Stearic acid-coated superhydrophobic Fe₂O₃/Fe₃O₄ composite film on N80 steel for corrosion protection

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1 **Stearic acid-coated superhydrophobic Fe₂O₃/Fe₃O₄ composite film on N80** 2 **steel for corrosion protection**

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12 13 **ABSTRACT**

14 Fe₂O₃/Fe₃O₄ composite films with micro-nanostructure are prepared on the N80 steel surface
15 by a two-step hydrothermal method, followed by heat treatment. The prepared dual-scale film,
16 after the modification with stearic acid, shows superhydrophobic property with a water contact
17 angle of 159.6° and sliding angle of 2.2°. The greatly decreased corrosion current density and
18 the largely increased impedance indicate the superhydrophobic surface can protect steel sample
19 well from corrosion. Furthermore, the superhydrophobic Fe₂O₃/Fe₃O₄ composite film also
20 showed excellent self-cleaning ability and was able to maintain its anti-wettability when
21 immersed in water. Our work finds that the concentration of NaOH in the second hydrothermal
22 method is a critical factor for the morphology of the Fe₂O₃ film and the annealing treatment
23 plays a significant role in realizing the superhydrophobic stearic acid coated micro-
24 nanostructure Fe₂O₃/Fe₃O₄ composite.

Keywords: superhydrophobicity, Fe₂O₃/Fe₃O₄ composite film, dual-scale film, corrosion resistance.

Highlights

- Micro-nanostructured Fe₂O₃ / Fe₃O₄ films are obtained after a two-step hydrothermal treatment and annealing
- The nanostructures on the micro-octahedral surface are affected by the concentration of NaOH
- The optimal superhydrophobic film displays a water contact angle of 159.6° and sliding angle of 2.2°
- The film also demonstrates more positive corrosion potential and much reduced corrosion current density

1. Introduction

Oil and natural gas pipeline, mostly made by N80 steel, is facing serious corrosion problems [1]. Preparing a superhydrophobic surface is a good strategy to prevent or alleviate the corrosion problem because it can effectively minimize the contact of the steel with the corrosive media. Superhydrophobic surface has been reported to possesses excellent properties in self-cleaning [2,3], anti-icing [4,5] and anti-corrosion [6,7].

Generally, the superhydrophobic surface is based on the hierarchical structures with low surface energy [8-10]. A composite film displaying surface features at different length scale will enable the formation of such hierarchical structure. Therefore, it is important to find the suitable

processing conditions in the preparation of the superhydrophobic surface on a steel surface [11-14]. For example, Zhang et al. used epoxy/polydimethylsiloxane (EP/PDMS) resins as the matrix and silica nanoparticles as the fillers to prepare superhydrophobic surface. They found the contact angle of the epoxy/polydimethylsiloxane-SiO₂ increased from 105° to 161°, and the structures was changed from bump to hollow grooves when the nano-SiO₂ increased from 5 to 30 wt% [15]. Koao et al. synthesized the octadecylamine (ODA)-capped ZnO nanostructures via the homogeneous precipitation method with annealing treatment. The flower-like particles of the ODA-capped ZnO were observed at 0.7 mol% ODA and the shape was transformed from flower-like structures to cylindrical nanorods when the ODA molar concentration increased from 5 to 15 mol% [16]. Moreover, Liu et al. bio-mimicked typical plant surfaces by a chemical immersion process. They found the structures on the surface of stainless steel changed from pits to lamellar when the FeCl₃ concentration increased from 0.5 M to 2 M, the corresponding water contact angle increased from 142.9° to 158.3° [17]. The concentration of the chemical solution would certainly influence the surface structures.

Herein, we report a simple two-step hydrothermal process to prepare micro-nanostructured Fe₂O₃/Fe₃O₄ composite thin film on N80 steel. The influence of the NaOH concentration on the surface morphology for the superhydrophobic sample is investigated. The micro-nanostructure was obtained after an annealing treatment. The results suggest that through hydrothermal and annealing treatments, appropriate hierarchical structures can be realized to display superhydrophobicity and excellent corrosion resistance after modification with stearic acid.

2. Experiment

68 2.1. Materials

69 The N80 (supplied by Yangzhou Keli environmental protection equipment Co., Ltd., the
70 composition in Table S1) sample was prepared from a steel rod with a diameter of 14.5 mm
71 using a wire-electrode cutting machine. A 100 ml Teflon-lined stainless-steel autoclave
72 (supplied by Xi'an Yi Chuang Laboratory Instrument and Equipment Co., Ltd., KH-100) was
73 used in this experiment. The chemical reagents used in our work include ethylenediamine
74 ($\text{C}_2\text{H}_8\text{N}_2$, EDA), Anhydrous ferric chloride (FeCl_3), sodium hydroxide (NaOH), stearic acid
75 ($\text{C}_{18}\text{H}_{36}\text{O}_2$), sulphuric acid (H_2SO_4 , 98%), anhydrous sodium sulfate (Na_2SO_4), sodium nitrate
76 (NaNO_3), and sodium chloride (NaCl) and ethanol. All of them were analytical grade,
77 purchased from Sinopharm, and used without further purification.

78 2.2. Experimental procedure

79 In a typical procedure, the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ micro-nanostructure were synthesized via a two-step
80 hydrothermal treatment followed by an annealing process. In the first hydrothermal treatment,
81 the circular N80 samples were ultrasonically cleaned in sequence with acetone, ethanol and
82 distilled water for 10 min each and dried in air. Then the samples were placed into a 100 ml
83 Teflon-lined stainless-steel autoclave with ethylenediamine aqueous solution (3.75 M, 20 ml)
84 at 165 °C for 7 h. Upon cooling, black samples (denoted as G1) were obtained after cleaning
85 by ethanol and distilled water. In the second hydrothermal treatment, a mixture of FeCl_3 (0.01
86 M) and NaOH (0.05 M, 0.1 M, 0.2 M, 0.3 M) was added into 20 ml distilled water and stirred
87 vigorously for several minutes. After that, the G1 samples were placed in the above solution in
88 a 100 ml Teflon-lined stainless-steel autoclave, heated at 90°C for 4 h. After cooling down, the
89 samples, denoted as G2, were cleaned by ethanol and distilled water. After the two-step
90 hydrothermal treatment, an annealing process was carried out for the G2 samples at 450 °C,
91 500 °C, 550 °C, and 600 °C for 2 h in air with the heating rate of 5 °C·min⁻¹. This temperature
92 will not greatly influence the metallographic structures and strength of the N80 steel (Figure S1

and S2). The annealed samples are named as G3. Subsequently, hydrophobic samples were obtained after modification with 8 mM stearic acid in ethanol solution for 5 h at room temperature, and the sample are named as G4. The procedure for the preparation of the hydrophobic samples is shown in Fig. 1.

Fig. 1. Schematic of the procedure on the preparation of the sample: G1, Fe₃O₄ film; G2, FeOOH/ Fe₃O₄ film; G3, Fe₂O₃/Fe₃O₄ film; G4, hydrophobic sample.

2.3. Sample characterization

X-ray diffraction (XRD) patterns of the samples were recorded by a Rigaku SmartLab X-ray diffractometer at a scanning rate of 0.2 per second with 2θ ranging from 20 to 80°, using Cu-K β radiation ($\lambda=1.3922$ Å). Fourier transform infrared spectrum (FTIR) was conducted on a VETEXV70 spectrometer from 3300 to 2300 cm⁻¹. Morphologies of the samples were studied by a field emission scanning electron microscope (FESME, ZEISS SIGMA). The water contact angles and sliding angles were measured with a JinHe JY-PHb contact angle measurement device. The electrochemical measurement was performed by CS350 electrochemical workstation at room temperature in 5 wt % NaCl aqueous solution. The conventional three-electrode system was used for the measurements with the saturated calomel electrode (SCE) as the reference electrode, Pt as the auxiliary electrode and the sample as the working electrode.

The working electrode was vertically immersed in the test solution and the constant steady state (open circuit) potential was recorded when it became virtually a constant. The scanning rate of the polarization measurement was $0.5 \text{ mV}\cdot\text{s}^{-1}$ and the electrochemical impedance measurements were explored in the frequency range from 10 mHz to 100 kHz with an amplitude of 10 mV.

3. Results and discuss

3.1. The wettability of the different sample surfaces

The water contact angle and sliding angle of the bare N80 and G4 sample with different NaOH concentrations are shown in Fig. 2.

Fig. 2. (a) Water contact angle of the bare N80 (SEM images in Figure S3). Optical image of the water contact angle and sliding angle of the G4 sample with different NaOH concentrations in the second hydrothermal treatment: (b) 0.05 M (c) 0.1 M (d) 0.2 M (e) 0.3 M. (f) Summary of the water contact angle and sliding angle of the G4 sample with different NaOH concentrations,

WCA stands for the water contact angle and SA stands for sliding angle.

As shown in Fig. 2a, the water contact angle on the bare N80 was 50.2°, which displayed the expected hydrophilicity. The water contact angles of G1, G2 and G3 sample for different conditions are displayed in Figure S4. The G1 sample is slightly hydrophobic, but G2 samples are hydrophilic. After annealing treatment, the G3 samples become more hydrophilic than G2. After modification with stearic acid, the G4 samples displayed great superhydrophobicity especially the one treated in 0.2 M NaOH solution. As indicated in Fig. 2b, the sliding angle was 13.3° for the G4 sample with 0.05 M NaOH although the water contact angle was higher than 150°. The water contact angles of G4 samples with 0.1 M, 0.2 M, 0.3 M NaOH (Fig. 2c, 2d and 2e) were all higher than 150°, and the sliding angles were less than 10°. The G4 sample with 0.2 M NaOH performed better than others, with a water contact angle of 159.6° and sliding angle of 2.2°. The results indicated that the different NaOH concentrations play a significant role in controlling the wettability for the G4 samples.

3.2. Electrochemical measurement

The potentiodynamic polarization of the G4 samples with different NaOH concentrations in 5 wt% NaCl aqueous solution was obtained by Tafel extrapolation method and shown in Fig. 3a. The corrosion current density (I_{corr}) and potential (E_{corr}) are displayed in Fig. 3b.

Fig. 3. (a) Potentiodynamic polarization curves measured in 5 wt% NaCl aqueous for the bare N80 and G4 samples with different NaOH concentrations in the second hydrothermal treatment. (b) the corresponding corrosion current density (I_{corr}) and corrosion potential (E_{corr}).

A lower corrosion current density (I_{corr}) and a higher corrosion potential (E_{corr}) means a better corrosion resistance and lower corrosion rate [18,19]. Compared with the bare N80, the corrosion potentials of the G4 samples with different NaOH concentrations were shifted positively, making the corrosion of the N80 surface more difficult to happen. Furthermore, the lower anodic current densities of the G4 sample in comparison to the bare N80 also indicates the film acts has decreased the corrosion rate of N80 steel. From Fig. 3b, the corrosion current density (I_{corr}) values decrease from 196.5 to 14.4 $\mu\text{A}\cdot\text{cm}^{-2}$ and the corrosion potential values increase from -0.542 to -0.318 V. Among the G4 samples with different NaOH concentrations, the corrosion current density is the smallest for the G4 sample with 0.2 M NaOH, which means the best inhibition of corrosion.

Electrochemical Impedance Spectroscopy (EIS) is the common method to investigate the corrosion inhibition process. Fig. 4 displays the Nyquist, Bode and phase angle plots for the bare N80 and the G4 samples with different NaOH concentration in 5 wt% NaCl aqueous

solution. The electrochemical behavior of G1, G2 and G3 samples also shown in Figure S5.

Fig. 4. (a) Nyquist poles, (b) Bode and (c) phase angle plots of the bare N80 and G4 sample with different NaOH concentrations in the second hydrothermal treatment after immersing in 5 wt% NaCl aqueous solution. (d) Equivalent electrical circuits for EIS results of (i) bare N80 and (ii) G4 samples.

As shown in Fig. 4a, diameter of the semicircle in the Nyquist loop of the G4 samples with different NaOH concentration is larger than that of the bare N80, which indicates a better corrosion resistance. The largest diameter of the semicircle was observed in the G4 sample with 0.2 M NaOH concentration. Fig. 4b and 4c show that the impedance of all G4 samples were higher than that of the bare N80, and the angle of the G4 samples was around 90° . This confirms the better corrosion resistance of the treated samples than the bare N80. Furthermore, there is

only one time constant for the bare N80, while there are two time constants for the G4 samples owing to the capacitance derived from the organic coating (Fig. 4c). Therefore, the equivalent circuits in Fig. 4d(i) and Fig. 4d(ii) are chosen for the bare N80 and G4 samples, respectively. The EIS data are shown in Table 1. The R_{ct} is the charge transfer resistance and the value of R_{ct} increased from the bare N80 of 85.36 to 4095 $\Omega \cdot \text{cm}^2$ for the treated sample. Furthermore, the C_{dl} is the capacitance of the double electrical layer and it decreased from the bare N80 of 367.8 to $3.803 \times 10^{-5} \text{ S} \cdot \text{sn}/\text{cm}^2$ for the treated sample. The higher value of R_{ct} and the smaller value of C_{dl} indicate the slower corrosion rate, which confirms that the G4 sample with 0.2 M NaOH concentration provides the best protection to the N80 steel.

The surface coverage is a significant parameter to evaluate the quality of the film, which could be calculated by Eq. (1).

$$\theta = 1 - \frac{R_{t0}}{R_t} \quad (1)$$

where the θ is the surface coverage of film on the electrode surface. R_{t0} is the resistance of the bare N80, and R_t is the sum of R_{ct} and R_f of the G4 samples [20,21].

Table 1. Electrochemical parameters of specimens obtained from EIS Equivalent electrical circuit

specimen	R_s ($\Omega \cdot \text{cm}^2$)	C_f ($\text{S} \cdot \text{sn}/\text{cm}^2$) (n)	R_f ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\text{S} \cdot \text{sn}/\text{cm}^2$) (n)	R_{ct} ($\Omega \cdot \text{cm}^2$)	θ (%)
Bare N80	7.577			367.8 (0.803)	85.36	
G4 sample with 0.05 M NaOH	0.211	4.83×10^{-7} (1)	79.34	2.09×10^{-4} (0.4406)	1355	94.05
G4 sample with 0.1 M NaOH	0.418	4.48×10^{-7} (1)	82.52	1.06×10^{-4} (0.5761)	2177	96.22

G4 sample with 0.2 M NaOH	0.327	3.70×10^{-7} (1)	253.1	3.80×10^{-5} (0.6101)	4095	98.04
G4 sample with 0.3 M NaOH	0.158	5.74×10^{-7} (1)	141.3	2.43×10^{-4} (0.492)	3770	97.82

Based on the calculations, the highest θ (98.04%) was obtained from the G4 sample with 0.2 M NaOH concentration, indicating it is most dense film among all.

3.3. Surface morphology

The surface of the micro-octahedral facets is smooth after hydrothermal treatment. In contrast, the surface of micro-octahedral structures become rougher and nanoparticles are observed after the annealing process, as shown in [Figure S6](#). The effect of NaOH concentration in the second hydrothermal treatment on the morphology was investigated and results are shown in [Fig. 5](#). At the low NaOH concentration of 0.05 M, some plate- or needle-like structures were found between the micro-octahedral structures. With the NaOH concentration increased to 0.1 M, the number of the plate or needle-like structures decreased. When the NaOH concentration was higher than 0.2 M, the sheet structures disappeared while small nanorods were observed on the edge of the micro-octahedral structure. This means that the NaOH concentration will significantly affect the location of the nucleation and the shape of the surface fine structures. Furthermore, the nanorods became smaller and thinner when the NaOH concentration reached 0.3 M ([shown in Figure S7](#)). From the water contact and sliding angle of the G4 samples with different NaOH concentrations, it could be found that the wettability of the G4 sample became more superhydrophobic with the decrease of the plate- or needle-like structures.

Moreover, the influence of the annealing temperature on the surface morphology was also

investigated, as shown in Figure S8. It could be found that the complete coverage by nanoparticles emerged only at the temperature higher than 500 °C. The micro-octahedral structure collapsed when the temperature exceeds 600 °C. Therefore, the annealing temperature in the range of 500~550 °C is the optimal for the complete coverage of nanoparticles without destroying micro-octahedral structures.

The dual-scale micro-nanostructures were obtained after a two-step hydrothermal method and an annealing treatment. The first hydrothermal treatment was conducted to form the micro-octahedron structure. The second hydrothermal treatment, using NaOH solution instead, plays the role of ensuring nanostructure formation, after the annealing, not only on the micro-octahedron surface, but also in-between the space of these octahedral. With the second hydrothermal treatment, the hierarchical micro-nanostructures are better spread out over the entire surface, warranting a better hydrophobicity and thus much improved corrosion resistance.

Fig. 5. SEM images of the G3 samples with different NaOH concentration (a) 0.05 M, (b) 0.1 M, (c) 0.2 M, (d) 0.3 M.

Fig. 6. XRD patterns of (a) the G2 sample under 0.2 M NaOH concentration and the G3 sample annealed under 550 °C with (b) 0.05 M, (c) 0.1 M, (c) 0.2 M and (d) 0.3 M NaOH concentration.

Fig. 6. shows the X-ray diffraction patterns of the G2 sample under 0.2 M concentration and G3 samples with different NaOH concentrations under the annealed temperature of 550 °C. All the diffraction peaks in Fig. 6a of the G2 sample could be indexed with the standard JCPDS card No.19-0629 for Fe_3O_4 [22] and No. 06-0696 for Fe. We believe FeOOH was present after the second hydrothermal treatment, which corresponds to the plate or needle-like structures [23,24]. However, this phase was not detected by XRD as it was in amorphous form. An evidence was given by the color of the solution after the second hydrothermal reaction, which was yellowish-brown (Figure S9). Based on the XRD patterns (Fig. 6b-e) for the G3 samples with different NaOH concentrations under the same annealed temperature, diffraction peaks are indexed to Fe_2O_3 (JCPDS card No.33-0664) [25], in addition to the ones from Fe_3O_4 and Fe phases. The (104) diffraction peak of the Fe_2O_3 in Fig. 6d is stronger than that in other XRD patterns, which indicates that the crystallinity of Fe_2O_3 under 0.2 M NaOH concentration is higher than that of other NaOH concentrations. Based on the above analyses, $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$

composite phases were obtained after the two-step hydrothermal treatment and annealing process. As confirmed by FTIR in Figure S10, stearic acid was successfully coated on the surface.

3.5. Anti-wettability behaviors of the superhydrophobic sample

The anti-wettability behaviors of the superhydrophobic sample were examined by water bouncing test, water jetting test, self-cleaning, and immersion test, as shown in Fig. 7.

Fig. 7. Photographs of (a) the bare N80 for water bouncing test and water jetting test. Tests on the superhydrophobic sample for (b) water bouncing test, (c) water jetting test, (d) self-cleaning and (e) immersion test. The optimal G4 sample was used in these tests.

From the photograph of the bare N80 (Fig. 7a), water droplets stayed on the surface of the bare N80 when they were in contact with the surface. In contrast, there was a great difference when the water droplets dropped on the surface of the superhydrophobic sample (the optimal G4 sample). As shown in Fig. 7b, the water droplets bounced away when they were dropped onto the surface of superhydrophobic sample. Similar behavior was displayed in Fig. 7c for the water

jetting test. When the continuous water jet hit the surface of superhydrophobic sample, the water jet was bounced off continuously. The self-cleaning test of the superhydrophobic sample is exhibited in Fig. 7d. The angle of inclination for the superhydrophobic sample was around 3°. The chalk crumbs sprinkled on the surface were taken away when the water droplets slid on the surface. Therefore, the superhydrophobic sample displayed great anti-wettability because of the air cushion and the lower surface energy. In order to prove the existence of the stable air cushion, the superhydrophobic sample was immersed under the water, as shown in Fig. 7e. The surface under the water showed a high reflectivity of light due to the presence of a layer of air cushion between the surface and water.

3.6. Wetting of different pH solutions

The contact angle and sliding angle on the superhydrophobic sample (G4 with 0.2 M NaOH) by solutions with different pH are displayed in Fig. 8. NaOH and H₂SO₄ solution were used to adjust the pH value. The change in the contact angle was relatively small in the range of 154.5~160.8°. When the pH value was at 1 or 14, the sliding angle showed a drastic change, reaching around 20°. In the range of 2~13, the sliding angle varied but was within 10°, a criterion for superhydrophobicity. The current study indicates that our coating could display excellent great anti-wettability in a wide range of pH values from 2 to 13.

Fig. 8. The variation of contact angle and sliding angle of the best G4 sample with different solution pH values.

Table 2. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) of bare N80 and the G4 sample with 0.2M in different corrosive solutions. The standard deviation is based on the I_{corr} of 3 samples for each condition.

samples	5 wt% NaNO ₃		5 wt% Na ₂ SO ₄		pH=1 H ₂ SO ₄		pH=14 NaOH	
	solution		solution		solution		solution	
	E_{corr} (V)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{corr} (V)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{corr} (V)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{corr} (V)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)
Bare N80	-0.377	80.5	-0.697	119.5	-0.417	1996.8	-0.174	45.9
G4 sample with 0.2 M NaOH	-0.266	5.3	-0.329	6.6	-0.521	1229.4	-0.227	10.5
Standard deviation of I_{corr} for G4 sample	5.54×10^{-7}		2.612×10^{-5}		3.54×10^{-4}		7.21×10^{-6}	

Besides the 5 wt% NaCl aqueous solution, the superhydrophobic sample also performed well again other corrosive media. The potentiodynamic polarization curves are displayed in Fig. 9a and 9b and the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are summarized in Table. 2. The corrosion current densities (I_{corr}) of the superhydrophobic sample were greatly decreased in 5 wt% Na₂SO₄, 5 wt% Na₂NO₃, extremely acidic (H₂SO₄, pH=1), and extremely alkaline (NaOH, pH =14) solutions.

Fig. 9. Potentiodynamic polarization and Nyquist plots of the bare N80 and superhydrophobic sample in different corrosive solutions: (a) (b) 5 wt% $NaNO_3$ aqueous solution and 5 wt% Na_2SO_4 aqueous solution, (c) (d) pH = 1 H_2SO_4 aqueous solution and pH = 14 NaOH aqueous solution.

The schematic diagram in Fig. 10 summarizes the reason for the composite film to have displayed the superhydrophobicity and the differences resulted from the treatment using different NaOH concentrations in the second hydrothermal treatment. The micro-octahedral structures for Fe_3O_4 were formed by the first hydrothermal treatment. Moreover, after the second hydrothermal treatment and annealing process, the nanoparticles appeared on the surface on the micro-octahedral structures. Nanorods scattered on the edge of micro-octahedral structures for the G3 sample with 0.2 M NaOH treatment and plate-like structures were

observed between micro-octahedral structures for the G3 sample with 0.05 M NaOH treatment.

The micro-nanostructures $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ composite film was formed on the N80 substrate, performing a great superhydrophobicity after the modification of stearic acid. The optimal is the G4 sample with 0.2 M NaOH, which displayed higher surface coverage, higher water contact angle and smaller sliding angle than that of the G4 sample with 0.05 M NaOH. A large amount of air pockets can be trapped in the hierarchical micro-nanostructures between liquid and solid, which could reduce the contact area of the water on the substrate, exhibiting great superhydrophobicity and anti-corrosion performance.

Fig. 10. Schematic diagram of the air pockets trapped by micro-nanostructure and the different NaOH induced the different surface morphology to exhibit different wettability.

4. Conclusion

In this paper, a new route to fabricate a micro-nanostructured $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ composite film on N80 steel surface was presented. It takes a two-stage hydrothermal treatment, followed by annealing treatment in air at 550 °C for 2 h. The obtained $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ composite film displayed

a water contact angle of 159.6° and sliding angle of 2.2° after the modification with stearic acid. The significant change in the micro-octahedral structures on the surface leads to the dual-scale roughness and has improved the anti-wetting performance. The superhydrophobic sample performed excellently in self-cleaning, water bouncing, and water jetting tests. It is also able to maintain great superhydrophobicity for the water droplets at a large pH range. Based on the electrochemical experiment, the optimal sample displayed the best corrosion resistance in different corrosive solutions. This work proves the micro-octahedron / nanorod structure formed on the N80 steel surface play an effective role for anti-corrosion performance. Lesson learnt from this study will be useful for the design of corrosion protection of other metals and alloys in the future.

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