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Superhydrophobic polyaniline/polystyrene micro/nanostructures as anticorrosion coatings

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ABSTRACT

In this paper, superhydrophobic polyaniline (PANI)/polystyrene (PS) micro/nanostructures were prepared by an electrospinning combining with drop-cast strategy for protecting carbon steel. The corrosion resistance ability and durance property of the resultant PANI/PS micro/nanostructures in 0.1 M H_2SO_4 were investigated and compared using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization technique. It is found out that effective anticorrosion performance can be provided by PANI/PS micro/nanostructures for carbon steel, and the corrosion protection efficiency (η) increases along with the water repellency of the PANI/PS micro/nanostructures. The protection properties of PANI/PS micro/nanostructures increased along with their water repellency. The PANI-PFOA/PS micro/nanostructures has the water contact angle value as high as 153°, demonstrating the most excellent anticorrosion properties with a promising anticorrosion efficiency of 99.48%.

1. Introduction

Metal corrosion often leads to performance degradation and loss function of life [1–4]. As is known to all, the corrosion of steel material can cause tens of billions of economic losses each year [5]. Covering the metal surface with protective coatings is a kind of economic effective and widely used method of achieving corrosion [6,7]. Traditional organic coatings containing Cr or Pb have been strictly prohibited by many countries because of their threats to human health and the environment. In recent years, the development of conducting polymers which protect the metals against corrosion is aimed at seeking a potential alternative to Cr or Pb for their environmental friendliness [8]. Among conducting polymers, polyaniline (PANI) has been considered as the most promising candidate because of good environmental stability, the resistance to pit corrosion and scratches, and good compatibility with the resin [9,10]. Besides simple and economic production process, it is the main advantage of PANI that formats a protective passivation oxide layer, maintaining and even repairing the native passive film on the metal, with a subsequent lowering the corrosion, and enhancing the protection [11,12].

Recently, superhydrophobic coatings with water contact angle of at least 150° have been widely used in many fields, such as self-cleaning windows, roof tiles, textiles, solar panels, biological medicine due to their special characteristics of water-repellent, self-cleaning properties, transparency, anisotropy, reversibility, and elasticity [13–15]. In particular, considerable interest has now been given to the use of superhydrophobic coatings as protective coating due to their superior water-repellent properties [16,17]. Liu et al. [18] utilized the hydrolysis of 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane and annealing on zinc substrates to fabricate stable super-hydrophobic films, which provided an effective corrosion-resistant protection for the underlying zinc in saline conditions. The superhydrophobic surface of biomimetic natural leaf shows outstanding corrosion protection in NaCl aqueous solution. More recently, considerable interest has been given to the use of superhydrophobic PANI coatings as the anticorrosion protective coatings. For example, C.W. Peng [19] fabricated superhydrophobic PANI coatings (CA = 156°) which provided excellent corrosion protections for cold rolled steel in 1.0 M HCl solution. Besides, superhydrophobic polyaniline micro/nanostructures with a water contact angle of 158° were prepared through a template-free method in our previous work [20]. And the prepared superhydrophobic PANI micro/nanostructures coatings can effectively prevent water from diffusion and restrain the corrosion process. However, superhydrophobic PANI coatings usually are prepared on the carbon steel by drop-casting, which resulted in uniformity and poor adhesion to the carbon steel for superhydrophobic PANI coatings, and further led to poor long-term anticorrosion properties. So overcoming the uniformity and poor adhesion of the superhydrophobic coatings can be accepted as a valuable means of

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developing long-term effective anticorrosion coatings.

In this work, PANI micro/nanostructures were deposited on the superhydrophobic electrospun polystyrene (PS) microfibers film to fabricate superhydrophobic PANI/PS anticorrosion coatings. By this approach, the adhesion between the coatings and the metal substrates can be improved efficiently. The corrosion behavior of carbon steel coated with superhydrophobic PANI/PS coatings was investigated in 0.1 M H_2SO_4, and it was the synergistic effect of the electrochemical anticorrosion of PANI and the superhydrophobic properties of PS microfibers to realize the efficient anticorrosion protection for the metals.

2. Experimental

2.1. Reagents and materials

The composition (%) of the Q235 carbon steel sheet used in this study (size 10 mm × 10 mm × 3 mm) was Mn 0.45, C 0.18, S 0.02, Si 0.02, P 0.01, with the balance iron, which was purchased from Shengxin Science and Technology Ltd., Yangxin, China. Poly(styrene) (PS), polymethyl methacrylate (PMMA), acetic acid (AA), lauric acid (LA), Ammonium persulfate (APS), sulfuric acid, tetrahydrofuran (THF), perfluoro caprylic acid (PFOA), butanol, anhydrous ethanol and ether were obtained from National Medicine Chemicals, China, and used without further purification. Aniline (National Medicine Chemicals of China) was distilled under vacuum before use.

2.2. Preparation of PS fibers

Electro-spun solution was PS solution (200 g L^{-1}) in THF or PMMA solution (70 g L^{-1}) in THF. The as-prepared PS or PMMA solution was positioned in a 5 mL plastic syringe which was fixed perpendicularly. A high-voltage DC direct generator (DW-P303-1ACF0, Dongwen High Voltage, Inc., China) was kept at 16 kV. In this test, the syringe was attached to a stainless steel needle used as a nozzle, and the needle had a diameter of 0.5 cm. The stainless steel needle connected to a high direct voltage source was located 16 cm away from the Q235 carbon steel electrode which was used as a collector. The non-woven, fibrous PS or PMMA mats with a thickness of about 50 μm were formed then dried in a vacuum oven at 60 °C for 10 h to allow the removal of remaining solvents.

2.3. Synthesis procedure of PANI

In the first step, aniline (2 mmol) was ultrasonicated in 5 mL of deionized water. And then, AA (1 mmol) and 5 mL of APS solution (0.4 mol/L) was added to the above mixture, stirring constantly. After 15 hours standing, the product was retrieved from the suspension using filtration funnel. The prepared sample (PANI-AA) was washed with deionized water and ethanol, respectively, followed by drying in a vacuum oven at 60 °C. Subsequently, PANI-LA and PANI-PFOA were obtained by replacing AA with 1 mmol LA and 0.1 mmol PFOA.

2.4. Preparation of PANI/PS coatings

PANIs were dispersed in butanol under ultrasonic condition and then were dropped on fibrous PS substrate. The obtained PANI/PS composites were marked as PANI-LA/PS, PANI-AA/PS and PANI-PFOA/PS, respectively. For comparison, PANI-PFOA dispersion was drop-cast on fibrous PMMA mats, and the obtained composite was marked as PANI-PFOA/PMMA.

2.5. Characterizations

The morphologies of the coatings were characterized by scanning electron microscope (SEM, Hitachi TM-1000). The coatings were covered on Q235 carbon steel sheet (10 mm × 10 mm × 3 mm). And then a layer of gold-palladium was coated on the prepared samples before being observed at an accelerating voltage of 5 kV. The surface roughness of coated Q235 carbon steel was measured with the MPLFLN10 objective lens through its 1 × zoom. The static water contact angle (CA) measurements were conducted on a Dataphysics OCA optical contact angle measuring device at room temperature using 2 μL of water. The static water contact angle was measured 5 times at different sites and the representative samples were chosen to present the result. The roughness and the surface topology were measured by 3D measuring laser microscope OLS4000. Tafel curves and electrochemical impedance spectroscopy (EIS) were recorded on an Autolab (PGSTAT302N) Potentiostat/Galvanostat (NOVA Software). A typical three electrode configuration was utilized in the circuit with the uncoated and coated Q235 carbon steel electrodes as the working electrodes, Pt as the counter electrode, and saturated calomel electrode (SCE) as reference electrode, respectively. All tests were performed in H_2SO_4 (0.10 M) corrosive environment, and the samples were immersed for 30 min before doing EIS measurements to make sure that the system is in steady-state. EIS measurements were tested in the frequency range of 100 kHz to 10 mHz with an amplitude of 10 mV at open circuit potential (OCP). The potentiodynamic current-potential curves were obtained by changing linearly the electrode potential automatically from − 250 mV to + 250 mV at a scan rate of 1 mV s^{-1}. All electrochemical experiments were operated in triplicate at room temperature to ensure reproducibility and statistical significance. The corrosion protection efficiency from Tafel polarization curves was calculated by the following formula:

$$\eta(\%) = [i_{corr} - i_{corr}(C)]/i_{corr} \times 100\% \quad (1)$$

In this equation, i_{corr} (C) and i_{corr} are corrosion current density of coated carbon steel and blank carbon steel [21], respectively.

3. Results and discussion

3.1. Morphologies and wettability

Fig. 1 shows the representative SEM images of PANI and PANI/PS composites. It can be clearly seen from Fig. 1a that the electrospun PS microfibers presents relatively uniform fibers whose average diameter are about 150 nm. Fig. 1b′ and c′ indicate that PANI-LA and PANI-AA are made of short fibers with several hundred nanometers in length. PANI-LA and PANI-AA have an average diameter of ~100 nm and 200 nm, respectively. It can also be explicitly observed that there are smaller nanoparticles on the surface of the PANI-AA. The PANI-PFOA are micro/nano-coexisted aggregates, on which there are short nanowires, as shown in Fig. 1d′. It is found that the SEM images (Fig. 1b–d) of PANI-LA/PS, PANI-AA/PS and PANI-PFOA/PS are the same as those of the responding PANI, indicating that PANI has covered on the surface of PS microfibers successfully.

The wettability of PANI and PANI/PS composites was characterized by water CA measurements, as demonstrated in the insets of Fig. 1. The surface of the PANI micro/nanostructures is significantly affected by the doping acid. The surface of the PANI-LA is strongly hydrophilic with a water CA as low as 40° (Fig. 1b′ inset). PANI-AA's water CA (71°) is higher than PANI-LA, exhibiting a hydrophilic character. The water CA of the PANI-PFOA, however, increased to 155°, showing a superhydrophobic characteristic. The hydrophobic properties are known to be strongly reliant on not only the chemical structures but also the surface roughness of the coating [22]. In Cassie state, the CA of a water droplet on a hydrophobic surface (θ_r) is associated with the CA (θ) on a smooth surface by the Cassie-Baxter equation [23]:

$$\cos\theta_r = f_1 \cos\theta - f_2 \quad (2)$$

where f_1 and f_2 are the fractions of solid surface and air in contact with water, respectively (i.e., $f_1 + f_2 = 1$). According to the Cassie-Baxter model hypothesis, a droplet of water is suspended on the rough surface,