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Anti-corrosion properties of oligoaniline modified silica hybrid coatings for low-carbon steel

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ABSTRACT

Novel electroactive silica-based hybrid coatings were synthesized on the surface of Q235 low carbon steel via one-step electrodeposition and were analyzed by FTIR, UV-vis, SEM, OCA20 contact angle (CA) analyzer and CHI-660E electrochemical workstation, respectively. The CA test indicated, in comparison with bare Q235 substrate, the silica hybrid material modified by N, N'-Bis(4′-(3-triethoxysilylpropylureido)-phenyl)-1,4- quinonenediimine (TSUPQD) exhibited an excellent hydrophobic properties. More importantly, the deposition potential significantly affected the corrosion resistance of TSUPQD modified silica hybrid material. By comparing with various deposition potentials (−1.1, −1.3, −1.5, −1.7 V) under the deposition time of 500 s, the coating prepared under the potential of −1.5 V presented the best anti-corrosion performance for Q235 steel in 3.5 wt.% NaCl solution. The XRD and SEM analysis of corrosion product beneath the hybrid coatings showed that the redox catalytic capability of aniline trimer unit induced the Q235 substrate to form the passive films which mainly consisted of α-Fe_2O_3 and Fe_3O_4.

1. Introduction

Metal corrosion is a serious problem to many industries and brought huge loss to world economy. Silica-based organic-inorganic materials possess many advantages, such as good strength, excellent barrier performance and the convenient processing, have been widely used in optical devices, catalysts, composites, and protective coatings [1–10]. For instance, Peng et al. [11] developed a novel organic-inorganic hybrid silica coating by the reaction of tetraethoxysilane (TEOS) and benzotriazole (BTA), and found that the anti-corrosion property was significantly improved after the substrate was covered by this coating. Ahmad et al. [12] prepared a silica-based hybrid coating via the combination between Linseed diol fattyamide (HELA) and tetraethoxysilane (TEOS) at 80 °C, followed by the addition of toluene-2,4-diisocyanate (TDI) at room temperature. The results showed that the as-prepared coating displayed a good protective performance against the corrosive medias of HCl (3.5 wt.%), NaOH (3.5 wt.%) and NaCl (5 wt.%). Zhang et al. [13] combined the organic benzotriazole and tetraethoxysilane (TEOS) to form a superhydrophobic hybrid coating which exhibited a better corrosion protection property than pure silica coating.

Meanwhile, some previous reports confirmed that embedding organic inhibitors into silica-based hybrid coatings can further enhance the corrosion resistance performance [14–16]. Polyaniline (PANi) as a typical conducting polymer has been broadly applied in anticorrosion coating due to its simple fabrication, low price and excellent electroactivity [17–20]. However, the poor processability of PANi is the main limitation for its application in many areas [21,22]. In contrast, oligoaniline not only owns a well-defined structure, but also possesses a similar electroactivity to that of PANi [23–26]. For example, Huang et al. [27] successfully prepared an electroactive epoxy thermoset coating containing amino-capped aniline trimer units, and showed that the anti-corrosion mechanism of such coating was attributed to the special redox behavior of the aniline trimer. Gu et al. [21] synthesized an electroactive siliceous hybrid material via one-step coupling reaction between phenyl-capped aniline tetramer (AT) and 3-(triethoxysilyl) propyl isocyanate (TESPIC). The study confirmed that the anti-corrosion ability of this obtained sol-gel coating was better than that of the pure sol-gel silica coating. Thus, oligoaniline as a corrosion inhibitor has a great potential to use for improving the corrosion resistance of silica-based hybrid coatings.

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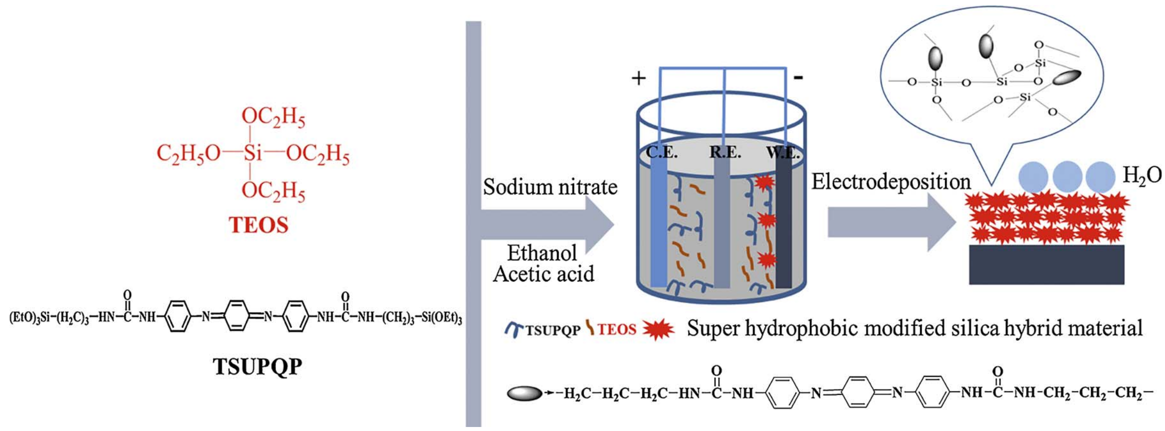

Fig. 1. The schematic diagram of modified silica coating.

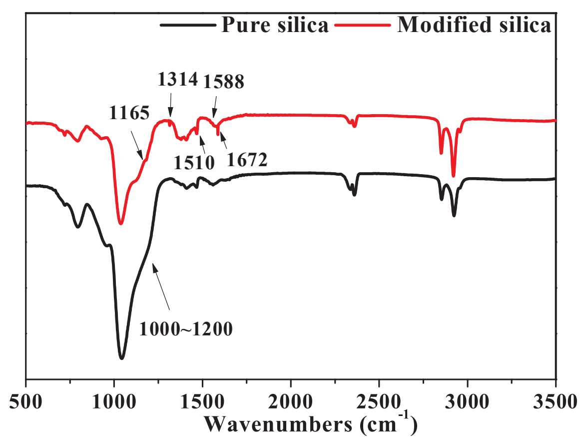

Fig. 2. The FTIR spectra of pure silica and modified silica coatings.

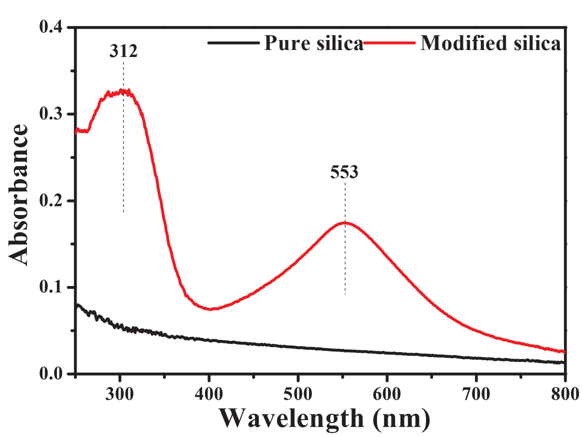

Fig. 3. The UV–vis spectra of pure silica and modified silica coatings.

In this study, we prepared a precursor of N, N′-bis (4′-(3-triethoxysilylpropyl-ureido) phenyl)-1,4-quinonenediimine (TSUPQD) via a one-step coupling reaction between the aniline trimer and triethoxysilylpropyl isocyanate. And the electrodeposition technology rather than the typical sol-gel method was chosen to prepare the modified silica hybrid coating on Q235 steel based on a mixed solution of tetraethyl orthosilicate (TEOS) and TSUPQD. The modified silica hybrid coatings were obtained under different deposition potentials, which were found to affect the thickness, morphology, surface contact angle and corrosion resistance of the coatings. The chemical composition, surface morphology and hydrophobicity were characterized by transform infrared spectroscopy (FTIR), scanning electron microscope (SEM)

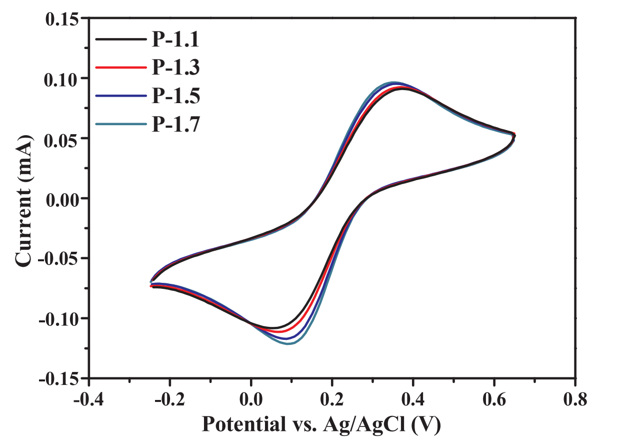

Fig. 4. The CV curves of these hybrid coatings in 0.1 M H_2SO_4 solution with the scan rate of 10 mV/s.

and contact angle analyzer. The Tafel curve and EIS spectra were used to investigate the relationship between deposition potential and anti-corrosion performance. The scanning electron microscope (SEM, FEG 250) and X-ray diffraction (XRD, D8 ADVANCE) were used to analyze the coating morphologies and the corrosion products, respectively.

2. Experiment section

2.1. Materials

Triethoxysilylpropyl isocyananate (TESPIC), anhydrous tetrahydrofuran (THF), *n*-hexane and tetraethoxysilane (TEOS) were purchased from Aladdin Industrial Corporation. N, N'-diamino-diphenylamine, ammonium persulfate, ammonium hydroxide, acetone, ethanol, sodium nitrate, hydrochloric acid and acetic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals and solvents were used as received without further purification. The Q235 carbon steel specimens (10 mm × 10 mm × 10 mm, with composition of 1.39 wt.% C, 0.29 wt.% Mn, 0.18 wt.% Al and balanced Fe (wt.%) were polished using 400, 800 and 1500-grit sand papers. After that, in order to remove the surface contaminants and prevent the electrode rust, the Q235 steel electrodes were rinsed by ultrasonication in acetone and ethyl alcohol, and finally dried in nitrogen. The aniline trimer (AT) and N, N'-Bis(4′-(3-triethoxysilylpropylureido)-phenyl)-1,4-quinonenediimine (TSUPQD) were produced according to the reported procedure [23].