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Synthesis of ZnO/Bi₂S₃ Core/Shell Nanowire Array Photoanodes for Photocathodic Protection of Stainless Steel

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Abstract: Nanocrystalline Bi₂S₃ shells were conformally deposited on ZnO nanowire arrays via a successive ionic layer adsorption and reaction approach. Microstructure, optical, and electric properties of the as-prepared ZnO/Bi₂S₃ core/shell nanowire heterostructures were thoroughly investigated using various characterization and electrochemical methods. Compared with the pristine ZnO photoanode (−734 mV and 0.57 mA·cm^{−2}), the ZnO/Bi₂S₃ photoanode with a type-II heterojunction exhibited a more negative shift in the coupled open circuit potential (−862 mV) and a higher photocurrent density (2.92 mA·cm^{−2}), achieving more effective photocathodic protections for the coupled 304 stainless steel under solar illumination.

Keywords: ZnO; Bi₂S₃; heterostructure; nanowire; photocathodic protection

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1. Introduction

Protection of stainless steel against localized corrosion, such as pitting and crevice corrosion, is of great significance for its engineering applications [1–3]. Cathodic polarization is an effective strategy to suppress steel corrosion of marine and underground structures [1]. As a green alternative technique, photocathodic protection (PCP) is attracting tremendous scientific interests for steel anticorrosion by harnessing sustainable solar energy [2,4–6]. The present challenge of PCP is to exploit effective *n*-type semiconductor photoanodes to generate photoelectrons via photoelectric conversion effect and then transfer photoelectrons to the coupled steels [7–10]. Representatively, *n*-type TiO₂ has been extensively investigated in the field of PCP, especially its composites with narrow-bandgap semiconductors [2,5–7,9–18]. Nevertheless, ZnO is significantly lagging behind TiO₂ in PCP research though ZnO is one of the most promising candidates for PCP due to its conduction band negative enough, environmental benignity, and low cost [19–21]. To overcome the limitation of ZnO's wide bandgap (~3.2 eV) and the corresponding UV-sensitive characteristic [22–27], nowadays, coupling ZnO with various narrow band gap semiconductors becomes indispensable for enhancing PEC properties in the visible light region [8,28–36].

Bi₂S₃ is a *n*-type semiconductor with a relatively narrow band gap (~1.3 eV) and is able to broaden the optical absorption range of ZnO to the visible part of solar light by hybridization [28,29,37]. More importantly, Bi₂S₃ possesses appropriate energy band alignments to form a type-II heterojunction with ZnO, which facilitates spatial charge separation via built-in electric field across the interface. Recently, ZnO/Bi₂S₃ heterostructures have been reported to reduce the recombination of charge carriers and enhance PEC properties [28,29,37–43], and moreover Bi₂S₃ has been also utilized to decorate TiO₂ for improving PCP performances [11,18,44]. Therefore, it would be desirable to promote PCP performance of ZnO photoanodes for steels by rational introduction of Bi₂S₃. Just recently, Zhang et al. reported a Bi₂S₃/ZnO nanocomposite with a good PCP effect on 304 stainless steel (304 SS) [45]. However, the electrodeposited ZnO nanowires were poorly aligned, and their lengths were only ~300 nm, which dramatically restricted the photoinduced current density for PCP (0.094 mA·cm^{−2}). To enhance the light absorption and increase the

photoinduced current density, rational construction of $\text{Bi}_2\text{S}_3/\text{ZnO}$ nanocomposites with the well-aligned ZnO nanowires of sufficient lengths will be promising for PCP.

In this study, ZnO/ Bi_2S_3 core/shell heterostructured nanowire arrays were synthesized via a seed-assistant hydrothermal method followed by successive ionic layer adsorption and reaction (SILAR). Microstructure, optical, and electric properties of the as-prepared ZnO/ Bi_2S_3 core/shell nanowire heterostructures were thoroughly investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDAX), X-ray photoelectron spectroscopy (XPS), ultraviolet–visible (UV–Vis), Electrochemical impedance spectroscopy (EIS), and Mott–Schottky plots. PCP performances of the ZnO/ Bi_2S_3 photoanode for the coupled 304 SS were investigated in details.

2. Materials and Methods

2.1. Photoanode Synthesis

All chemicals were of analytical grade. ZnO nanowire arrays were synthesized by using a seed-assistant hydrothermal method [24]. Firstly, fluorine-doped tin oxide (FTO) conductive glasses were thoroughly cleaned by ultrasonic treatment in acetone, ethanol, and deionized water for 15 min, dried in an electrically heated convection oven at 90 °C, and treated before use with oxygen plasma for 3 min. Then, 100 μL of 25 mM zinc acetate aqueous solution was dropped on the cleaned FTO glasses and dried at 60 °C for 3 min. This drop-dry process was repeated 4 times. To form a thick ZnO seed layer, the pre-coated FTO glasses were calcined in a muffle furnace at 350 °C for 1 h with a heating rate of 5 °C·min^{−1}. Lastly, ZnO-seeded FTO glasses were hydrothermally treated in a Teflon-lined stainless-steel autoclave filled with 50 mL of aqueous solution containing 2.5 mmol of ZnCl_2 and 2.5 mmol of hexamethylenetetramine at 125 °C for 4 h. Deposition of particulate Bi_2S_3 on ZnO nanowire arrays was realized by a successive ionic layer adsorption and reaction (SILAR) method [11,18,44,46,47]. During each cycle, the substrates were immersed into separate Bi^{3+} and S^{2-} precursor solutions for adsorption and reaction and subsequently rinsed with deionized water after each immersion to remove excess ions and hinder homogeneous precipitation. The absorption, reaction, and rinse times were 50, 60, and 30 s, respectively. The Bi^{3+} precursor solution contained 0.125 mmol of $\text{Bi}(\text{NO}_3)_3$ dissolved in 25 mL of ethylene glycol, and the S^{2-} precursor solution contained 0.625 mmol of Na_2S dissolved in 25 mL of deionized water. The substrates were dried at 85 °C for 5 min after each cycle, and optimal ten cycles of SILAR were implemented in total.

2.2. Characterization

Surface morphologies were observed by a field emission scanning electron microscope (FE-SEM, SU8020, Hitachi, Tokyo, Japan) operated at an accelerating voltage of 3 kV. Crystal phases were determined by a X-ray diffractometer (Ultima IV, Rigaku, Tokyo, Japan) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Surface chemical compositions and states were examined by a X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo, Waltham, MA, USA) with Al K α radiation ($h\nu = 1486.6 \text{ eV}$). Microstructures and elemental mappings were obtained by a high-resolution transmission electron microscope (HRTEM, Talos F200X, FEI, Lausanne, Switzerland) equipped with an energy dispersive X-ray spectroscopy (EDAX) detector. Optical absorption properties were investigated by an ultraviolet–visible (UV–Vis) spectrometer (UV-3600, Shimadzu, Tokyo, Japan).

2.3. Electrochemical Measurements

For photoelectrochemical measurements, a system comprised of an electrochemical workstation (CS350H, CorrTest, Wuhan, China) and a three-electrode cell was adopted (see the schematic diagram in our previous work [24]). The as-prepared photoanodes (1 cm $\times$ 1 cm) served as the work electrode, Pt foil as the counter electrode, and Ag/AgCl as the reference electrode. An aqueous solution of 0.2 M NaOH was used as the electrolyte, and 0.1 M Na_2S was used as the hole scavenger. The simulated irradiation source was a

500 W xenon lamp (CHF-XM500, Perfectlight, Beijing, China) equipped with an AM 1.5 G filter, and the light intensity was fixed at $100 \text{ mW} \cdot \text{cm}^{-2}$ using an optical power meter (PL-MW2000, Perfectlight, Beijing, China). The open circuit potential (OCP) measurements were conducted in a H-type electrochemical cell separated with a Nafion membrane between two chambers [24]. The as-prepared photoanodes were electrically connected with 304 SS placed in another chamber containing 3.5 wt. % NaCl aqueous solution. Electrochemical impedance spectroscopy (EIS, $10^{-2} \sim 10^5 \text{ Hz}$) and Mott–Schottky measurements (100 Hz) were performed on a Gamry Interface 1010E electrochemical workstation with 10 mV alternating current amplitude under dark.

3. Results and Discussion

Crystal phases of the as-prepared ZnO/Bi₂S₃ core/shell nanowire arrays were analyzed by powder XRD patterns in Figure 1. For the ZnO photoanode, the collected diffraction peaks can be divided into two groups. One group of diffraction peak located at 31.8° , 34.4° , 36.3° , 47.5° , 56.6° , 62.9° , 68.0° , and 69.1° matched well with (100), (002), (101), (102), (110), (103), (112), and (201) reflections of hexagonal ZnO (JCPDS# 36-1451) [22,24]. Another group of diffraction peak centered at 26.6° , 33.9° , 37.9° , 51.8° , 54.8° , 61.9° , 65.9° , and 78.7° was indexed to (110), (101), (200), (211), (220), (310), (301), and (321) reflections of tetragonal SnO₂ (JCPDS# 41-1445) from FTO conductive glasses. After coating with Bi₂S₃ on ZnO via the SILAR method, no additional diffraction peak was detected in the ZnO/Bi₂S₃ photoanode. For instance, there was no peak for orthorhombic Bi₂S₃ (JCPDS# 17-0320) in Figure 1. The absence of Bi₂S₃ reflection may be caused by the poor crystallinity and low content of Bi₂S₃.

Figure 1. Powder XRD patterns of ZnO and ZnO/Bi₂S₃ photoanodes.

Figure 2 shows the representative SEM images of ZnO and ZnO/Bi₂S₃ photoanodes. The ZnO/Bi₂S₃ photoanode exhibited similar surface morphologies with the ZnO photoanode. Dense nanowires with the lengths between 1.5 and 2.1 μm and the diameters between 35 and 150 nm were vertically aligned and uniformly distributed on the entire FTO substrate. It was noted that the surface of nanowires changes from smooth for the

pristine ZnO (Figure 2b) to rough for the Bi_2S_3 overcoated ZnO (Figure 2e). Obviously, a great number of Bi_2S_3 nanoparticles [48] are tightly deposited on the outer wall of ZnO nanowires so that ZnO nanowire cores are successfully covered by conformal Bi_2S_3 shells.

Figure 2. Top-view and cross-sectional view of SEM images: (a–c) ZnO and (d–f) ZnO/ Bi_2S_3 photoanodes.

The information of microstructures and composition distributions was obtained by HRTEM and EDAX elemental mappings. Figure 3a shows a typical core/shell structured nanowire with a diameter of ~ 100 nm and a highly porous shell composed of nanoparticles. In the lattice-resolved TEM image (Figure 3b), the lattice fringe with an interplane spacing of 0.261 nm is ascribed to the (002) plane of ZnO from the nanowire core. Importantly, a distinct interplane spacing of 0.33 nm was clearly observed, which can be attributed to the (021) crystal plane of orthorhombic Bi_2S_3 (JCPDS# 17-0320) [11,18,44,47]. Near the outermost wall of the nanowire, lattice fringes show short-range order and long-range disorder, which is the characteristic of nanocrystalline or amorphous Bi_2S_3 . These analyses support the

absence of Bi_2S_3 diffraction peaks in the XRD pattern. The core/shell nanostructure was further unveiled by STEM and the corresponding elemental mapping images in Figure 3c–g. The Zn and O elements were mostly constrained in the nanowire core, while the Bi and S elements were mostly distributed in the shell region. The merged image of Zn, O, Bi, and S elements in Figure 3h displays that the core/shell nanowire has a shell thickness of ~ 15 nm. In brief, both HRTEM and EDAX analyses demonstrate the successful coating of the nanocrystalline Bi_2S_3 shell on the ZnO nanowire core.

Figure 3. The ZnO/ Bi_2S_3 photoanode: (a) TEM, (b) HRTEM, (c) STEM images, and the corresponding EDAX elemental mappings of (d) Zn, (e) O, (f) Bi, (g) S, and (h) the merged image of Zn, O, Bi, and S elements.

Chemical compositions and states of the ZnO/ Bi_2S_3 photoanode were studied by X-ray photoelectron spectroscopy (XPS). The survey spectrum in Figure 4a reveals the existence of various bind energies from Zn, O, Bi, and S elements. The high-resolution Zn 2p spectrum in Figure 4b displays two peaks centered at 1021.7 and 1044.8 eV, ascribing to Zn 2p_{3/2} and Zn 2p_{1/2} of Zn^{2+} , respectively. In Figure 4c, the predominant O 1s spectrum

can be deconvoluted into two peaks located at 531.1 and 532.4 eV, corresponding to oxygen vacancies and chemisorbed oxygen, respectively [24,49]. In the Bi 4f spectrum (Figure 4d), two main peaks at 158.3 and 163.6 eV are attributed to Bi 4f_{5/2} and Bi 4f_{7/2} of Bi³⁺, respectively. The remained peak at 160.9 eV in Figure 4d is related to S 2p_{3/2}. The S 2s peak at 225.3 eV (Figure 4e) further proves the presence of S^{2−} [50,51]. The appearance of S 2s peak at 232.2 eV is indicative of the formation of sulfates (SO₄^{2−}), arising from the hydrolysis of sulfides [50]. Therefore, XPS analyses prove the presence of Bi³⁺ and S^{2−}, suggesting the formation of Bi₂S₃ on the surface of nanowires.

Figure 4. (a) XPS survey spectrum, and high-resolution (b) Zn 2p, (c) O 1s, (d) Bi 4f, and (e) S 2s spectra of the ZnO/Bi₂S₃ photoanode.

Figure 5a shows the optical absorption properties of ZnO and ZnO/Bi₂S₃ photoanodes measured via UV–Vis spectroscopy. It was seen that the ZnO photoanode can only absorb UV light with an absorption edge at 385 nm. Obtained from the slope in $Tauc$ plots of $(\alpha h\nu)^2$ to photo energy (Figure 5b), the band gap value of the ZnO photoanode was 3.22 eV. By contrast, the absorption edge of the ZnO/Bi₂S₃ photoanode was extended to 614 nm,

indicating an optical band gap of 2.02 eV. Obviously, the ZnO/Bi₂S₃ photoanode exhibits a significantly enhanced absorption capability in the visible part of solar spectrum when Bi₂S₃ is composited with ZnO.

Figure 5. (a) UV-Vis absorption spectra and (b) Tauc plots of ZnO and ZnO/Bi₂S₃ photoanodes.

To understand the PCP performance of the ZnO/Bi₂S₃ photoanode, the photoinduced open circuit potential (OCP) variation of coupled 304 SS and transient photocurrent responses were measured under intermittent illumination of simulated solar light (AM 1.5 G). As shown in Figure 6a, OCP of 304 SS moderately shifts to the negative direction in the dark while coupled with the ZnO and ZnO/Bi₂S₃ photoanodes. Once exposed to white

light, the ZnO/Bi₂S₃ photoanode shows a dramatic shift to -862 mV in the coupled OCP, suggesting a better PCP performance than the ZnO photoanode (-734 mV). According to the large photoinduced potential drop, it is speculated that the photoelectrons of ZnO/Bi₂S₃ photoanode excited from its valence band maximum (VBM) to conduction band minimum (CBM) by white light can be transferred to the connected 304 SS for efficient cathodic polarization and protection. Figure 6b exhibits positive photocurrent responses for the ZnO and ZnO/Bi₂S₃ photoanodes, characteristic of PCP for 304 SS. Importantly, the ZnO/Bi₂S₃ photoanode ($2.92 \text{ mA}\cdot\text{cm}^{-2}$) presents five times higher photocurrent than the ZnO photoanode ($0.57 \text{ mA}\cdot\text{cm}^{-2}$) in the final of first cycle, demonstrating a better PCP performance than the just-reported ZnO/Bi₂S₃ nanocomposites ($0.094 \text{ mA}\cdot\text{cm}^{-2}$) [45].

Figure 6. (a) Time evolution of photogenerated OCP for 304 SS coupled with ZnO or ZnO/Bi₂S₃ photoanodes under intermittent illumination. (b) Transient photocurrent responses of ZnO and ZnO/Bi₂S₃ photoanodes.

Figure 7 displays a long-term photoinduced OCP variation of 304 SS coupled with the ZnO/Bi₂S₃ photoanode. Under continuous illumination of simulated solar light, OCP of the ZnO/Bi₂S₃ photoanodes coupled with 304 SS was stabilized at -0.9 V for 6 h, validating a superior PCP durability for 304 SS.

Figure 7. Long-term OCP variation in 304 SS coupled with the ZnO/Bi₂S₃ photoanode under continuous illumination for 6 h.

To obtain the flat-band potentials of ZnO and ZnO/Bi₂S₃ photoanodes, Mott–Schottky plots were recorded at an applied frequency of 100 Hz in the dark. The linear fitting of Mott–Schottky plots in Figure 8 shows positive slopes, typical of *n*-type semiconductors [52,53]. Based on the *x*-axis intercepts of the fitted tangent lines, the flat-band potentials of ZnO and ZnO/Bi₂S₃ photoanodes were estimated to be approximately -0.01 and -0.20 V vs. Ag/AgCl, respectively. Thus, the CBM values of *n*-type ZnO and Bi₂S₃ can be considered as -0.21 and -0.40 V, respectively [52,53]. In terms of the optical band gaps, VBM of *n*-type ZnO and Bi₂S₃ can be speculated at 3.01 and 1.62 V, respectively. As shown in the inset, a type-II semiconductor heterojunction was constructed between ZnO and Bi₂S₃, which is beneficial for the spatial charge separation in the ZnO/Bi₂S₃ photoanode. Clearly, hybridization of Bi₂S₃ with ZnO not only broadens the absorption spectrum but also increases the charge separation efficiency, which is of great importance to boost PCP performances of the ZnO/Bi₂S₃ photoanode.

To investigate the charge transfer properties, EIS was used to record Nyquist plots of the ZnO and ZnO/Bi₂S₃ photoanodes under the dark. Generally, the charge transfer resistance (R_{ct}) can be estimated from the diameter of the semicircle in the high-frequency region, and a smaller radius of impedance arc indicates a more decreased R_{ct} [22,23]. As fitted by EClab software using the proposed equivalent circuit model (see the inset in Figure 9), the R_{ct} value of ZnO/Bi₂S₃ photoanode was 12.7 k Ω , which was much smaller than that of the ZnO photoanode (50.8 k Ω). Therefore, the ZnO/Bi₂S₃ photoanode exhibits the significantly improved charge transfer kinetics, resulting in the enhanced PCP performance.

Figure 8. Mott-Schottky plots of ZnO and ZnO/Bi₂S₃ photoanodes under dark. The inset is the schematic diagram of energy band alignments.

Figure 9. EIS Nyquist plots of ZnO and ZnO/Bi₂S₃ photoanodes under dark. The small circles and squares in the plots represent the experimental data, and the solid lines represent the fitting results. The inset is the proposed equivalent circuit model, in which R_s is the solution resistance; CPE is the capacitance phase element for the semiconductor/electrolyte interface; and R_{ct} is the charge transfer resistance across the interface.

4. Conclusions

In summary, Bi₂S₃ was successfully deposited on ZnO nanowire arrays via a SILAR approach. The as-prepared ZnO/Bi₂S₃ core/shell nanowire heterostructures were thoroughly investigated by XRD, SEM, TEM, EDAX, XPS, UV-Vis, EIS, and Mott-Schottky plots. Compared with the ZnO photoanode (385 nm, −734 mV, and 0.57 mA·cm^{−2}), the ZnO/Bi₂S₃ photoanode with a type-II heterojunction exhibited an optical absorption red-shift (614 nm), a more negative shift in the coupled OCP (−862 mV), and a higher photocurrent density (2.92 mA·cm^{−2}), achieving more effective photocathodic protections for the coupled 304 SS under solar illumination.

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