Fabrication of cerium myristate coating for a mechanochemically robust modifier-free superwettability system to enhance the corrosion resistance on 316L steel by one-step electrodeposition

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ABSTRACT

Redundant deposits formation on steel through interaction with liquids is an integral problem that results the reduction in function and durability. Here, we report a new method to form a modifier-free durable superhydrophobic and highly anti-corrosive surface by one-step electrodeposition method. Surface morphologies, chemical composition and wettability characterized by field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), laser Raman spectroscopy (LRS), Fourier transform infrared spectroscopy (FT-IR) and optical contact angle measurements, respectively. The highest average water contact angle (CA) $167.7 \pm 2.4^\circ$ on fabricated surface achieved

numerically and experimentally. The phase-field simulation for transient evolution of water droplet performed for superhydrophobic surface revealed that the rate of contact angle increase is greater at beginning and smaller at the equilibrium state. Superwetting surfaces exhibit enhancement of corrosion resistance based on electrochemical impedance spectroscopy, Tafel polarization curves and shear abrasion tests with excellent mechanical durability. Furthermore, the characteristics of as-fabricated mechanically durable and the stabilization of chemicals on the surface were observed. This work gives a new pathway to attain chemically and mechanically stable, eco-friendly, and corrosive-resistant superhydrophobic coating with low surface energy hydrophobicity index ($\beta_s = -0.937$) on steel 316L and should have a reassuring future in increasing range of industrial applications.

Keywords: Superhydrophobicity, Electrodeposition, Phase field simulation

1 Introduction

Degradation of metals and their alloys triggered via chemical and electrochemical corrosion that leads to harmful consequences on the world's ecological and economic system. Globally, corrosion costs more than four trillion dollars per year [1]. For this aspect, such defensive liquid barrier coating is oftentimes utilized for corrosion prevention. The speculation on the corrosion impact of superhydrophobic surface morphology has received a lot of attention due to effectively protection from corrosive species, like ions and water [2]. In the earlier decades, superhydrophobic (SHP) surfaces has been created by numerous methods such as vapor deposition [3], etching [4–7], sol-gel technique [8], lithography [9], self-assembly [10], femtosecond laser pulsing [11,12], electro spinning [13], templating [14] and electrodeposition [15]. Few of the fabrication techniques introduced in the literature for making superhydrophobic surfaces are costly and complex to scale-up. However, some methods like templating

have fantastic potential for commercial level manufacture, these are not for hardened specimens. Electrodeposition process has demonstrated as auspicious method to construct the excellent hydrophobic coating due to cost efficiency, simplicity, adaptability and scalability for broad range of using substrates [16].

Recently, electrodeposition is a renowned coating method, appropriate to make uniform coating on large and small surface areas of countless shapes. Nevertheless, morphological instabilities produced while electrodeposition at high concentration and voltage which results in irregular augmentation of accumulates at the surface of working electrode. That gives an appropriate surface morphology for superhydrophobic (SHP) surfaces. By varying electrodeposition voltage and time, superhydrophobicity can be achieved during electrodeposition method. By electrodeposition, the formation of superhydrophobic surface accomplished by controlled adhesion. The previous research reported that by change in deposition time parameters, the effect of surface morphology on wettability and adhesion can be compared [17]. Anti-corrosive SHP surfaces were developed on aluminum alloy by one step electrodeposition and showed that the performance of corrosive resistance was enhanced significantly by as-prepared SHP surfaces [18]. Electrodeposition technique improved abrasion resistance of superhydrophobic magnesium alloy surface by deposition of nickel and modification of chemicals. Superhydrophobicity retained after mechanical abrasion for 700mm with 800 grit sandpaper [19].

Steels are used ubiquitously from biomedical surgical instruments and devices, construction, marine environment, household equipment, transport, industrial equipment, and architecture because of their exceptional mechanical properties such as elasticity, corrosion resistance, ductility and shear abrasion. Several steel alloys have been assembled to meet diverse application requirements permitting their integration into an infrastructure in all atmospheres; for example, corrosion resistant austenitic

steels are used in aquatic environment, chemical industry, construction, medical and surgical instruments [20,21]. Superhydrophobic and Superhydrophilic TiO₂/epoxy coatings were formed with TiO₂ and fluoroalkylsilane functionalized TiO₂ nanoparticles deposited on AISI 316L steel alloy and produced the durable surface [22]. Particularly, cathodic electrodeposition has an essential advantage for an industrial application. The superhydrophobic surfaces manufactured on magnesium AZ-91D alloy by electroless plating of nickel and copper by modifying the fluoroalkylsilane (FAS) [23]. Whereas, mostly the deposition methods generally require special circumstances, costly materials, and complicated multi-step procedure to limit their practical applications. Moreover, to accomplish a low surface energy, various techniques involve in consumption of biological toxic materials, like fluoroalkylsilane (FAS).

Currently, researchers have taken an advantage by using two-step electroplating method to fabricate rough cauliflower morphology on copper specimen. Firstly, deposits form with a compact branching morphology were weakly bonded with the surface. Secondly, these loose connected sediments were strengthened by applied lower over-potential for a small period [16]. For the fabrication of superhydrophobic Ni [24], Cu [25], Co [26], and Mn [27] surfaces by electrodeposition process using electrolytic solutions consists of salts of Mn, Ce, La, Ni, Cu or Co, myristic acid and ethanolic solution. Myristic acid is promising a less expensive and powerful reagent to reduce the surface energy [28–30] of material surface as compared to the polymers using fluorination. Among the formation of superhydrophobic coating on different substrates, long term durability is the main concern that confines their practical and industrial applications [31–34].

The theoretical simulations of phase field modeling of droplet on superhydrophobic surfaces were established in which whole transition from Cassie-Baxter to Wenzel [35] of a droplet evaporation on micropillars of a substrate revealed by using Quasi-Newton

continuation technique to solve non-linear equations [36]. This article opens a new window proposed for the treatment of stainless steel surface leading to modifier-free one-step electrodeposition process to form the SHP surface to achieve the extreme robustness against corrosive media, which will be applicable for constructional and marine projects to develop a cost effective and eco-friendly technique to fabricate water repellent surfaces, specifically for the protection of steel substrate for long term storage time. To achieve the commercial applications and surface durability, robustness of the surface improvement is critical in such diverse areas.

To circumvent the above problems, herein, we took the unreported and low cost electrodeposition process utilized to fabricate modifier-free superhydrophobic coating on AISI 316L stainless steel. The phase field simulation for transient evolution of water droplets over the superhydrophobic surface was performed and the kinematical features for varying initial flatness of water droplet over fabricated surface was evaluated with Cahn-Hilliard equation by using finite element method (FEM) in Multiphysics Object Oriented Simulation Environment (MOOSE) Framework software. After fabrication of superhydrophobic film on substrate, the effect of voltage and procedural duration on morphology of surface was examined. The stabilization of electrochemical tests, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies were examined the resistance of corrosion for superhydrophobic coated specimens in NaCl solution.

2 Experimental

2.1 Methodology for theoretical design

In this work, all calculations were based upon a generalized Landau type of free energy function for a continuum phase field variable (ϕ) and Cahn-Hilliard equation was

solved using finite element method (FEM) in Multiphysics Object Oriented Simulation Environment (MOOSE) Framework software [37].

2.2 Experimental Realization

2.2.1 Materials and reagents

For the pre-treatment of austenitic stainless steel AISI 316L specimens were cut into $20 \times 15 \times 2.0 \text{ mm}^3$. The specimens were mechanically grinded with waterproof silicon carbide abrasive papers upto 2000 grit and polished by diamond spray (up to $1 \mu\text{m}$), then each specimen cleaned ultrasonically in absolute ethanol for 15 min in ultrasonic agitation (40 kHz, 360 W, F-060S, Fuyang, China) and then dried in atmospheric air. A platinum mesh was used as an anode with a size of $30 \times 20 \times 0.2 \text{ mm}^3$. The reagents myristic acid ($\text{C}_{14}\text{H}_{28}\text{O}_2$) and cerium (III) nitrate hexahydrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ were obtained from Sinopharm chemical Co., Ltd. For the suspension of water droplets on the fabricated surface to measure water contact angle, water purified from millipore purification system used with the resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$.

2.2.2 Fabrication of superhydrophobic films

The deposition method was conducted by using two electrode system, in which a pretreated AISI 316L stainless steel substrate was employed as working electrode and the (Pt) platinum mesh used as a reference electrode. The constant direct current used for electrodeposition process by using a direct current power supply (CHI 630d, CHI Instrument, Shanghai, China).

The applied potential was varied from 20 V to 70 V for the fabrication of surface and the time of electrochemical deposition process was firstly took constant at 10 min in each case. Moreover, after measuring the highest water contact angle, the electrodeposition process was taken from 5 to 20 min at fixed potential 40 V. Anodic platinum mesh and the cathodic specimen was separated by 2 cm during the process. The electrolytic aqueous solution was prepared by the mixing (0.2 M) concentration of

myristic acid ($C_{14}H_{28}O_2$) in as received reagent and (0.1 M) concentration of cerium nitrate hexahydrate $[Ce(NO_3)_3 \cdot 6H_2O]$ in absolute ethanol solution. After electrodeposition process, as-prepared sample rinsed completely with ethanol and dried under atmospheric temperature.

2.2.3 Surface characterization

The average water contact angle (CA) of as-prepared samples was evaluated by contact angle analyzer (DSA-100, KRUSS, Germany) for which 10 μ L drops were dispersed on the surface of the sample at atmospheric temperature of 26.5 ± 0.2 °C and contact angles of water droplets were measured by using Young-Laplace fitting method. The average CA for a fabricated surface was determined by measuring contact angles at five separate spots on the surface. The morphology of fabricated surface of the specimen was characterized by using field emission scanning electron microscope (ULTRA-55 FE-SEM, Zeiss-Supra Company, Germany) also equipped with energy dispersive X-ray spectroscopy (EDS) for surface composition characterization. The composition of chemicals on the fabricated surface of specimen was examined by X-ray photoelectron spectroscopy a thermo fisher ESCALAB250 Xi⁺ system with monochromatic X-ray source XPS (1486.6 eV, 14.4 kV, 13.6 mA, 150 W) and by Fourier transform infrared spectroscopy (FT-IR) in the range of 4000–400 cm^{-1} .

2.2.4 Chemical stabilization of superhydrophobic surface

The chemical stabilization of superhydrophobic surface was evaluated in a three electrode cell in which a graphite mesh (counter electrode), Ag/AgCl (reference electrode) and electrodeposited specimen (working electrode) with the surface exposure of 1.0 cm^2 were employed in a system. All electrochemical measurements were achieved in 3.5 wt% sodium chloride (NaCl) medium via potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS) at an atmospheric

temperature using CS electro-chemical & corrosion workstation. Corrosion parameter values such as corrosion density (I_{corr}), corrosion potential (E_{corr}), corrosion resistance and corrosion rate were achieved from Tafel curves using CS studio (ver. 5.4) software. The polarization Tafel plots were evaluated at the scan rate of 0.5 mV/s. The electrochemical impedance spectroscopy (EIS) evaluations achieved at the frequency from 100 kHz–0.01 Hz with an amplitude signal of 10 mV. Saline water having 1–5 M NaCl aqueous mixture used to examine the ionic strength and stability of the as-prepared specimen. Silane water drops were distributed on as-prepared samples prepared at 40 V.

3 Results and discussion

3.1 The effect of electrodeposition voltage on wettability

Success of the electrodeposition process of cerium myristate [$\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3$] modifier-free surface depends to a great extent on the applied voltage. To characterize wetting static contact angles, droplets of water having 10 μL volume were calculated on five separate spots for the surface of every specimen. The reproducibility of evaluating the water contact angle (CA) defined as the root mean square (R.M.S) deviation of the angles for five consecutive images of the drop was better than 0.1° . The effect of electrodeposition potential is summarized in Fig. 1.

Fig. 1(a) demonstrates that the average water contact angle (CA) and average contact angle hysteresis (CAH) measurements in a graphical representation with error bars (The error bars for each plot indicates the minimum and maximum average water CA and corresponding CAH). The as-fabricated surface obtained at an applied potential of 20V provided the mean water contact angle of $132.2 \pm 3.0^\circ$. The as-prepared sample obtained at applied potential of 30V gave an average value of water CA of $156.8 \pm 2.3^\circ$. The average CA value obtained from applied potential of 40 V was $167.7 \pm 2.4^\circ$, which

represents the maximum superhydrophobic surface, whereas some areas of the fabricated surface revealed water contact angle (CA) nearly 173.7° (approximately ideal superhydrophobic coating) [38]. The sample which was prepared by electrodeposition at an applied potential of 50 V showed the average CA value of $159.1 \pm 2.03^\circ$. Whereas, by increasing the electrodeposition voltage to 60 V, the CA was slightly reduced to $157.1 \pm 1.92^\circ$ and when 70 V was applied it reduced again a smaller amount of CA to $155.1 \pm 1.3^\circ$.

Fig. 1 (a) Variation in average water contact angles (CA) and average contact angle hysteresis (CAH) of the surfaces as a function of different applied electrodeposition voltages. The error bars for each plot indicate the maximum and minimum water contact angles. (b) Molecular structure of myristic acid (C₁₄H₂₈O₂) and cerium nitrate hexahydrate [Ce(NO₃)₃·6H₂O].

It was noted that except for the as-fabricated surface at an applied voltage of 20 V, the advancing contact angle (θ_a) of all the samples prepared at different applied voltages had more than 150° and the average contact angle hysteresis (CAH) were less than 10° as shown in Fig. 1(a), which exhibits excellent superhydrophobicity. It is worth noting that the wettability was controlled by the parameters of morphological structure made by the chemicals. The droplet was stuck on the surface even it turned upside down at applied voltage of 20 V. The hierarchical micro/nanoscale papillae rough structure has better ability of air traps which increases superhydrophobicity compared with sheet-like structure. Therefore, the micro/nanostructure composed of cerium myristate

[Ce(CH₃(CH₂)₁₂COO)₃] can improve hydrophobicity of the surface and decrease contact angle hysteresis by reducing the contact area of solid–liquid interface.

The as-prepared coatings fabricated at electrodeposition potentials for instance 30 V, 50 V, 60 V and 70 V illustrated nearly zero rolling angle which shows Cassie–Baxter state infrequent areas but on some points where the water drop was adhered to the surface due to some point defects or partial wetting shows the intermediate wetting states between Wenzel and Cassie–Baxter state, the drop can have metastable wetting states where it reaches its local energy [39]. The surface at applied potential of 40 V demonstrated the minimum number of defected points, where (Movie S1 shown in the supporting information) bouncing of the drop from a height revealed on the fabricated surface more than two times and the droplet slides after bouncing on the coated surface that implies very small sliding angle ($<1^\circ$) due to surface morphology and low surface energy. Fig. 1(b) shows the molecular structure of myristic acid (C₁₄H₂₈O₂) and cerium nitrate hexahydrate [Ce(NO₃)₃·6H₂O].

3.2 The influence of electrodeposition time on wettability

After evaluation of the highest water contact angle CA at potential of 40 V, the effect of electrodeposition time on wettability was measured, the process was conducted from 5 to 20 min at constant potential of 40 V. The variations in average CA and average CAH at constant applied potential of 40 V with different time intervals demonstrated in Fig. 2. Bare specimen showed average CA of $94 \pm 0.3^\circ$. By increasing the duration of electrodeposition process after 5 min, the average water contact angle (CA) value also enhanced to $137.6 \pm 0.3^\circ$ and average contact angle hysteresis was observed greater than 10° . However, the average CA values were observed at different time periods of 10, 15, 20 min at an enhancement of $167.7 \pm 2.4^\circ$, $164.9 \pm 1.8^\circ$, $155.7 \pm 2.5^\circ$, respectively. The contact angle hysteresis except 5 min electrodeposition time were observed as less than 10° , which exhibits good hydrophobicity under the applied

voltage of 40 V. There was no significant improvement in water contact angle with further prolongation period of electrodeposition. This could be a plausible reason for surface of steel owing to an insulating attribute of superhydrophobic surface facing in the direction of an electrolyte.

Fig. 2 Variation in average water contact angles and average contact angle hysteresis of the surfaces fabricated at different electrodeposition times at constant voltage of 40 V. All the plots show averaged values of water contact angle and contact angle hysteresis at five different points on the same sample. The error bars for each plot indicate the maximum and minimum water contact angles and corresponding contact angle hysteresis.

3.3 The influence of electrodeposition potential and duration on the morphology of the surface

Dendritic crystals with fascinating morphological structures are prepared at higher potential and higher concentrations in electrocrystallization. For the dendritic crystals formation in electrocrystallization, the uncertainty of a diffusion field in the aqueous solution is considered as a driving force. After reaching a limiting requirement, the deposition will become diffusion controlled, and the transfer of mass in this situation supports the development of haphazard protrusions of the coating and improves instabilities of morphology. Previous research work demonstrates that the ion deposition leads to the involvement of instability in the diffusion process and an unstable electrocrystallization on cathode results the asymmetrical evolution of the electrode surface [40]. Previous research of electrodeposition indicates that the surface

energy, electric field and limiting current are the main key factors to control the stability of the surface [41].

Fig. 3(a-f) shows FE-SEM topographical images of the surfaces formed at different applied potentials. Fig. 3(a) illustrates that the surface is observed to alter with applied voltages formed by applying 20 V depicted irregular deposition of nanoparticles which forms non-uniform distribution of florets. Fig. 3(b) shows sample formed at 30 V demonstrated that nanoparticles began the agglomeration of papillae-like deposits scattered arbitrary on the fabricated surface and form larger particles as compare to 20 V applied potential, where a drastic improvement in water contact angle is observed.

The morphological structure prepared at 40 V resembles cauliflower-like morphology in Fig. 3(c). Remarkably, the tip of radii observed $\sim 3.78 \mu\text{m}$ on the surface, which is near to the tip radii of lotus-leaf (~ 3.8 to $4.4 \mu\text{m}$) [42]. The agglomeration of nanoparticles was same as the wax tubules of lotus-leaf, same structure of 70 nm size combined on the surface was observed on each papillae structure marked in Fig. 3(c) the inset magnified image. The agglomeration of nanoparticles could result in an irregular morphological surface with nanoscale spaces comprised of small parabolic convexities plus some large protrusions decorating its surface forming an irregular cauliflower-like morphology. Such type of surface morphology is suitable for the fabrication of SHP surface. However, samples obtained at 50, 60 and 70 V papillae structures were also observed having blemished and diffused surface nanoparticles on micro-sized florets, that might be due to applied high voltage which shows that the cluster of particles of over potential increased the irregularity of the surface.

Fig. 3 (a-f) FE-SEM micrographs of the as-prepared superhydrophobic surfaces obtained at different electrodeposition voltages: (a) 20 V, (b) 30 V, (c) 40 V, (d) 50 V, (e) 60 V and (f) 70 V. The right side of the images is magnified view of the left side images.

To obtain the highest water repellence, a stable air cushion remains trapped under the droplet of the surface, thus it makes a spherical shape and minimum contact to prevent wetting of the specimen [43]. Depending on chemical composition and morphology, the droplet can have several preferable, metastable wetting states where it reaches its local minimum energy. Koishi et al. [44] presented a simulation evidence of co-existence and transition of Cassie/Wenzel state for water droplets on a hydrophobic pillared surface. In this model, the free energy barrier separates the Cassie and Wenzel

states computed on molecular level, based on raining experiments and a statistical-mechanics method.

The surface formed at 20 V did not depict superhydrophobic behavior, it might be a reason for the lack of hierarchical micro nanostructure. By increasing the applied potential, the constant growth time reduced where more instabilities of morphology are possible which can cause the fractional structures of various length scales [16]. Fabrication of hierarchical structures is an effective way to decrease the adhesion of droplet because the microstructure entraps large air pockets under the grooves of pillars and thus reduce the liquid–solid interface. For the fabrication of robust Cassie state, nanostructures are necessary to achieve high impalement pressure and high apparent receding contact angle at the same time [45].

To further investigate the effect of immersion time in the process of electrodeposition on wettability, FE-SEM micrographs of the fabricated sample coated with different electrodeposition time at applied potential of 40 V were attained in Fig. 4(a-d). After deposition for 5 min, Fig. 4(a) shows nanosheets like structure aligned at inclined angles with respect to the surface. By extending the electrodeposition time to 10 min illustrated in Fig. 4(b), the small papilla started to attach with each other and agglomerate as large papilla which formed a cauliflower-like hierarchical micro/nanostructure having air cushions between them. Fig. 4(c and d) showed that when the process duration was extended to 15 and 20 min, the surfaces covered with the film having some small cracks on it (Fig. 4(d) magnified image). Those small microcracks exist on the surface lowers the durability of substrates. These cracks on the surface might have been produced due to the shrinkage in volume because of the evaporation of ethanolic solution molecules while prolonged period.

Fig. 4 (a-d) FE-SEM of as-prepared surface topographies deposit obtained at 40 V with different electrodeposition time: (a) 5 min, (b) 10 min, (c) 15 min and (d) 20 min. The right side of the images is magnified view of the left side images.

3.4 Mechanism of electrodeposition

X-ray photoelectron spectroscopy (XPS) spectra was analyzed the chemical composition of the superhydrophobic samples exhibited that the surface was extremely insulating in nature and containing low surface energy which is basic ingredient to increase the superhydrophobicity (Fig. 5). The presence of Ce, C, and O on the superhydrophobic surface can be observed in Fig. 5(a). The survey spectrum exhibited that the high asymmetrical and broad peaks moving towards high binding energy, is the reference of standard peak of C 1s at 284.9 eV is attributed to $-\text{CH}_2$; which indicates an extremely positive charging. Thus, for the minimization of the effect of surface

charging and external low surface energy of (1 eV) an electron source utilized to neutralize the surface charging. Fig. 5 depicts an XPS spectrum of SHP sample after correction of surface charging.

Fig. 5 High resolution spectrums of XPS of as-prepared superhydrophobic surface: (a) survey spectrum, (b) Ce 3d core level spectrum of Ce 3d_{3/2} and Ce 3d_{5/2}, (c) O 1s spectrum, (d) C 1s spectrum, respectively.

It was determined that the higher resolution peaks are asymmetric and broad leads to lower binding energy site. As a result, C 1s in Fig. 5(d) spectrum contains two peaks, which showed the existence of C=O (288.8 eV) and -CH/C-C (284.9 eV). In Fig. 5(c), O 1s spectrum peaks illustrates the existence of peaks at 531.5 eV and 532.4 eV assigned to Ce-O and O=C respectively [28]. Due to incomplete charge neutralization of the surface, the short peaks of C 1s and O 1s having low binding sites at 530.5 eV & 283.5 eV, respectively. Remarkably, in Fig. 5(b) 3d spectrum of Ce is not demonstrating the existence of +4 oxidation state. Different peaks of Ce 3d_{3/2} and 3d_{5/2} were shown while Ce was supposed to be in +3 oxidation state at superhydrophobic surface. The atomic composition of Ce, C and O obtained from XPS are estimated to

be 1.9, 82.9 and 14.6%, respectively. We can conclude from the results that cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ with lower surface energy is present on the outer most surface of fabricated superhydrophobic film.

Figure 6 (a) Schematic illustrating mechanism of fabrication of cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ and $\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_4$ ions on stainless steel 316L specimen (b) FT-IR spectrum of cerium myristate coated stainless steel 316L at 40 V (c) Laser Raman spectrum of cerium myristate fabricated stainless steel 316L at different applied electrodeposition voltages.

Fig. 6(a) shows the emergence of yellowish color close to the anode proves Ce^{3+} to Ce^{4+} oxidation. Ce^{4+} ions arrive at the cathode because Ce^{4+} ions are greater than that of Ce^{3+} ions during electrodeposition, which leads the exceptional electrodeposition of $\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_4$. More shifting of Ce^{4+} ions towards the working electrode is delayed because of insulating behavior of inner layer. Thereby, Ce^{3+} ions close to the working electrode surface which cooperate with myristic acid and make $\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3$.

Fourier Transform infrared spectroscopy (FT-IR) and laser Raman spectroscopy (LRS) was used to analyze the composition of chemicals. Fig. 6(b) portrays the FT-IR spectrum of as-fabricated specimen at 40 V applied potential. In the maximum frequency area of the curve, the spectra of as-prepared surface demonstrated peaks related to H–C antisymmetric and symmetric stretching vibrations at maximum frequency area (2915 & 2848 cm^{-1}), which resembles the peaks of commercial myristic

acid (2918 and 2850 cm^{-1}) [46]. The peak for the carboxylic carbonyl stretching vibration at 1702 cm^{-1} was not present in FT-IR spectra of the SHP sample while compared to myristic acid peaks in the previous studies of research work [28]. Although, two peaks at 1446 & 1535 cm^{-1} in superhydrophobic surface specimen, which were ascribed the antisymmetric and symmetric peaks of O–C bond of cerium myristate.

Fig. 6(c) reveals the LRS (Raman spectra) of the SHP coated specimens. The spectrum exhibited the characteristics of stretched band associated with O–Ce at 442 cm^{-1} [47]. Stretching peak of C–C (1063, 1129 cm^{-1}), twisting peak of CH_2 (1297 cm^{-1}), stretching peak of O=C (1636 cm^{-1}), symmetric stretching peak of C–H in CH_2 (2847 cm^{-1}) and H–C in CH_3 (2883 cm^{-1}) attributes to the corresponding Raman shifts. Raman peak intensity was progressively enhanced while increasing applied potential from 20 V–70 V, which indicates the increased amount of deposits at higher potential without any composition change of the surfaces. On the contrary, the rate of deposition enhanced with an increased potential, the water contact angle values remain constant, suggests that changes in morphological surface have significant role in the contribution of water repellency of the as-fabricated specimens.

Table 1 Elemental concentration of as-fabricated SHP surface determined by energy dispersive X-ray spectroscopy.

wt%				atom%			
Fe	Ce	C	O	Fe	Ce	C	O
2.02	18.33	65.68	13.96	0.56	2.01	84.03	13.41

Fig. 7(a) demonstrates that energy-dispersive X-ray spectroscopy (EDS) of the specimen prepared at 40 V; the elemental concentrations on as-fabricated SHP surface are enumerated in Table 1. The atomic ratio of O/C/Ce was observed 6.6:41.8:1, respectively. We can deduce that cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ atomic ratio

of O/C/Ce was observed in XPS is 6.2:39.3:1. These results indicate on the basis of chemical valences that the surface could be composed of Ce^{3+} ions and myristate ions $\text{CH}_3(\text{CH}_2)_{12}\text{COO}^-$ in the aqueous medium. Thus, cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ with low energy can be found on outer most surface of fabricated film.

Fig. 7 (a) Chemical composition analysis of durable superhydrophobic surface by energy dispersive X-ray spectroscopy (EDS), (b) variation in water contact angles (CA) and contact angle hysteresis (CAH) of superhydrophobic surface prepared at electrodeposition voltage of 40 V as a function of ionic strength of NaCl solution. The error bars for each plot indicate the maximum and minimum water contact angles and corresponding contact angle hysteresis.

3.5 Chemical and mechanical stability

Fabrication of SHP surface coatings were provided corrosion protection and enhancement in the effectiveness to the specimens in harsh and corrosive environment. The condition for durable corrosion capability is feasible to the chemical stabilization of the as-fabricated coatings in continuous interaction with neutral, acidic or basic aqueous solution. Fabrication of specimens are proposed to protect from environmental corrosion in coastal region. Ionic strength and stability of as-fabricated SHP coatings were tested by variation in the concentration of NaCl in chloride medium.

Fig. 7(b) portrays the measurement of water CA and CAH at distinctive ionic strength of sodium chloride aqueous mixture on as-fabricated durable superhydrophobic surface coating at 40 V. The measurement was done after 30 s by suspension of chloride aqueous solution drops on the as-prepared surface. Fabricated surface coating

maintained its superhydrophobic efficiency up to 5 M chloride medium, this illustrates its stability in the vicinity of such harsh NaCl aqueous solution. Although, decrease in contact angles (CA) and increase in contact angle hysteresis (CAH) by increasing the concentration of NaCl in solution was observed. The cerium myristate modified SHP surface still retained its superhydrophobic behavior. When a droplet of NaCl solution is placed on the superhydrophobic modified coating, van der Waals forces are favorable for sodium (Na^+) and chloride (Cl^-) ions adsorption on modified coating [48,49], thus compromising the hydrophobic behavior of modified surface. Gouy—Chapman theory [50] also supports this argument that with the increase in ionic strength, free energy also decreases to fabricate charged monolayer; thus modified superhydrophobic coating endorsed by the adsorption of solute. Thereby, an agglomeration of adsorbent species on the surface promotes hydrophobic decrease, which affects the air cushions [51] and leads to Wenzel state. For this scenario, the coating of cerium myristate is chemically inert, therefore Na^+ and Cl^- ions accumulated on modified coating and cerium myristate coated stainless steel 316L specimen in such corrosive environment showed excellent repellency and sustained the water CA $> 150^\circ$ and CAH $< 10^\circ$ up to the concentration of 5 M sodium chloride. This ability enhances the scope of the as-fabricated SHP surface in corrosive environment.

Traditional abrasion tests and shear abrasion tests based on sandpaper were conducted to characterize the mechanical robustness of as-fabricated SHP coated samples. To analyze the traditional abrasion test which employ water drops to interact the surface and results the damaged surface. Continuous bombardment of the water droplets (volume: 20 μL , drop rate: 1 drop/s, impingement height: 5 cm) was performed as shown in Fig. S.1 (as shown in supplementary data) and no mechanical damage of even the finest nano-feature was observed.

In order to check the mechanical properties of superhydrophobic surface, the degradation in superhydrophobicity of the sample prepared at 40 V was dragged on 1000 grit SiC paper under a load of 2.46 kPa nearly 50 g assessed by measuring water contact angle (CA) and contact angle hysteresis (CAH) as a function of abrasion cycles as shown in Fig. 8(a). The values represented in Fig. 8(a) indicates the averaged values for water CA and CAH measured on five different locations on a sample prepared at 40 V applied potential. It is observed that the water CA decreases, and CAH increases with the parameter contributing to an increased number of abrasion cycles.

Fig. 8 (a) Variations in average water contact angles (CA) and average contact angle hysteresis (CAH) on superhydrophobic surface as a function of number of abrasion cycles (the inset schematic illustration is of shear abrasion test), (b) a photograph of spherical interface of water droplets on superhydrophobic surface obtained at 40 V after scratch test and inset minimum value of water contact angle, (c) topographical view of coated surface after abrasion test by optical microscope, (d) optical microscopic image after knife scratch test.

After 50 cycles, some loss in superhydrophobicity was observed resulting in a reduced average contact angle of $151.1 \pm 1.02^\circ$ and increased average hysteresis of about $8.3 \pm 0.6^\circ$. However, the sample retained its superhydrophobicity and was not wetted by water. The steady reduction in non-wetting properties is because of the combined

impact of its parameters i.e., number of abrasion cycles, pressure load and abrasion surface roughness. The inset diagram of abrasion test process is explained in Fig. 8(a). An optical microscopic view of abrasion test can be seen in Fig. 8(c). Although, a durable surface fabricated by middle connecting layers and formed a net-like structure encompasses the silica particles modified by hexamethyldisilazane (HMDS) lost its superhydrophobic behavior after 45 cycles on 1200CW sandpaper under 3 kPa applied pressure [52].

To determine the mechanical robustness of the superhydrophobic surface, knife scratching tests were also conducted as demonstrated in Fig. 8(b), water droplets still maintained its $CA > 150^\circ$ and sliding angle $\leq 10^\circ$. This may happen due to loss of chemical functionalization or loss of surface texture or complete removal of fabricated surface [53]. As shown in the supporting information (Movie S2), droplets of water still easily rolled off on the surface, indicating that the surface could endure severe damages. Fig. 8(d) is the optical microscopic view of knife scratching test. These results indicate that as-fabricated SHP surface showed an excellent mechanical durability.

3.6 Corrosion resistance studies

Fig. 9(a) exhibited the Tafel characterization analysis of the uncoated and SHP specimen formed at discrete applied potentials in 3.5 wt% sodium chloride aqueous mixture. Table 2 describes the corresponding polarization parameter values listed as follows. The corrosion potential of the bare samples is -0.23871 V with the current density of round 1.70×10^{-6} A/cm², confirms the uncoated 316L specimen is susceptible to the resistance of corrosion as compare to surface. Fig. 9(a) describes the Tafel plots, corrosion potential (E_{corr}) of the SHP formed at 20 V moves towards more negative potential (-0.25397 V) but corrosion density (I_{corr}) is considerably reduced to 2.31×10^{-6} A/cm². On the contrary, the increment in applied voltage the superhydrophobic

sample prepared at 30 V, E_{corr} shifts towards positive corrosion potential of about – 0.23028 V but I_{corr} decreased significantly.

Table 2 Comparison of different polarization parameters for superhydrophobic surfaces and uncoated specimen in corrosive 3.5 wt% sodium chloride medium.

Sample	E_{corr} (V)	I_{corr} (A/cm ²)	$R_p(\Omega)$	Corrosion rate (mm/y)
Bare	–0.23871	1.70×10^{-6}	$4.16 \times 10^{+4}$	4.89×10^{-4}
20 V	–0.25397	2.31×10^{-6}	$4.13 \times 10^{+4}$	6.58×10^{-4}
30 V	–0.23028	7.45×10^{-7}	$1.89 \times 10^{+5}$	2.11×10^{-4}
40 V	0.0056798	3.50×10^{-8}	$1.98 \times 10^{+6}$	9.96×10^{-6}
50 V	–0.30431	3.29×10^{-7}	$7.34 \times 10^{+4}$	1.48×10^{-4}
60 V	–0.051251	3.36×10^{-7}	$5.47 \times 10^{+5}$	9.57×10^{-5}
70 V	–0.17983	3.15×10^{-7}	$2.40 \times 10^{+5}$	9.04×10^{-5}

Generally, better corrosion resistance identifies lower rate of corrosion, corresponds to the more positive E_{corr} and a lower I_{corr} [54]. Superhydrophobic sample fabricated at 40 V, the maximum shift can be seen towards positive corrosion potential (E_{corr}) about 0.0056798V, and the lowest current density (I_{corr}) of about 3.50×10^{-8} A/cm². By further increment in applied potential prepared sample at 50 V, exhibited rapid decrease in E_{corr} and a decrease in I_{corr} . Furthermore, E_{corr} of the SHP samples at 60 and 70 V, showed slight shift towards positive corrosion potential and I_{corr} shift towards negative as shown in Table 2. It also demonstrates the change in corrosion resistance (R_p) and corrosion rate (mm/y).

The specimen prepared at 40 V demonstrates the minimum rate of corrosion (mm/y), exhibited highest surface roughness, lowest surface energy and permitted the maximum entrapped air between cauliflower-like compact morphology. The decrease in I_o and increase in E_{corr} , indicates that the SHP surface of applied potential 40 V improved corrosion resistance significantly about > 2 orders of magnitude in NaCl corrosive solution.

Fig. 9 (a) Tafel curves of modifier-free superhydrophobic surfaces at variable applied potential and bare specimen in 3.5 wt% sodium chloride (NaCl) medium, (b) schematic diagram of bare specimen and as-fabricated cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ based superhydrophobic sample in sodium chloride (NaCl) solution.

Fig. 9(b) illustrates the schematic diagram of corrosion resistant SHP coating on AISI 316L specimen in NaCl solution. Based on the previous observations, bare sample can freely react with neighboring water molecules. On the other hand, superhydrophobic coatings with micro-nano scale rough structure having air cushions among the lumps of cauliflower-like morphology and the trapped air cushions act as a barrier for chloride ions to prevent the surface of substrate from chloride media and resulted in the improved E_{corr} as results shown in Fig. 9(a). There are two reasons for enhancement of corrosion resistance: chemical composition of cerium (Ce) ions [55,56] in cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ coating resulted the enhancement in corrosion resistance and superhydrophobicity of the film. Superhydrophobic surface prepared at 40 V with hierarchical roughness and high water CA will have air pockets between protrusions on SHP surface. The fabrication of layered double hydroxides (LDHs) film and superhydrophobic coating at different time in simulated body fluid (SBF) medium and observed that superhydrophobic surfaces can block the penetration of corrosive ions in SBF electrolytic solution [57].

Anti-corrosive properties based on cerium myristate superhydrophobic surface are examined by electrochemical impedance spectroscopy (EIS) Nyquist plots. Impedance

was measure by immersion of bare and SHP specimen in 3.5 wt% sodium chloride medium. Fig. S.3 clearly indicates that Nyquist plots of coated and bare samples formed at distinctive applied voltage. The capacitive loop diameter was maximum for all superhydrophobic specimens in the comparison with uncoated specimen in Fig. S.3(a). This shows an enhancement in charge transfer resistance [58], that described the existence of a protecting film at the metal–mixture interface [59]. The range of the impedance circle diameter for the bare specimen was in $k\Omega$, but the range for as-fabricated SHP specimen at 40 V was in $G\Omega$ range, that proves the preferential E_{corr} of cerium myristate-based SHP surface.

In order to investigate the impedance moduli, BOD plot of uncoated and SHP coating specimen was plotted of as-prepared different applied potentials as shown in Fig. S.3(b). The impedance moduli of the SHP specimens are greater than the bare substrate. An excellent protecting film was fabricated at 40 V having modulus $>10^6 \Omega \text{ cm}^2$ at lower region of frequency $\sim (-3)$. The enhancement in impedance of the 40 V specimen depicts a pure capacitive nature of the specimen. Closely packed cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ layer to specimen have a factor in the high impedance value for the fabricated SHP surfaces. High frequency modulus of the stainless steel 316L substrate and superhydrophobic specimen fabricated at 20 V and 30 V were almost resembled, but the values of impedance modulus for superhydrophobic specimens fabricated at 40 V, 50 V, 60 V and 70 V were comparatively much higher in the value of its magnitude. Therefore, the BOD plot showed higher resistance barrier for corrosion reaction for those specimens which fabricated SHP surfaces and indicate an enhancement in corrosion protection.

3.7 The influence of low surface energy for multifunctional coating

The numerical solutions presented the phase field variables over the three faces corresponding to the lowest energy states at hydrophobicity index values varied between 0 to -1 in Fig. 11. The method of contact deformation to departure and approach of $10\ \mu\text{L}$ droplet suspended on a syringe over superhydrophobic coating as shown in Fig. 10 and Movie S3 shown in the supporting information. The suspended water droplet was difficult to be pulled down by the as-fabricated superhydrophobic surface due to low surface energy theoretically calculated ($\beta_s = -0.937$) and high roughness, even the droplet was deformed severely as shown in Fig. S.2.

Fig. 10 (a–d) The process of contact, deformation, and approach of $10\ \mu\text{L}$ water droplet suspending on syringe on cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ based superhydrophobic surface coating obtained at 40 V electrodeposition voltage.

4 Computational simulations

4.1 Numerical simulation of water droplet evolution on superhydrophobic surface

The water droplet put on the top of the superhydrophobic (surface treated 316L steel) can be considered as a structured surface-droplet system, in which three immiscible phases namely, steel solid (consisting of electrodeposited micropillars), liquid (droplet) and gas (air) are in contact [60]. This contact line problem can be studied theoretically or numerically by a phase field model which is based upon a generalized Landau type of free energy function for a continuum phase field variable (ϕ) [61].

Considering ϕ as a conserved variable, the spatio-temporal evolution of this variable can be represented by the Cahn-Hilliard equation as follow:

$$\partial\phi/\partial t = \nabla \cdot M \nabla \left(\partial f_{bulk} / \partial \phi - \nabla \cdot (\kappa \nabla \phi) \right) \quad (1)$$

As shown in Fig. 11(a), the water droplet (liquid phase) is defined as $\phi = 1$, and air (gas phase) is characterized by $\phi = -1$. The diffuse interface between the liquid and gas phases is characterized by $-1 < \phi < 1$. In Eq. 1, f is the free energy of the bulk phases, M is the mobility and κ is the gradient energy coefficient. The radius of the water droplet of volume $10 \mu\text{L}$ is about 1.3 mm . The computational domain is a square of length 5 mm . Since the scale of the simulation is in the range of mm [see Fig. 11(a)], the micron sized electrodeposited pillars ($3\text{--}4 \mu\text{m}$) at the solid/gas or solid/liquid interfaces are not visible. Nevertheless, the hydrophobic behavior shown by this structured solid surface can be implemented in the phase field model by introducing a wettability parameter or hydrophobicity index (β_s) in the free energy term. The bulk free energy of the phases can be represented by the following expression:

$$f_{bulk} = (\phi^2 - 1)^2 + \left(\frac{1-\alpha}{8} \right) \tau (\phi - \beta_s)^2 \quad (2)$$

The value of the parameter α in Eq. 2 is assigned as 1 for liquid/gas phases and -1 for the solid phase. With this differentiated value of α in solid and fluid phases, it can be inferred from Eq. 2, that the bulk free energies of liquid/gas phases are characterized by double-well potential, whereas that of solid phase is represented by a single well [61]. In the equation, τ is an arbitrary constant which must be sufficiently large in magnitude to ensure the notable presence of the surface, but not too large to cause spurious solutions [60]. In this study, τ is given a value of 1 .

Fig. 11 As shown in images (a) and (b), the phase field variable ϕ has a value of 1 in liquid phase (water droplet) and -1 in gas phase (air). In image (a), the solid phase (steel) corresponds to the case with hydrophobicity index (β_s) = 0, and it is to be noted that the system has yet not reached the lowest energy state. For the equilibrium energy states of water droplet on steel surfaces with β_s values corresponding to 0, -0.2 , -0.4 , -0.6 , -0.8 and -1.0 are presented in image (b), it is important to observe the change in colors of the solid steel surfaces in line with the numerical magnitudes of the hydrophobicity index (β_s). The fitted curve in image (c) that shows the functional relationship between contact angle and hydrophobicity index ($R^2 = 0.994$) is obtained using the method of polynomial regression. In accordance to the curve, the contact angle of 167.7° corresponds to $\beta_s = -0.937$

In the bulk free energy expression (Eq. 2), the wettability parameter (β_s) is related to the contact angle (θ_c) and thus determines the extent of hydrophobicity of the surface.

The solid phase (steel with micropillars at the surface) has an energy minimum at $\phi = \beta_s$. For water-repellant or hydrophobic surfaces, the numerical values of β_s are < 0 . To input experimental contact angle for the superhydrophobic surface, it is important to outline numerical correlation ship between θ_c and β_s . With the initial geometry represented by Fig. 11(a) and for values of β_s varied between 0 and -1.0 , Eq. 1 is solved using finite element method (FEM) in Multiphysics Object Oriented Simulation Environment (MOOSE) Framework software [37,62].

At the boundary in contact with the solid steel, dirichlet boundary condition with $\phi = \beta_s$ is imposed. The value κ of is kept as 5.25×10^{-4} . The mobility (M) is implemented as a function of phase field variable [63] by the following expression:

$$M(\phi) = 1 + \tanh(4\phi + 1.5) \quad (3)$$

The numerical solutions of ϕ variables over the three faces corresponding to the lowest energy states at hydrophobicity index values varied between 0 to -1 , are presented in Fig. 11(b). The measured values of equilibrium contact angles at this energy state is graphically represented as a function of hydrophobicity index (β_s) in Fig. 11(c). For the wettability parameter of -1 corresponds to the equilibrium contact angle of 180° , and $\beta_s = 0$ corresponds to $\theta_c = 90^\circ$. Moreover, for $-1 < \beta_s < 0$, it is obvious from the Fig. that $180^\circ > \theta_c > 90^\circ$. A polynomial regression analysis is performed for the data of contact angle and wettability parameter represented in Fig. 11(c). The degree of polynomial features for the polynomial regression is chosen as 2, thus, implying that the contact angle is fitted as a quadratic function of hydrophobicity index. The relationship between the contact angle and the hydrophobicity index as established from the polynomial fitting is expressed by the following quadratic equation:

$$\theta_c = a_0 - a_1 \times \beta_s + a_2 \times (\beta_s)^2 \quad (4)$$

where, $a_0 = 90.0^\circ$, $a_1 = 40.37^\circ$ and $a_2 = 45.46^\circ$. For the regression analysis, R^2 was obtained as 0.994, which suggests that there is a strong functional relationship between contact angle and the hydrophobicity index. In context of the experimental superhydrophobic surface sample, corresponding to 40 V and electrodeposition time of 10 min, having the contact angle of 167.7° , the corresponding value of β_s given by Eq. 4 is -0.937 .

Having obtained the wettability parameters in the free energy expression for the experimental sample (40 V, electrodeposit duration = 10 min), we proceed towards

performing transient simulation for studying the behavior of this superhydrophobic surface in context of liquid with different flatness. The differing initial flatness conditions are encountered in real experimental tests with varying pressure, external loads, needle morphology, temperature fluctuation etc. In context of nearly circular drop at initial time (t) as shown in Fig. 12(a1–e1), the drop evolves to a perfect sphere with virtually negligible flatness at $t = 2500$.

Fig. 12 (a) Transient evolution of a nearly circular drop (smaller flatness at interface) at initial regime over a superhydrophobic surface with $\beta_s = -0.937$ ($\theta_c = 167.7^\circ$) at $t =$ (a1) 0.35, (b1) 25.5, (c1) 93.5, (d1) 543.5, and (e1) 2500 (b) Transient evolution of an initially hemispherical drop (larger flatness at interface) over a superhydrophobic surface with $\beta_s = -0.937$ ($\theta_c = 167.7^\circ$) at $t =$ (a2) 0.35, (b2) 25.5, (c2) 93.5, (d2) 543.5, and (e2) 2500.

Another drop initially of semicircular morphology as shown in Fig. 12(a2–e2) also takes the duration of $t = 2500$ to attain the perfect circular morphology when treated over a superhydrophobic surface similar to the experimental sample (40 V, electrodeposition duration = 10 min). Although at $t = 0.35, 25.5$ and 93.5 ; the morphologies of these droplets are different; there are identical at $t = 543.5$ where they still bear a smaller flatness at the interface. This shows that the evaluation kinematics of the droplet of random initial flatness at superhydrophobic surface is faster at the initial period and get slower when it reaches the equilibrium morphology. In other

words, the rate of increase of contact angle from its non-equilibrium state to its final equilibrium contact angle is larger at the beginning whereas the increment becomes smaller as the droplet-surface system approaches towards its equilibrium contact angle. To summarize the numerical and experimental results, the different initial flatness conditions are encountered in real experimental tests with varying pressure, external loads, temperature fluctuation etc. The time duration in this simulation has an arbitrary unit and when observing the experimental duration, the water droplet attains spherical morphology within a fraction of second when it is put over the superhydrophobic surface. Experimental deformation (hemispherical) of water droplet and recirculation time was evaluated via computer simulation. Performing the numerical simulation with the known unit of electrodeposition time by comparing with experimental measurements is considered the scope of future study.

5 Conclusion

A fast one-step electrodeposition method used to produce rough surface austenitic steel. Electrodeposition parameters were optimized and obtained higher water CA and lower CAH on coating fabricated at applied potential of 40 V for 10 min. Water drop acquires spherical shape on superhydrophobic steel surface with average water CA of $167.7 \pm 2.4^\circ$ and average CAH $\leq 1^\circ$. The array of water drops eventually bounces off the surface without damaging the surface features retained its superhydrophobicity. Regardless of the degree of initial flatness of droplets and the effect of surface energy interface of liquid/solid phase over superhydrophobic surface, the phase field simulation for transient evolution of water droplets over the superhydrophobic surface (40V, t = 10 min) has revealed that the rate of contact angle increase is greater at the beginning and smaller at the equilibrium state. Furthermore, the as-prepared surface associated to the maximum fluid repellency and the lowest rolling angle due to the formation of

hierarchical micro/nano structural feature and the air trapped between the protrusions appears on the topographical view of the surface which enhanced corrosion resistance and reduced the corrosion rate up to nearly three order in the aggressive chloride media. This work also explains the wetting property in accordance with lotus-like superhydrophobic surface structure in nature after prolonged exposure of surface area intact with chloride water and suitable for the protection of surfaces during storage periods in coastal environments. This work demonstrates an effective pathway for designing and preparing a low cost, facile and durable coating on a large-scale industrial manner with controllable wettability.

Associated Content

Supporting information

Bouncing and Rolling off droplet on surface Movie S1 (mp4)

Water droplet after knife scratching test Movie S2 (mp4)

Water droplet on superhydrophobic surface Movie S3 (mp4)

Supporting information (Pptx)

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List of Figure Captions

Fig. 1 (a) Variation in average water contact angles (CA) and average contact angle hysteresis (CAH) of the surfaces as a function of different applied electrodeposition voltages. The error bars for each plot indicate the maximum and minimum water contact angles. (b) Molecular structure of myristic acid ($C_{14}H_{28}O_2$) and cerium nitrate hexahydrate $[Ce(NO_3)_3 \cdot 6H_2O]$.

Fig. 2 Variation in average water contact angles and average contact angle hysteresis of the surfaces fabricated at different electrodeposition times at constant voltage of 40 V. All the plots show averaged values of water contact angle and contact angle hysteresis at five different points on the same sample. The error bars for each plot indicate the maximum and minimum water contact angles and corresponding contact angle hysteresis.

Fig. 3 (a–f) FE-SEM micrographs of the as-prepared superhydrophobic surfaces obtained at different electrodeposition voltages: (a) 20 V, (b) 30 V, (c) 40 V, (d) 50 V, (e) 60 V and (f) 70 V. The right side of the images is magnified view of the left side images.

Fig. 4 (a–d) FE-SEM of as-prepared surface topographies deposit obtained at 40V with different electrodeposition times: (a) 5 min, (b) 10 min, (c) 15 min and (d) 20 min. The right side of the images is magnified view of the left side images.

Fig. 5 High resolution Spectrums of XPS of as-prepared superhydrophobic surface: (a) survey spectrum, (b) Ce 3d core level spectrum of Ce $3d_{3/2}$ and Ce $3d_{5/2}$, (c) O 1s spectrum, (d) C 1s spectrum, respectively.

Fig. 6 (a) Schematic illustrating mechanism of fabrication of cerium myristate $[Ce(CH_3(CH_2)_{12}COO)_3]$ and $Ce(CH_3(CH_2)_{12}COO)_4]$ ions on stainless steel 316L specimen (b) FTIR spectrum of cerium myristate coated stainless steel 316L at 40 V (c) Laser Raman spectrum of cerium myristate fabricated stainless steel 316L at different applied electrodeposition voltages.

Fig. 7 (a) Chemical composition analysis of durable superhydrophobic surface by energy dispersive X-ray spectroscopy (EDS), (b) variation in water contact angles (CA) and contact angle hysteresis (CAH) of superhydrophobic surface prepared at electrodeposition voltage of 40 V as a function of ionic strength

of NaCl solution. The error bars for each plot indicate the maximum and minimum water contact angles and corresponding contact angle hysteresis.

Fig. 8 (a) Variations in average water contact angles (CA) and average contact angle hysteresis (CAH) on superhydrophobic surface as a function of number of abrasion cycles (the inset schematic illustration is of shear abrasion test), (b) a photograph of spherical interface of water droplets on superhydrophobic surface obtained at 40 V after scratch test and inset minimum value of water contact angle, (c) topographical view of coated surface after abrasion test by optical microscope, (d) optical microscopic image after knife scratch test.

Fig. 9 (a) Tafel curves of modifier-free superhydrophobic surfaces at variable applied potential and bare specimen in 3.5 wt% sodium chloride (NaCl) medium, (b) schematic diagram of bare specimen and as-fabricated cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ based superhydrophobic sample in sodium chloride (NaCl) solution.

Fig. 10 (a–d) the process of contact, deformation, and approach of 10 μL water droplet suspending on syringe on cerium myristate $[\text{Ce}(\text{CH}_3(\text{CH}_2)_{12}\text{COO})_3]$ based superhydrophobic surface coating obtained at 40 V electrodeposition voltage.

Fig. 11 As shown in images (a) and (b), the phase field variable ϕ has a value of 1 in liquid phase (water droplet) and -1 in gas phase (air). In image (a), the solid phase (steel) corresponds to the case with hydrophobicity index $(\beta_s) = 0$, and it is to be noted that the system has yet not reached the lowest energy state. For the equilibrium energy states of water droplet on steel surfaces with β_s values corresponding to 0, -0.2 , -0.4 , -0.6 , -0.8 and -1.0 are presented in image (b), it is important to observe the change in colors of the solid steel surfaces in line with the numerical magnitudes of the hydrophobicity index (β_s) . The fitted curve in image (c) that shows the functional relationship between contact angle and hydrophobicity index ($R^2 = 0.994$) is obtained using the method of polynomial regression. In accordance to the curve, the contact angle of 167.7° corresponds to $\beta_s = -0.937$

Fig. 12 (a) Transient evolution of a nearly circular drop (smaller flatness at interface) at initial regime over a superhydrophobic surface with $\beta_s = -0.937$ ($\theta_c = 167.7^\circ$) at $t =$ (a1) 0.35, (b1) 25.5, (c1) 93.5, (d1) 543.5, and (e1) 2500 (b) Transient evolution of an initially hemispherical drop (larger flatness at

interface) over a superhydrophobic surface with $\beta_s = -0.937$ ($\theta_c = 167.7^\circ$) at $t =$ (a2) 0.35, (b2) 25.5, (c2) 93.5, (d2) 543.5, and (e2) 2500.

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Table 1 Elemental concentration of as-fabricated SHP surface determined by energy dispersive X-ray spectroscopy.

Table 2 Comparison of different polarization parameters for superhydrophobic surfaces and uncoated specimen in corrosive 3.5 wt% sodium chloride medium.

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Fig. S.1 Photograph of Spherical droplets on fabricated surface after traditional abrasion test

Fig. S.2 Transient evolution of an initially hemispherical drop deformed and recirculation (larger flatness at interface) over a superhydrophobic surface

Fig. S.3 (a) Nyquist plots of as-fabricated modifier-free steel 316L and bare sample prepared at variable electrodeposition voltages (b) Plots of Bode $\log(|Z|)$ with $\log(f)$ of SHP modifier-free steel 316L and bare sample.

List of Movies Captions of Supporting Information

Movie S1 Bouncing and Rolling off droplet on surface.

Movie S2 Water droplet after knife scratching test.

Movie S3 Water droplet on superhydrophobic surface.