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Enhanced photoelectrochemical cathodic protection performance of H_2O_2-treated In_2O_3 thin-film photoelectrode under visible light

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ABSTRACT

In this work, a H_2O_2-treated indium oxide (In_2O_3) semiconductor material was prepared. The photoelectrochemical cathodic protection performance and the photoelectrochemical behaviors of the H_2O_2-treated In_2O_3 were investigated. Under visible light illumination, the H_2O_2-treated In_2O_3 exhibits enhanced photoelectrochemical conversion efficiency (the photoinduced current density was increased by approximately 50%) and enhanced photoelectrochemical cathodic protection performance (the photoinduced cathodic protection current density was increased by approximately 81.8%). The concentrations of adsorbed oxygen and oxygen vacancy in In_2O_3 were increased after H_2O_2 treatment, resulting in the enhancement of visible light absorption activity of the H_2O_2-treated In_2O_3. With the increase of the concentration of oxygen vacancy, the Fermi level of In_2O_3 negatively shifts, which promotes the photoelectrochemical cathodic protection performance of the H_2O_2-treated In_2O_3. The increased surface adsorbed oxygen groups is beneficial for capturing the photoinduced electrons, resulting in the promotion of the separation efficiency of the photogenerated electron–hole pairs and the electron transfer capability, and hence leading to the increase of the photoelectrochemical cathodic protection performance of the H_2O_2-treated In_2O_3.

1. Introduction

Corrosion of metals is a widespread phenomenon in the nature, and it will cause not only huge economic losses, but also serious environmental pollution and even disastrous accidents [1]. Traditional corrosion protection techniques for metals, such as cathodic protection and organic coating, possess some disadvantages, including material consumption, energy wastage and environmental pollution [2]. Recently, the metals coated with semiconductor materials were found to possess enhanced corrosion resistances under light illumination [3]. When the semiconductor coating is exposed under light illumination, it will offer photogenerated electrons for the coupled metal substrate and the photoelectrochemical cathodic protection is achieved [3,4]. This new technique by utilizing solar energy for the cathodic protection for metals has attracted increasing attentions [5–10]. Under illumination of light with the energy equal to or greater than the band gap of the semiconductor material, the electrons in the valence band (VB) of the semiconductor will be excited to its conduction band (CB), resulting in the formation of photoinduced electrons [5–10]. Importantly, when the CB potential of the semiconductor is more negative than the corrosion potential of the coupled metal, the photoinduced electrons can migrate to the coupled metal and participate into the oxygen reduction reactions there, resulting in the suppression of the corrosion of the coupled metal [5–10]. In this system, the semiconductor material theoretically acts as a non-sacrificial photoanode because the anodic reactions need no decomposition of the semiconductor material, but the oxidation of water and/or adsorbed organic pollutants by the photogenerated holes [5].

Indium oxide (In_2O_3) is a very important semiconductor with the band gap showing a direct one of approximately 3.6 eV and an indirect one of approximately 2.8 eV [11], and it has been widely used in transparent conductive coatings, modern electronics and optoelectronics as electrically conductive thin films [12], antireflection coatings for silicon solar cells [13] and photocatalysis [11]. Importantly, In_2O_3 has also been demonstrated to possess a negative CB potential ($E_{CB} = -0.6$ V vs. Standard Hydrogen Electrode (SHE)), which is beneficial for the photoelectrochemical cathodic protection for metals. Furthermore, In_2O_3 possesses photoelectrochemical conversion activities under both UV and visible light.

Recently, the adsorbed oxygen (O_A) and oxygen vacancy (Vo), which act as the important surface activity states for a semiconductor, have received worldwide concerns for their prominent impacts on the photoelectrochemical conversion performance [14,15]. The Vo in a semiconductor will naturally involve in the photoelectrochemical conversion processes [14,15] and will effectively promote the photoelectrochemical conversion property for a semiconductor material [16]. As reported in a previous work from the authors' laboratory, the presence of Vo dramatically enhanced the photoelectrochemical cathodic protection performance of Ni-doped TiO_2 [6]. The Vo, acted as active sites, effectively promoted the electron transfer capability

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[17] and enhanced the photocatalytic performance [18]. Increasing the concentration of Vo in In_2O_3 will effectively expand the visible light absorption region by narrowing the band gap of In_2O_3 [12,14,19] and thus enhance the photoelectrochemical conversion property of In_2O_3.

By comparing with other conventional doping methods, increasing the concentration of Vo in a semiconductor is a kind of self-doping without introducing any impurity elements, which is more favorable on preserving the intrinsic crystal structures of the semiconductor and hence leads to an enhanced photocatalytic performance. It was reported that heat treatment under H_2 or Ar atmosphere could increase the concentration of Vo. Recently, some simple methods were also found to increase the concentration of Vo in a semiconductor material. Gan et al. reported that the phase transformation from $In(OH)_3$ to In_2O_3 could introduce Vo into In_2O_3 [14]. Uekawa et al. synthesized nonstoichiometric ZnO nanoparticles with Vo by decomposing zinc peroxide (ZnO_2) precursors [15]. Chavillon et al. obtained the stable and nonstoichiometric N-doped ZnO with Vo using ZnO_2 precursors [20]. Innovated by these reports, it could be a simple strategy to increase the concentration of Vo in In_2O_3 crystal lattices via H_2O_2 treatment.

In the present work, the authors pretreated the $In(OH)_3$ precursor using H_2O_2 solution and then annealed it to obtain In_2O_3. The change of the concentrations of O_A and Vo in In_2O_3 was investigated by comparing H_2O_2-treated In_2O_3 with untreated In_2O_3. The photoelectrochemical cathodic protection performance of the H_2O_2-treated In_2O_3 and untreated In_2O_3 was characterized by measuring the photoinduced potential variations of the coupled 304 stainless steel (SS) electrode and the photoinduced current density between the coupled In_2O_3 photoelectrode and the 304 SS electrode. The effect of O_A and Vo on the electrochemical properties of In_2O_3 was also studied. Based on the experimental results obtained in this work, a mechanism for narrowing the band gap of In_2O_3 and enhancing the photoelectrochemical conversion performance due to the increased concentrations of O_A and Vo in In_2O_3 was proposed.

2. Experimental

2.1. Preparation of In_2O_3

The In_2O_3 nanoparticles were prepared based on the method used by Uekawa et al. for synthesizing ZnO with Vo [15]. In detail, 0.4 $mol \cdot L^{-1}$ NaOH was added into 100 mL of 0.2 $mol \cdot L^{-1}$ $In(NO_3)_3 \cdot 4.5H_2O$ to adjust the pH value to 7, and stirred for 2 h. The precipitate was separated by filtration. Subsequently, the precipitate was divided into two equal parts. One part was annealed at 600 °C for 2 h, and the untreated In_2O_3 nanoparticles, denoted as r-In_2O_3, were obtained. The other part was dispersed into 100 mL of 1 $mol \cdot L^{-1}$ H_2O_2. The dispersed solution was kept at 75 °C for 2 h in a beaker with a lid covered on it, and it was subsequently evaporated at 75 °C until the precipitate was dry. The $In(OH)_3$ precursor, denoted as v-$In(OH)_3$, was obtained. The as-prepared v-$In(OH)_3$ was then annealed at 600 °C for 2 h, and the H_2O_2-treated In_2O_3, denoted as v-In_2O_3, was obtained.

2.2. Fabrication of the In_2O_3 thin-film photoelectrode and the 304 SS electrode

The In_2O_3 thin-film photoelectrode was fabricated by evenly depositing the prepared In_2O_3 powder onto the surface of the fluorine-doped tin oxide (FTO) conductive glass. Commercialized FTO was used in the present study. The FTO glass was of 13 × 10 mm^2 in size. Prior to the deposition, the FTO glass was ultrasonically cleaned in acetone of analytical grade for 5 min and rinsed with deionized water. The FTO glass was then dried with a clean dry airflow. One edge of the long conductive side of the FTO glass was carefully covered with insulating tapes, and the exposed effective area of the FTO glass was 10 × 10 mm^2. Then, 0.01 g of the prepared In_2O_3 powder was mixed with 0.1 mL of deionized water in an agate mortar, and the mixture was carefully ground for 10 min to form slurry. The slurry was then evenly spread over the exposed effective area of the FTO glass. The insulating tape on the edge of the FTO glass was removed after the slurry had dried in ambient air. After that, the FTO glass deposited with the as-prepared powder was heated to 120 °C for 2 h. The optical image of the obtained In_2O_3 powder coated FTO glass is shown in Fig. 1a. A copper wire was connected to the conductive side of the FTO glass using silver conductive adhesive (Fig. 1b). Uncoated parts of the conductive side of the FTO glass were isolated with parafilm after the silver conductive adhesive had dried. The optical image of the final obtained In_2O_3 thin-film photoelectrode is shown in Fig. 1c.

The chemical composition (wt.%) of 304 SS is as follows: C (≤0.08), Si (≤1.00), Mn (≤2.00), S (≤0.03), P (≤0.05), Cr (18.00–20.00), Ni (8.00–10.50), and the remaining is Fe. The 304 SS electrode was made by embedding a 10 × 10 × 10 mm^3 cubic 304 SS in the mixture of 25 mL epoxy resin and 2 mL diethylenetriamine (DETA), and the exposed area of 304 SS for testing was 10 × 10 mm^2. The exposed surface of the 304 SS electrode was wet ground with SiC paper to 2400 grit before ultrasonically cleaned in analytical grade ethanol for 5 min. Before the test, the electrode was put into a desiccator for 24 h.

2.3. Characterizations of the prepared In_2O_3 powder

The crystalline structures of the prepared powder were identified using an X-ray diffraction (XRD) (D/MAX-2500/PC; Rigaku Co., Tokyo, Japan). The morphologies and the microstructure of the prepared powder were analyzed using a scanning electron microscope (SEM) (SU8020, Hitachi Company, Japan). The elemental compositions and the bonding information of the synthetic products were analyzed using an X-ray photoelectron spectroscopy (XPS) on a Thermo VG scientific spectrometer; model ESCALAB 250 (Al Kα, $h\nu$ = 1486.6 eV; Mono X-ray source). The binding energy was calibrated according to the signal of adventitious carbon (binding energy = 284.8 eV). The optical absorption properties were investigated using a UV/Vis Spectrophotometers (SHIMADZU UV-2600, Japan) equipped with an integration sphere.

2.4. Photoelectrochemical measurements

Photoelectrochemical cathodic protection performance was studied using the variations of the photoinduced current density with time (i–t curve) and the photoinduced variations of the potential, which were performed using a CHI 660D electrochemical work station (Shanghai Chenhua Instrument Co., Ltd., China). Fig. 2 shows the schematic illustrations of the experimental setup used for measuring the photoinduced current density (Fig. 2a) and the photoinduced variations of potential (Fig. 2b). A similar arrangement has been used previously [7]. This experiment setup, which is a model one based on the working principles of the production of hydrogen and oxygen from photoelectrochemical water splitting, can simultaneously record the values of the current density and potential.

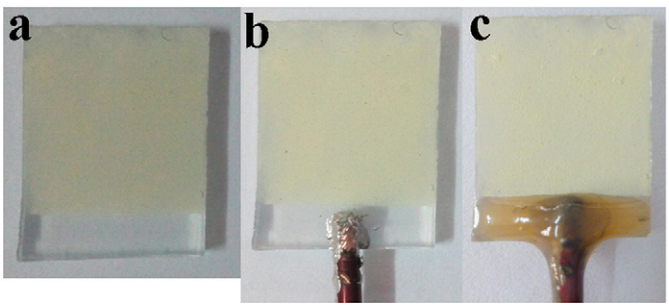

Fig. 1. The optical images of the obtained In_2O_3 powder coated FTO conductive glass (a), the In_2O_3 powder coated FTO glass and subsequently connected with a copper wire on the conductive side of the FTO glass using silver conductive adhesive (b), and the final obtained In_2O_3 thin-film photoelectrode (c).