

Simple Fabrication of Superhydrophobic Nickel Surface on Steel Substrate via Electrodeposition

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Received: 23 September 2016 / Accepted: 9 November 2016 / Published: 12 December 2016

Preparation of artificial superhydrophobic surfaces are in urgent demand in a specific domain. In the study, we obtained superhydrophobic nickel surface on steel substrates via electrodeposition nickel process and stearic acid modification, which are facile, time-saving and eco-friendly. The surface wettability, morphologies and chemical composition were analyzed by contact angle measurement, scanning electron microscope and Fourier transform infrared spectrometry. The results indicated that the $-CH_2-$ and $-CH_3$ groups of low surface energy were introduced into rough surface by modification with stearic acid, the rough surface was modified from superhydrophilic to superhydrophobic. When electrodeposition current density was 60 A/dm^2 , the as-prepared nickel surface showed excellent superhydrophobicity with a contact angle of 154.4° and a sliding angle of about 2.0° , and possessed micro-nano rough structures. Besides, the superhydrophobic nickel surface also had a good anti-corrosion performance. It is believed that the presented approach should have a prosperous future in industrial applications for the superhydrophobic surface fabrication on steel substrates.

Keywords: superhydrophobic; steel; electrodeposition; modification; anti-corrosion

1. INTRODUCTION

The surface which has a water contact angle (CA) greater than 150° and a sliding angle (SA) smaller than 10° is defined as superhydrophobic surface [1]. In nature, this kind of non-wettable surface can be commonly found on plants and insects, such as lotus leaf surface, rose petals, butterfly wings and fly eyes [2-5]. On superhydrophobic surface, water drops can form a sphere shape and roll off easily with little resistance. Additionally, coupled with its excellent performance in anti-fogging [6,7], self-cleaning [8,9] and oil-water separation [10,11], the superhydrophobic surface has a great application potential in life and industry. It is found that this kind of surfaces has both low surface

energy and dual-scale surface roughness, which play an important role in the development of the superhydrophobic theory [12,13]. After years of research, numerous methods have been developed for the preparation of artificial superhydrophobic surfaces, including sol-gel method [14,15], laser fabrication [16,17], solution-immersion process [18,19], etc.

As the most widely used metallic material, steel has better physical and mechanical properties than pig iron. Due to its reactive chemical properties, however, steel is easy to be corroded by oxygen in the air or other corrosive media. Preparation of artificial superhydrophobic surfaces on steel substrates is an efficient way to prevent or inhibit the corrosion [20,21]. In recent years, some methods to prepare superhydrophobic surface on steel substrate have been reported. Latthe et al. fabricated microstructured superhydrophobic surfaces via etching in acid solution for 12 hours and then followed by 2 hours subsequent hydrophobic silane treatment [22]. Motlagh et al. obtained silica sols by magnetically stirring the mixture of tetraethoxysilane-acetone solution and ammonium hydroxide-acetone solution for 20 hours and then sprayed them on the substrates to build superhydrophobic surface [23]. Nevertheless, the long fabrication duration and complex process have restricted its widespread application. A simple and highly-effective fabrication process is supposed to be developed.

As known, electrodeposition of nickel (Ni) is fast and effective for industry production and the stearic acid is a low-priced and nontoxic chemical reagent with a low surface free energy. In the work, we developed a facile and environmental friendly method of fabricating the superhydrophobic surface. The surface roughness structure was obtained via electro nickel plating, followed by reducing its surface energy via stearic acid modification. The process only needs 10 minutes. Furthermore, the as-prepared surface not only exhibited excellent waterproof property, but also showed a good anti-corrosion performance.

2. MATERIALS AND METHODS

2.1. Materials

Steel substrates with 60 mm×20 mm×1 mm were obtained from Baosteel Group Corp. Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was supplied by Tianjin Guangfu Fine Chemical Research Institute, China. Stearic acid (STA) was supplied by Tianjin Fuyu Fine Chemical Co., Ltd. All other reagents were of analytical grade and used without further purification.

2.2 Pretreatment of steel substrates

For preparation, the steel substrate was immersed in an alkaline solution containing 0.08M Na_2CO_3 , 0.5M NaOH, 0.2M $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 2 g/L emulsifier OP-10 at 60 °C for 3 minutes. Then the presented sample was immersed for 30s in a 0.4M H_2SO_4 at room temperature to remove the oxide film of the surface and subsequently flushed with deionized water.

2.3 Electrodeposition of Ni

The electrodeposition process was performed at a constant current supplied by a direct current (DC) power at room temperature, where the sample mentioned above was used as the cathode and Ti-IrO₂ as the anode [24]. The electrolyte solution contained 0.5M NiSO₄ and the distance between the sample and the Ti-IrO₂ plate was 1 cm. After electrodepositing for 5 minutes, the sample was removed from the solution, followed by rinsing with deionized water and drying. The reaction processes can be expressed as follows:



2.4 Chemical modification

To modify the electrodeposited Ni surface, the sample was immersed in 0.02M STA ethanol solution for 1 minute at room temperature. After dried with cold air, the superhydrophobic Ni surface was obtained. Fig. 1 shows the schematic illustration of the fabrication of the superhydrophobic Ni surface on the steel substrate.

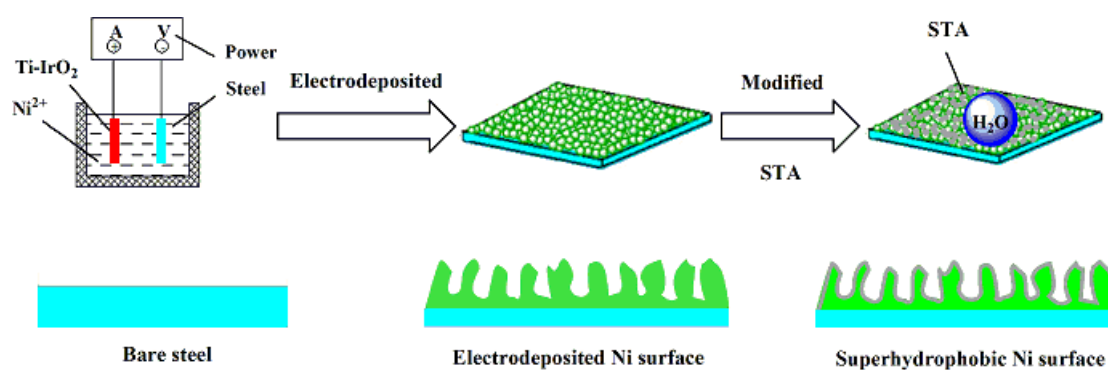


Figure 1. Schematic illustration of the fabrication of superhydrophobic Ni surface on the steel substrate.

2.5 Characterization

The CAs and SAs for water were measured by an optical contact angle meter (JCY-2, Fangrui) with a 3 μL water droplet at room temperature. All CAs were measured at five different positions and then averaged. The morphologies of the samples were characterized by scanning electron microscopy (SEM, Carl Zeiss AG Ultra Plus, Germany) equipped with an energy dispersive spectrometer (EDS). The roughness of the surface was measured by laser scanning confocal microscope (LSCM, OLS3100, Japan). Fourier transform infrared (FTIR) spectra were recorded with a VERTEX 70 Fourier transform infrared spectrophotometer (Bruker, Germany) in the range 4000 to 500 cm^{-1} . The polarization curves were obtained on an electrochemical workstation (Wuhan Corrtest, CS350) with a three-electrode

configuration, and the polarization curves were fitted using the Corrview software. The samples with an exposed area of 1.0 cm^2 were used as the working electrode. A platinum electrode and a saturated calomel electrode were used as auxiliary electrode and reference electrode, respectively. Polarization curves were measured with the scanning rate of 2 mV/s .

3. RESULTS AND DISCUSSION

3.1 Effect of current density on wettability

For the superhydrophobic surface, many factors affect the electrodeposition process, such as the pH value of electrolyte solution, time and temperature of electrodeposition, and the current density [25,26]. In this paper, the effect of current density was mainly considered. From Fig. 2, it can be shown that the CA of the superhydrophobic Ni surface changed significantly with the rise of current densities. The CA of the bare steel modified by STA was only 95.4° ; however, with the increasing of the current density, the CA had a gradual promotion. When the current density added up to 60 A/dm^2 , the modified samples showed the best superhydrophobicity with the CA of 154.4° and the SA of about 2.0° , then the CA began to decrease as the current increased. It is important to mention that the CA was less than 120° when the current density exceeded 80 A/dm^2 , because binding force between coating and metal base reduced markedly with obvious phenomenon of coating exfoliating. Therefore, it can be concluded that the current density of electrodeposition has a major impact on the surface hydrophobic property.

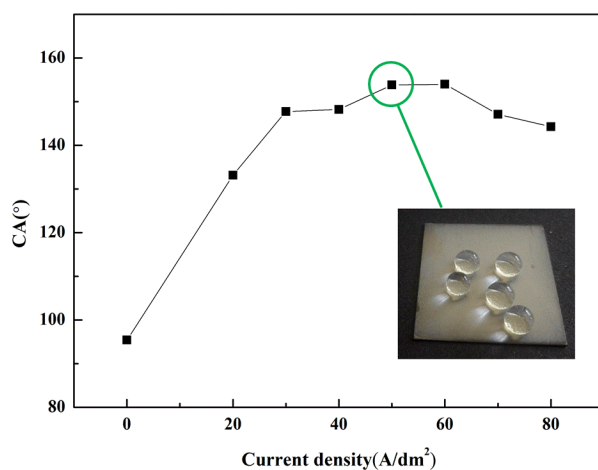


Figure 2. Effect of current density on the CAs of the sample surfaces.

3.2 Microstructure of the superhydrophobic Ni surface

In Fig. 3a-d, the images show the bare steel and the superhydrophobic Ni surface. The bare steel had an approximately smooth flat surface (except for the scratches during processing) with a CA of 68° (Fig. 3a-b). The superhydrophobic Ni surface composed with a large amount of micrometer-scale laminated crystals, forming micro-nano rough structures, and its CA increased to 154.4° (Fig. 3c). After further amplification, it can be seen that the surface was riddled with homogeneously

tortoise-shell-like structures with an average of 300 nm in which air can be trapped among the gaps (Fig. 3d). Fig. 4 shows LSCM topographical images of the steel surface and the superhydrophobic Ni surface. In Fig. 4a, the surface roughness (R_a) of bare steel surface was 0.167 μm . After electrodeposition and modification, the R_a of the sample increased to 2.036 μm (Fig. 4b), indicating that the air can be trapped easily in the interspaces for the roughness of the surface.

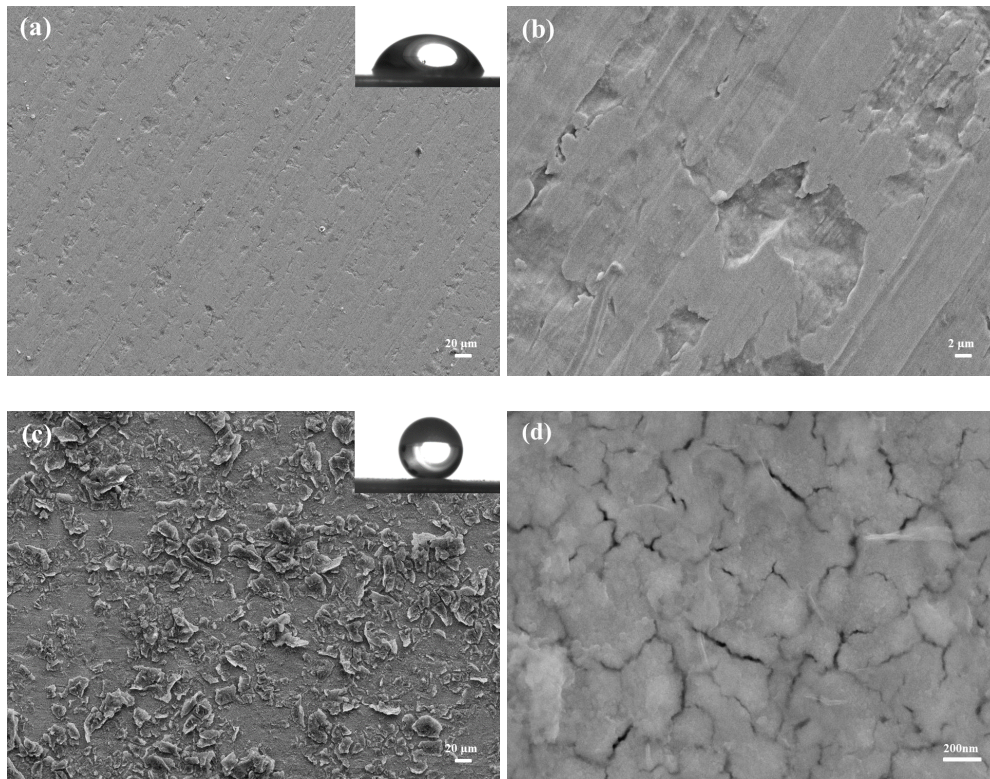


Figure 3. SEM images of the sample: (a) and (b) bare steel surface, (c) and (d) superhydrophobic Ni surface. The insets correspond to the CAs in (a) and (c).

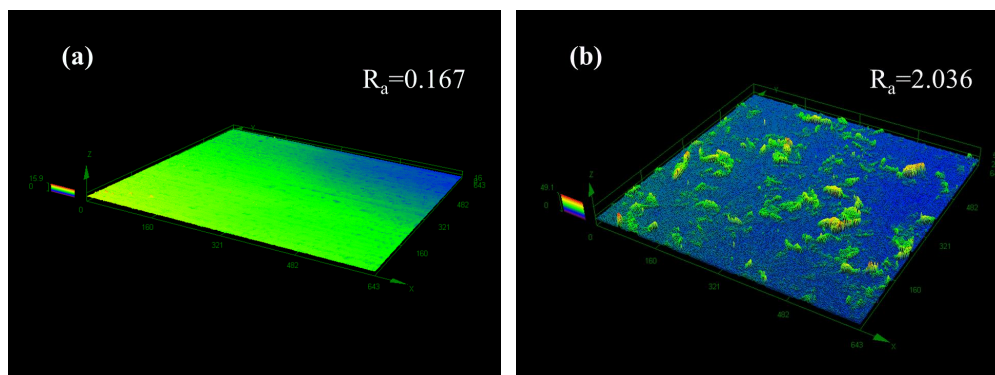


Figure 4. LSCM topographical images of bare steel surface (a) and superhydrophobic Ni surface (b).

In general, the Cassie-Baxter model can describe the superhydrophobicity [27], where the superhydrophobic Ni surface is seemed as a porous medium consisting of air. The CA was written as:

$$\cos\theta_r = f_1 \cos\theta_0 - f_2 \quad [4]$$

where f_1 and f_2 represent the fractional areas of the solid surface and air in contact with the liquid, respectively; θ_r (154.4°) and θ_0 (107°) represent the CAs on the STA modified rough and smooth surfaces, respectively [28]. Given that $f_1 + f_2 = 1$, f_1 and f_2 can be estimated at 0.143 and 0.857. That revealed that 85.7% of the contact area between water droplet and the sample was occupied with air. As the air is absolutely hydrophobic, the trapping air can largely enhance the surface hydrophobicity.

3.3 Chemical compositions of the superhydrophobic Ni surface

After electrodeposition and modification, the changes of the surface chemical components can be characterized via FTIR and EDS. Fig. 5a-b exhibit the FTIR spectra of the electrodeposited Ni surface before and after modification. Fig. 5c shows the EDS spectra of the superhydrophobic Ni surface.

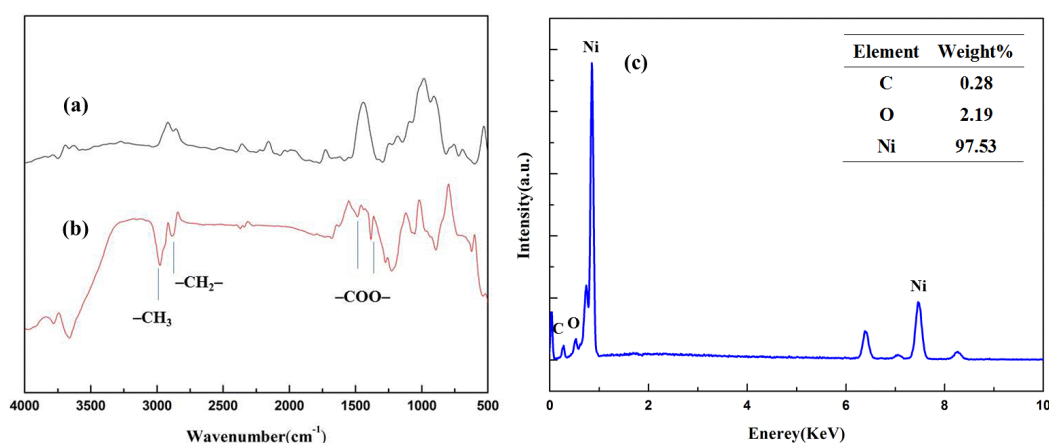


Figure 5. FTIR spectra of the electrodeposited Ni surface: (a) before modification and (b) after modification; (c) EDS spectra of the superhydrophobic Ni surface.

In the low frequency region, the -COO- vibration peak appears clearly at 1480 cm^{-1} and 1388 cm^{-1} in STA modified surface spectra [29], indicating that the adhesion of STA with electrodeposited Ni surface was successful. In the high frequency region, the peaks at 2972 cm^{-1} and 2880 cm^{-1} are attributed to the asymmetric stretching vibrations of the -CH_3 and $\text{-CH}_2\text{-}$ groups from STA, respectively [30]. Due to the existence of the -CH_3 and $\text{-CH}_2\text{-}$ groups, the free energy of electrodeposited Ni film was significantly decreased. Fig. 5c shows the EDS spectra of the electrodeposited Ni surface after modification. The Ni surface after STA modification contained the elemental C and O, which further explained that the STA molecules have successfully assembled to the electrodeposited Ni film.

3.4 Anti-corrosion performance

The potentiodynamic polarization measurement was widely performed to evaluate the anti-corrosion behaviors of the samples [31]. Fig. 6a displays the polarization curve of the bare steel,

electrodeposited Ni surface and superhydrophobic Ni surface measured in 3.5 wt.% NaCl solution. The corrosion current density (I_{corr}), can be calculated from the polarization curve by using Tafel extrapolation, the evaluation of the polarization parameters leads to the determination of the corrosion rate (V_{corr}) [32]. In addition, the corrosion resistances (R_{corr}) of samples were calculated from the Stearn-Geary equation [33]:

$$R_{corr} = \frac{b_a \cdot b_c}{2.303 \times I_{corr} (b_a + b_c)} \quad [5]$$

where b_a and b_c represent the Tafel slopes ($\Delta E/\Delta \log I$) of anode and cathode, respectively. All the values were shown in Table 1.

The surface with a low I_{corr} generally has a low V_{corr} and a high R_{corr} , which possesses a good corrosion resistance. As expected, it can be seen that the I_{corr} of superhydrophobic Ni surface is nearly a half of the bare steel and a sixth of the electrodeposition sample (Fig. 6b). The V_{corr} of superhydrophobic Ni surface is also the lowest, which is approximately 36.5% that of the bare steel and 16.9% that of the electrodeposition sample (Fig. 6c). Moreover, the superhydrophobic Ni surface has the highest corrosion resistance that is 3.3 times of the bare steel and 3.9 times of the modified steel (Fig. 6d). It can be confirmed that the superhydrophobic Ni surface has the best corrosion protective properties compared to the bare steel and the electrodeposited Ni surface. Interestingly, the electrodeposited Ni surface has the lowest corrosion resistance, because bare steel surface turned from hydrophilic to superhydrophilic after electrodeposition.

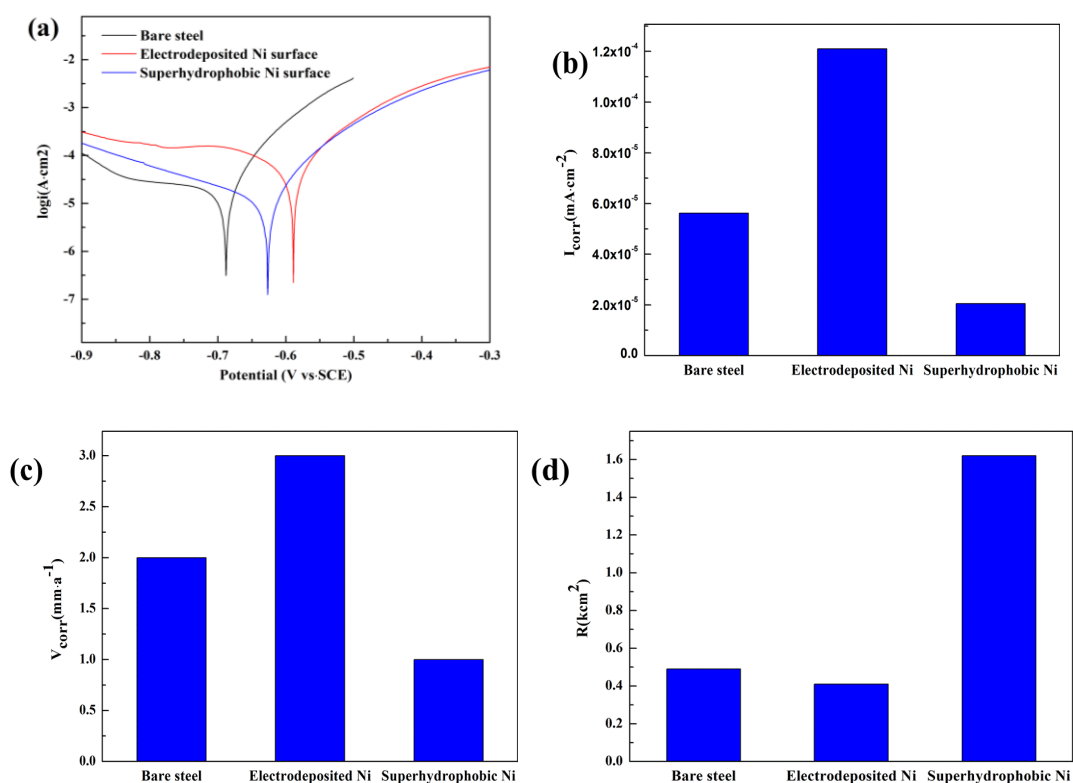


Figure 6. (a) Polarization curves, (b) I_{corr} , (c) V_{corr} and (d) R_{corr} of bare steel, electrodeposited Ni surface and superhydrophobic Ni surface.

Fig.7a illustrates the anti-corrosive mechanism of as-prepared coatings. The bare steel can be corroded easily, due to direct exposure to corrosive liquids without any protection. After electrodeposited and modified, the as-prepared superhydrophobic Ni surface was wrapped in structures on the micro and nanometer scales, which can simply trap the air between “peaks” in corrosive liquid, blocking the penetration of the corrosive medium into the substrate directly [34-36]. Section of the superhydrophobic Ni surface was shown in Fig. 7b, which confirmed that numerous peaks and gaps existed on the surface, contributing to the separation of corrosive medium and the substrate. Thus, superhydrophobic Ni surface has high performance in anti-corrosive.

Table 1. E_{corr} , I_{corr} , V_{corr} and R_{corr} of different samples.

Samples	$E_{corr}(\text{mV})$	$I_{corr}(\text{mA}/\text{cm}^2)$	$V_{corr}(\text{mm}/\text{a})$	$R_{corr}(\text{k}\Omega \cdot \text{cm}^2)$	$b_a(\text{V}/\text{dec})$	$b_c(\text{V}/\text{dec})$
Bare steel	-688	5.62×10^{-5}	0.82	0.49	0.42	0.075
Electrodeposited Ni surface	-589	1.21×10^{-4}	1.77	0.41	0.87	0.13
superhydrophobic Ni surface	-626	2.05×10^{-5}	0.30	1.62	0.51	0.09

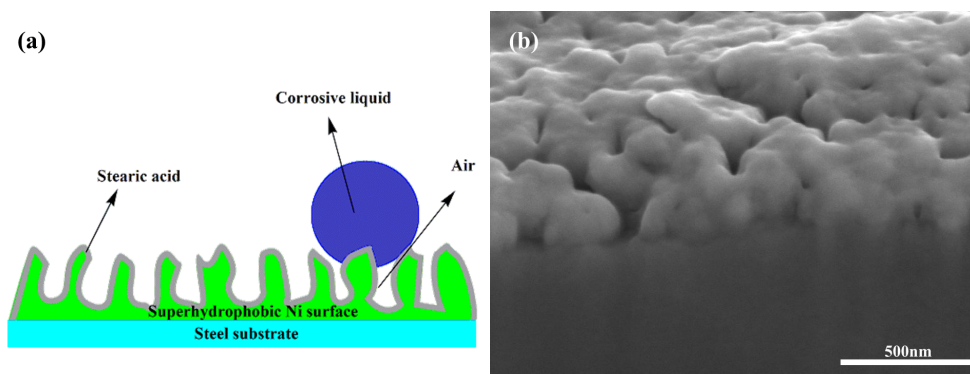


Figure 7. (a) Interface model for the corrosion mechanism of the superhydrophobic Ni surface. (b) SEM images of the superhydrophobic Ni surface section.

4. CONCLUSIONS

In summary, a simple, fast and eco-friendly preparation method for superhydrophobic Ni surface on steel substrate has been found. The electrodeposition current density has a major impact on the surface hydrophobic property, and shows the best effect at the current density of $60 \text{ A}/\text{dm}^2$. In this condition, the as-prepared superhydrophobic Ni surface with micro-nano rough structures has a CA of 154.4° and a SA of about 2.0° . After electrodeposition and modification, the R_a of the surface has a significant upgrade, increasing from 0.167 to $2.036 \mu\text{m}$. Moreover, The FTIR and EDS spectra show that the STA of low surface energy is successfully assembled on electrodeposited Ni surface. The polarization curve shows that the superhydrophobic Ni surface has a nice property of corrosion

resistance that can efficiently protect the steel substrates from corrosion. We believe that such a technique will have a promising future in expanding industrial applications for preparation of superhydrophobic surfaces on steel substrates.

ACKNOWLEDGMENTS

The authors thank the National Training Program of Innovation and Entrepreneurship for Undergraduates (No. 201610145034) and Fundamental Research Funds for the Central Universities (N130810001). Author-one (J.Y. Tan) and Author-two (J.J. Hao) contributed equally to this work.

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