

Article

Development of Waterborne Heavy-Duty Anticorrosive Coatings with Modified Nanoscale Titania

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Abstract: The steel structures of coastal engineering in the moist tropics and subtropics are always under a C5/CX level corrosion environment with high temperature, high humidity, and high salt fog. Anticorrosive waterborne coatings with high weatherability and reliability are urgently to be developed. In this work, one kind of waterborne heavy-duty anticorrosive coatings, with the advantages of excellent corrosion resistance, self-repairing ability, self-cleaning ability, and high film compactness, was successfully achieved through modifying the side chains on the surface morphologies of the spherical nanoscale titania. The micromorphology and structure of the coating were characterized by a scanning electron microscope (SEM), transmission electron microscope (TEM), and atomic force microscope (AFM). The anticorrosion characteristics and forming mechanism of the modified nanoscale titania coating were analyzed. The salt spray tests showed that the neutral salt spray resistance time of the modified nanoscale titania coating was 1440 h. Its durability reached the H level and met the design requirements for 15 years of anticorrosion lifetime. The modified nanoscale titania coatings had been large-scale commercially applied at some typical steel structures under an extreme harsh corrosion environment in one coastal thermal power plant. The results showed that no rusting, peeling, or crack phenomena were observed after 3 years of service under different harsh coastal corrosion conditions.

Keywords: heavy-duty anticorrosive coating; waterborne coating; modified nanoscale titania; coastal engineering; steel structure



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1. Introduction

Steel structure has been widely used in many infrastructure constructions and industrial engineering fields due to its high strength, convenient processing, and low cost [1]. The corrosion rate of steel structures increases sharply under the harsh environment of high temperature, high humidity, and high salt fog in tropical and subtropical coastal engineering. The corrosion of steel structures leads to deformation, fracture, or even collapse, which will cause serious economic losses and safety accidents [2,3]. It is a common and effective method to use coating materials to protect steel structures from corrosion in a corrosive environment [4], and coating materials can act as physical barriers and isolate corrosive substances [5]. Organic coatings, especially heavy-duty anticorrosion coatings, have been widely utilized to confront the severe corrosion issue because of their excellent corrosion resistance [6], such as polyurethane coatings, epoxy resin coatings, and acrylic coatings [7]. However, organic solvents are normally used as the fundamental solution environment of organic ingredients in coatings, which inevitably bring in large damage to the environment. Thus, more and more attention has been paid to the research and application of waterborne coatings. However, due to the poor strength of ordinary waterborne coatings, the anticorrosion lifetime of waterborne coatings is short, and it is difficult to meet the anticorrosion requirements, which limits the scope of application of waterborne coatings.

In recent decades, lots of inspired studies have reported that the corrosion resistance of waterborne coatings can be improved by adding some ceramic nanoparticles [8], such as ZrO_2 [9], SiO_2 [10], h-BN [11], and TiO_2 [12]. Radoman et al. [13] reported that the epoxy composite coating containing 1 wt% gallic-acid-ester-modified TiO_2 nanoparticles provided effective corrosion protection in both 3 wt% NaCl solution and 0.1 M H_2SO_4 solution for more than 60 days. Ejenstam et al. [14] found that polydimethylsiloxane composite coatings with 20 wt% hydrophobic silica nanoparticles possessed a high impedance modulus value of $10^9 \Omega \cdot cm^2$ at 0.01 Hz and an effective corrosion protection in 3 wt% NaCl solution for nearly 80 days. Chen et al. [15] reported that conducting polypyrrole coating containing molybdate-loaded TiO_2 nanotubes was successfully electropolymerized using the cyclic voltammetry method. The TiO_2 -modified coating retained its fine corrosion resistance after 720 h immersion in 3.5 wt% NaCl solution. The underlying enhancement mechanism of nanoparticles was explored, which demonstrated that the nanoparticles could form a dense layered or reticulated structure on the surface of the coating, enhancing the barrier performance of the coating.

Besides, the modification role of nanoparticles also endows coatings with self-cleaning ability and self-repairing ability, thereby greatly benefiting from the enhancement of the corrosion resistance. Wang et al. [16] suggested that polytetrafluoroethylene/ TiO_2 coating prepared by plasma electrolytic oxidation exhibited a kind of hydrophobic behavior with a water contact angle of 138° , consequently establishing a good self-cleaning ability. Qing et al. [17] modified TiO_2 with trimethoxy-silane by the hydrothermal method and introduced hydrophobic $-CF_2-$ and $-CF_3-$ groups, a superhydrophobic TiO_2 /polyvinylidene fluoride composite coating with excellent self-cleaning ability, and a water contact angle of 160.1° was prepared. The self-cleaning ability could lead to the potentially enhanced corrosion resistance of the coatings by the escapement of dust and corrosive medium. Ghomi et al. [18] reported that 1 wt% triethoxysilyl-propyl-methacrylate-modified TiO_2 contributed to the self-repairing ability of the epoxy coating, and the self-repairing efficiency measured by electrochemical impedance spectroscopy reached 98%, which was due to the migration of the modified nanogel composite and its swelling property. Ye et al. [19] prepared carbon-dot-modified graphene/epoxy waterborne coatings, and the scanning vibrating electrode technology analysis of artificial defect coating showed that the coating containing 0.5 wt% carbon-dot-modified graphene had the lowest current density of local defect and the best self-repairing performance in NaCl solution. The self-repairing ability of the coatings is always pursued by anticorrosion research, which could bring in the desirable recovery of the microstructure and corrosion resistance of long-working coatings. Self-repairing behaviors diminished the corrosion sites and paths and resulted in the enhanced corrosion resistance of the coatings.

Although lots of great achievements have been obtained in the field of waterborne heavy-duty anticorrosive coatings modified by TiO_2 nanoparticles, current studies focus on experimental investigation, which still has not been proved by simulation or application studies. Especially in tropical or subtropical coastal surroundings with large temperature differences between day and night, aging crack failure is easy to appear in waterborne solvent coatings, deteriorating the corrosion resistance of the coatings. Therefore, the anti-corrosion mechanism and performance of waterborne heavy-duty anticorrosive coatings modified by TiO_2 nanoparticles in a coastal surrounding need to be deeply explored, which is greatly meaningful for widening the applications of coatings.

In this work, one kind of modified nanoscale titania was used to prepare waterborne hyperbranched polymer coating with the abilities of heavy-duty anticorrosion, self-cleaning, and self-repairing. The corrosion resistance of the coating was evaluated by neutral salt spray tests and coupon corrosion tests. The micromorphology and structure of the coating were characterized by SEM, TEM, and AFM. The film-forming and self-repairing mechanism of the coating was analyzed. Large-scale commercial applications on coastal equipment confirmed that the waterborne coating had excellent durability and reliability under the harsh corrosion environment at the C5/CX level.

2. Materials and Methods

2.1. Materials

The waterborne epoxy resin (AB-EP-20) was provided by Zhejiang Anbang New Material Development Co., Ltd. (Jiaxing, China). Nanoscale titania (rutile) with an average size of 40 nm was obtained from the Aladdin Company. A silane coupling agent (KH-560) was purchased from Guangzhou Zhongjie Chemical Technology Co., Ltd. (Guangzhou, China). A film-forming agent (XS-12C) was provided by Zhengzhou Hongboli Chemical Products Co., Ltd. (Zhengzhou, China). Oxalic acid, wetting agent, dispersant, and defoamer were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphene coating and metal flake coating were self-made in the laboratory. Q235 steel plates with a size of 150 mm × 70 mm × 4 mm were used for coupon corrosion tests. Table 1 shows the chemical composition of the Q235 steel studied in the tests. In all processes, deionized water, ethanol, and acetone were utilized for cleaning and as solvents.

Table 1. Chemical composition and percentage content of Q235 steel.

Chemical Composition	C	Si	Mn	P	S
Content/wt%	0.17	0.35	1.4	0.04	0.04

2.2. Preparation of Coatings and Samples

The nanoscale titania and KH-560 were mixed in ethanol, and oxalic acid was added to adjust the pH value between 4 and 5. The mixed solution was ultrasonically dispersed for 20 min and then added into a three-necked flask at 45 °C maintained with a water bath, and continuously stirred at 600 rpm for 3 h. The mixed solution was centrifuged to obtain precipitate, dried precipitate in an oven at 120 °C, then ground to obtain the modified nanoscale titania. The waterborne epoxy resin and deionized water were mixed at a mass ratio of 3:1. Then, 8 wt% of the modified nanoscale titania and 0.5 wt% of the dispersant were added to the above mixture and stirred at 800 rpm for 6 h. The wetting agent, film-forming agent, and defoamer were added and stirred at 100 rpm. After stirring evenly, the waterborne hyperbranched polymer heavy-duty anticorrosive coating was obtained.

Prior to preparing the samples, the surface of a Q235 steel plate was pretreated to the level of Sa 2.5 by sandblasting, and then the surface was cleaned with acetone to remove grease and other pollutants. The modified nanoscale titania coating, graphene coating, and metal flake coating were sprayed on the Q235 steel plate by air spraying, dried at room temperature with air humidity over 30%, and cured for 5 days to obtain the coating samples.

2.3. Corrosion Tests

2.3.1. Neutral Salt Spray

The neutral salt spray tests were carried out according to the ISO 9227:2017 standard in the salt chamber. Corrosion tests were performed in triplicate for each group. The samples were placed at an angle of 20° to the vertical. A mist of 5 wt% NaCl solution was sprayed in the salt chamber at a temperature of 35 ± 2 °C, and the condensation rate was 1–2 mL/h per 80 cm² of the surface.

2.3.2. Coupon Corrosion Test

The coupon corrosion test was carried out at some typical steel engineering structures in one coastal thermal power plant of China. The steel structures in the thermal power plant were under typical a C5/CX level corrosion environment with high temperature, high humidity, and high salt fog. At the same time, in order to test the anticorrosion performance of the coating in the case of scratches, coating samples at 150 mm × 70 mm, with X scratches and no scratches, were suspended in the seriously corroded area of the steel structure in the power plant. The suspended samples were kept a distance of 50 mm to ensure that all of them were completely exposed to the corrosive environment and sunlight. The surface of the samples was observed regularly, and the anticorrosion performance of the coating was

tracked. The protective effects of three kinds of anticorrosion coatings in a harsh corrosion environment were compared and analyzed.

2.4. Characterization

A SEM (ZEISS Gemini 300, Oberkochen, Germany) was used to observe the morphology of the modified nanoscale titania coating. A TEM (FEI Talos F200X, Hillsborough, OR, USA) was used to characterize the structure of the coating. An AFM (Bruker, Dimension Icon, Karlsruhe, Germany) was used to characterize the surface structure of the coating, and the roughness of the coating was measured. The scanning range of X–Y was $5\ \mu\text{m} \times 5\ \mu\text{m}$. An optical contact angle meter (Dataphysics OCA50AF, Stuttgart, Germany) was used to measure the contact angle of the water droplet of the coating.

2.5. Commercial Application on Coastal Steel Structures

In order to further verify the actual anticorrosion protection performance of the modified nanoscale titania coating, three typical steel structures with severe corrosion located in coastal areas, namely, pipeline valve, dome support of coal yard, and boiler connecting bolt in the power plant, were selected for practical engineering application. The coatings were observed regularly, and the anticorrosion effects of the coatings were compared with that of usual polyurethane oily anticorrosive coating.

3. Results and Discussion

3.1. Corrosion Resistance of Coatings

3.1.1. Neutral Salt Spray Results

According to the ISO 10289:1999 standard, the failure of the coating was identified as being three or more pits per sample or coating delamination. Samples were inspected every 24 h to evaluate the corrosion resistance of the coating during the test. Table 2 shows the performance parameters of salt spray resistance of four coatings. It can be seen that the neutral salt spray resistance time of the modified nanoscale titania coating is 1440 h, which is five times that of the waterborne epoxy resin coating and 408 h longer than that of metal flake coating. The durability of the modified nanoscale titania coating and graphene coating reached the H level. The modified nanoscale titania coating has excellent salt spray resistance and meets the design requirements of more than 15 years' lifetime in a C5/CX level corrosion environment.

Table 2. Comparison of neutral salt spray resistance of different coatings.

Coating Types	Neutral Salt Spray Resistance time/h	Durability Level	Weatherability Level
Waterborne epoxy resin	264	L	C5/CX
Metal flake coating	1032	M	C5/CX
Modified nanoscale titania coating	1440	H	C5/CX
Graphene coating	1512	H	C5/CX

3.1.2. Coupon Corrosion Test Results

The protective effects of these coatings after 1 year of coupon corrosion test are shown in Figure 1. As can be seen from Figure 1a,d, the surface of the modified nanoscale titania coating is clean and smooth, and there is no rust, spalling, or cracking, which indicates that the modified nanoscale titania coating has excellent corrosion resistance and self-cleaning ability. A new protective film is formed at the scratches of the coating, which indicates that the coating has self-repairing ability. As shown in Figure 1b,e, the surface of the graphene coating is blistered and slightly corroded, and a small amount of pollutants are attached to the coating surface. As shown in Figure 1c,f, the metal flake coating is obviously blistered and corroded, and the width of the corrosion at the X scratches exceeds 2 mm. Moreover, the large amount of pollutants attached to the surface accelerates the corrosion rate of the

coating [20]. After 1 year of coupon corrosion test, the modified nanoscale titania coating remains well, and its comprehensive anticorrosion performance is better than that of the graphene coating and metal flake coating.

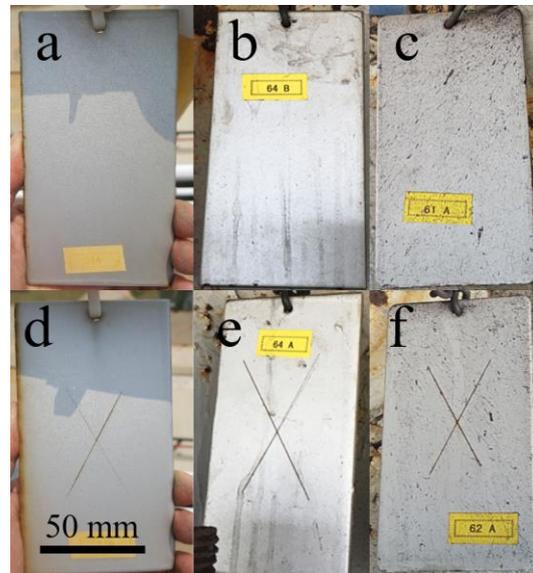


Figure 1. Protective effect of different coatings after 1 year of coupon corrosion test: (a) modified nanoscale titania coating, (b) graphene coating, (c) metal flake coating, (d) coating (a) with X, (e) coating (b) with X, (f) coating (c) with X.

3.2. Surface Morphology of the Modified Coating

To explore the underlying anticorrosion mechanism of the coating, the morphology of the modified coating was observed by SEM, as shown in Figure 2. From Figure 2a,b, it is observed that the overall appearance of the coating is flat and crack-free. As shown in Figure 2c, quantities of spherical-like structures are uniformly distributed on the coating surface, the white spheres are nanoscale titania particles, and the gray portion is epoxy resin. The modified nanoscale titania particles were dispersed uniformly by silane molecules. Such arrangement is similar to a honeycomb, which improves the compactness of the coating [21]. As can be seen from Figure 2d, the diameter of the single particle is about 200 nm, which confirms that the side chain of the resin has been successfully grafted onto the surface of the modified spherical nanoscale titania. After modification, the organic groups grafted on the surface of the particles introduced steric repulsion, thus preventing their aggregation [22]. The existence of these nanoparticles makes the coating surface form a micro-nano structure, which makes the coating have high compactness. The anticorrosion performance of the coating is enhanced with the increase in the compactness of the coating [23]. This is also an important reason why the modified nanoscale titania coating can still provide reliable protection for steel structures in an environment of high humidity and high salt fog.

The same micro-nano structure is also observed by AFM. As shown in Figure 3, many bumps are distributed on the surface of the coating. The root mean square roughness (RMS) of the coating is 13.9 nm. This kind of protruding structure is similar to the hierarchical structure of the lotus leaf surface, which has both microscale and nanoscale roughness [24]. The protruding structure with micro-nano roughness could form a hydrophobic surface [25]. Generally speaking, the water contact angle of a hydrophobic surface is greater than 90°, which makes it possess a self-cleaning ability [26]. As shown in Figure 4a,b, the water contact angle of the coating before corrosion and after coupon corrosion test are 118° and 103°, respectively. This indicates that the coating is hydrophobic and also can maintain lasting hydrophobic properties under harsh corrosion environments, consequently

establishing the self-cleaning ability. In fact, the modified nanoparticles are assembled on the coating surface to form a hydrophobic surface so that water droplets can easily roll off the coating. The rolling water droplets accumulate corrosive substances and other pollutants attached to the coating surface, and then fall off together [27]. The AFM images and contact angle test are consistent with the results of the above coupon corrosion tests. It is the special micro-nano rough structure that makes the coating have excellent self-cleaning ability.

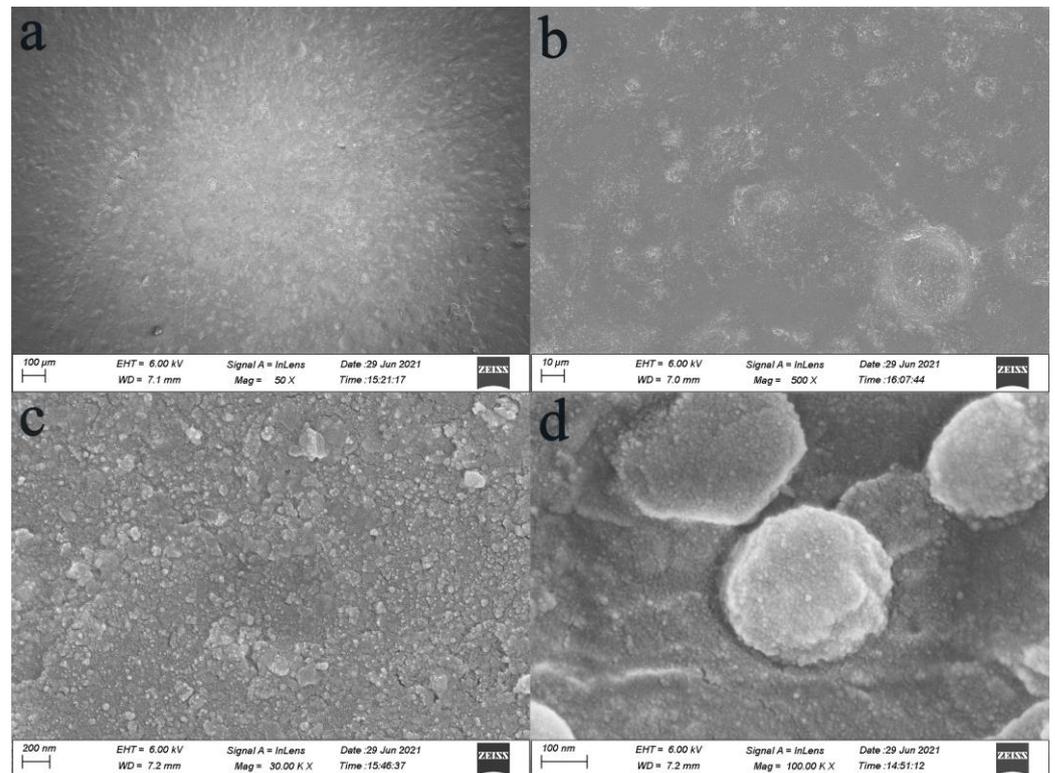


Figure 2. SEM images of the modified nanoscale titania coating: (a,b) overall appearance, (c) distribution of particles, (d) single particle.

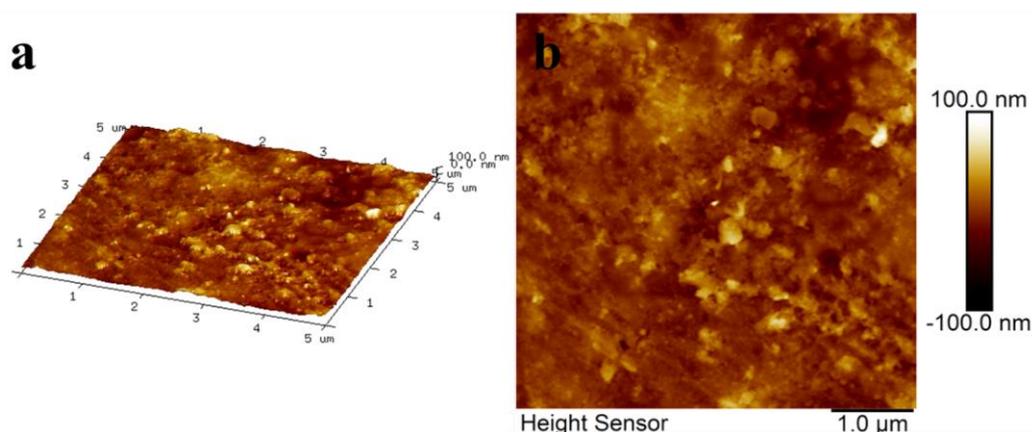


Figure 3. AFM images of the modified nanoscale titania coating: (a) 3D stereogram, (b) 2D topography.

3.3. Forming Mechanism of the Modified Nanoscale Titania Coating

To further explore the film-forming and self-repairing mechanism of the coating, the morphology and structure of the modified nanoscale titania coating were investigated by TEM, as shown in Figure 5. From Figure 5a,b, it is observed that the spherical particles of the coating are connected together by the overlap of side chains. In the modified nanoscale

titania coating, the side chains of the modified spherical nanoscale titania stretch out, and resin molecules are grafted on the spherical surface to form a fluffy sphere with many side chains, as shown in Figure 6. Countless particles form a tight film by virtue of the overlapping and winding of their side chains [28]. The cross-linking makes the film's density increase after moisture volatilization; then an ultradense anticorrosive coating is formed.

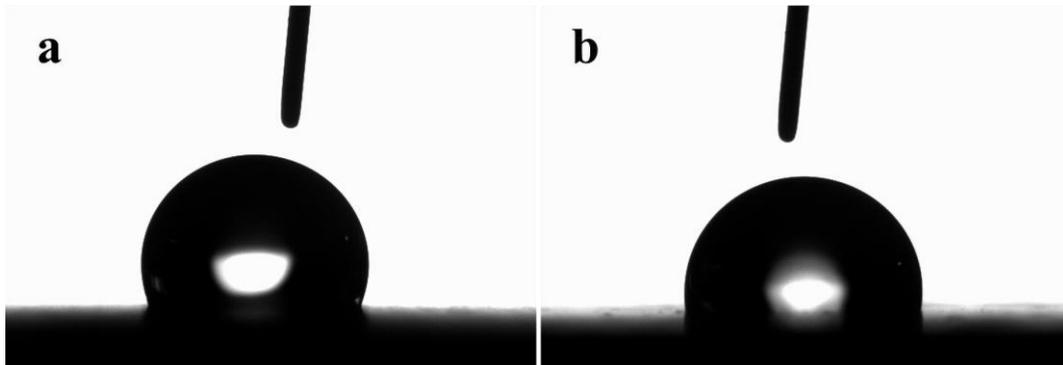


Figure 4. Images of water droplet (4 μL) on the surface of the modified nanoscale titania coating: (a) original coating, (b) coating after coupon corrosion test.

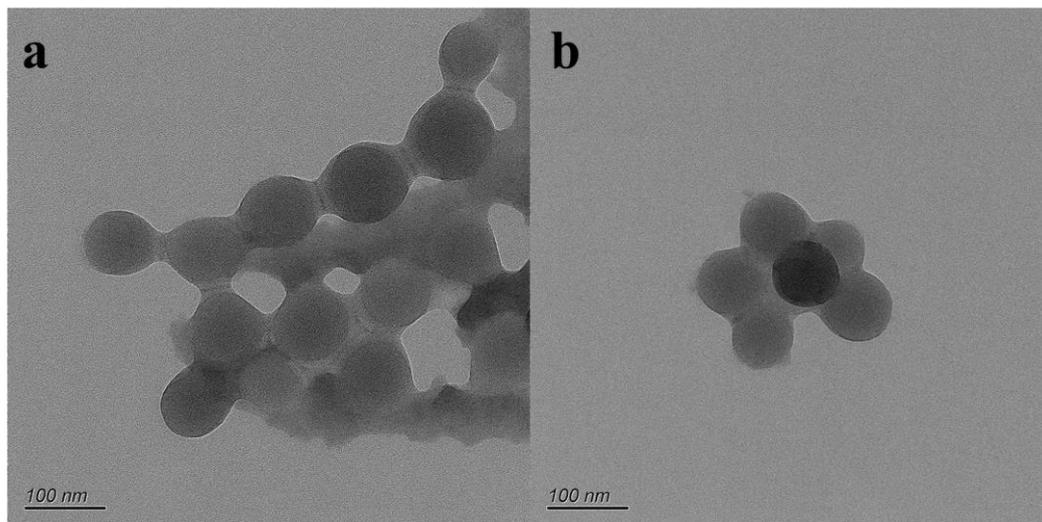


Figure 5. TEM images of modified nanoscale titania coating diluted with deionized water: (a) dilute 10 times, (b) dilute 20 times.

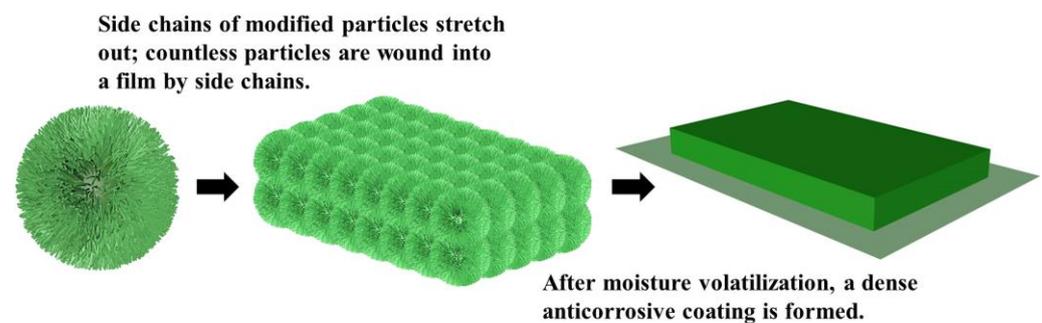


Figure 6. Forming mechanism of the modified nanoscale titania coating.

The superiority of the modified nanoscale titania coating is related to the excellent anti-ultraviolet aging performance of TiO_2 [28,29]. Furthermore, the existence of side

chains makes the coating have good flexibility [30]. When the coating is cracked due to the external expansion of steel substances under the blazing sun, the side chains of adjacent particles will relap together to form a new protective film to repair the damaged coating, as shown in Figure 7. The anticorrosion performance of the modified nanoscale titania coating is greatly improved because of its excellent anti-ultraviolet aging performance and self-repairing ability.

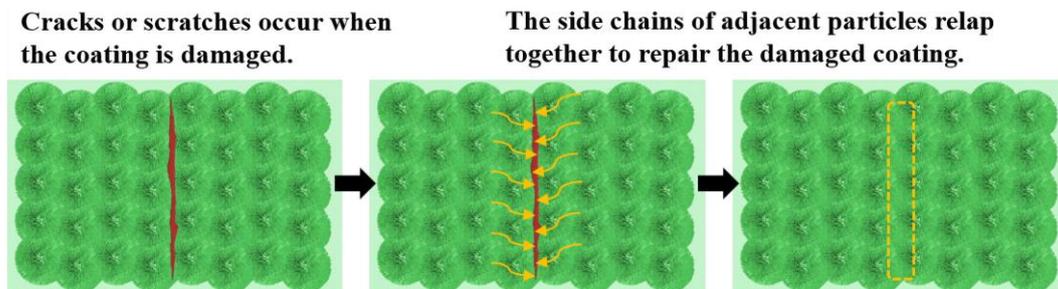


Figure 7. Self-repairing mechanism of the modified nanoscale titania coating.

3.4. Commercial Application on Coastal Steel Structures

The modified nanoscale titania waterborne coating was commercially applied on the steel structures under an extreme coastal corrosion environment with high temperature, high humidity, and high salt fog at the Huaneng Haimen Power Plant, Shantou, China. The protective effects of the usual polyurethane oily anticorrosive coatings and modified nanoscale titania coating are compared in Figures 8 and 9. As seen in Figure 8, the polyurethane oily anticorrosive coating has a large area of blistering and rust, and even a small part of the coating has fallen off. After 6 months of service, the polyurethane oily anticorrosive coating has lost its anticorrosion ability, which indicates that the ordinary anticorrosive coating cannot provide long-term and effective anticorrosion protection for steel structures in a coastal corrosion environment. As shown in Figure 9, after 3 years of service, the surface of the modified nanoscale titania coating is still clean and smooth, without blistering, rust, or shedding.



Figure 8. Protective effect of the usual polyurethane oily anticorrosive coating after 6 months: (a) pipeline valve, (b) dome support of coal yard, (c) boiler connecting bolt.

In addition, an artificial scratching test was carried out on the coating at the boiler connecting bolt. Two holes with an area larger than 100 mm² were dug out in the coating. The left hole was carved in recent time after the modified nanoscale titania coating experienced 3 years' testing. As shown in Figure 10, there is almost no corrosion on the steel matrix under the left hole. The right hole was carved 3 years before. Although there is serious corrosion in the right hole, the corrosion spreads slightly to the surround coating around the hole. This demonstrates that the coating has an ability to inhibit the spread of the corroded area, and can still provide effective protection even in the case of large area damage. The modified nanoscale titania coating has excellent anticorrosion performance, which leads to a long service life under a harsh coastal corrosion environment.



Figure 9. Protective effect of the modified nanoscale titania coating after 3 years: (a) pipeline valve, (b) dome support of coal yard, (c) boiler connecting bolt.



Figure 10. Scars on the modified nanoscale titania coating under artificial scratching: (left hole) new damage, (right hole) damaged 3 years before.

4. Conclusions

In this work, the extended side chains were grafted onto spherical nanoscale titania modified by silane coupling agent. Countless particles formed a hierarchical coating by virtue of the overlapping and winding of side chains, which greatly enhanced the strength and toughness of the coatings. The coating exhibited a kind of hydrophobic behavior with a water contact angle of 118° . The hierarchical grafting structure improves the stress resistance of the coating and makes the coating have high weatherability and high reliability. The modified nanoscale titania waterborne coating can provide long-term and reliable anticorrosion protection for steel structures under a coastal corrosion environment with high temperature, high humidity, and high salt fog. It has certain practical application value in the field of heavy-duty anticorrosion of steel structure. On the basis of the experimental study of waterborne anticorrosive coatings, more attention should be paid to the research of solidification simulation and microstructure analysis. Environmentally friendly waterborne anticorrosive coatings are expected to replace traditional organic solvent coatings.

(1) The salt spray tests showed that the neutral salt spray resistance time of the modified nanoscale titania coating was 1440 h, and the durability reached the H level.

(2) The coupon corrosion test showed that the modified nanoscale titania coating had no blistering, rust, or cracking after 1 year. The coating surface was clean and smooth. Especially, a new protective film would be spontaneously formed at the crack due to the overlapping and winding of side chains on the surface of the modified nanoscale titania particles. The modified nanoscale titania coating had excellent self-repairing ability and self-cleaning ability.

(3) The large-scale commercial application of the modified nanoscale titania coating on coastal steel structures showed that the coating remains well after 3 years' service in the heavy corrosion environment with high temperature, high humidity, and high salt fog.

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X.W.; writing—review and editing, S.W. All authors have read and agreed to the published version of the manuscript.

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