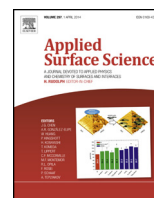




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Preparation of porous TiO₂/ZnO composite film and its photocathodic protection properties for 304 stainless steel

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ABSTRACT

TiO₂/ZnO composite films with porous structure were prepared on the 304 stainless steel (304SS) by the sol-gel method and heating treatment. The crystalline phase and morphology of as-prepared TiO₂/ZnO composite films were characterized systematically by X-ray diffraction (XRD), scanning electron microscope (SEM) and ultraviolet–visible (UV–vis) spectroscopy, respectively. The influences of Ti/Zn molar ratio and the annealing temperature on the photoelectric property of the samples have been investigated and their photocathodic protection performances for 304 stainless steel under dark and UV conditions have also been evaluated in 3.0% NaCl solution by the electrochemical measurements. The results indicate that porous TiO₂/ZnO composite film has a great enhancement of the light absorption and photoelectric property under UV illumination. This can be ascribed to the mutual effect of TiO₂/ZnO heterojunctions and the porous structures in the composite films, which provide a better photogenerated cathodic protection for 304SS.

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1. Introduction

Anticorrosion of steels is always an important project in many fields. Although various methods such as coating [1–3], sacrificial anode [4] and impressed current cathodic protection [5] have been investigated and applied during the past centuries, the environment-friendly, high-performance and long-lasting anticorrosion technology is still one of main targets of scientists nowadays. Recently, the applications of TiO₂ semiconductor films to the photogenerated cathodic protection of metals have received much attention of corrosion researchers [6–9]. As a metal coated with TiO₂ film is illuminated by ultraviolet (UV) light, photogenerated electrons will inject into the underlying metal substrate, which results in a potential shift of metal substrate to the corrosion immunity region and the corrosion prevention of metals known as photogenerated cathodic protection is achieved [10]. In this case, the TiO₂ coating is not sacrificial and allowed to have defects. Additionally, TiO₂ itself is of high chemical stability, low cost and nontoxic nature. The above advantageous properties make TiO₂ or TiO₂-based composite coatings applied to photogenerated cathodic protection become a promising technique for corrosion prevention, and get the quick development in recent years [11–16]. However,

the photo-induced charge carrier in single bare TiO₂ particles has a very short lifetime due to the rapid recombination of photo-generated electrons and holes, which reduces the photocathodic protection effect of TiO₂ films. An efficient approach is to composite TiO₂ with some semiconductors to form heterojunctions, such as WO₃ [16], SnO₂ [17,18], CdS [19], CeO₂ [20], V₂O₅ [21] etc., which can enhance interfacial electrons transfer to the underlying metal substrate.

ZnO is an important semiconductor with a band gap of 3.37 eV and exhibits higher electron mobility and longer life time of carriers than TiO₂ [22,23]. Recently, a few investigations have been carried out for design and preparation of nanocomposites containing ZnO and TiO₂ [24–34]. It has been realized that mixed ZnO–TiO₂ polycrystals display profoundly improved properties and high efficiency as compared to the pure ZnO and TiO₂ materials. For example, Agrawal et al. [27] reported the fabrication of a shell of the ZnO–TiO₂ mixed metal oxides by template assisted approach and demonstrated enhanced overall performance of ZnO–TiO₂ hollow spheres over pure ZnO and TiO₂ hollow spheres for the photocatalytic degradation of rhodamine 6G. In another study, Liu et al. [33] coated the ZnO shell on the TiO₂ nanotube by cathodic electrodeposition method to enhance the performance of dye-sensitized solar cells, which improved both the short-circuit photocurrent and the open-circuit voltage. The conversion efficiency of the solar cells is more than double that for bare TiO₂ nanotubes. At present, most of studies were focused on photocatalysts [27–29], solar cell [30–33]

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and UV detector [34] et al., but few have been reported ZnO-TiO₂ applied to the photogenerated cathodic protection of metal.

In our previous researches on the photocathodic protection of TiO₂/ZnO composite films for metals, we found that the photocathodic protection property was rather poor as the composite films prepared by heating the mixture of TiO₂ and ZnO sols, but as the composite films prepared by layered coating and double-step heating method, they exhibit the good photo-electrochemical effect for 304 stainless steel under UV irradiation. It is clear that the interference and interaction between TiO₂ and ZnO in the crystallizing process restrains the formation of TiO₂/ZnO heterojunctions to a larger extent. Nevertheless, the layered coating and double-step heating method need careful control of the reaction parameters and tedious preparing process, which make it impractical and high-cost. In this work, we choose the commercial TiO₂ (P25) and ZnO sol to prepare the TiO₂/ZnO composite films with homogeneously distributed nanoparticles and micropores on the 304SS, which exhibits the better photocathodic protection effect for 304SS.

2. Experimental

2.1. Preparation of TiO₂/ZnO films on the 304SS

TiO₂/ZnO films were prepared using a simple hybrid sol-gel-powder method. For preparing ZnO sol, a certain amount of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, 99.5%)(0.04 mol, 0.04/3 mol, 0.04/5 mol, 0.004 mol) was first dissolved 30 ml mixture solution containing C₂H₅OH and monoethanolamine (MEA, C₂H₇NO, 99.0%) at room temperature. The molar ratio of MEA to zinc acetate was kept at 1.0. Then the resulting mixture were stirred at 60 °C for 3 h until they became clear and homogeneous solution. After 1 day aging, 0.04 mol commercial TiO₂ (Degussa P25, 80% anatase, 20% rutile) was dispersed into the above ZnO sols via the ultrasonic cell disruptor to get the uniform TiO₂/ZnO composite sols, making the molar ratios of Ti to Zn were 1:1, 3:1, 5:1 and 10:1, respectively. 304 stainless steel plates (10 mm × 10 mm × 3 mm) were used as substrates in this study. The tested sides of the specimens were mechanically polished to a mirror finish with SiC abrasive papers, and then ultrasonically cleaned in acetone, ethanol and deionized water for 20 min, respectively. The substrates were spin-coated with the sol with a speed of 3000 rpm for 30 s and dried in air at 80 °C for 30 min, and then calcined at 500 °C for 2 h to obtain the TiO₂/ZnO composite films. Pure ZnO and TiO₂ films were prepared separately in the same conditions for comparison.

2.2. Characterization of TiO₂/ZnO composite films

The structure and morphology of the synthesized samples were characterized using a X-ray diffraction (XRD, Bruker D8 advanced X-ray diffractometer) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), a scanning electron microscope (SEM, Hitachi S-4800). The chemical composition of the films was analyzed by energy dispersive X-ray spectroscopy (Hiroba EDX). The photoabsorption properties of the samples were recorded by a UV-vis-NIR spectrophotometer (UV-2550, Shimadzu, Japan).

Photoelectrochemical measurements were performed in a three-electrode experimental system using CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The back and edges of the working electrodes were all covered with epoxy resin to expose only the front active surface (10 mm × 10 mm) to the electrolyte solution. A platinum coil and a saturated calomel electrode (SCE) used as the counter electrode and reference electrode, respectively. The center of the platinum coil left a square hole (13 mm × 13 mm) for the UV light to pass through. The light source used was a 250 W Hg lamp in front of a

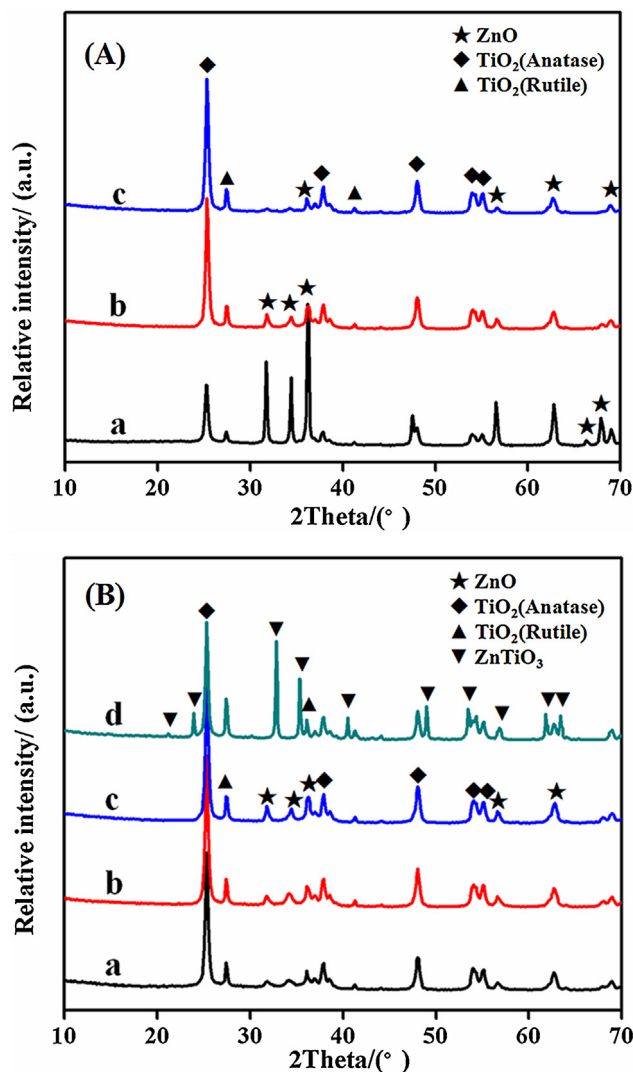


Fig. 1. XRD patterns of TiO₂/ZnO composite films with (A) different molar ratios: (a)1:1, (b)5:1, and (c)10:1; (B) different annealing temperatures: (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C, respectively.

quartz window incorporated into a conventional electrolytic cell. The electrolyte used in the photoelectrochemical test was 3.0% NaCl aqueous solution. All experiments for the different specimens were done in triplicate to confirm the reproducibility of the measurements.

3. Results and discussion

Fig. 1A shows the XRD patterns of TiO₂/ZnO composite films with the different molar ratios of Ti to Zn after annealed at 500 °C for 2 h in air atmosphere. All diffraction peaks can be indexed as hexagonal wurtzite ZnO (JCPDS 36-1451) and TiO₂ of anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phases. No characteristic peaks for impurity are observed. Furthermore, by comparing the three curves of a, b, c in Fig. 1A can be found that both the intensities of the peaks of TiO₂ (anatase) and TiO₂ (rutile) increase by increasing the amount of TiO₂ with respect to ZnO, but that of ZnO decreases, actually, some peaks even disappear.

The XRD patterns of the TiO₂/ZnO composite films with molar ratio of 5:1 annealed at different temperatures are shown in Fig. 1B. Obviously, the characteristic peaks of anatase TiO₂ and rutile TiO₂ as well as wurtzite ZnO can be observed simultaneously after being calcined at 300, 400, 500 °C, respectively (curves a–c). The peaks of

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