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Full Length Article

Sb_2S_3/Sb_2O_3 modified TiO_2 photoanode for photocathodic protection of 304 stainless steel under visible light

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ABSTRACT

A series of $Sb_2S_3/Sb_2O_3/TiO_2$ (SS/SO/T) composites with different reactant concentrations were synthesized via anodic oxidation and a one-pot hydrothermal method. The chemical compositions, morphologies, and optical absorption properties of prepared samples were characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, energy disperse spectroscopy, elemental mapping and ultraviolet–visible diffuse reflectance spectroscopy. Photocathodic protection performances of these samples were studied using time-dependent open circuit potential, time-dependent photoinduced current density, and photoinduced volt-ampere characteristic. The SS/SO/T composite with a 48 mmol/L antimony source exhibited optimal performance for 304 stainless steel (304SS). This excellent performance origins from the synergistic effect of the ternary system. The narrow band gap Sb_2S_3 promoted visible light harvesting. The p-n junction between p-type Sb_2S_3 and n-type SO/T provides a driving force for the separation and transfer of carriers. Well crystallized Sb_2O_3 rods offer a direct pathway for the carriers migration.

1. Introduction

304 stainless steel (304SS) is widely used for various engineering structures due to its good corrosion resistance. However, stainless steel is prone to corrosion when immersed in an electrolyte containing Cl^-, which destroys the protective oxide film on the metal and subsequently induces pitting corrosion [1]. It has been reported that corrosion costs accounts for about 1–5% of the gross national product (GNP) in countries such as, the USA, the UK, and Japan [2]. Therefore, improving the anti-corrosion performance of 304SS is an urgent economic necessity.

Recently, photocathodic protection as an environment-friendly and energy saving technology for anti-corrosion applications has drawn considerable attention [3]. Yuan and Tsujikawa reported that TiO_2 is a suitable photocathodic protection material for copper [4], and since then, it has been a promising photoanodes in cathodic protection with high efficiency, low cost, low toxicity, and good chemical stability [5–7]. Nevertheless, the further utilization of TiO_2 under visible light is limited by its wide band gap (3.2 eV) and poor separation efficiency of photoexcited carriers [8,9]. To overcome these limitations, various approaches have been employed to modify TiO_2 [10–15]. Coupling TiO_2 with narrow-gap semiconductors has been shown to not only enhance the separation of electron-hole pairs via the formation of suitable heterojunction structures, but contribute to the absorption of visible light [16,17].

Antimony(III) sulfide (Sb_2S_3) is a p-type semiconductor with a narrow band gap (~1.7 eV) and large absorption coefficient ($> 5 \times 10^4\ cm^{-1}$) [18,19]. The conduction band (CB) and valence band (VB) potentials of Sb_2S_3 and TiO_2 are −3.7/−4.2 eV and −5.4/−7.4 eV *vs.* absolute vacuum scale (AVS), respectively, which is favorable for the construction of a staggered alignment (type II) heterojunction, thus restraining the carriers recombination. In addition, given its environmental friendliness and easy preparation [18,20], Sb_2S_3 is often applied to modify TiO_2 for application in dye-sensitized solar cell [21], water splitting [22], and pollutant degradation [23]. In photoinduced cathodic protection, the CB potential is essential for the protection performance [24,25]. The negative CB potential of Sb_2S_3 is beneficial for more electrons transfer to 304SS. Hence, upon coupling with Sb_2S_3, the protection performance of TiO_2 for the metal is

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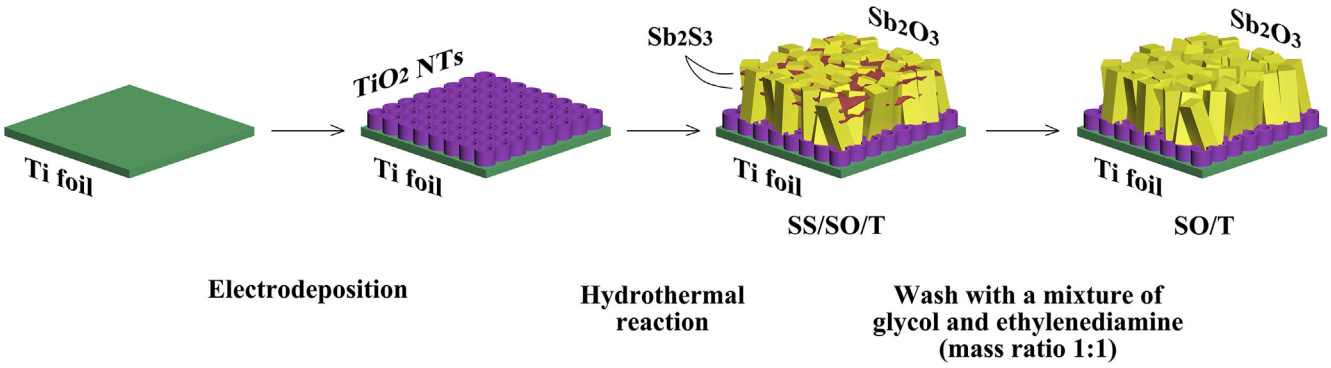

Fig. 1. Diagram of the preparation process for the SS/SO/T and SO/T heterojunctions.

improved. Another antimony-based semiconductor, antimony(III) oxide (Sb_2O_3), is an n-type semiconductor with a band gap (3.0 eV) near that of TiO_2 [26,27]. It is extensively used in flame retardants, optical devices, and conductive materials [28]. Recently, it was also used in photocatalysis by coupling with WO_3 [26], ZnO [28], and TiO_2 [29], and exhibited good performance in reducing the recombination of photogenerated electron-hole pairs.

To the best of our knowledge, Sb_2S_3 and Sb_2O_3 co-sensitized TiO_2 photoanodes has not been studied in photocathodic protection to date. In this study, TiO_2 nanotubes (NTs) was prepared by potentiostatic anodization and modified with Sb_2S_3 and Sb_2O_3 using a one-pot hydrothermal method. The morphology, chemical composition, and photochemical properties of these composites were characterized. The mechanism of the improved photocathodic protection performance for prepared samples was also analyzed.

2. Experimental

2.1. Chemicals and materials

Ti foil (99.96% purity) was purchased from BaoTi Group Co., Ltd., China and cut into small pieces (40 mm × 10 mm × 0.3 mm) before use. Ammonium fluoride (NH_4F), antimony potassium tartrate ($K(SbO)C_4H_4O_6{\cdot}0.5H_2O$), sodium sulfide ($Na_2S{\cdot}9H_2O$), sodium sulfite ($Na_2SO_3$), glycol, ethylenediamine and anhydrous ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All reagents were of analytical grade and used without further purification. Ultrapure water (18.0 MΩ·cm) was used to prepare aqueous solutions.

2.2. Preparation of TiO_2 NTs

TiO_2 NTs were synthesized using potentiostatic anodization method. Prior to oxidation, the Ti pieces were ultrasonically cleaned in ethanol for 30 min and subsequently in deionized water for 10 min. The pieces were then polished for 30 s in an aqueous solution containing 3.56 wt% NH_4F, 41.37 vol% HNO_3, and 41.37 vol% H_2O_2 to remove surface oxides. The samples were rinsed with deionized water and ethanol several times before being dried under a cold air stream. After pretreatment, the polished pieces were anodized at 20 V for 1 h using a Pt plate as a counter electrode in an electrolyte composed of 0.55 wt% NH_4F, 9.09 vol% H_2O, and 90.91 vol% ethylene glycol. The samples were subsequently washed with deionized water and ethanol again. Finally, the oxidized pieces were calcined at 450 °C for 2 h in a muffle furnace at a heating rate of 5 °C/min.

2.3. Preparation of SS/SO/T and SO/T composites

The SS/SO/T composite was fabricated by one-pot hydrothermal method. In the typical process, 0.6 mmol of $K(SbO)C_4H_4O_6{\cdot}0.5H_2O$ was dissolved in 50 mL water and magnetically stirred for 15 min to prepare the 12 mmol/L antimony source. Subsequently, Na_2S particles were added to the above solution under vigorous stirring. The molar amount of Na_2S was twice that of $K(SbO)C_4H_4O_6{\cdot}0.5H_2O$. After stirred for another 35 min, the mixed solution was transferred into a 100 mL Teflon-sealed autoclave containing horizontally arranged TiO_2 NTs and heated at 180 °C for 12 h. Then, this composite was took out from the autoclave and flushed with deionized water and ethanol. Finally, the composite was dried in a vacuum drying oven under 70 °C for 4 h. Using the same general process, the other two samples were synthesized with different antimony source concentrations (48 and 120 mmol) and corresponding amounts of Na_2S. The obtained dark-red samples were termed SS/SO/T-12, SS/SO/T-48, SS/SO/T-120, respectively.

For comparison, a Sb_2O_3/TiO_2 (SO/T) composite was also prepared by removing Sb_2S_3 in SS/SO/T-48 sample. Specifically, the SS/SO/T-48 sample was immersed in a mixture of glycol and ethylenediamine (1:1 mass ratio) at 40 °C for 50 min to dissolve Sb_2S_3, during which the solution was stirred intermittently. Then, the composite was thoroughly washed with water and ethanol to remove the Sb_2S_3, and dried under a cold air stream. The obtained white composite was named SO/T-48. A schematic diagram for constructing these composites is shown in Fig. 1.

2.4. Characterization

The phase compositions and crystal structures of the samples were examined using an X-ray diffractometer (XRD, Bruker AXS D8 Advance, Germany) with Cu Kα radiation at a scanning rate of 10°/min with 2θ ranging from 10° to 80°. The chemical states of the elements in the samples were analyzed using an X-ray photoelectron spectrometer (XPS, Thermo Escalab 250Xi, USA) with an Al Kα X-ray. The morphologies of the composites were observed by scanning electron microscope (SEM, Hitachi S-4800, Japan). The elemental distributions and compositions were recorded using a scanning electron microscope (Hitachi SU8220, Japan) equipped with an electron diffraction spectrometer (EDS, Bruker Quantax, Germany). The optical properties of the prepared samples were determined using UV–visible diffuse reflectance spectrophotometer (UV–vis DRS, Hitachi U-3900H, Japan).

2.5. Electrochemical measurements

The prepared samples work as photoanodes in electrochemical measurements. The variations in the open circuit potential (OCP-t) and photoinduced current density with time (i-t) of the photoanodes were measured using an electrochemical workstation (PARSTAT 4000+, USA) in a double electrolytic cell device, as shown in Fig. 2. The photoanode cell containing 0.1 mol/L Na_2SO_3 and the corrosion cell filled with a 3.5 wt% NaCl solution were connected by a Nafion membrane. For the OCP-t test, the prepared composites as photoanodes were immersed in the electrolyte of photoanode cell and coupled with 304SS by a wire. The corrosion cell contained a three-electrode system, where a Pt electrode worked was used as the counter electrode (CE), saturated