°, it should exhibit the self-cleaning property. This was tested in lab-scale experiment, in which both uncoated and coated steel surfaces were sprinkled with dust particles and water was dropped on dust containing samples as shown in Fig. 5. It shows that water immediately spreads over the uncoated steel surface due to its hydrophilic nature. Water is unable to clean the surface and leaves the messy surface. This test further shows that when water droplets fall on the dust

**Table 1** Corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) values obtained from potentiodynamic polarization curves for steel surfaces before and coating in 3.5% NaCl solution for 30 min

| Specimen | $E_{corr}$ (V) | $I_{corr}$ (mA/cm$^2$) |
|---|---|---|
| Uncoated steel | 0.131 | 0.008 |
| Coated steel | 0.169 | 0.002 |

containing superhydrophobic steel surface, these droplets roll from the surface because of low adhesion between the droplets and surface. By rolling of water droplets, they take away the dust particles from the superhydrophobic surface due to low adhesion between dust particles and surface. It results in the cleaning of the surface, indicating the great self-cleaning ability of the coating.

Water vapour present in atmospheric air generally condensates on the metallic bodies and corrodes. In general, there are several methods to protect the metals from condensation of water vapour (fogging). Considering this, antifogging test on the coated steel sample was performed by exposing the chilled sample to humid atmosphere. In this regard, coated sample along with uncoated sample was kept in deep freezer for overnight and then exposed to open environment. It is observed that uncoated steel is wetted with a thin layer of water after condensing of air moisture (Fig. 5) due to its hydrophilic nature and no water droplet on superhydrophobic surface is observed because of the excellent

**Fig. 4** Potentiodynamic current–potential curves for steel surfaces before and coating in 3.5% NaCl solution for 30 min

## Self-cleaning test

### Unmodified

### Superhydrophobic
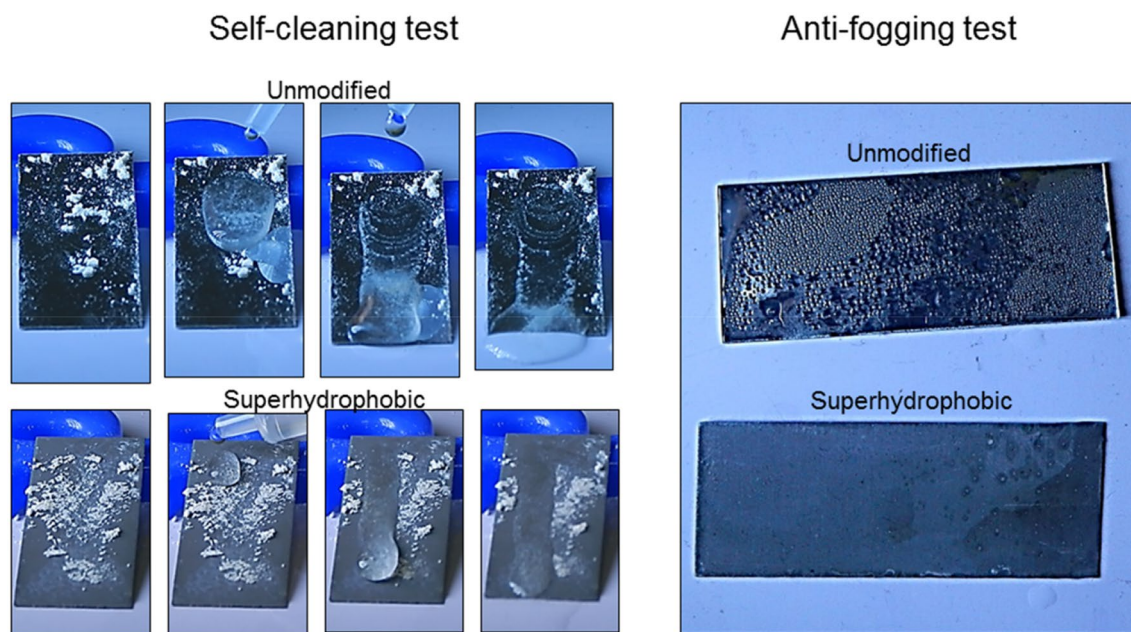
## Anti-fogging test

Unmodified

Superhydrophobic
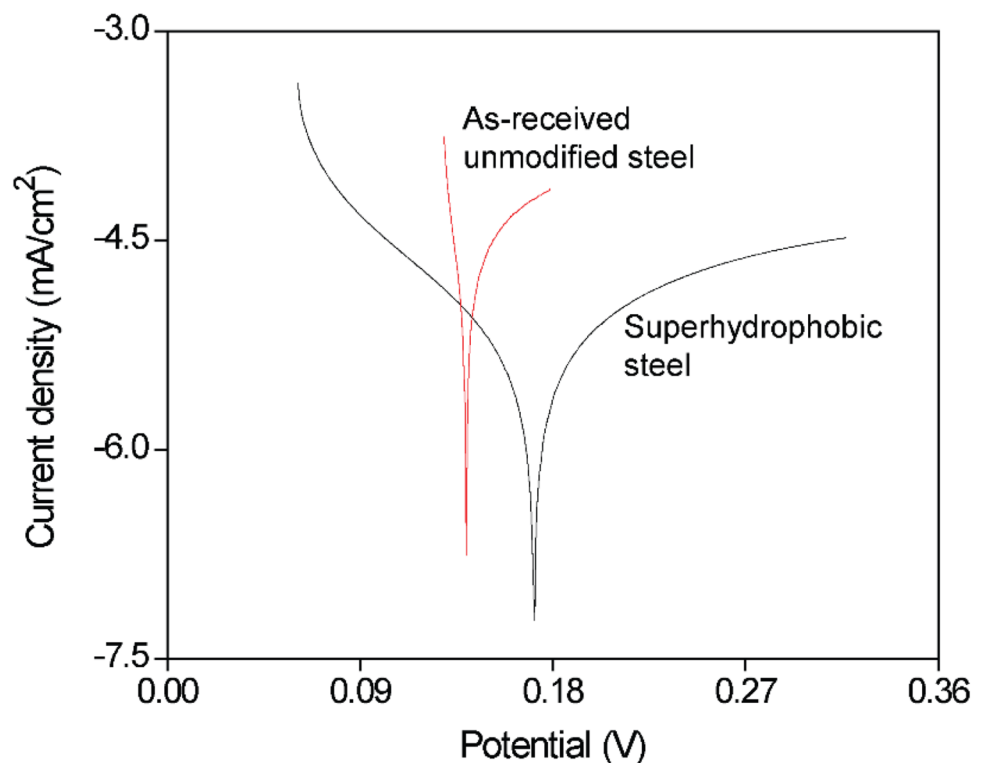
**Fig. 5** Optical images of self-cleaning behaviour of steel surface before and after coating. Optical images of condense droplets on chilled uncoated and coated steel surfaces, revealing anti-fogging property of coating

water repellent nature of the surface. Thus, superhydrophobic steel sample exhibits the excellent anti-fogging property.

### 3.1 Wetting Stability Under External Disturbances

External disturbances, like chemical, thermal, mechanical, and other environmental factors, influence the surface properties, such as morphology, texture, and wettability. Therefore, it is essential to examine the wetting properties in harsh conditions. Mechanical durability of coating can be done by performing water droplet and jet impact, adhesive tape peeling, floating, abrasive with sand paper, and bending tests. If high kinetic energy water droplet and jet falls on the surface, it can destroy the surface textures. Therefore, in this work we have studied the water droplet and jet impact on the superhydrophobic steel surface. Figure 6 shows the water droplet impact behaviour on the coated steel surface. In this study, the droplets were dropped from different height and they impacted on the surface with different impact velocities. Nondimensional Weber (Wb) and Reynolds (Re) numbers are calculated by using Eqs. (4) and (5):

$$\text{Wb} = \frac{\rho v^2 D}{\gamma}, \tag{4}$$

$$\text{Re} = \frac{\rho v D}{\mu}, \tag{5}$$
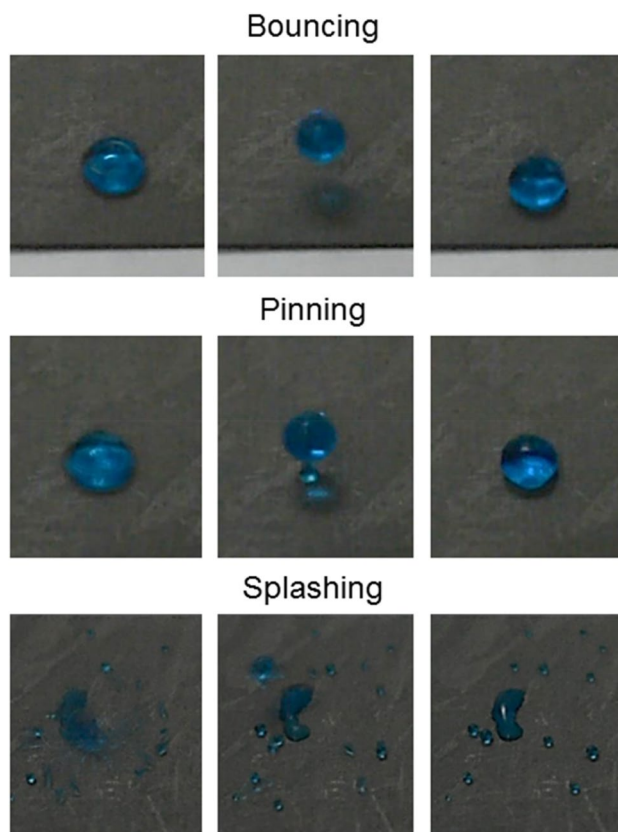
Bouncing

Pinning

Splashing

**Fig. 6** Optical photographs showing water drop impact behaviour on coated steel surface. Bouncing of droplet at low velocity, pinning of droplet at critical velocity, and splashing of water droplet at very high velocity are observed

where ρ is the density of water, D the diameter of water droplet, v the impact velocity, γ the surface tension of water, and μ is the viscosity of water. Different droplet behaviours have been observed at different impact velocities. With low kinetic energy ($v = 0.45$ m/s, Wb = 2.2, Re = 450), water droplet rebounds and bounces back from the surface as shown in Fig. 6. In this situation, kinetic energy of water droplet is lower than surface energy of coated surface and elastic collision of droplet occurs. On increasing dropping height of droplet, kinetic energy of impacted droplet is enough to replace the air trapped in roughed grooves and at high kinetic energy ($v = 0.63$ m/s, Wb = 4.34, Re = 632), only partial rebound of water droplet takes place and remaining water remains sticky on the surface as shown in Fig. 6. Due to sufficient kinetic energy of water droplet Cassie state converts into Wenzel State and pining of droplet takes place. With very high impact kinetic energy, droplet completely replaces the air trapped in roughed grooves, and splashing of water droplet coated surface is regenerable observed (Fig. 6).

A continuous high-speed water also destroys the texture and surface properties. Figure 7 shows the water jet impact test on uncoated and coated steel samples. Since uncoated steel surface is hydrophilic in nature, so water immediately wets the surface and spreads without showing any bouncing nature. On the other hand, due to excellent water repellent nature of coated steel surface, water does not wet the surface and bounces in the opposite direction as shown in Fig. 7. This test has continued on one spot of sample for one min and it is observed that surface continuously bounces off the water jet stream in opposite direction without fail. This means coating can sustain water jet impact and confirms the mechanical stability of coating.

Figure 7 also exhibits floating test of coated sample on water surface. It shows that coated steel surface remains floated when it retains over the water surface. It is mainly due to its excellent water repellent nature and similar observation has also observed in previous studies [17, 18]. On the contrary, uncoated steel sample sinks immediately in the water due to its hydrophilic nature. To check its floating ability, coated steel alloy sample was kept on water surface for four weeks. It is noticed that coated steel alloy sample remains continuously floated, exhibiting the excellent water repellent nature of coating.

In another test for mechanical durability test, superhydrophobic coated steel sample was folded in such a way it makes itself 90° as shown in Fig. 7. It was also completely folded and unfolded. Wettability was checked in kink/bend areas and it is found that surface folding or bending does not
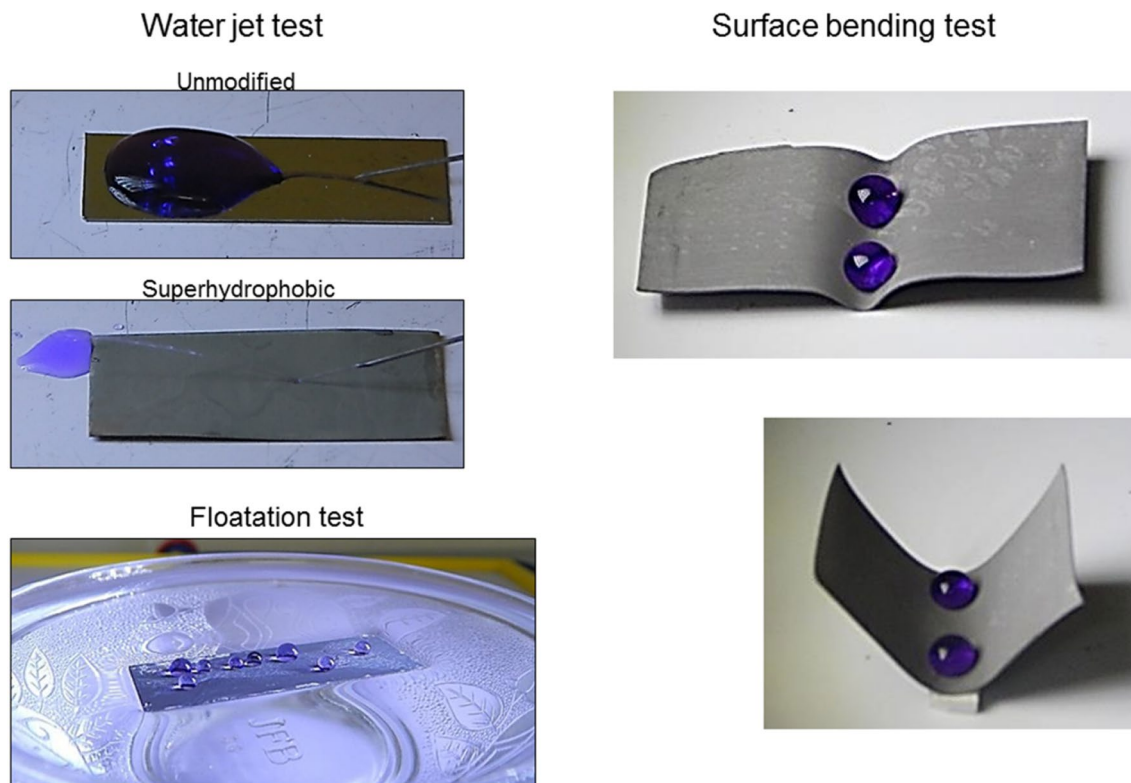


Fig. 7 Optical images of water jet, floatation, and surface bending tests. In water jet, water wets the uncoated surface, whereas it bounces back in opposite direction for coated surface. In water floatation test, superhydrophobic steel sample floats on the water surface. In surface bending tests, coating survives after several folding

have much effect on the wettability and superhydrophobicity. It is experimentally confirmed that wettability of coated steel sample does not amend till 8 times of folding and de-folding. After 10 times of folding and de-folding, water static contact angle does not change and remains more than 150°, but tilt angle is found to be more than 10°, i.e. it attains the sticky superhydrophobicity. In this situation, surface starts to worn out.

In this paper, sand abrasion and tape peeling tests were performed to evaluate abrasion resistance and adhesive strength of coating, respectively. In sand abrasion test, coated steel sample was rubbed in forth and back directions on the sand paper with 0.2 g weight as shown in Fig. 8. Coated sample remains unaffected up to 45 times rubbing on the sand paper. However, coating starts deteriorating after 50 abrasion cycles due to repeatedly rubbing on sand paper and water static contact angle is found to be $105° \pm 9°$ with tilt is found greater than 60°.

Figure 9 demonstrates the steps in tape peeling test to examine adhesive strength of superhydrophobic steel sample. In this, an electrical insulation tape was glued and unglued several times and at regular interval of test, wetting properties were measured. Wetting properties of coating is found to be unchanged even after 30 times of tape peeling. However, coating loses its superhydrophobicity after 40 cycles, and achieves sticky superhydrophobicity due to destroying the coating surface by multiple gluing and de-gluing of tape on the surface.

In industrial work, pipelines, reactors, tanks, and other equipment are made of steel or steel-based alloys and these surfaces are to be exposed to elevated temperature; therefore, thermal stability of present coating should be examined. In order to do this, coated steel samples were annealed at elevated temperatures varying from 25 to 250 °C in a hot air oven for 1 h. After cooling, water contact angle of annealed samples were measured and results are shown in Fig. 10. It shows that water static contact and tilt angles remain constant after annealing the coated steel sample under the temperature range of 25 to 125 ℃, showing thermal stability of coating. Annealing at 150 °C and 175 °C, water static contact angle slightly decreases and it is found to be 155° and 150°, respectively; however, tilt angle increases rapidly, i.e. after annealing at 150–175 °C coating shows the sticky superhydrophobicity. After annealing at 200 °C or more, surface no longer remains superhydrophobic because of damaging of coating under this temperature range.
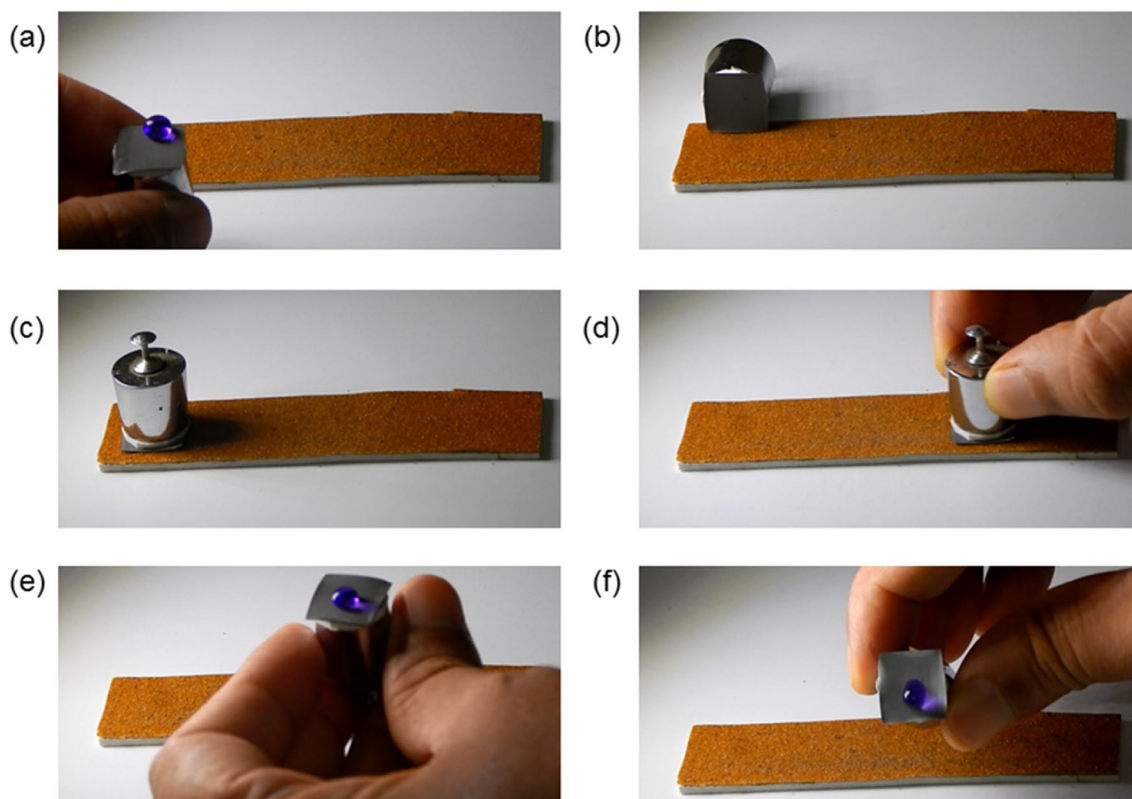


**Fig. 8** Optical images of superhydrophobic steel surface **a** before, **b–d** during, **e** after 45 cycles, and **f** after 50 cycles of abrasion tests by sand paper with 0.2 N force
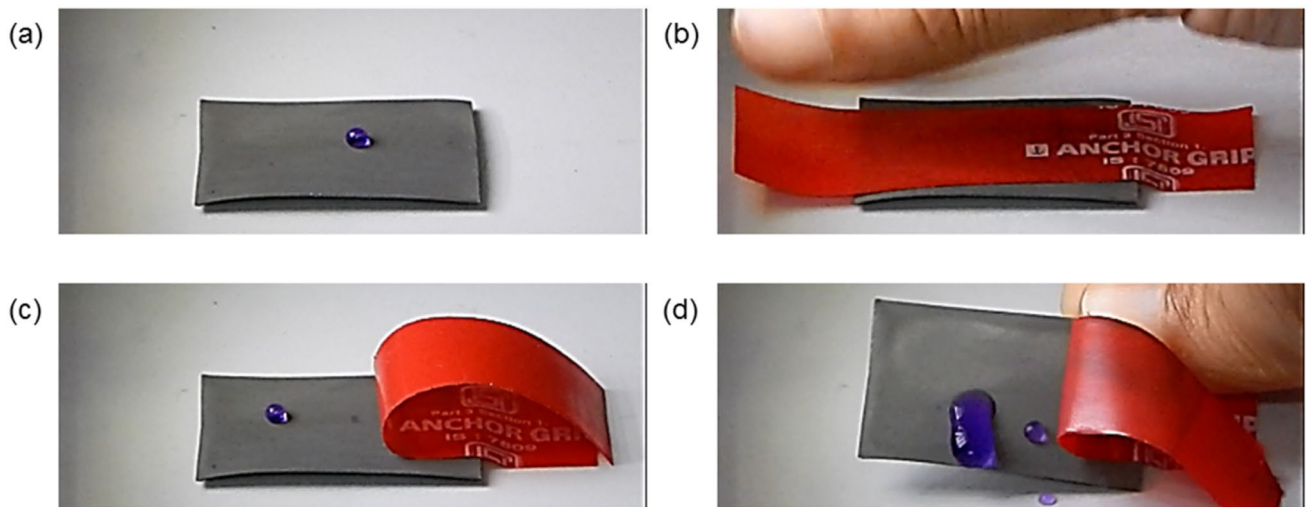
**Fig. 9** Optical images of superhydrophobic steel sample **a** before, **b–d** during, **e** after 30 cycles, and **f** after 40 cycles of tape peeling tests by insulation tape
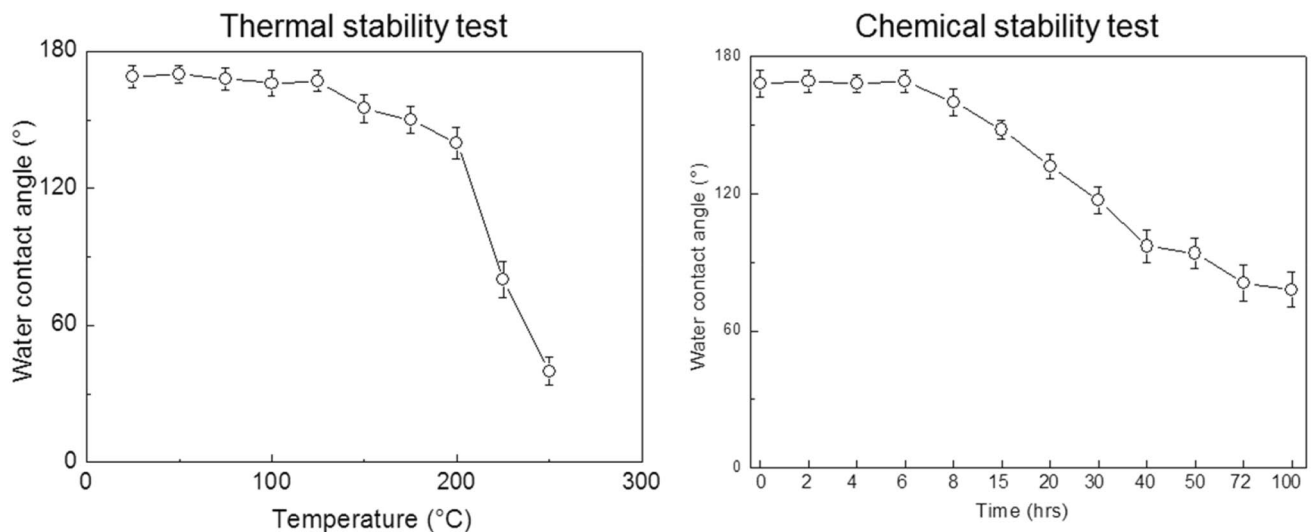


**Fig. 10** Water static contact angle of superhydrophobic steel samples as a function of annealing temperature and immersing time of sample in 3.5% NaCl solutions

Furthermore, it is important to evaluate chemical stability of coating for practical applications. In order to inspect the longevity of coating, superhydrophobic steel samples were immersed in sea water (3.5% NaCl solution, pH 8) and wetting properties of immersed samples were measured after regular interval of 2 h. Results of this study are shown in Fig. 10. It is found that coating remains unaffected up to 6 h of immersion in pH 8 solution, showing the chemical stability of coating. After that, water contact angle slowly decreases with immersion time as shown in Fig. 10 due to the damaging of the surface.

After partial or complete damaging of coating sample, it is necessary to repair the coating without further delay. In this, coating was destroyed by continuously annealed at temperature of 300 °C for 6 h and it can damage the surface. The water static contact angle is found to be less than 10°, i.e. coating has completely damaged. To regenerate superhydrophobicity on the surface, damaged sample was again immersed in ethanol solution of lauric acid for 24 h. After air dried, water contact angle was measured. Water static contact and tilt angles are found to be about 165° and 5°, respectively, showing regenerability of coating.

## 4 Conclusions

In this work, a superhydrophobic coating on steel surface was prepared by using chemical etching process with $HCl + HNO_3$ solution and simple immersion in lauric acid solution. With etching time, surface roughness and water contact angle also increase. By optimizing the etching process parameter, superhydrophobicity with water static contact angle of 170° and sliding angle of 5° is successfully achieved. A rough micropattern on the coated surface is confirmed by SEM analysis. FTIR and EDS analyses confirm the coating formation.

Mechanical durability of coating was experimentally evaluated by water droplet and jet impact, adhesive tape peeling, floating, abrasive with sand paper, and bending tests. From water droplet impact test, if water is dropped at low velocity on the coated surface, it remains in superhydrophobic (Cassie) state, but if water is dropped with high velocity, it does not remain in superhydrophobic (Wenzel) state. Wetting properties of coating does not change even after flow of continuous water jet, folding and bending the sample, repeatedly scratching with sand paper, and multiple time gluing and ungluing the adhesive tape. Coating remains in superhydrophobic state even after several hours of immersion in sea water and annealing at temperature range of 25–150 °C, indicating the excellent chemical and thermal stability of coating. In this work, easy regenerability of coating is experimentally verified. Present coating shows the excellent self-cleaning and anti-fogging properties. It also exhibits excellent corrosion resistance. The aforesaid durable and regenerable superhydrophobic steel surfaces have potential industrial applications.

## Declarations

**Conflict of interest**  There is no conflict to declare.

## References

1. Bhadeshia HKDH, Honeycombe SR (2006) Steels: microstructure and properties, 3rd edn. Butterworth-Heinemann, Oxford
2. Anonymous (1994) In Annual book of ASTM standards, Metals test methods and analytical procedures, ASTM standard 3–89 (volume 03.02, wear and erosion; metal corrosion), Philadelphia, PA
3. Anonymous (2005) In Corrosion of metals and alloys-electrochemical test methods-guidelines for conducting potentiostatic and potentiodynamic polarization measurements, ISO 17475:2005. American National Standards Institute. Washington, DC
4. Bhushan B (2018) Biomimetic: bioinspired hierarchical-structured surfaces for green science and technology, 3rd edn. Springer International, Cham
5. Nanda D, Sinhamahapatra A, Kumar A (2020) Superhydrophobic metal surface. In: Karapanagiotis I, Hosseini M (eds) Materials with extreme wetting properties: methods and emerging industrial applications. Springer, New York
6. Nanda D, Kumar A (2019) Methods and fabrication techniques of superhydrophobic surfaces. In: Samal S, Mohanty S, Nayak SK (eds) Superhydrophobic Polymer coatings: fundamentals, design, fabrications, and applications, 1st edn. Elsevier, Amsterdam
7. Motlagh NV, Birjandi FC, Sargolzaei J, Shahtahmassebi N (2013) Durable, superhydrophobic, superoleophobic and corrosion resistantcoating on the stainless steel surface using a scalable method. Appl Surf Sci 283:636–647
8. Wen N, Peng S, Yang X, Long M, Deng W, Chen G, Chen J, Deng W (2017) A Cycle-etching approach toward the fabrication of superamphiphobic stainless steel surfaces with excellent anticorrosion properties. Adv Eng Mater 19:1600879
9. Hao L, Sirong Y, Xiangxiang H (2016) Fabrication of CuO hierarchical flower-like structures with biomimetic superamphiphobic, self-cleaning and corrosion resistance properties. Chem Eng J 283:1443–1454
10. Meena MK, Tudu BK, Kumar A, Bhushan B (2020) Development of polyurethane based superhydrophobic coatings on steel surfaces. Phil Trans R Soc A 378:20190446
11. Li H, Yu S (2016) Facile fabrication of micro–nano-rod structures for inducing a superamphiphobic property on steel surface. Appl Phys A. https://doi.org/10.1007/s00339-015-9544-y
12. Xia B, Liu H, Fan Y, Zhu W, Geng C (2017) Preparation of robust $CuO/TiO_2$ superamphiphobic steel surface through chemical deposition and sol–gel methods. Adv Eng Mater 19:1600572
13. Motlagh NV, Sargolzaei J, Shahtahmassebi N (2013) Super-liquid-repellent coating on the carbon steel surface. Surf Coat Technol 235:241–249
14. Li W, Zaloga J, Ding Y, Liu Y, Janko C, Pischetsrieder M, Alexiou C, Boccaccini AR (2016) Facile preparation of multifunctional superparamagnetic PHBV microspheres containing SPIONs for biomedical applications. Sci Rep 6:23140–23151
15. Wen R, Huang Z, Huang Y, Zhang X, Min X, Fang M, Liu Y, Wu X (2016) Synthesis and characterization of lauric acid/expanded vermiculite as form-stabilized thermal energy storage materials. Energy Build 116:677–683
16. Cassie ABD, Baxter S (1944) Wettability of porous surfaces. Trans Faraday Soc 40:546–551
17. Varshney P, Lomga J, Mohapatra SS, Kumar A (2018) Durable and regenerable superhydrophobic coatings for aluminium surfaces with excellent water-repellent self-cleaning and anti-fogging properties. Tribol Int 119:38–44
18. Varshney P, Mohapatra SS, Kumar A (2016) Superhydrophobic coatings for aluminium surfaces synthesized by chemical etching process. Int J Smart Nano Mater 7:248–264

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