

Synergistic effect of nano-silica and copper grains on the superhydrophobicity and corrosion resistance of silane coatings on carbon steel

Jinjian Liu

Shandong University of Aeronautics

Ziyan Feng

Zyfengphd@163.com

Shandong University of Aeronautics

Mingwei Cui

Shandong University of Aeronautics

Yujie Sui

Shandong University of Aeronautics

Research Article

Keywords: Q235B steel, superhydrophobic coating, nano-SiO₂, micro-nano structure, corrosion protection

Posted Date: October 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10368045/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Synergistic effect of nano-silica and copper grains on the superhydrophobicity and corrosion resistance of silane coatings on carbon steel

Jinjian Liu^a, Ziyang Feng^{a*}, Mingwei Cui^a, Yujie Sui^a

^aCollege of Chemical Engineering and Materials, Shandong University of Aeronautics, Binzhou, Shandong, China

Abstract: Q235B carbon steel is one of the most widely used structural materials in the field of industrial engineering. However, the corrosion failure problem in harsh service environments restricts its service life and application safety. Existing anticorrosive coatings generally have defects such as high preparation costs, complicated processes, and poor eco-friendliness. In order to address these issues, this study utilized a simple chemical displacement deposition and silane synergistic modification method to prepare a superhydrophobic composite anti-corrosion coating on carbon steel. The experiment focused on investigating the effects of the doping strategy and concentration of nano-silica on the micro-nano morphology, surface wettability, and electrochemical protection effect of the coating. The results demonstrate that the direct doping of nano-SiO₂ in the deposition solution destroys the physical continuity of the surface structure, leading to a negative impact on the overall hydrophobicity and corrosion resistance of the coating. After process optimization, a uniform micro-nano hierarchical rough structure can be constructed on micron-sized copper grains by chemical deposition for 50 s combined with a silane modification solution containing 0.3 wt% nano-SiO₂. Under this optimal condition, the static water contact angle of the coating reaches 160°. Electrochemical tests indicate protective properties, exhibiting an approximately 4.5-fold enhancement in polarization resistance and a nearly 75% reduction in corrosion current density relative to the bare substrate, which suppresses the interfacial corrosion kinetics. Furthermore, under long-term continuous immersion in a 3.5 wt% NaCl solution (>500 h), the coating maintained a physical and chemical shielding barrier, halving the cumulative macroscopic corrosion rate compared to the unprotected steel. The composite preparation scheme proposed in this study provides a simple and reliable technical reference for the low-cost anti-corrosion treatment of carbon steel components.

Keywords: Q235B steel; superhydrophobic coating; nano-SiO₂; micro-nano structure; corrosion protection

1. Introduction

With the rapid development of modern industry, metal material protection has become a key engineering challenge. Metal corrosion is a natural phenomenon in which metals react with the external environment to form stable compounds such as oxides and sulfides, which severely compromises the structural integrity and utility of metals[1]. Therefore, effectively

* Corresponding author at: College of Chemical Engineering and Materials, Shandong University of Aeronautics, Binzhou, 256600, China.

E-mail address: zyfengphd@163.com

mitigating corrosion is crucial, as it not only saves resources and reduces maintenance costs but also significantly prolongs the service life of equipment and materials[2]. With excellent performance and cost advantages, Q235B carbon steel is widely used in oil gathering and transportation pipelines, marine engineering and various industrial infrastructures. However, in the harsh environment containing chloride ions, electrochemical corrosion is prone to occur, which will not only lead to a sharp decrease in the service life of the equipment, but also lead to potential safety hazards and economic losses such as pipeline perforation and medium leakage[3]. Traditional anti-corrosion methods mainly rely on organic coatings or electroplating. Although they can delay corrosion in a short period of time, they inevitably have application problems such as easy aging and peeling of coatings, internal micro-pore defects, and environmentally unfriendly preparation processes[4].

To overcome the limitations of traditional anti-corrosion technologies, bionic surface modification technology has gradually become a research hotspot in the field of metal protection. In recent years, superhydrophobic coatings based on the lotus leaf effect have provided a promising technical path for long-term corrosion protection of metals[5]. The protection and antifouling properties of superhydrophobic coatings are synergistically regulated by multi-level micro-nano rough morphology and low surface energy components[6,7]. This composite rough structure can greatly reduce the solid-liquid contact area, make the water droplets show a high static contact angle and roll off quickly, effectively block the adsorption and infiltration of corrosive media such as water and chloride ions on the surface of the matrix, and inhibit the corrosion interface reaction from the source[8].

In addition to anti-corrosion, the special micro-nano structure also endows the surface with multiple practical functions such as self-cleaning and oil-water separation. Water droplets on superhydrophobic surfaces exist in a metastable state; even slight inclination causes them to roll and carry away surface contaminants, effectively reproducing the 'lotus leaf effect'[9]. The transparent superhydrophobic coating prepared by Yoon et al. on glass by electrospraying has a light transmittance of 90% and exhibits excellent dust removal and self-cleaning ability[10]; The coating prepared by Tong using carbonaceous soot can make the acid and alkali solution and all kinds of domestic sewage quickly bounce off and achieve efficient self-cleaning[11]. In addition, taking advantage of the significant difference in surface tension between water and oil (water is about 72.8 mN/m, most oil < 40 mN/m), the superhydrophobic-superoleophilic synergistic characteristics can be achieved by regulating the surface energy of the coating, which can be extended to the field of oil-water separation[12]. Wang et al. used the superhydrophobic surface constructed by impregnated porous materials with dopamine and silane to efficiently adsorb organic solutes in water and have the ability to recycle[13].

Although superhydrophobic surfaces perform well in multi-functional applications, their core value in the field of metal protection still lies in their excellent anti-corrosion mechanism. Its microstructure can capture a large amount of air and form an 'air cushion' at the solid-liquid interface, effectively avoiding large-area contact between the liquid and the substrate, thereby inhibiting electron transfer and reducing the corrosion rate[14]. The composite coating prepared by Feng et al. exhibited excellent electrochemical corrosion resistance in 3.5 wt% NaCl solution[15]; The dual protective composite coating constructed by Li et al. on the surface of magnesium alloy not only can actively resist corrosion, but also

has the ability of micro-damage self-healing. Electrochemical tests have confirmed its excellent protective performance[16].

With the in-depth study of anti-corrosion mechanism, the preparation process of superhydrophobic surface is also increasingly rich. At present, the mainstream methods include etching[17,18], electrochemical deposition[19], spraying[20] and other technologies. In terms of laser and etching, Sun et al. coated composite materials on the laser-treated aluminum surface to obtain a superhydrophobic surface with high wear resistance and self-cleaning properties[21]; Khan et al. used chemical etching to construct a silver-based superhydrophobic layer on a copper substrate, which reduced the corrosion current by 4.47 times and significantly improved the corrosion resistance[22]; Sun et al. innovatively used neutral electrolyte to etch stainless steel to achieve superhydrophobic and anti-icing functions[23]. In terms of spraying process, Zhang et al. constructed a coating with photothermal self-healing function by spraying, which took into account both corrosion resistance and chemical stability[24]; Goraleczyk et al. prepared Fluoropor superhydrophobic materials by spraying and photopolymerization of fluorinated monomers[25]. In the field of electrodeposition, Zheng et al. constructed a coating in situ on magnesium alloy by one-step electrodeposition, and the immersion test confirmed its long-term protection[26]; Xu et al. constructed a sponge-like micro-nano structure based on laser-enhanced local electrodeposition technology, which exhibited excellent superhydrophobic properties after modification with low surface energy materials[27].

Although the existing preparation routes can achieve high-performance superhydrophobic surface construction, they generally have shortcomings such as long preparation process, high investment cost of high-end equipment, and dependence on highly toxic fluorine-containing low surface energy reagents, which seriously limit their large-scale industrial application. In contrast, chemical displacement deposition can grow a metal rough layer in situ on a metal substrate, which has outstanding advantages such as simple operation, short preparation cycle, and easy large-area film formation[28]. Nano-SiO₂ is an ideal inorganic filler for constructing hierarchical micro-nano composite framework due to its low raw material cost, excellent thermochemical stability and rich polar hydroxyl groups on the surface[29]. The combination of nano-SiO₂ and fluorine-free long-chain alkylsilane can not only form a dense cross-linked network through hydrolysis condensation reaction to reduce the surface free energy, but also significantly improve the overall mechanical durability and corrosion resistance of the coating by means of the physical inlay of nanoparticles[30].

Based on this, this paper proposes a low-cost and easy-to-implement collaborative composite preparation method. Using Q235B steel as the substrate, micron-sized copper grains are grown in situ on its surface by controlling the deposition time of the substrate in an acidic copper sulfate solution. Subsequently, leveraging the hydrolytic condensation reaction of octadecyltrimethoxysilane in combination with varying mass fractions of nano-SiO₂, a binary "micron-nano" composite layered structure was fabricated on the micron-scale copper layer. This paper focuses on comparing and investigating the effects of nano-SiO₂ doping concentration and doping strategies on the evolution of coating microstructure and surface wettability, while systematically evaluating the anticorrosive mechanisms of the coatings.

2. Experimental Section

2.1. Experimental materials

Octadecyltrimethoxysilane (ODTMS), $\geq 95\%$, Shandong Keyuan Biochemical Co., Ltd.; anhydrous ethanol, $\geq 99.7\%$, Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd.; anhydrous copper sulfate, $\geq 99\%$, Tianjin Tianli Chemical Reagent Co., Ltd.; concentrated sulfuric acid, $95\% \sim 98\%$, Yantai Far East Fine Chemical Co., Ltd.; nano-silica (W0.05 μm), Changsha Xinhui Electronic Technology Co., Ltd.

2.2. Characterization methods

In this study, a variety of methods were used to systematically characterize the structure and properties of the composite coating. In terms of chemical composition and phase analysis, the molecular structure and functional groups of the modified silane layer were characterized by Nicolet iS50 Fourier transform infrared spectrometer, and the test band was set to $400 \sim 4000 \text{ cm}^{-1}$; The crystal structures of CuO/ODTMS-SiO₂ coatings with different mass fractions were determined by Ultima IV X-ray diffractometer. The scanning range was set to $10^\circ \sim 80^\circ$; The surface element composition and chemical state changes of the coating before and after immersion were analyzed by Thermo ESCALAB Qxi X-ray photoelectron spectrometer.

In terms of micro-morphology, the micro-nano morphology characteristics of the coating surface were observed by scanning electron microscopy, and the three-dimensional morphology data and roughness parameters of the surface were extracted by non-contact 3D confocal microscopy.

In terms of performance evaluation, the surface hydrophobicity was measured by the SDC-100H contact angle measuring instrument. Each sample was randomly selected at three different positions on the surface to measure the contact state of the droplets and take the average value. The electrochemical corrosion resistance of the coating was analyzed by Shanghai Chenhua CHI series electrochemical workstation. The main test items include potentiodynamic polarization curve and electrochemical impedance spectroscopy.

2.3. Preparation of composite coating

In order to explore the best doping strategy of nano-SiO₂ and its effect on the microstructure and final corrosion resistance of the coating, two different composite preparation methods were designed as controls based on the above preparation mechanism. CuO-SiO₂/ODTMS coatings were prepared by introducing nanoparticles (deposition solution doping) into the micro-structure construction stage and CuO/ODTMS-SiO₂ coatings were prepared by introducing nanoparticles (modification solution doping) into the final modification stage.

2.3.1. Preparation of CuO/ODTMS-SiO₂ coating

The preparation process of CuO/ODTMS-SiO₂ composite superhydrophobic coating is shown in Figure 1. The process mainly includes three stages: cleaning and pretreatment of the substrate surface, construction of micron-scale rough structure on the surface, and final formation of micro-nano composite hierarchical structure. First, the surface-activated Q235B was immediately immersed in 0.2 M acidic copper sulfate solution, and the deposition time was controlled to be 50 s. After removal, it was rinsed with anhydrous ethanol and dried, and naturally oxidized in air at room temperature for 1h to construct active sites. Then the silane

modified solution (1.0 wt% octadecyltrimethoxysilane, 2.0 wt% deionized water, 2.0 wt% glacial acetic acid and 95 wt% anhydrous ethanol) was prepared. On this basis, 0 wt% (control group), 0.1 wt %, 0.2 wt %, 0.3 wt % and 0.4 wt % nano-SiO₂ particles were added according to the mass fraction. The mixed solution was magnetically stirred for 2-4 h to promote the hydrolysis of silane, and then ultrasonic treatment for 10 min was carried out to ensure the uniform dispersion of nanoparticles. Finally, the sample of the pre-deposited copper layer was immersed in the above modified solution for 60 min, and the sample was taken out and heat-treated in an oven at 120 °C for 1 h to form a stable superhydrophobic anti-corrosion coating by condensation reaction.

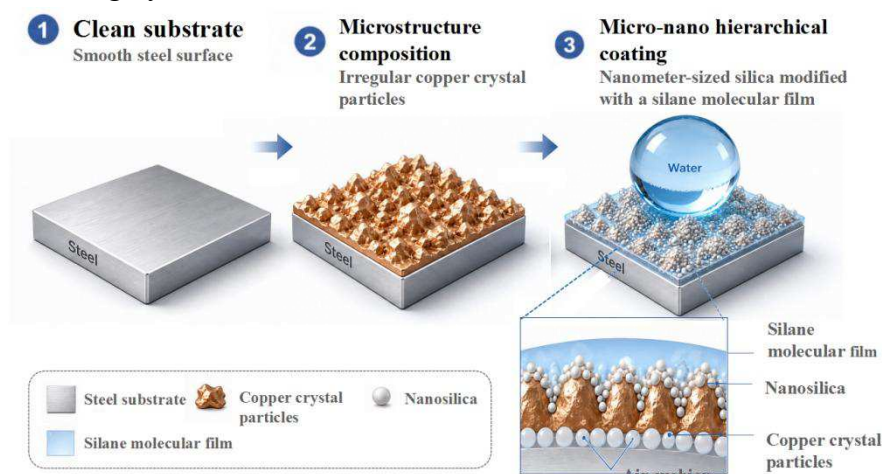


Figure 1. Schematic illustration of the fabrication process for the CuO/ODTMS-SiO₂ composite superhydrophobic coating

2.3.2. Preparation of CuO-SiO₂/ODTMS coating

For comparison, the effect of introducing nanoparticles in the chemical replacement stage on the properties of the coating was studied. The 0.2 M copper sulfate deposition solution was prepared, and nano-SiO₂ with mass fractions of 0 wt%, 0.1 wt%, 0.2 wt%, 0.3 wt% and 0.4 wt% was added according to the experimental groups. Subsequently, ultrasonic dispersion was carried out for 10 minutes, and the activated sample was immersed in the deposition solution containing nanoparticles for 50 s, so that nano-SiO₂ was deposited on the surface of the substrate in situ with copper grains. The samples were washed with ethanol, dried and oxidized at room temperature for 1 h, and then immersed in silane modified solution without nanoparticles for 60 min. Finally, the sample was cured at 120 °C for 1 h to complete the preparation of the composite coating.

3. Results and discussion

3.1. Coating characterization

(1) XRD analysis

The composite coatings with different mass fractions were analyzed by XRD. Figure 2 shows the XRD patterns of CuO/ODTMS-SiO₂ coatings doped with different mass fractions of nano-SiO₂.

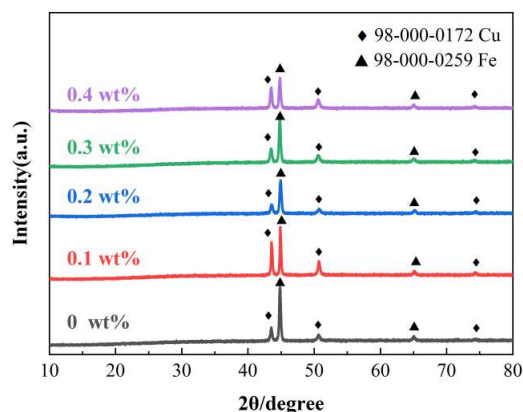


Figure 2. XRD patterns of CuO/ODTMS-SiO₂ coatings with different mass fractions

As illustrated in Figure 2, prominent diffraction peaks are observed at 43.3°, 50.4°, and 74.1° across all nano-SiO₂ doping levels, which can be indexed to the (111), (200), and (220) crystallographic planes of face-centered cubic (FCC) metallic copper (Cu), respectively. This result proves that the metal copper has been successfully reduced in situ and crystallized on the surface of the steel substrate by chemical displacement reaction. At the same time, the diffraction peak with the highest intensity in the spectrum is located near 44.7°, corresponding to the α -Fe phase of the Q235B steel substrate. The much higher Fe peak intensity compared to that of the Cu deposition layer indicates that the copper layer formed during the deposition time of 50 s is thinner and presents a micro-nano rough structure with high porosity, which not only provides a solid physical basis for the roughness required for the superhydrophobic surface, but also provides sufficient active sites for the subsequent chemical bonding of silane molecules.

In addition, it can be found that after doping different mass fractions of nano-SiO₂ in the modified solution, the diffraction peak positions and half-peak widths of Cu and Fe in each curve did not shift or change significantly, indicating that the introduction of nanoparticles did not affect the crystal structure of the underlying metal deposition layer. Since the selected nano-SiO₂ is an amorphous structure, it is uniformly loaded on the surface of the coating and the load is relatively low. The weak signal is masked by the metal substrate signal with extremely high crystallinity, so no obvious SiO₂ characteristic diffraction peak is detected in the spectrum.

(2) FTIR analysis

In order to further verify whether the hydrophobic long-chain molecules and nano-SiO₂ particles were successfully grafted and constructed a micro-nano composite network, the coatings prepared under CuO/ODTMS-SiO₂ and CuO-SiO₂/ODTMS systems were characterized by FTIR (Figure 3).

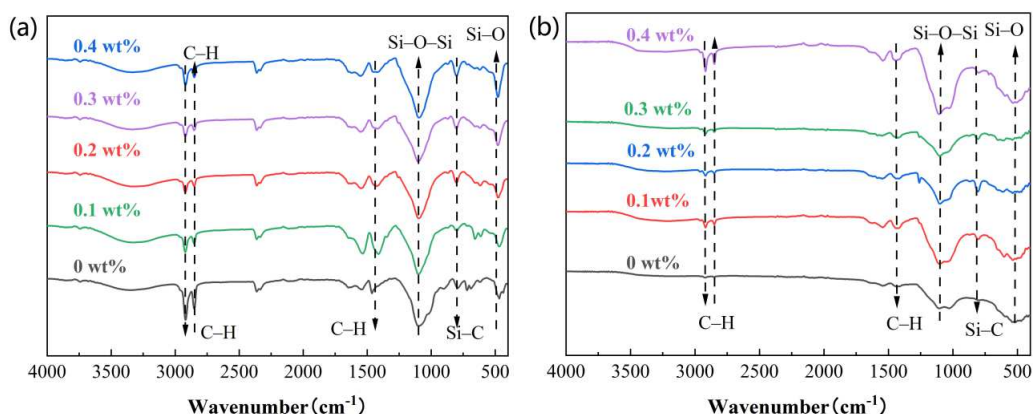


Figure 3. FTIR spectra of two composite coatings: (a)CuO/ODTMS-SiO₂; (b)CuO-SiO₂/ODTMS

In all test curves, strong and sharp absorption peaks at 2919.6 cm⁻¹ and 2850.6 cm⁻¹ appear, which correspond to the asymmetric and symmetric stretching vibrations of octadecyl long-chain methylene (-CH₂-), respectively. At the same time, the -CH₂- shear vibration peak was also observed at 1456.1 cm⁻¹. The appearance of these C-H bond characteristic peaks indicates that the long-chain alkyl with low surface energy has been successfully grafted onto the surface of the coating. More importantly, the spectrum exhibits a broad and strong absorption band in the range of 1093.7-1100.6 cm⁻¹, which is attributed to the asymmetric stretching vibration of the Si-O-Si bond. In addition, the stretching vibration of Si-C bond and the bending vibration of Si-O bond were detected at 800.3 cm⁻¹ and 460 cm⁻¹, respectively. The existence of these chemical bonds confirms that the silane molecules are not only physically attached to the rough structure, but also react with the nano-SiO₂ particles and the hydroxyl groups on the surface of the activated substrate through hydrolysis condensation reaction to form a highly dense and cross-linked three-dimensional covalent network. This stable chemical network can firmly anchor low surface energy groups on the micro-nano rough skeleton, endowing the coating with a long-lasting ability to resist water molecule penetration at the chemical level.

Comparing the spectra of different nano-SiO₂ doping concentrations, it can be found that with the change of SiO₂ mass fraction, the density of covalent crosslinking network changes regularly. For the CuO/ODTMS-SiO₂ coating system Figure 3(a), when no nano-SiO₂ (0 wt%) is added, the Si-O-Si characteristic absorption band already exists, which is mainly due to the condensation of ODTMS silane molecules themselves. With the increase of nano-SiO₂ concentration in the modified solution (from 0.1 wt% to 0.4 wt%), the absorption intensity of the main peak of Si-O-Si in the range of 1093.7~1100.6 cm⁻¹ and the characteristic peak of Si-O at 460 cm⁻¹ showed an obvious deepening and broadening trend. This feature reflects that the introduction of an appropriate amount of nanoparticles provides a richer free silicon hydroxyl group for the system, which makes the Si-O-Si crosslinking network density on the coating surface gradually increase with the increase of concentration. In contrast, in the CuO-SiO₂/ODTMS coating system directly doped with nanoparticles in the deposition solution (Figure 3b), the silicon-containing characteristic peaks show some irregularity with the change of concentration, and the overall peak intensity is generally weaker than that of the former.

(3) Surface micro-morphology analysis (SEM)

In order to observe the microstructure characteristics of the coating surface under different preparation processes, three groups of representative samples were characterized by SEM, and the results were shown in Figure 4.

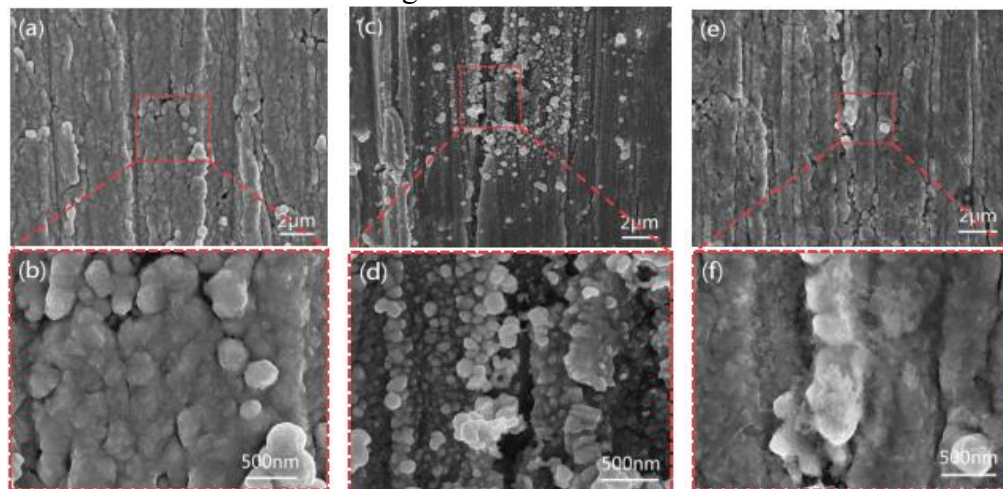


Figure 4. SEM images showing the surface morphology of the coatings under different preparation processes: (a, b) deposition layer; (c, d) CuO-SiO₂/ODTMS (0.3 wt%); (e, f) CuO/ODTMS-SiO₂ (0.3 wt%)

Figure 4 (a,b) show the surface morphology of the Q235B steel substrate after only 50 s deposition in 0.2 M acidic copper sulfate solution. It can be seen from the low-magnification image that the overall surface of the substrate is relatively flat. With the increase of magnification, the high-magnification image shows that the metal copper in situ generates small granular protrusions on the surface of the substrate. These copper particles are relatively dispersed, showing only a single micron-scale roughness and lack of nano-scale structural characteristics.

Figure 4 (c,d) show the morphology of CuO-SiO₂/ODTMS (0.3 wt%) coating. It can be seen from the figure that the nanoparticles have obvious agglomeration on the surface of the substrate, forming irregular clusters with larger size. High magnification images further show that these aggregates are randomly and disorderly stacked on the surface, resulting in extremely uneven distribution of microstructure on the surface of the coating. This large agglomerate hinders the uniform deposition of the underlying copper grains and destroys the physical continuity of the surface, which is not conducive to the subsequent formation of a uniform and dense low surface energy layer.

Figure 4 (e,f) shows the morphology of CuO/ODTMS-SiO₂ (0.3 wt%) coating. Compared with the first two groups, the coating exhibits an ideal 'micron-nanometer' bi-level composite structure. The micron-sized copper particles construct a strong underlying support network, while the fine nano-SiO₂ particles are evenly distributed and embedded in the surface and micropores of the copper grains. This uniform multi-level rough structure can capture and retain air to the greatest extent, and form a continuous and stable 'air cushion' (Cassie-Baxter state) at the solid-liquid interface, thereby giving the surface excellent superhydrophobic properties.

(4) Three-dimensional morphology and roughness analysis of deposition layer

In order to explore the effect of different nano-SiO₂ doping amounts in the deposition

solution on the micro-roughness of the coating, the surface morphology of the samples that only completed the chemical replacement deposition step (without silane modification) was characterized by a non-contact 3D confocal microscope. The surface features are quantified by extracting the average absolute value of the surface profile within the reference length (R_a) and the height of the highest peak in the profile curve at the reference length (R_p). The results are shown in Figure 5.

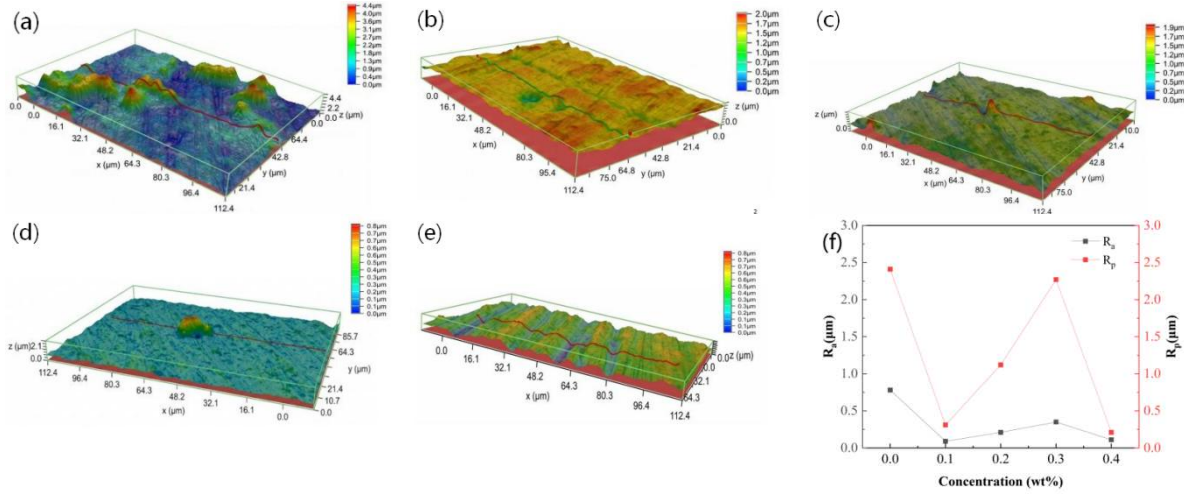


Figure 5. Three-dimensional confocal laser scanning microscopy images of CuO-SiO₂/ODTMS coatings with different mass fractions: (a) 0 wt%, (b) 0.1 wt%, (c) 0.2 wt%, (d) 0.3 wt%, (e) 0.4 wt%; and (f) variation curves of R_a and R_p

As shown in Figure 5 (a), when nano-SiO₂ is not added, micron-sized copper grains construct a relatively uniform distribution of hill-like undulations. However, after the introduction of nano-SiO₂ in the deposition solution, Figure 5 (b-e) intuitively shows that the three-dimensional morphology of the coating surface has changed, not only the original micron-scale rough skeleton has disappeared in a large area, but also the roughness parameters have fluctuated drastically. From the roughness parameter variation curve of Figure 5 (f), it can be observed that when nano-SiO₂ is not added, micron-sized copper grains build the basic surface roughness. At this time, R_a is about 0.8 μm and R_p is about 2.4 μm . After the introduction of nano-SiO₂ in the deposition solution, the roughness parameters of the coating did not change regularly, but fluctuated violently. When the doping amount is 0.1 wt% and 0.4 wt%, both R_a and R_p decrease significantly, and R_a decreases to about 0.1 μm . When the doping amount is 0.3 wt%, R_a remains at a low level (about 0.35 μm), but R_p increases sharply to about 2.3 μm . Combined with the previous SEM morphology analysis, the abnormal fluctuation of roughness parameters is closely related to the agglomeration effect of nanoparticles. The nanoparticles in the deposition solution are disorderly agglomerated, which obscures the reactive sites and interferes with the uniform replacement and crystal growth of the micron-sized copper grains at the bottom, resulting in a significant decrease in R_a . The sudden increase of R_p at 0.3 wt% directly reflects the formation of local large-scale irregular clusters. The reason why hydrophobic surfaces can achieve excellent performance is highly dependent on dense and uniform micro-nano hierarchical pores as microscopic ‘gas storage chambers’. In the deposition solution, the disordered agglomerated nanoparticles mask the activation sites of the substrate, resulting in the inability of the bottom micron-sized copper grains to uniformly nucleate and grow. This defect morphology of large-area flattening and

local isolated protrusions cannot construct a three-dimensional capillary network with sufficient depth and high connectivity. The lack of micro-nano hierarchical structure means that the surface cannot provide sufficient physical space to accommodate air, resulting in the loss of the basic physical conditions for the coating to stabilize and retain a large amount of air during the structural forming stage.

3.2. Effect of nano-SiO₂ doping strategy on surface wettability

Wettability is a key indicator to measure the waterproof and anticorrosive potential of coatings. Figure 6 shows the evolution of the water contact angle of the coating surface with the addition amount under two different nano-SiO₂ doping strategies.

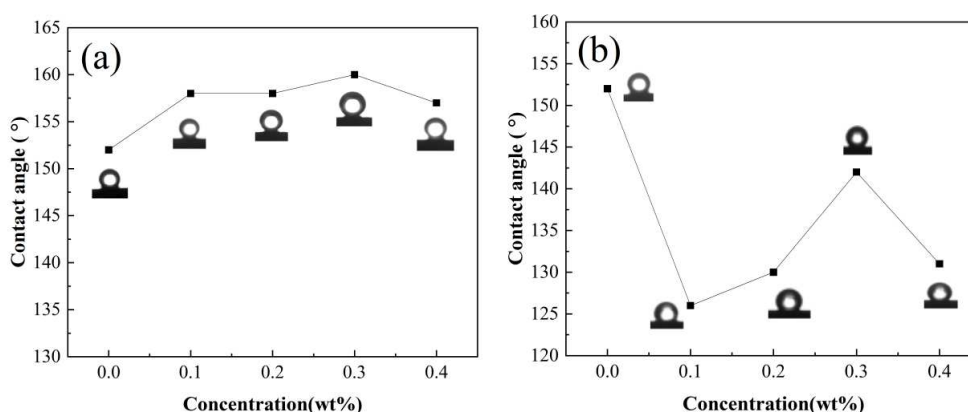


Figure 6. The effect of nano-SiO₂ on the contact angle of the composite coating:
(a)CuO/ODTMS-SiO₂; (b)CuO-SiO₂/ODTMS

For the CuO/ODTMS-SiO₂ system, the contact angle of the coating increases first and then decreases with the increase of nano-SiO₂ doping amount (Figure 6a). When the doping amount increased from 0 wt% to 0.3 wt%, the contact angle increased steadily and reached a maximum of 160°, showing good superhydrophobic properties. Combined with the previous SEM morphology (Figure 4e,f) analysis, it can be seen that the appropriate amount of nanoparticles are evenly distributed and embedded on the surface of the underlying micron-sized copper grains at this stage, and a dense 'micron-nanometer' two-stage composite rough structure is successfully constructed. Combined with the low surface energy provided by silane modification, this uniform multi-level rough skeleton can retain air to the greatest extent, forming a continuous and stable Cassie-Baxter gas film at the solid-liquid interface, thereby giving the coating good water repellency. However, when the doping amount is further increased to 0.4 wt%, the excessive nano-SiO₂ is prone to local agglomeration on the surface, which destroys the uniform distribution of the hierarchical structure, resulting in the damage of the stability of the gas-liquid three-phase interface and the obvious decrease of the contact angle.

In contrast, the CuO-SiO₂/ODTMS system with direct addition of nano-SiO₂ in the deposition solution has a poor overall hydrophobic performance (Figure 6b). Under this process, with the increase of doping amount, the contact angles of most experimental groups fluctuated sharply and failed to reach the superhydrophobic standard of 150°. This phenomenon of wettability deterioration can be directly explained by the abnormal surface morphology and roughness characteristics. The three-dimensional morphology and roughness

test (Figure 5) shows that the roughness parameters of the coating fluctuate irregularly after the introduction of nanoparticles in the deposition solution, especially the R_p increases suddenly in the local area. Combined with the microscopic morphology (Figure 4c,d), it was confirmed that the nano-SiO₂ was disorderly agglomerated in the acidic system, forming a large-sized irregular cluster. These large aggregates obscure the reactive sites on the surface of the substrate and interfere with the uniform nucleation and replacement growth of micron-sized copper grains, resulting in a large area of planarization and local isolated protrusions on the surface of the coating. Due to the loss of physical continuity and the failure to construct a micro-nano capillary network with sufficient depth and connectivity, the coating surface cannot provide sufficient physical space to stabilize the bound air. The lack of gas film barrier directly leads to the easy infiltration of droplets into Wenzel state, which is manifested as the decrease of contact angle and the failure of superhydrophobicity.

3.3. Effect of nano-SiO₂ doping on the electrochemical properties of the coating

In order to quantitatively evaluate the physical barrier ability of the coating to the corrosive medium, Tafel and EIS tests were carried out on the coatings of different systems by electrochemical workstation.

3.3.1. Electrochemical properties of CuO/ODTMS-SiO₂ coating

The polarization curve test results in Figure 7 and Table 1 show that the E_{corr} of the control group of Q235B bare steel is -0.902 V, and the i_{corr} is $10.13 \times 10^{-5} \text{ A} \cdot \text{cm}^{-2}$. In the CuO/ODTMS-SiO₂ system, with the increase of nano-SiO₂ addition, E_{corr} showed a significant positive shift trend, and reached the maximum value of -0.747 V when the addition amount was 0.3 wt%. The i_{corr} of each experimental group was significantly lower than that of the blank control group. This indicates that the introduction of nanoparticles effectively improves the thermodynamic stability of the coating surface and kinetically inhibits the occurrence of corrosion reactions.

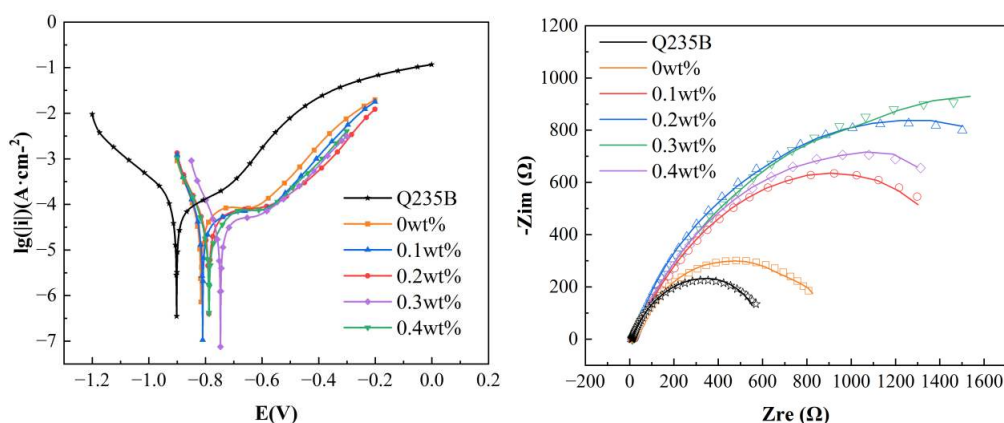


Figure 7. Polarization curves (a) and electrochemical impedance spectra (b) of CuO/ODTMS-SiO₂ coatings with different nano-SiO₂ concentrations.

Table 1. Polarization curves and EIS parameters of the CuO/ODTMS-SiO₂ coatings at different mass fractions

Nano-SiO ₂ content	E_{corr} (V)	i_{corr} ($10^{-5} \text{ A} \cdot \text{cm}^{-2}$)	R_s ($\Omega \cdot \text{cm}^2$)	CPE-T	CPE-P	R_p ($\Omega \cdot \text{cm}^2$)	η (%)
----------------------------------	--------------------------	---	---	-------	-------	---	---------------

(wt%)							
Q235B	-0.902	10.13	9.614	0.001008	0.7345	652.2	-
0 wt%	-0.816	4.196	11.43	0.002306	0.7286	934.7	30.22
0.1 wt%	-0.81	2.572	10.41	0.002994	0.6565	1341	51.36
0.2 wt%	-0.788	2.803	10.33	0.01834	0.4574	2085	68.72
0.3 wt%	-0.747	2.572	11.57	0.00243	0.702	2949	77.88
0.4 wt%	-0.787	2.381	11.19	0.002831	0.696	1083	39.78

The EIS fitting data further revealed that the polarization resistance (R_p) of the coating increased first and then decreased with the increase of the addition amount. The R_p of the blank control group was only $652.2 \Omega \cdot \text{cm}^2$; when the addition amount increased from 0 wt% to 0.3 wt%, R_p gradually increased to $2949 \Omega \cdot \text{cm}^2$, showing a good interface charge transfer impedance. Combined with the above characterization, it can be seen that the improvement of electrochemical protection efficiency is due to the synergy of micro-physical morphology and chemical structure: SEM test shows that a uniform and dense 'micron-nanometer' two-level rough skeleton is constructed on the surface of the 0.3 wt% group, and FTIR spectrum confirms that a high-density Si-O-Si crosslinking network is formed at this concentration. This ideal composite structure can retain air at the solid-liquid interface to the greatest extent and form a stable Cassie-Baxter gas film, thus effectively blocking the penetration of water and Cl^- and other corrosive media into the substrate. However, when the addition amount continues to increase to 0.4 wt%, the R_p decreases to $1083 \Omega \cdot \text{cm}^2$, indicating that excessive nano- SiO_2 will lead to a decrease in the compactness of the coating and a deterioration in the corrosion resistance.

3.3.2. Electrochemical properties of CuO-SiO₂/ODTMS coatings

Figure 8 and Table 2 show the electrochemical data of the CuO-SiO₂/ODTMS coating prepared by another process. Compared with the results of the previous group, the addition of nano-SiO₂ directly in the deposition solution showed different characteristics on the improvement of the corrosion resistance of the coating. From the polarization curve, the E_{corr} of the samples at each doping concentration mostly fluctuates between -0.80 V and -0.82 V , and the overall positive shift is not obvious. Although the i_{corr} data was lower than that of the control group, the difference between the groups was relatively small. From the EIS fitting results, the polarization resistance of the system coating showed an upward trend with the increase of nano-SiO₂ doping amount, and reached the maximum value at 0.4 wt%. However, compared with the highest polarization resistance of the former process, it can be found that the overall charge transfer impedance is relatively low when the nanoparticles are directly added to the deposition solution. Combined with micro-morphology analysis, this doping strategy is prone to causing the agglomeration of nanoparticles, destroy the compactness of the coating as a whole, and fail to effectively construct a uniformly distributed anti-corrosion shielding layer, so the upper limit of anti-corrosion on electrochemical performance is low.

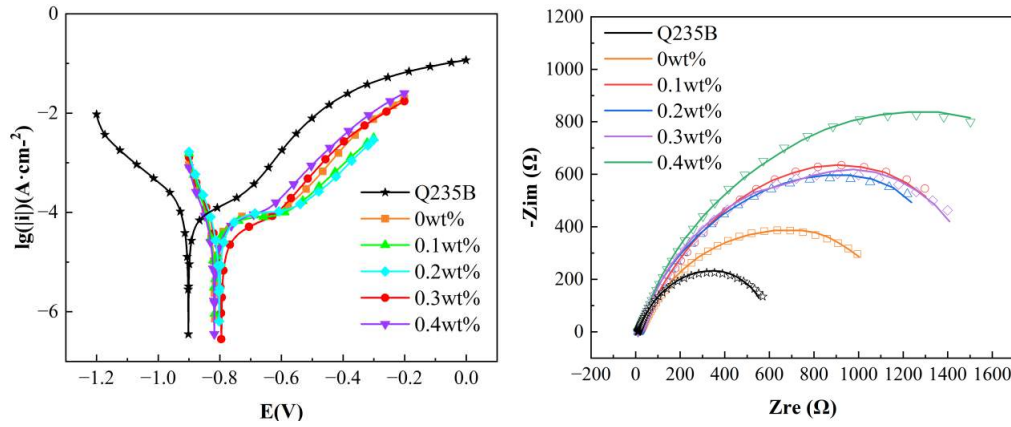


Figure 8. Polarization curves (a) and electrochemical impedance spectra (b) of CuO-SiO₂/ODTMS coatings with different nano-SiO₂ concentrations.

Table 2. Polarization curves and EIS parameters of the CuO-SiO₂/ODTMS coatings with different mass fractions.

Nano-SiO ₂ content (wt%)	E _{corr} (V)	i _{corr} (10 ⁻⁵ A·cm ⁻²)	R _s (Ω·cm ²)	CPE-T	CPE-P	R _p (Ω·cm ²)	η (%)
Q235B	-0.902	10.13	9.614	0.001008	0.7345	652.2	-
0 wt%	-0.816	4.196	11.43	0.002306	0.7286	934.7	30.22
0.1 wt%	-0.817	2.477	10.41	0.002984	0.6775	1241	47.45
0.2 wt%	-0.802	3.068	12.36	0.001681	0.812	1739	62.49
0.3 wt%	-0.795	1.922	12.5	0.001663	0.7596	1771	63.17
0.4 wt%	-0.818	2.358	10.32	0.002035	0.4573	2080	68.72

3.4. Long-term immersion test

In order to evaluate the protective ability of the composite coating in simulated harsh environment, the weight loss method was used to determine the corrosion rate of the CuO/ODTMS-SiO₂ optimal coating group immersed in 3.5 wt% NaCl solution. The experimental data are shown in Figure 9.

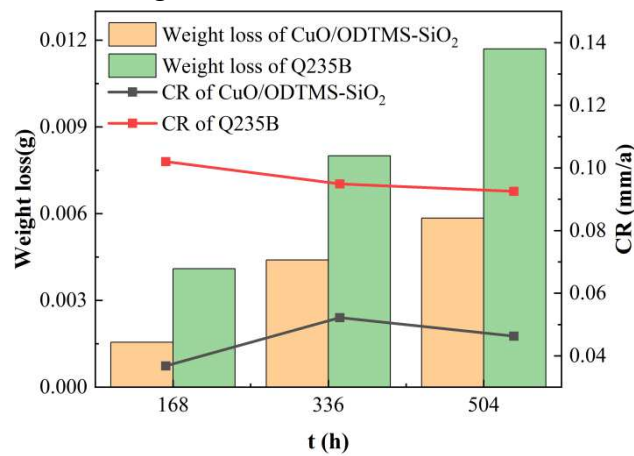


Figure 9. Weight loss and corrosion rate of the optimized CuO/ODTMS-SiO₂ coating and bare steel over immersion time

In the early stage of immersion (168 h), the coating has good corrosion resistance, the

weight loss is only 0.00155 g, and the corrosion rate is as low as 0.0368 mm/a. This is attributed to the synergistic effect of the micro-nano composite rough structure and the low surface energy of silane, which intercepts air at the interface to construct a stable Cassie-Baxter gas film, effectively shielding the infiltration of corrosive media such as water and Cl^- .

With the extension of immersion time to 336 h, the weight loss of the coating increased to 0.0044 g, and the corrosion rate increased to 0.0522 mm/a. This is because, due to prolonged hydrostatic pressure, the local gas film on the surface dissolves or breaks, and the interface gradually changes to the Wenzel state, and the infiltration of the medium along the micropores leads to accelerated corrosion.

When immersed to 504 h, the cumulative weight loss of the coating was 0.00585 g, but the corrosion rate decreased slightly to 0.0463 mm/a. Compared with the bare steel sample (weight loss 0.0117 g, corrosion rate 0.0925 mm/a) under the same conditions, the coating after soaking for 504 h still has protective effect. The decline trend of corrosion rate may be due to the gradual accumulation of internal corrosion products in the later stage of immersion, which fills the infiltration pores, resulting in a 'physical self-sealing effect'.

In order to further clarify the surface chemical changes before and after soaking the experimental samples, XPS characterization was carried out. As shown in the XPS survey spectrum of Figure 10 (a), the coating surface before immersion is mainly composed of four elements: C, O, Cu and Si, and their atomic percentages are 54.69%, 28.00%, 11.91% and 5.40%, respectively. At this time, the signal of Fe element in the substrate was not detected, indicating that the composite structure composed of the bottom micron copper and the surface nano- SiO_2 /silane realized the complete coverage of the steel substrate. As observed in the high-resolution Cu 2p spectrum (Figure 10b), the characteristic peaks of both Cu_2O and CuO , along with the satellite peaks of CuO , are detected. This reflects that the surface of the copper layer is moderately oxidized during the preparation stage, which provides the necessary active sites for the subsequent hydrolysis and condensation of silane molecules.

After 504 h long-term immersion, the chemical composition of the coating surface changed significantly. Compared with the full spectrum test results of Figure 10 (c), the atomic percentages of C and Si elements are reduced to 23.27% and 2.94%, respectively, and the Cu element is also reduced to 2.80%. At the same time, the proportion of O element increased to 57.07%, and 13.91% Fe 2p signal appeared. It shows that with the extension of immersion time, the corrosive medium has gradually penetrated the pores of the coating and reached the steel substrate. Combined with the further analysis of the high-resolution spectrum after immersion, the intensity of $\text{Cu}(\text{OH})_2$ -related characteristic peaks in the Cu 2p spectrum of Figure 10 (d) is significant, indicating that the micron copper grains in the bottom layer are involved in the corrosion reaction. In the Fe 2p spectrum of Figure 10 (e), the main peak position corresponds to the chemical state of Fe^{3+} , confirming that a large amount of Fe_2O_3 or FeOOH corrosion products are formed on the surface. Based on the changes in the proportion and chemical state of the above elements, a large number of insoluble iron oxides, iron hydroxyl oxides and copper hydroxides were formed and accumulated in situ in the coating at the later stage of immersion. These insoluble corrosion products block the further infiltration channels of water and chloride ions, resulting in a 'physical self-sealing effect', which leads to a macroscopic decline in the 504 h corrosion rate.

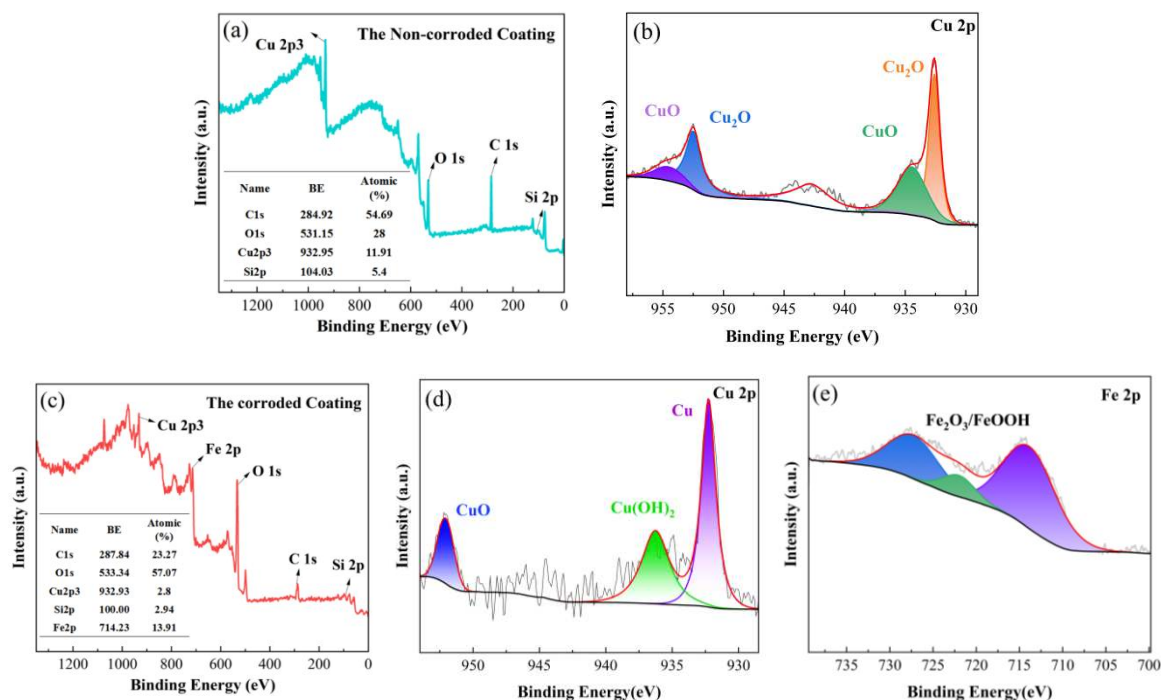


Figure 10. XPS spectra of the optimized coating before and after immersion: (a) XPS survey spectrum before immersion; (b) high-resolution Cu 2p spectrum before immersion; (c) XPS survey spectrum after immersion; (d) high-resolution Cu 2p spectrum after immersion; (e) high-resolution Fe 2p spectrum after immersion

3.5. Anticorrosion mechanism and corrosion kinetics

The anti-corrosion performance of CuO/ODTMS-SiO₂ composite coating is essentially the result of the synergistic effect of multi-level micro-nano physical barrier and chemical crosslinking network. The micro-mechanism of anti-corrosion is shown in Figure 11. In terms of physical barrier, a dense 'micron-nanometer' two-stage structure was constructed by in-situ deposition of micron-sized copper particles and uniformly embedded nano-SiO₂, which can effectively intercept air and form a highly stable Cassie-Baxter gas film at the solid-liquid interface. As a low dielectric insulating layer, this layer of gas film greatly reduces the actual contact area between the corrosive media such as water molecules and Cl⁻ ions and the underlying metal. In terms of chemical stability, the hydrolysis and condensation of octadecyltrimethoxysilane formed a dense three-dimensional network containing Si-O-Si and Si-C covalent bonds on the surface. This stable chemical crosslinking network not only endows the coating with extremely low surface free energy, but also firmly anchors the hydrophobic long chain on the micro-nano skeleton, further seals the erosion channel from the molecular scale, and constructs a composite defense line against medium penetration together with the micro-nano physical gas film.

From the perspective of the evolution of corrosion kinetics, the protection of the substrate by the CuO/ODTMS-SiO₂ composite coating is essentially the improvement of the interface charge transfer barrier and the dynamic blocking of the ion mass transfer path. In the early stage of immersion, the stable Cassie-Baxter gas film on the coating surface and the dense silane crosslinking network synergistically constructed an insulating physical barrier with low dielectric constant. This barrier greatly raises the charge transfer barrier at the

solid-liquid interface, which severely hinders the iron dissolution reaction ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) in the anode region and the oxygen reduction reaction ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$) in the cathode region due to the lack of charge transfer channels. Macroscopically, the interface charge transfer resistance is significantly improved, and the diffusion of highly active Cl^- to the metal surface is effectively blocked in space. At this time, the corrosion kinetics of the system is completely controlled by the charge transfer step.

With the extension of soaking time, the local gas film in the micropores breaks or dissolves under long-term hydrostatic pressure, and the gas-liquid-solid interface gradually changes to the Wenzel state. Cl^- first penetrates along the water-permeable microchannel and reaches the metal substrate, causing anodic activation of the substrate micro-area. In this bimetallic system, the iron substrate with lower potential is preferentially dissolved as an anode ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$), while the micron copper particles with higher potential are initially protected as a cathode. When the dissolved Fe^{2+} diffuses outward, it reacts with the OH^- enrichment in the cathode region to form complex iron hydroxyl oxides (such as $4\text{Fe}^{2+} + \text{O}_2 + 8\text{OH}^- \rightarrow 4\text{FeOOH} \downarrow + 2\text{H}_2\text{O}$). At the same time, the copper oxide pre-deposited on the surface of the coating at the initial stage of preparation undergoes hydration evolution in a long-term immersion and erosion environment, and a slight interfacial reaction occurs in the local area where the galvanic effect is weakened in the later stage of corrosion, which ultimately contributes to the formation of a complex insoluble layer containing iron oxides. These solid-state insoluble corrosion products are limited by the physical space of micro-nano pores, and do not lose a lot to the bulk solution, but gradually accumulate and fill inside the erosion channel, triggering a 'physical self-sealing effect'. This physical plugging of micropores makes the permeability path of the medium extremely tortuous and narrow, which sharply increases the spatial steric hindrance of the inward diffusion of external Cl^- and water molecules and the outward migration of internal metal cations. At this point, the corrosion control step of the system is gradually transformed from the initial charge transfer control to the ion diffusion control limited by the product layer. It is the continuous blocking of this mass transfer channel that eventually leads to a slight decrease in the macroscopic corrosion rate in the later stage of immersion.

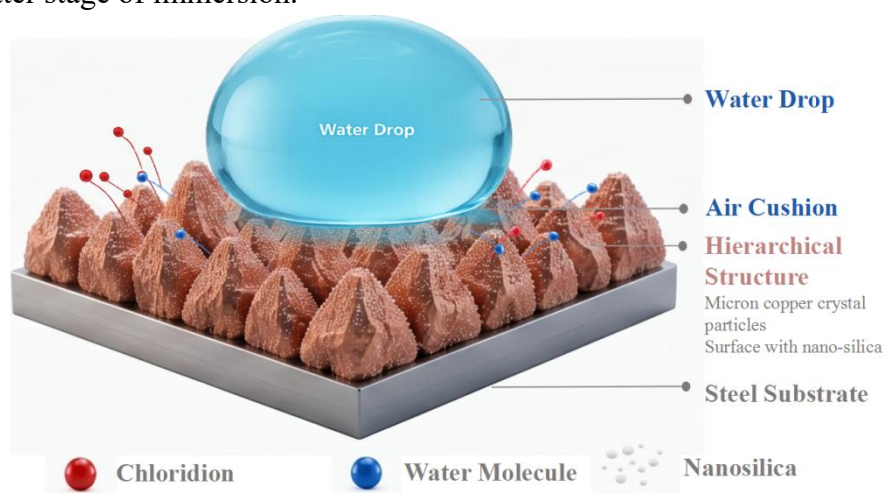


Figure 11. Schematic illustration of the anti-corrosion mechanism for the composite coating

4. Conclusions

In this study, a composite superhydrophobic coating was prepared on the surface of Q235B steel by a chemical displacement deposition and silane synergistic modification process. The experimental results show that the direct doping of nano-SiO₂ in the deposition solution destroys the physical continuity of the coating, which has a negative impact on the coating performance, leading to the deterioration of hydrophobicity and corrosion resistance. However, the CuO/ODTMS-SiO₂ modification strategy effectively overcomes this defect. Under this strategy, nano-SiO₂ is uniformly embedded on the micron-sized copper grains to successfully construct a dense 'micron-nanometer' two-stage composite rough structure. This physical structure cooperates with the low surface energy crosslinking network of silane to make the static water contact angle of the coating reach 160°. Accordingly, the coating exhibits higher polarization resistance and lower corrosion current density, maintaining a good protective effect after long-term immersion in 3.5 wt% NaCl solution. The corrosion resistance of the composite coating benefits from the synergistic mechanism of the micro-nano physical barrier and the low surface energy chemical curing network, which provides a simple and efficient theoretical reference for the industrial preparation of low-cost, long-term multifunctional superhydrophobic coatings.

Acknowledgements

This work was supported by the Postgraduate Innovation Fund (No. SHSYCX2505).

Data Availability

All relevant data are included in the paper or its Supplementary Information.

Competing Interests

The authors declare that they have no conflict of interest.

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Jinjian Liu, Ziyang Feng, Mingwei Cui, and Yujie Sui. The first draft of the manuscript was written by Jinjian Liu, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Reference

- [1] Zhao Y Y, Lei L L, Wang Q, et al. Study of superhydrophobic concrete with integral superhydrophobicity and anti-corrosion property[J]. *Case Studies in Construction Materials*, 2023, 18: e01899.
- [2] Bastidas, David M. Corrosion and protection of metals[J]. *Metals*, 2020, 10 (4): 458.
- [3] Jin M H, Li K H, Zhao L. Research progress on oilfield scaling, its control and mechanisms[J]. *Chemical Technology and Development*, 2013, 42(4): 18-21.
- [4] Liu S P. Preparation and performance of polymer-based anti-corrosion and anti-scaling functional coating[D]. Daqing: Northeast Petroleum University, 2022.
- [5] Zhao L. Research progress on superhydrophobic materials and their coatings[J]. *Surface Technology*, 2024, 53(24): 54-68.
- [6] Jiang Y J, Wang C C, Liu Z, et al. Anti-corrosion and anti-fouling superhydrophobic silicone coating with continuous micro/nano structure[J]. *Prog Org Coat*, 2024, 188: 108230.
- [7] Yu Y H, Dong Y H, Ning H L, et al. A robust superhydrophobic coating with multi-dimensional micro-nano structure on 5052 aluminum alloy[J]. *Surf Coat Technol*, 2023, 465: 129564.
- [8] Luo Z, Liu K, Zhou X, et al. Synthesis and performance of superhydrophobic microstructured surface coatings on underwater target shells[J]. *Materials Protection*, 2022, 55(11): 22-27.
- [9] Khan A, Huang K, Sarwar M G, et al. Self-healing and self-cleaning clear coating[J]. *Journal of Colloid and Interface Science*, 2020, 577: 311.
- [10] Yoon H, Kim H, Latthe S S, et al. A highly transparent self-cleaning superhydrophobic surface by organosilane-coated alumina particles deposited via electrospraying[J]. *Journal of Materials Chemistry A*, 2015, 3(21): 11403-11410.
- [11] Tong W, Wu Z, Xiong D, et al. Transparent superhydrophobic coating based on a carbonaceous soot framework for the self-cleaning of glass[J]. *Sustainable Materials and Technologies*, 2023, 37.
- [12] Chen C L, Weng D, Mahmood A, et al. Separation mechanism and construction of surfaces with special wettability for oil/water separation[J]. *ACS Applied Materials & Interfaces*, 2019, 11(11): 11006-11027.
- [13] Wang N, Wang Y, Shang B, et al. Bioinspired one-step construction of hierarchical superhydrophobic surfaces for oil/water separation[J]. *Journal of Colloid and Interface Science*, 2018, 531: 300-310.
- [14] Song J L, Lu Y, Huang S, et al. Progress in research and applications of extreme wettability surfaces[J]. *Science & Technology Review*, 2015, 33(15): 92-10.
- [15] Feng Y, Li H, Zhang M, et al. Preparation of BTA@PDA/PANI microcapsules and anti-corrosion performance of self-healing epoxy coatings on low carbon steel[J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2022, 649: 129414.
- [16] Li Q, Zhang X, Ben S, et al. Bio-inspired superhydrophobic magnesium alloy surfaces with active anti-corrosion and self-healing properties[J]. *Nano Research*,

2023, 16(2): 3312-3319.

[17] Zheng H K, Chang S N, Ma G J, et al. Anti-icing performance of superhydrophobic surface fabricated by femtosecond laser composited dual-layers coating[J]. *Energy Build*, 2020, 223: 110175.

[18] Zhang X, Zhao J, Mo J L, et al. Fabrication of superhydrophobic aluminum surface by droplet etching and chemical modification[J]. *Colloid Surf A-Physicochem Eng Asp*, 2019, 567: 205-212.

[19] Huang Q, Zeng X G, Cao K, et al. Preparation and properties of Co-LDH superhydrophobic film fabricated by electrodeposition[J]. *Surface Technology*, 2022, 51(7): 314-323.

[20] Zhang X G, Yang J Y, Zhang W, et al. Facile preparation of durable superhydrophobic coating with microstructure self-repairing function by spraying method[J]. *Prog Org Coat*, 2024, 187: 108166.

[21] Sun J Y, Zhu L, Liu Z. Preparation of a Wear-Resistant, Superhydrophobic SiO₂/Polymethyl Methacrylate Composite Coating on Aluminum Surface Processed with Nanosecond Laser[J]. *Materials*, 2023, 16(19): 6485.

[22] Khan M A, Hussain W, Hassan N, et al. Fabrication of Ag nanoparticles on a Cu-substrate with excellent superhydrophobicity, anti-corrosion, and photocatalytic activity[J]. *Alexandria Engineering Journal*, 2022, 61(8): 6507-6521.

[23] Sun Y K, Liu J Y, Ming P M, et al. Wire electrochemical etching of superhydrophobic 304 stainless steel surfaces based on high local current density with neutral electrolyte[J]. *Appl Surf Sci*, 2022, 571: 151269.

[24] Zhang J, Zhao X, Wei J, et al. Superhydrophobic coatings with photothermal self-healing chemical composition and microstructure for efficient corrosion protection of magnesium alloy[J]. *Langmuir*, 2021, 37(45): 13527-13536.

[25] Goralczyk A, Savichev S, Montazeri R, et al. Spray-coating of superhydrophobic coatings for advanced applications[J]. *Adv Eng Mater*, 2023, 25(8): 2201314.

[26] Zheng T, Hu Y, Pan F, et al. Fabrication of corrosion-resistant superhydrophobic coating on magnesium alloy by one-step electrodeposition method[J]. *Journal of Magnesium and Alloys*, 2019, 7(2): 193-202.

[27] Xu K, Shen W R, Yang S, et al. Laser-enhanced electrodeposition preparation technology of superhydrophobic micro-nano structure coating[J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2023, 657: 130507.

[28] Laleh M, Kargar F, Rouhollahi A. Superhydrophobic properties of silver-coated films on copper surface by galvanic exchange reaction[J]. *Applied Surface Science*, 2011, 257(16): 7300-7305.

[29] Liang T T, Yuan H Y, Li C C, et al. Corrosion inhibition effect of nano-SiO₂ for galvanized steel superhydrophobic surface[J]. *Surface and Coatings Technology*, 2021, 406.

[30] Hu G J, Xiao Y X, Ying J. Nano-SiO₂ and silane coupling agent co-decorated graphene oxides with enhanced anti-corrosion performance of epoxy composite coatings[J]. *International Journal of Molecular Sciences*, 2021, 22(20): 11087.