Surface & Coatings Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Self-healing active anticorrosion coatings with polyaniline/cerium nitrate hollow microspheres

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ARTICLE INFO

Keywords:
Anticorrosion coatings
Rare earth elements
Polyaniline hollow microspheres

ABSTRACT

Polyaniline (PANI) hollow microspheres have been synthesized by self-assembly method and doped with Poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) and Ce ions. PANI/$Ce(NO_3)_3$ hollow microspheres of large specific area (10.9 m^2/g) and ultrahigh electrical conductivity (46.8 S/cm) were applied as additives and dispersed in epoxy coating. EIS and Tafel polarization tests indicated that PANI/$Ce(NO_3)_3$ coating exhibiting excellent anticorrosion performance. Raman spectra revealed that compact and thin Fe_3O_4 layer has been formed on steel surface to block aggressive electrolytes. In addition, Ce ions promoted the formation of passivation layer and assured protection against corrosion without toxic inhibitor.

1. Introduction

Among all conducting polymers, polyaniline (PANI) has received considerable attention due to its easy synthesis, good environmental stability, high electrical conductivity and anticorrosion ability. Various forms of micro/nanostructures of PANI, such as nanoparticles [1,2], nanotubes [3,4], microspheres [5,6], nanofibers [7,8], nanowires [9,10], nanosticks [11,12], have been synthesized via chemical oxidation of aniline or electrochemical methods. PANI has found wide applications in semiconductors, electrodes, supercapacitors, electromagnetic shieldings and anticorrosion coatings [13–17] etc. To protect metallic structure against corrosion-caused degradation, many strategies have been used and PANI coating has been demonstrated as one of the effective anticorrosion protections [18]. Since protective effect of PANI on steel has been found by DeBerry, anticorrosion application has attracted many researchers' interest [19]. In spite of some controversies on protection mechanism, polyaniline remains one of the most promising anticorrosion materials due to its high electrical conductivity and good environmental stability.

PANI hollow microspheres presented unique structure. Many approaches have been used to prepare PANI hollow microspheres [20–22]. One of them is self-assembly method, which can eliminate the need to remove hard templates in subsequent process. The key factor to obtain uniform hollow microspheres is to choose proper surfactants. Although many papers reported that salicylic acid, β-naphthalene sulfonic acid, *m*-aminobenzenesulfonic acid [23–25] etc., can be used in the synthesis of PANI hollow microspheres, their diameters were larger than 1 μm. For example, PANI hollow microspheres provided by D. Tran were ranging from 50 nm to 5 μm in diameter with a shell thickness on the order of 10–100 nm [26]. In general, smaller particle sizes often lead to larger specific surface area. For PANI hollow microspheres, small diameters show higher electrochemical activity and better anticorrosion properties. Therefore, it is desirable to develop uniform PANI hollow microspheres with smaller diameters.

Corrosion inhibitors have been employed for anticorrosion protection, the most representative ones are Cr (VI)-based compounds, which have unrivaled ability in self-healing activity of conversion coatings on metals. However, Cr (VI)-species corrosion inhibitors have been banned in many countries due to their high toxicity and carcinogenic effect [27]. Therefore, it is desired to develop environmental friendly and effective corrosion inhibitors. Recently, rare-earth metals, especially cerium salts have been found to be good candidate as corrosion inhibitors due to their excellent corrosion inhibition, low toxicity and low cost. Cerium chloride [28], cerium salicylate [29], cerium molybdate [30], etc., have been used as corrosion inhibitors on different metals and alloys.

Poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) is a type of polymeric acid synthesized via 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomers [6]. PAMPS was employed as surfactant and dopant in synthesis of PANI with high electrical conductivity and water solubility by self-assembly method [31]. Of excellent hydrophily and adsorption for ions sulfonic acid group in side chains, PAMPS was good candidate to prepare PANI/rare earth composites.

The main objective of this study is to prepare Ce ions doped PANI

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https://doi.org/10.1016/j.surfcoat.2017.11.054
Received 25 June 2017; Received in revised form 17 October 2017; Accepted 18 November 2017

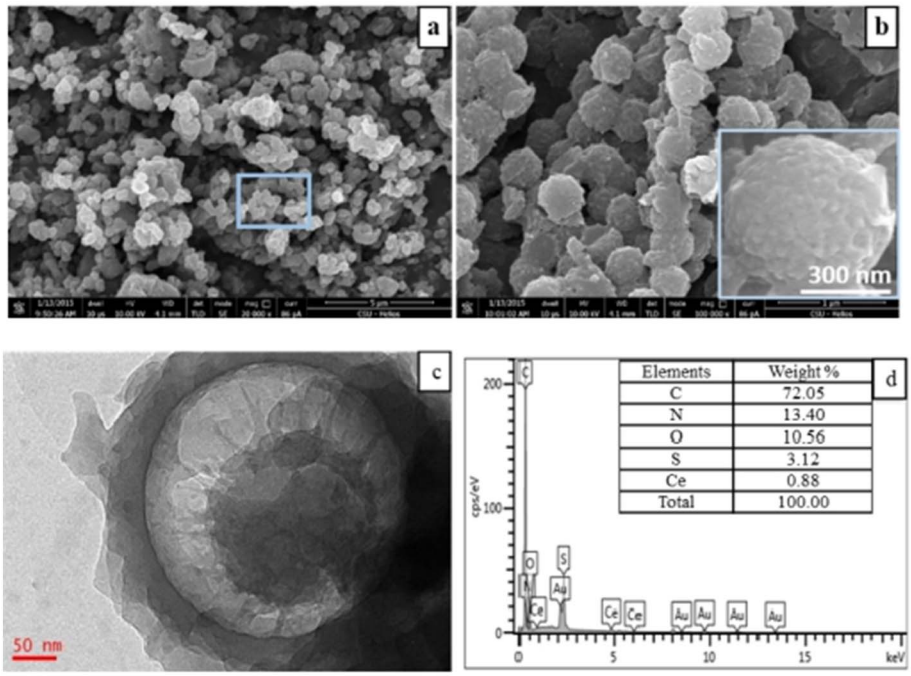

Fig. 1. Morphology of PANI/$Ce(NO_3)_3$ hollow microspheres: (a) 20,000 × (SEM image); (b) 100,000 × (SEM image); (c) EDX spectrum; (d) TEM image.

hollow microspheres as anticorrosion additives for epoxy coating. Structural and morphological of PANI/$Ce(NO_3)_3$ will be characterized by FT-IR, UV–Vis, SEM and TEM, respectively. Anticorrosion properties of composite coatings with PANI/$Ce(NO_3)_3$ will be examined by electrochemical impedance spectroscopy (EIS) and Tafel polarization in detail. The possible protective mechanism imparted by PANI/$Ce(NO_3)_3$ will be discussed and examined by Raman spectra.

2. Experimental

2.1. Materials

PAMPS was synthesized by free radical polymerization of AMPS (Purity, 99.23% and supplied by Shouguang Yuyuan Green Technology Co., Ltd., China). The number-average molecular weight and weight-average molecular weight of PAMPS were 2006 kg mol^{-1} and 2015 kg mol^{-1}, respectively. Aniline was distilled before used. Cerium nitrate, ammonium persulfate, alcohol and acetone were analytical grade and commercially obtained from local chemical shops. Epoxy resin (E-51) and polyamide hardener (651) were supplied by Changsha Chemical Industry Research Institute.

2.2. Synthesis of PANI/$Ce(NO_3)_3$ hollow microspheres

PAMPS (2.08 g), absolute ethanol (6.32 g), distilled water (72.00 g) and Aniline (1.86 g) were mixed together in a flask forming homogeneous suspensions with stirring at 80 °C for 10 min. Then, 40 mL ammonium persulfate aqueous solution (114 mg/mL) was preheated to 80 °C and added to the homogeneous mixture rapidly. The initial reaction was sustained at 80 °C for 1 min under stirring. Subsequently, the flask was transferred to ice-water bath rapidly. After 12 h, acetone was applied for demulsification, PANI precipitates were washed with deionized water and absolute alcohol. These PANI hollow precipitates were dispersed in 40 mL cerium nitrate aqueous solution (4.5 mg/mL) with magnetic stirring for 12 h at room temperature. Afterwards, PANI/Ce$(NO_3)_3$ precipitates were obtained after washing with deionized water and dried under vacuum at 70 °C.

2.3. Preparation of epoxy coating containing PANI/$Ce(NO_3)_3$

Q235 mild steel sheets with dimension of 150.0 × 70.0 × 1.0 mm were ground to 1000-grits with emery paper and degreased in acetone and dried in air. PANI/$Ce(NO_3)_3$ composites (5.0 wt%) were dispersed in xylene and further dispersed in epoxy resin, and a certain amount of polyamine hardener was added to the mixture. PANI/$Ce(NO_3)_3$ coating was ground by cone mill (QZM) and painted on Q235 steel panels to form thin films. Average thickness of dry films measured by coating thickness gauge (QUC-200) was 150 ± 10 μm for immersion test and 35 ± 5 μm for electrochemical test.

2.4. Characteristics

Fourier transform infrared spectroscopy (FT-IR) was obtained on spectrophotometer (NICOLET 6700). Ultraviolet-visible spectra of PAMPS, PANI and PANI/$Ce(NO_3)_3$ were performed on ultraviolet spectrophotometer (TU 1900) ranging from 200 nm to 900 nm, concentration of samples in *N*-methyl-pyrrolidone was 50 mg/kg. Morphology of PANI/$Ce(NO_3)_3$ was observed by scanning electron microscopy (SEM, Helios Nanolab 600i) and transmission electron microscopy (TEM, JEM-2100F). BET surface areas were measured by N_2 adsorption in Monosorb Autosorb. X-ray photoelectron spectroscopy (XPS) was performed by ESCALAB 250Xi spectrometer, with Al Kα X-ray source. Electrical conductivity of compressed samples with 14 mm (prepared under 15 MPa) was measured by four-probe method at room temperature. Electrochemical properties of PANI/$Ce(NO_3)_3$ were investigated in 0.5 M H_2SO_4 solution on electrochemical station (CHI660C). The working electrodes were made of PANI/$Ce(NO_3)_3$, acetylene black and polytetrafluoroethylene at a ratio of 8:1:1. Impedance of PANI/$Ce(NO_3)_3$ was recorded from 0.01 Hz to 100 kHz with ac amplitude of 10 mV. Anticorrosion performances of coatings were mainly evaluated via electrochemical impedance spectroscopy and Tafel polarization using CHI660C electrochemical station. Saturated calomel electrode and platinum electrode were used as reference electrode and counter electrode, respectively. Impedance measurements of coatings were carried out ranging from 0.01 Hz to 100 kHz with ac amplitude of 10 mV. The test area of working electrode was 1cm^2. A "×" scratch with width of 0.5 mm exposing steel substrate