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Preparation of Sb₂O₃/Sb₂S₃/FeOOH composite photoanodes for enhanced photoelectrochemical water oxidation

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Abstract: A novel $Sb_2O_3/Sb_2S_3/FeOOH$ photoanode was fabricated via a simple solution impregnation method along with chemical bath deposition and post-sulfidation. The X-ray diffractometry, Raman measurement, and X-ray photoelectron spectroscopy show that the $Sb_2O_3/Sb_2S_3/FeOOH$ thin films are successfully prepared. SEM–EDS analyses reveal that the surface of Sb_2O_3/Sb_2S_3 thin films becomes rough after the immersion in the FeCl₃ solution. The optimized impregnation time is found to be 8 h. The FeOOH co-catalyst loaded Sb_2O_3/Sb_2S_3 electrode exhibits an enhanced photocurrent density of 0.45 mA/cm² at 1.23 V versus RHE under simulated 1 sun, which is approximately 1.41 times compared to the photocurrent density of the unloaded one. Through the further tests of UV–Vis spectroscopy, the electrochemical impedance spectra, and the PEC measurements, the enhancement can result from the increased light-harvesting ability, the decreased interface transmission impedance, and the remarkably enhanced carrier injection efficiency.

Key words: Sb₂O₃/Sb₂S₃; FeOOH co-catalyst; photoanode; carrier injection efficiency

1 Introduction

Over the past few decades, the rapid growth of technology has seen the massive consumption of fossil fuels, bringing energy crisis and environmental pollution to the whole world. To exploit clean and sustainable energy resource manufacturing methods is an urgent task for the researchers worldwide [1]. Photoelectrochemical (PEC) water splitting is a fascinating process during which solar energy can be utilized to split water into hydrogen and oxygen [2]. Solar hydrogen aroused widespread interest on account of its representation of clean and efficient energy source. Since FUJISHIMA and HONDA [3] first reported the marvelous hydrogen production ability via TiO₂

photoanode in 1972, a great deal of attention had been paid to the artificial photosynthesis especially by the metal oxide semiconductors such as TiO_2 [4–6], ZnO [7], WO₃ [8], Fe₂O₃ [9] and Cu₂O [10].

Sb₂O₃, among the various metal oxide semiconductors, has emerged as a highly promising material owing to its excellent chemical stability, non-toxicity, and low cost [11]. Unfortunately, due to its wide band-gap (3–3.6 eV) [12], only a very small part of the solar spectrum can be harvested, which greatly limited its application. Besides, Sb₂S₃, as another antimony-based semiconductor, is also an original photoelectric material attributed to its suitable energy band-gap (1.7–2.3 eV) and high absorption coefficient (>10⁴ cm⁻¹) [13]. Correspondingly, Sb₂S₃ has a wide range of

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applications in the field of solar cells and photoelectrocatalysis [14–17]. DENG et al [14] developed a facile and efficient method to fabricate a full-inorganic epitaxial Sb₂S₃ solar cell device and obtained an efficiency of 5.4%. DU et al [15] prepared plate-like Mo-doped WO₃ films deposited which achieved an enhanced with Sb_2S_3 , photocurrent density of 0.42 mA/cm² at extremely low input energy (1 mW/cm²), nearly 20 times as high as that of 5%Mo-WO₃ film. Besides, DAI et al [17] designed a well-defined hierarchically ordered C-Sb₂S₃-TNTA ternary photoanode, and with the introduction of Sb₂S₃ nanocrystals, the solar light harvesting and conversion ability rose to a high level.

Our present work indicates that a Sb₂O₃/Sb₂S₃ heterojunction composite structure can he fabricated via chemical bath deposition and post-sulfidation [18]. The composite of Sb_2S_3 can extend light absorption into the visible region compared to the pure Sb₂O₃, resulting in an enhanced photocurrent density of 0.35 mA/cm² at 1.23 V vs RHE under simulated sunlight. However, the obtained photocurrent of the Sb₂O₃/Sb₂S₃ thin film is still far less than the theoretically maximum photocurrent of Sb₂S₃, which is nearly 19 mA/cm² [19]. Till now, many strategies could be taken to improve the photoelectrochemical performance of a photoelectrode, including doping [20–22], heterojunction construction [23,24], co-catalyst loading [25,26] and plasmonic effect [27]. Given that the heterostructures have already been fabricated, it is feasible that co-catalyst loading could be adopted further to enhance the PEC performance of the Sb₂O₃/Sb₂S₃ composite. Recently, widespread interest has been provoked by the iron and nickel oxyhydroxide [28-30] co-catalyst on account of their low overpotential and good contact with the interface. particular, semiconductor In iron oxyhydroxide even (FeOOH) has broader applications in photoanode construction since the iron element is abundant enough in the earth just behind O, Si, and Al, resulting in its low price [31]. For instance, ZHANG et al [32] reported that the deposited FeOOH on nanostructured BiVO₄ significantly improved the sluggish kinetics of the oxygen evolution reaction and thus a remarkable photocurrent density of 4.3 mA/cm² was achieved.

Herein, we demonstrated a facile method to

fabricate the $Sb_2O_3/Sb_2S_3/FeOOH$ composite photoelectrode. Briefly, the FeOOH nanolayers were later deposited on the surface of the Sb_2O_3/Sb_2S_3 composite electrode through the impregnation method after the photoelectrode was prepared by the chemical bath deposition and post-sulfidation. Moreover, the mechanism for the enhancement of the photocurrent was investigated.

2 Experimental

2.1 Preparation of Sb₂O₃/Sb₂S₃/FeOOH composite photoelectrode

All chemical reagents in the experiment were of analytical grade and used without further purification. The Sb₂O₃/Sb₂S₃ composite thin film was prepared by a chemical bath deposition method followed by post-sulfidation treatment from previous literature [18]. First, a certain amount of triethanolamine was added to form a transparent solution after 0.05 mol/L SbCl₃ (99.0%; Aladdin) was dissolved in 60 mL of deionized water. Then, the saturated NaOH (99.0%; Sigma-Aldrich) was added to adjust the pH. After that, the cleaned fluorine-doped tin oxide (FTO) glass slides were vertically immersed into the above precursor solution and maintained at 60 °C for 15 min to form Sb₂O₃ thin films. After full drying, the as-prepared films were transferred to the tubular furnace, which was in static argon with sulfur vapor mixed atmosphere at the temperature of 350 °C and the pressure of about -0.07 MPa for post-sulfidation treatment.

The FeOOH co-catalysts were prepared by solution impregnation. Thus, the Sb_2O_3/Sb_2S_3 photoelectrodes were immersed in the 0.05 mmol/L FeCl₃·6H₂O (99.0%; Aladdin) solution for varying duration time (6, 8, 10 and 12 h) at room temperature. After the reaction, the obtained thin films were dried in air for several hours.

2.2 Characterization

The crystal structures of the as-prepared samples were identified by an X-ray diffractometer (XRD, Rigaku3014) equipped with Cu K_a radiation (λ =1.54 Å). The morphology of the obtained films was observed by a scanning electron microscope (SEM, Zeiss, MERLIN compact at 10 kV accelerating voltage), and the composition was examined by energy-dispersive X-ray spectroscopy

(EDX). Raman measurements were carried out on a Jobin Yvon LabRAM HR800 Horiba instrument. The chemical state of the products was probed by X-ray photoelectron spectroscopy (XPS) with a PHI5600 spectrometer. The UV-2450 equipment (SHIMADZU) was applied to evaluating the optical absorption property.

All PEC measurements were performed with a standard three-electrode system on Princeton Applied Research PARSTAT 4000. In detail, the as-prepared photoanode acted as the working electrode, a high-purity graphite plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The 1.0 mol/L Na₂SO₄ (pH=5.92) solution was served as the supporting electrolyte. And 1.0 mol/L Na₂SO₃ (pH=9.82) solution was applied to investigating the carrier injection efficiency. A 300 W xenon lamp with an AM 1.5G filter was adopted to supply the light source. The scan rate of linear sweep voltammetry was 3 mV/s. All potentials relative to SCE were converted to reversible electrode (RHE) values using the Nernst equation:

$$\varphi_{\rm RHE} = \varphi_{\rm SCE} + 0.05916 \text{pH} + 0.2483 \tag{1}$$

The electrochemical impedance spectra (EIS) were tested at an amplitude of 10 mV with frequency ranging from 0.1 Hz to 100 kHz.

3 Results and discussion

Figure 1(a) shows the XRD patterns of pure Sb₂O₃, Sb₂O₃/Sb₂S₃ and Sb₂O₃/Sb₂S₃/FeOOH thin films. For pure Sb₂O₃, all pronounced diffraction peaks are well assigned to orthorhombic phase β -Sb₂O₃ (JCPDS No. 11-0689) in addition to the peaks of FTO [11]. After the post-sulfidation treatment, the 2θ angles of 29.2°, 34.4°, 46.7° and 54.4° match those for orthorhombic Sb_2S_3 [13] (JCPDS No. 42-1393) and only the angle of 44.2° is indexed to Sb₂O₃, indicating the successful preparation of Sb₂O₃/Sb₂S₃ composite material. However, no diffraction peaks of FeOOH are observed after the impregnation of the FeCl₃ solution, possibly due to the fact that the assynthesized FeOOH is amorphous or the content is insufficient. Figure 1(b) displays the Raman spectra of the Sb₂O₃/Sb₂S₃ and Sb₂O₃/Sb₂S₃/FeOOH photoelectrode. The two sharp peaks at 110 and 147 cm^{-1} indicate the formation of the Sb₂S₃ crystalline phase, and the peaks at 281 and 302 cm^{-1} are



Fig. 1 XRD patterns (a) and Raman spectra (b) of Sb_2O_3 , Sb_2O_3/Sb_2S_3 and $Sb_2O_3/Sb_2S_3/FeOOH$ thin films

consistent with the symmetric vibrations of Sb_2S_3 pyramidal units [33,34]. Besides, the peaks at 190, 254, 373, 450, 508 and 710 cm⁻¹ are related to the presence of Sb_2O_3 . All signals below 400 cm⁻¹ belong to the external lattice mode regime, while those above 400 cm⁻¹ belong to the internal vibrations [35]. The position of the peaks has hardly changed before and after the impregnation of the FeCl₃ solution, which is consistent to the results of XRD patterns. Consequently, other testing methods are required to verify the existence of FeOOH further.

The as-obtained Sb₂O₃/Sb₂S₃/FeOOH photoelectrode was later investigated by XPS. The results shown in Fig. 2(a) demonstrate that the elements of Sb, S, C, O and Fe are detected. The peak of C may be derived from CO₂ in the atmosphere. The binding energy of C 1s is usually utilized to calibrate the XPS spectrum. Figures 2(b–d) exhibit the high-resolution XPS spectra of Sb 3d, Fe 2p and O 1s. As demonstrated in Fig. 2(b), the peaks at 530.7 eV (Sb $3d_{5/2}$) and 540.1 eV (Sb $3d_{3/2}$) are



Fig. 2 XPS spectra of Sb₂O₃/Sb₂S₃/FeOOH thin films (a-d) and EDX elemental mappings for Sb, S, Fe and O (e-i)

indexed to Sb³⁺ in Sb₂O₃. Meanwhile, the observed peaks at 529.5 eV (Sb 3d_{5/2}) and 538.7 eV (Sb 3d_{3/2}) correspond to Sb³⁺ in Sb₂S₃ [36]. As shown in Fig. 2(c), there are three distinct peaks. Specifically, the peak at 529.8 eV corresponds to the binding between oxygen atoms and metal atoms which refers to the Fe—O bond, the peak at 531.9 eV is associated with the absorption of water molecules, and the peak at 530.4 eV is assigned to the oxygen vacancies. For the Fe 2p core-level spectra (Fig. 2(d)), the binding energies of 711.2 and

714.0 eV are assigned to Fe $2p_{3/2}$, and 724.4 and 726.4 eV to Fe $2p_{1/2}$, indicating the successful preparation of FeOOH [32]. Also, the relative intensity of Fe²⁺ is higher than that of Fe³⁺, which may be attributed to the formation of oxygen vacancies [37]. As a result, the successful preparation of FeOOH can be well illustrated by the XPS analysis.

The energy dispersive X-ray (EDX) analysis was carried out to figure out the elemental distribution of the electrode. As shown in Fig. 2(d), it is clear that the elements of Sb, S, Fe and O evenly distribute on the substrate. Moreover, the weak signal of the Fe element indicates its low content, which is in accordance with the results of XRD and Raman spectra. Hence, it is certain that the FeOOH is undoubtedly loaded onto the surface of the Sb_2O_3/Sb_2S_3 photoelectrode by EDX elemental mapping along with the XPS analysis.

The morphology of the as-obtained films is observed by SEM. As presented in Fig. 3(a), the

 Sb_2O_3/Sb_2S_3 thin film is composed of rod-like structures. After the impregnation of the FeCl₃ solution, the surface of the sample becomes rough without destroying the original morphology, which may be due to the generated FeOOH covering the surface of the electrode.

The photoelectrochemical response of the as-obtained thin films is of great significance for assessing the potential for solar water splitting as a photoanode. Figure 4(a) shows linear voltammetry



Fig. 3 SEM images of Sb₂O₃/Sb₂S₃ (a) and Sb₂O₃/Sb₂S₃/FeOOH (b) composite films



Fig. 4 Photocurrent–potential curves (a), UV–Vis absorption spectra (b), electrochemical impedance spectra (c), and PEC measurements (d) of Sb₂O₃/Sb₂S₃ and Sb₂O₃/Sb₂S₃/FeOOH photoelectrodes

sweeps on the Sb₂O₃/Sb₂S₃ and Sb₂O₃/Sb₂S₃/ FeOOH photoanodes under chopped illumination in 1 mol/L Na₂SO₄ solution. As for the FeOOH-free electrode, the photocurrent is only 0.32 mA/cm² at 1.23 V versus RHE. Interestingly, an enhanced photocurrent density of 0.45 mA/cm² over the FeOOH loaded electrode is achieved, which is nearly 1.4 folds of the unloaded one at the same potential. This may be due to the excellent electrocatalytic activity of the FeOOH which can act as a hole transfer layer, thus reducing the recombination rate [38]. Therefore, the kinetics of the oxygen evolution reaction is dramatically accelerated as a result of the increased holes involved in the water oxidation reaction.

To further explore the mechanism of the enhanced photoelectrochemical performance, the optical absorption behavior by using UV–Vis absorbance spectroscopy is shown in Fig. 4(b). Both for Sb_2O_3/Sb_2S_3 and $Sb_2O_3/Sb_2S_3/FeOOH$ photoanodes, the absorption edge located at around 800 nm remains almost unchanged, while the optical absorption of FeOOH loaded photoelectrodes increases significantly. The improved light absorption for $Sb_2O_3/Sb_2S_3/FeOOH$ might be caused by the rough surface (as shown in Fig. 3(b)), which can increase the specific surface area, hence increasing the PEC performance.

Figure 4(c) demonstrates the electrochemical impedance spectra of Sb₂O₃/Sb₂S₃ composite photoelectrode before and after the impregnation of the FeCl₃ solution. EIS measurements are utilized to evaluate the interface separation and migration properties of the carriers. It can be observed that the FeOOH loaded Sb₂O₃/Sb₂S₃ photoelectrode exhibits a smaller radius in the low-frequency region, indicating that the loading of FeOOH can remarkably decrease the resistances in the charge transfer process. In other words, FeOOH co-catalyst accelerates the charge transfer across the interface of the Sb₂O₃/Sb₂S₃/FeOOH electrode and the electrolyte, resulting in the suppression of electron-hole recombination. In addition, the results of EIS measurements match the PEC test results well.

The appropriate thickness of photoelectric materials plays a vital role in its photoelectronchemical performance. On one hand, very thin films may deteriorate the light absorption ability since light can pass through the films easily. On the other hand, excess material may enlarge the carrier diffusion length, thus enhancing the likelihood of carrier recombination. LI et al [38] reported that the hole transfer layer of Fe₂O₃ deposited on the surface of pure BiVO₄ promoted the hole transfer from the bulk of the semiconductor to the electrode surface. Nevertheless, the thickness of the Fe₂O₃ layer has a great influence on the BiVO₄ photoanode owing to the short carrier diffusion length of Fe₂O₃. So, it might be reasonable to infer that the thickness of the FeOOH layer is one of the decisive factors in the PEC properties of the Sb₂O₃/Sb₂S₃/FeOOH composite electrode. Here, the thickness of the FeOOH thin films might be mainly controlled by the immersion time, and the photoelectrochemical performances of Sb₂O₃/Sb₂S₃ with varied duration time are shown in Fig. 4(d). It is obvious that the different photoanodes after 6, 8, 10 and 12 h immersion exhibit distinct photocurrents of 0.33, 0.45, 0.24 and 0.07 mA/cm², respectively, at 1.23 V versus RHE under simulated illumination. The photocurrent density starts to decline after immersing for over 8 h, which agrees with the hypothesis that the thickness does have an impact on photoelectrochemical properties. This is possibly attributed to the thickness of the film exceeding the carrier diffusion length, which leads to an increase in carrier recombination rate and a decrease in PEC properties.

The solar-to-hydrogen (STH) conversion efficiency is a considerable parameter to characterize the photoelectrochemical properties of a photoelectrode. Generally speaking, STH efficiency can be judged by the light absorption efficiency (η_{abs}), the charge separation efficiency (η_{sep}) and the charge injection efficiency (η_{inj}) [39]:

$$j_{\rm H_2O} = j_{\rm max} \cdot \eta_{\rm abs} \cdot \eta_{\rm sep} \cdot \eta_{\rm inj} \tag{2}$$

where j_{max} corresponds to the theoretical maximum photocurrent density, while $j_{\text{H}_2\text{O}}$ refers to the STH efficiency expressed by current density. Supposing that the PEC measurements are carried out in Na₂SO₄ solution, the STH efficiency can be expressed by Eq. (3). Na₂SO₃ as a hole scavenger can immediately consume the holes transferred to the semiconductor/electrolyte interface, which means that the injection efficiency of the photoelectrochemical process is 100%. Then, Eq. (3) can be simplified to Eq. (4) in Na₂SO₃ solution: Yang PENG, et al/Trans. Nonferrous Met. Soc. China 30(2020) 1625-1634

$$j_{\text{Na}_2\text{SO}_4} = j_{\text{max}} \cdot \eta_{\text{abs}} \cdot \eta_{\text{sep}} \cdot \eta_{\text{inj}}$$
(3)

$$j_{\text{Na}_2\text{SO}_3} = j_{\text{max}} \cdot \eta_{\text{abs}} \cdot \eta_{\text{sep}} \tag{4}$$

The same photoelectrode has the same theoretical maximum photocurrent density. Hence, the injection efficiency (η_{inj}) in Na₂SO₄ solution can be obtained via dividing Eq. (3) by Eq. (4):

$$\eta_{\rm inj} = \frac{j_{\rm Na_2SO_4}}{j_{\rm Na_2SO_3}} \tag{5}$$

The photoelectrochemical measurements of Sb_2O_3/Sb_2S_3 and $Sb_2O_3/Sb_2S_3/FeOOH$ photoelectrodes were carried out in Na_2SO_4 and Na_2SO_3 solution, respectively (as presented in Figs. 5(a) and 5(b)). The photocurrents measured in Na_2SO_4 and



Fig. 5 PEC measurements of Sb_2O_3/Sb_2S_3 and $Sb_2O_3/Sb_2S_3/FeOOH$ photoelectrodes: (a) Photoelectrochemical response curves in Na_2SO_4 solution; (b) Photoelectrochemical response curves in Na_2SO_3 solution; (c) Net photocurrent density plots in Na_2SO_4 solution; (d) Net photocurrent density plots in Na_2SO_3 solution; (f) Injection efficiency

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Na₂SO₃ solution have significant differences, indicating the existence of slow water oxidation kinetics. The net photocurrent density is calculated by simply subtracting the dark current from the light current, and the results are shown in Figs. 5(c)and 5(d). It is worth noting that there is no significant difference between the photocurrent density of Sb₂O₃/Sb₂S₃/FeOOH and Sb₂O₃/Sb₂S₃ in Na₂SO₃ aqueous solution, which indicates that the loading of FeOOH co-catalyst can also accelerate surface oxidation thermodynamics the and eliminate the surface recombination of charges, same as the Na₂SO₃ [40]. The carrier injection efficiency demonstrated in Fig. 5(e) is obtained according to Eq. (4). The η_{inj} of Sb₂O₃/Sb₂S₃/ FeOOH photoelectrode is higher than that of the Sb₂O₃/Sb₂S₃ electrode throughout the overall voltage range. The injection efficiency of FeOOH loaded and unloaded electrodes at the bias of 1.10 V versus RHE are 35% and 17%, respectively. This is consistent with the fact that the Sb_2S_3 has a poor water oxidation kinetics. Consequently, the FeOOH nanolayer serving as co-catalyst can tremendously enhance the carrier injection efficiency, thus accelerating the surface water oxidation kinetics, which is the principal consideration for the enhanced photoelectrochemical performance.

4 Conclusions

(1) The Sb₂O₃/Sb₂S₃/FeOOH composite photoelectrodes have been successfully fabricated via a simple solution immersion method along with chemical bath deposition and post-sulfidation. And the SEM-EDS analyses reveal that the surface of Sb₂O₃/Sb₂S₃ thin films becomes rough after the immersion in the FeCl₃ solution.

(2) The Sb₂O₃/Sb₂S₃/FeOOH photoelectrode displays an enhanced photocurrent density of 0.45 mA/cm² at 1.23 V versus RHE in Na₂SO₄ solution under simulated 1 sun, which is about 1.41 folds that of Sb₂O₃/Sb₂S₃ electrode. And the optimized impregnation time is found to be 8 h.

(3) The mechanism of the enhanced UV-Vis photocurrent is investigated by spectroscopy, the electrochemical impedance spectra, and the PEC measurements. And the improved photo-electrochemical performance of Sb₂O₃/Sb₂S₃/FeOOH composite photoelectrode is attributed to the increased light absorption capacity,

the decreased interface transmission impedance, and the remarkably enhanced carrier injection efficiency.

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用于增强光电化学水氧化的 Sb₂O₃/Sb₂S₃/FeOOH 复合光阳极的构建

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摘 要:通过简单的溶液浸渍法以及化学水浴沉积法和后硫化处理制备新型 Sb₂O₃/Sb₂S₃/FeOOH 光阳极。X 射线 衍射、拉曼光谱和 X 射线光电子能谱分析表明成功制备 Sb₂O₃/Sb₂S₃/FeOOH 薄膜。SEM-EDS 分析表明, FeCl₃ 溶液浸泡后的 Sb₂O₃/Sb₂S₃ 薄膜表面变得粗糙,最优的浸渍时间为 8 h。在模拟太阳光和偏压 1.23 V(vs RHE)下, FeOOH 助催化剂负载的 Sb₂O₃/Sb₂S₃ 电极表现出 0.45 mA/cm² 的光电流密度,为未负载 FeOOH 光电极的 1.41 倍。 通过紫外-可见光谱、电化学阻抗谱和 PEC 测试表明,光电性能的提高是由于 FeOOH 的复合可增强光电极的光 捕获能力、降低界面传输阻抗、提高载流子注入效率。

关键词: Sb₂O₃/Sb₂S₃; FeOOH 助催化剂; 光阳极; 载流子注入效率

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