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Short Communication

Corrosion Resistance Research of ZnO/polyelectrolyte Composite Film

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A composite film consisting of zinc oxide (ZnO) and polyelectrolyte, poly (diallyldimethylammonium chloride) (PDDA), has been successfully fabricated on a carbon steel substrate by a simply electrochemical deposition method. The fabrication mechanisms are based on electrophoretic deposition of PDDA and electrolytic deposition of ZnO. FT-IR results indicate the existence of PDDA. SEM results show that compared with ZnO film, the composite film becomes more compact and smooth. It demonstrates that the surface morphology of the film is increased because of the existence of PDDA. Polarization curves show that the substrate coated with composite film has a lower corrosion current density and a more positive corrosion potential value than bare and ZnO coated samples. The superior corrosion resistance can be attributed to PDDA, which can improve the stability of the film. The resulted film may be a potential anticorrosion coating for metal corrosion protection.

Keywords: ZnO; PDDA; composite film; carbon steel; corrosion

1. INTRODUCTION

Organic/inorganic composites have attracted widely attention. Composite materials with various nanostructured have been fabricated in recent years. These materials exhibit new thermal, mechanical, optical, magnetic and electrical properties [1-5].

Zinc oxide (ZnO) is one of the most talented materials with extensive applications. It has many outstanding properties, such as high piezoelectricity, photoelectric conversion, good biocompatibility and has potential application in optoelectronic devices and chemical sensors [6-9]. Recent studies indicate that nano-sized ZnO particles may offer cathodic protection to stainless steel in organic coating matrix [10].

Electrochemical method with the advantage of short operation time, simple process, compositional control easily, and better homogeneity has been widely used to fabricate ZnO films. However, it may lead to the agglomeration and poor adhesion of ZnO particles to the substrate surface. This disadvantage is very obvious especially when the film is used in corrosion protection.

Poly (diallyldimethylammonium chloride) (PDDA) is a familiar material used for the fabrication of organic/inorganic composite flims. It is a strong polycation because of the quaternary ammonium groups and the degree of dissociation of the ionic groups is almost pH-independent in a wide pH range [11-14]. PDDA may act as adhesive for improving adhesion of colloidal particles to the surface of an electrode for it has inherent binding properties. Also, the electrostatic repulsion of the PDDA macromolecules can be reduced. The PDDA macromolecules can be compensated by the negative charge of the colloidal particles formed at the electrode surface [15].

In this study, we report the simultaneously deposition of ZnO and PDDA onto a carbon steel substrate using a mixed solution of zinc nitrate ($Zn(NO_3)_2$) and PDDA via a electrochemical method involving the electrodeposition and electrophoretic deposition process. The main advantage of this method is that the ZnO nanoparticle can be produced in situ in the PDDA and many possible problems about the disperse ability of nano-size materials in organic matrix can be avoided. The anticorrosion property of the ZnO/PDDA composite film was investigated by Tafel curve.

2. EXPERIMENTAL

2.1 Chemical and materials

All chemicals are analytical grade. Sodium chloride (NaCl) and zinc nitrate ($Zn(NO_3)_2\cdot 6H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. PDDA (20%, MW 100 000 − 200 000) was purchased from Aldrich.

The samples used in this study are carbon steel rod (5 mm diameter) and enclosed with epoxy resin to offer a work area of 0.196 cm^2. The chemical composition (wt. %) of the substrate is 0.1 C, 0.4 Mn, 0.12 Si, 0.02 S, 0.05 P, and the others is iron.

2.2 Fabrication of ZnO and ZnO/PDDA films

Prior to electrodeposition, the substrate was polished with No. 2000 silicon carbide paper and 1 μm alumina powder. After rinsed by purified water (Millipore, USA), it was cleaned with ultrasonic ultrasonic machine in purified water for 5 min, and then rinsed by purified water again to be used for electrodeposition.

The reaction solutions were prepared with purified water and contained 5 mM $Zn(NO_3)_2$. The composite film was fabricated by adding 2 g L^{-1} of PDDA in solution.

The ZnO and ZnO/PDDA films were fabricated at the potential of −1.2 V (vs. Ag/AgCl) for 20 min on substrates in a three-electrode cell. The temperature of reaction solution was kept at 50 ^{o}C. The carbon steel was used as working electrode. A silver/silver chloride (Ag/AgCl) (3 M KCl) was used as reference electrode and a platinum wire electrode (CH Instruments, Inc.) was used as counter electrode.

2.3 Characterization

Crystal structure analysis was detected by X-ray diffraction (XRD) with a diffractometer (D/MAX-RB, Rigaku Corporation) using monochromeatized Cu K_α radiation at a scanning speed of 1.2 ^{o} min^{-1}. The morphologies analysis of the films was studied using a scanning electron microscope (KYKY-2800B, KYKY Technology Development Ltd., China). FT-IR spectrum was demonstrated in the range of 4000-400 cm^{-1} as KBr pellets on spectrometer (Nicolet iSIO, Thermo Electron Scientific Instruments LLC).

2.4 Electrochemical measurements

All the electrochemical experiments, including electrochemical deposition and Tafel curve, were carried out by electrochemical system (CHI 760C，CH Instruments Inc., USA). Tafel curve was used to detect the corrosion resistance of the films. It was recorded in a potential range of −800 to −200 mV (1 mV s^{-1}). 3.5wt. % NaCl solution was used as electrolyte. All the experiments were carried out at room temperature (about 25 ^{o}C) and the test samples were immersed in NaCl solution for a 30 min to ensure stability of open circuit potential (E_{ocp}).

3. RESULTS AND DISCUSSION

3.1 Fabrication of ZnO and ZnO/PDDA films

Electrodeposition of ZnO is based on the generation of hydroxide ions (OH^-) by the cathodic reduction of an oxygen precursor in a Zn^{2+} solution [16] . The reaction (1) takes place when NO_3^- is used as oxygen precursors for ZnO electrodeposition [16]. The Zn^{2+} and OH^- ions react together, leading to ZnO fabrication on the surface of substrate(reaction (2)) [17].

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad (1)$$
$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \qquad (2)$$

The ZnO/PDDA composite film was fabricated by adding 2 g L^{-1} of PDDA in $Zn(NO_3)_2$ solution. In previous work, the ZnO/PDDA composite fabrication is controlled by the electrostatic attraction of colloidal ZnO particles and PDDA macromolecules. The surfaces of colloidal ZnO particles may become positively or negatively charged depending on pH: [18]

$$Zn\text{-}OH + H^+ \rightarrow Zn\text{-}OH_2^+ \qquad (3)$$
$$Zn\text{-}OH + OH^- \rightarrow Zn\text{-}O^- + H_2O \qquad (4)$$

The cathodic reaction (1) results in pH increase at the cathode surface. It is important to note that the isoelectric point of ZnO was reported in the range of 8.1-10.3. Therefore, ZnO particles formed on steel surface could be negatively charged. It has been shown that the strong electrostatic repulsion of PDDA macromolecules could be compensated by ZnO particles with negative charge. In this case, composite film deposition is achieved via heterocoagulation of oppositely charged PDDA and negatively charged colloidal ZnO particles formed at the steel surface [19].

3.2 Characterization of ZnO and ZnO/PDDA films

The phase information of the films was determined by XRD. The XRD designs of ZnO and ZnO/PDDA films coated on steel surface are showed in Fig. 1. As shown, all peaks of ZnO film match well with the hexagonal structure of ZnO [JCPDS card No. 36-1451]. The peaks at 2θ = 31.80 ^{o}, 34.42 ^{o}, 36.22 ^{o} are assigned as the (*100*), (*002*), (*101*) reflection lines of ZnO, respectively. For the ZnO/PDDA composite film, the characteristic peak position of ZnO has nearly no changes and the peak intensity has a decrease. Moreover, except the characteristic peaks of Fe, there are on other peaks appeared, suggesting that PDDA has no significant effect on the fabrication mechanism of ZnO.

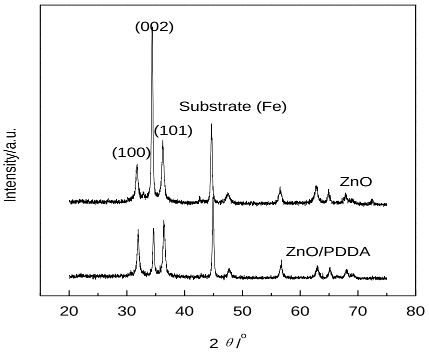

Figure 1. XRD patterns of ZnO and ZnO/PDDA composite films.

Fig. 2 shows the FT-IR spectra of ZnO and ZnO/PDDA composite. The absorption band at 433 cm^{-1} is typical Zn–O–Zn absorption [20]. The broad peak at 3373 cm^{-1} is due to the –OH group on the surface of ZnO [21]. Compared to the FT-IR spectrum of ZnO, the composite film has several additional absorption peaks near wavenumber 1474 and 1100 cm^{-1}, which can be assigned to the asymmetric bending of $–CH_2$ and C–N symmetric stretching vibration in PDDA, respectively [21]. This demonstrates the existence of PDDA in the composite film.

The morphologies of ZnO and ZnO/PDDA films were measured with SEM, and the typical SEM images are shown in Fig. 3. As shown in Fig. 3a, ZnO particles with diameters of smaller than 1 μm aggregate severely. This may be attributed to high surface energy of nano-sized particles. However, in ZnO/PDDA composite film, the aggregation of ZnO particles is greatly reduced and the film becomes more compact and smooths (Fig. 3b). This indicates the addition of PDDA make the quality of film increase.

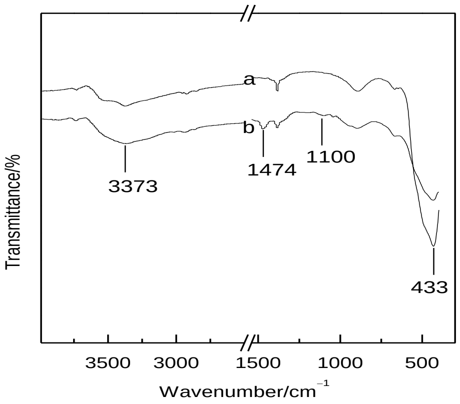

Figure 2. FT-IR spectra of ZnO (a) and ZnO/PDDA (b) composite particles.

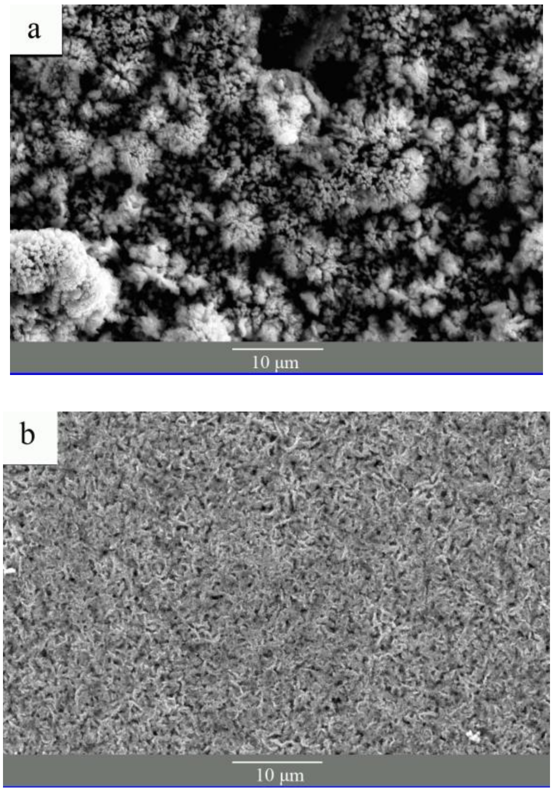

Figure 3. SEM images of ZnO (a) and ZnO/PDDA (b) composite films.

3.3 Electrochemical measurements

The polarization curves obtained for samples coated with ZnO and ZnO/PDDA films are shown in Fig. 4. The corrosion parameters of all the polarisation curves were calculated by software on the basis of the cathodic and anodic potential versus current density characteristics in the Tafel region. The values of the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) are shown in Table 1.

It is shown that i_{corr} of ZnO and ZnO/PDDA films was reduced from 79.39 μA cm^{-2} to 58.19 and 32.84 μA cm^{-2} respectively. Indicating that both the ZnO and ZnO/PDDA film could provide corrosion protection to substrate and ZnO/PDDA composite film provides better protection than ZnO.

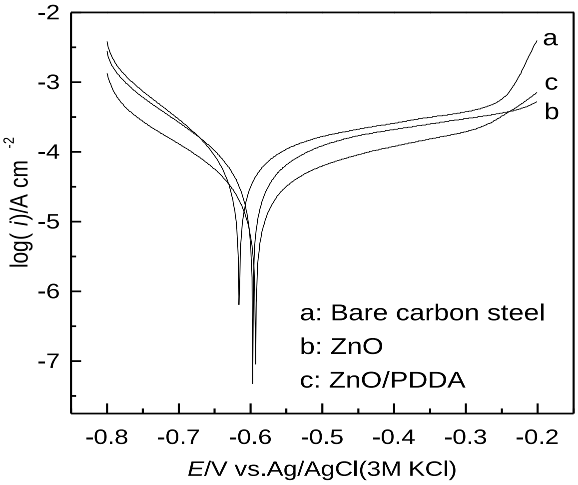

Figure 4. Polarization curves for bare and different films coated carbon steel obtained in 3.5% NaCl solution.

Table 1. Electrochemical parameters of the polarization curves.

Sample	i_{corr} (μA cm^{-2})	E_{corr} (mV)	b_a (mV/dec)	b_c (mV/dec)
Carbon steel	79.39	−616	117	453
ZnO	58.20	−597	142	448
ZnO/PDDA	32.84	−593	150	458

Temperature and potential are crucial factors in the electrodeposition of ZnO. When the potential is higher than –1.2 V, the growth rate of ZnO is relatively low and it is hard to form uniform films at the same time periods. And when the potential is lower than –1.2 V, there is aggregation of deposits and no uniform film could form [22]. Although former study indicated that ZnO could deposit at low temperature (34 ^{o}C) [23], many researchers still chose higher temperature (e.g. 70 ^{o}C) [24] because at lower temperature the deposits may have no well-defied crystallographic facets. What's more, in this work we also find that no uniform deposit is observed when the temperature is higher than 50 ^{o}C. This may because the corrosion rate of carbon steel increases with the increase of temperature [25, 26]. Accordingly, the deposit is difficult to form.

It has also been revealed that organic macromolecule is important to prevent agglomerations and increase the adhesion of the particles formed at the substrate surface [27]. This may be the main reason why ZnO/PDDA composite film has a superior corrosion resistance than that in without PDDA. However, when PDDA concentration is higher than 2 g/L, the composite film is also difficult to fabricate. Previous investigations highlighted the importance of optimization of polymer concentration in solutions for the fabrication of thick oxide films and composites [19]. It was established that the electrosynthesis rate of inorganic phase could be reduced significantly by high PDDA concentration [28].

Other studies show that the oxide layer on metal surface may only inhibit the anodic reaction [29]. In NaCl solution, the corrosion reaction at carbon steel surface consists of the cathodic reduction of the dissolved oxygen and the anodic dissolution of iron [30]:

$$Fe - 2e^{-} \rightarrow Fe^{2+} \qquad (5)$$

$$(1/2)O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \qquad (6)$$

Previous researches indicate that ZnO can inhibit oxygen reduction reaction [31]. Cathodic Tafel slope for substrate, ZnO and ZnO/PDDA are 117 mV/dec, 142 mV/dec and 150 mV/dec respectively. This means ZnO and ZnO/PDDA can inhibit the cathodic reaction of reduction of the dissolved oxygen. Surface morphology results indicate that the composite film becomes smoother than pure ZnO film. This makes the surface area decrease and the current of oxygen reduction reaction also reduce [27]. However, anodic Tafel slope for substrate, ZnO and ZnO/PDDA are 453 mV/dec, 448 mV/dec and 458 mV/dec respectively. It indicates that ZnO and ZnO/PDDA film have no significant effects on the anodic reaction of steel.

4. CONCLUSIONS

A ZnO/PDDA composite film has been prepared on carbon steel surface from the solution containing $Zn(NO_3)_2$ and PDDA by an electrochemical method involving the electrodeposition of ZnO particles and electrophoretic deposition of PDDA macromolecules. Electrochemical measurements indicate that ZnO/PDDA composite film has a better anti-corrosion behavior than ZnO. The reason can be ascribed to the improvement of ZnO film’s quality by the addition of PDDA. What’s more, this process can be easily extended to industrial production and a large number of metal oxides/polyelectrolyte complex functional films can be prepared by using this strategy.

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