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Article

Synthesis, characterization and application of BiVO₄ photoanode for photoelectrochemical oxidation of chlorate

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ABSTRACT

A high-quality polycrystalline bismuth vanadate (BiVO₄) film was prepared on a fluorine-doped tin oxide substrate via a facile two-step strategy involving electrodeposition and annealing processes. The morphology and structural characterization of the resulting film were investigated by different methods including scanning electron microscopy, transmission electron microscopy, X-ray diffraction (XRD), and Fourier transform infrared, ultraviolet-visible (UV-vis) absorption, and Raman spectroscopies. XRD patterns as well as optical measurements revealed that BiVO₄ film crystallized with a pure monoclinic scheelite structure. The prepared BiVO₄ film was used for heterogeneous oxidation of chlorate ions in aqueous solution via electrochemical (EC), photochemical (PC), and photoelectrochemical (PEC) processes. The decrease in concentration of chlorate was monitored using UV-vis absorption spectroscopy. The results revealed that BiVO₄ could effectively perform chlorate oxidation under light irradiation through a PEC method. The kinetics of chlorate oxidation was consistent with a first-order reaction, and the rate constant for the PEC process was found to be much higher than those of EC and PC. Furthermore, a possible photocatalytic oxidation mechanism for chlorate mainly based on the formation of perchlorate ions is proposed.

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1. Introduction

During the past decades, a large variety of advanced oxidation processes have been developed for degradation of various organic and inorganic materials [1–5]. These powerful oxidation methods are chemical, photochemical (PC), and electrochemical (EC) processes that are based on the in situ generation of highly reactive species [6–8]. Among these processes, photocatalysis is a promising advanced oxidation technology because of its ability to detoxify bacteria and photodegrade a large variety of contaminants cheaply and efficiently [9–11]. Thus, great attention has been paid to the photocatalytic reactions that occur on semiconductor materials [12,13]. It is generally agreed that upon exposing a semiconductor surface to

light of sufficient energy ($h\nu \geq$ band gap, E_g), charge separation is induced, resulting in the formation of reactive electrons (e^-) and holes (h^+). These charge carriers can initiate oxidation reactions either directly or by producing secondary oxidizing species such as hydroxyl radicals, hydroperoxyl radicals, hydrogen peroxide, and superoxide [14]. Considerable work in this area has been devoted to the oxidative degradation of pollutants on TiO₂, which suffers from the drawback of operating mainly under ultraviolet (UV) light irradiation [15,16]. To overcome this drawback, an alternative suitable visible light-sensitive photocatalyst is required for practical applications. Bismuth vanadate (BiVO₄) is one of the most promising photoanode candidates that shows visible-light photoactivity [17–20]. The narrow E_g of BiVO₄ (~2.4 eV) implies that it can

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absorb about 11% of the solar spectrum compared with 4% for a standard TiO_2 photocatalyst [17]. Moreover, the position of the valance band (VB) edge of BiVO_4 (located at ca. 2.4 V vs. RHE), provides sufficient overpotential for photogenerated holes to exhibit favorable photocatalytic activity for oxidation of materials [21].

Because of the quick recombination of excited electrons and holes, photoelectrocatalysis (PEC) has recently been demonstrated as an efficient way to further accelerate PC reactions. PEC involves applying an external potential to drive away electrons from the conduction band of a photocatalyst to a counter electrode, thereby increasing photocatalytic efficiency by preventing charge recombination.

Recently, Parkinson et al. [22] reported that TiO_2 -based semiconductors could photo-oxidize chloride to perchlorate ions in aqueous solutions. They also mentioned that the potential of the oxygen p-band in most semiconducting oxides was very oxidizing, suggesting that other oxides such as hematite could also induce this reaction. In other work, You et al. [23] reported that photooxidation of ClO_3^- at the surface of a $\text{Cu-TiO}_2/\text{SiO}_2$ system resulted in the formation of ClO_4^- . As stated above, BiVO_4 has been identified as a promising photoanode material [24–28]. However, chlorate oxidation by BiVO_4 has not been reported. In the present work, a BiVO_4 film is prepared by electrodeposition followed by annealing. The film is optically and structurally characterized using different characterization methods and subsequently used for PEC oxidation of chlorate in aqueous solution.

2. Experimental

2.1. Instrumentation

PEC experiments were conducted in a single-compartment custom-made reactor. A micro-Autolab EC workstation (PG-STAT) was used to bias the BiVO_4 photoanode against a platinum-wire counter electrode and Ag/AgCl reference electrode. Chlorate oxidation experiments were carried out in a quartz cell containing test solution (30 mL) at room temperature. PC and PEC reactions were carried out under a light intensity of $200 \text{ mW}/\text{cm}^2$ and the photoactive area of the photoanode was 1 cm^2 . Oxidation of chlorate was monitored by a spectrophotometric method according to a procedure previously described in the literature [29]. This method was based on the reaction of chlorate with a solution containing concentrated HCl and a small amount of bromide ions. The products of PEC oxidation of chlorate were monitored by a chromatograph (Knauer, Germany) equipped with a dual-piston pump, PRP-X110S analytical column ($4.1 \times 250 \text{ mm}$), and conductivity detector. An aqueous solution of Na_2CO_3 ($9.0 \text{ mmol}/\text{L}$) at a flow rate of $1.3 \text{ mL}/\text{min}$ was used as the eluent.

2.2. Synthesis of the BiVO_4 film

Bi metal was electrodeposited on the surface of a clean fluorine-doped tin oxide (FTO) substrate from a solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ($20 \text{ mmol}/\text{L}$) in ethylene glycol. The deposition

was carried out by passing a charge density of $0.04 \text{ C}/\text{cm}^2$ at a potential of -1.8 V vs. Ag/AgCl through the substrate, followed by a resting time of 2 s. This cycle was repeated eight times to pass a total charge of $0.32 \text{ C}/\text{cm}^2$ through the substrate. After electrodeposition, the film was carefully washed with ethanol and dried in air. To convert Bi to BiVO_4 , $\text{VO}(\text{acac})_2$ ($56 \mu\text{L}$, $0.15 \text{ mol}/\text{L}$) in dimethyl sulfoxide was placed on the surface of the Bi electrode (geometric area 1 cm^2) to fully cover its surface. The film was dried at about 80°C and then heated at 500°C for 2 h in air (ramp rate $2^\circ\text{C}/\text{min}$). During the heating process, Bi metal and VO^{2+} oxidized and reacted with each other to form BiVO_4 . Finally, after cooling to room temperature, the residual V_2O_5 was removed by soaking the electrode in NaOH ($1.0 \text{ mol}/\text{L}$) solution for 30 min with stirring.

3. Results and discussion

3.1. Characterization of the BiVO_4 film

The structural and optical characterization of the as-grown BiVO_4 film was carried out using different techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman scattering, and UV-visible (UV-vis) spectroscopy. Fig. 1 presents SEM images of metallic Bi and BiVO_4 films. The morphologies of the Bi and BiVO_4 films were in good agreement with those reported elsewhere [30]. Fig. 1(a) reveals that the as-synthesized black Bi film was composed of uniform nanodendritic structures with dendrite trunks more than $1 \mu\text{m}$ long and branches with diameters of less than 100 nm . The highly ordered branches were distributed on both sides of each

Fig. 1. SEM images of electrodeposited bismuth (a, b) and BiVO_4 films (c, d). Left images are top views and right images are cross-sectional views. TEM (e) and HR-TEM (f) images of BiVO_4 .

Fig. 2. XRD pattern of the as-grown BiVO_4 film on a FTO substrate.

trunk to produce three-dimensional structures with high surface area. Moreover, a cross-sectional SEM image of the Bi film (Fig. 1(b)) confirmed the uniformity of this structure in the film with a thickness of about 1.4 μm . The structure and thickness of the BiVO_4 film differed from those of the original Bi film. As shown in Fig. 1(c), BiVO_4 formed a granular, more compact film with a thickness of about 400 nm (Fig. 1(d)). The BiVO_4 film contained some pores and cavities between grains, which may shorten the pathway for photogenerated holes to reach the surface of BiVO_4 . The crystal structure of BiVO_4 was further evaluated by conventional transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM), as illustrated in Fig. 1(e) and (f), respectively. The HR-TEM image reveals a lattice spacing of 0.31 nm, which can be assigned to the (121) crystalline plane of monoclinic scheelite BiVO_4 [18]. To investigate the crystal phase composition of the BiVO_4 film, XRD and Raman scattering measurements were also carried out.

It has been reported that BiVO_4 crystallizes in a monoclinic

scheelite (clinobisvanite) phase upon calcining at temperatures higher than 400 $^{\circ}\text{C}$ [31]. XRD analysis of the film confirmed the high crystallinity of BiVO_4 . As it can be seen in Fig. 2, the patterns of the BiVO_4 film were consistent with a monoclinic structure (JCPDS No.14-0688), which is considered the most active BiVO_4 phase for photocatalysis or PEC applications [32,33]. The monoclinic nature of the film was confirmed from the two prominent peaks at 18.7 $^{\circ}$ and a sharp peak at 30 $^{\circ}$, which correspond to the (011) and (112) reflections of BiVO_4 , respectively. The presence of minor peaks that could be attributed to (101), (004), (121), (015), (204), and (116) reflections further confirmed the film was highly crystalline monoclinic BiVO_4 that was free from any other phases.

The Raman spectrum of the BiVO_4 film was consistent with XRD results and indicated that BiVO_4 had a monoclinic phase based on the characteristics of stretching and bending vibrations of VO_4^{3-} tetrahedra. Fig. 3(a) displays the Raman scattering spectrum of the crystalline BiVO_4 film, which main peaks at around 125, 206, 321, 362, and 820 cm^{-1} are characteristics of the typical vibration bands of a pure monoclinic scheelite structure. In accordance with reported data [34–36], the most intense band at 820 cm^{-1} was attributed to the symmetric stretching mode of V–O (A_g symmetry) and the weak bands at about 629 and 705 cm^{-1} were assigned to the asymmetric V–O stretching mode (B_g symmetry). The symmetric and asymmetric bending modes corresponding to deformation of VO_4 tetrahedra were observed at 362 and 321 cm^{-1} , while the bands around 206 and 125 cm^{-1} were attributed to external rotation and translation modes, respectively. Fig. 3(b) shows a Fourier transform infrared spectrum of the BiVO_4 film from 600 to 1500 cm^{-1} . The absorption bands in the 600–900 cm^{-1} region were characteristic of the stretching vibrations of the V–O bond [37]. A broad, strong absorption band at 682 cm^{-1} was assigned to the asymmetric stretching of VO_4^{3-} and the absorption band at 820 cm^{-1} was assigned to the symmetric stretching of VO_4^{3-} .

To characterize the optical properties of the BiVO_4 film, we studied its UV-vis absorption properties (Fig. 4). The absorption spectrum of BiVO_4 agreed well with those previously re-

Fig. 3. Raman (a) and Fourier transform infrared spectra (b) of an as-grown BiVO_4 thin film deposited on FTO as a supported electrode.

Fig. 4. UV-vis diffuse reflectance absorption spectrum of BiVO₄. The dashed line was used to determine the band gap of the film.

ported for the monoclinic phase [38], exhibiting a prominent absorption edge in the visible region of the solar spectrum. The absorption edge of BiVO₄ was observed at around 520 nm, and its band gap was estimated to be around 2.35 eV according to the intercept on the wavelength axis (Fig. 4).

3.2. Oxidation of chlorate

The EC, PC, and PEC processes for chlorate degradation in aqueous solutions were performed on the BiVO₄ electrode (Fig. 5). In the EC process, a bias of 1.5 V (DC mode) was applied to the BiVO₄ anode relative to the Ag/AgCl reference electrode. The EC and PC processes of chlorate oxidation over the BiVO₄ anode were negligible after 150 min, showing the high stability of chlorate ions under these conditions. Conversely, in the PEC process, about 76% of the chlorate was degraded after 150 min. These results indicate that the applied bias potential (1.5 vs. Ag|AgCl|KCl) effectively inhibited the recombination of the photogenerated e⁻-h⁺ pairs, prolonging the life of photogenerated charge carriers. In the PEC oxidation process, PEC oxygen evolution is the main side reaction, so the current efficiency will decrease as the concentration of chlorate decreases. This behavior can be seen clearly in Fig. 5(a). First-order kinetics were observed for the oxidation reaction (Fig. 5(b)), with first-order rate constants, k , for the PC, EC, and PEC processes of 0.0035, 0.085, and 0.61, respectively. It is clear that under the conditions used, the degradation rate of chlorate in the PEC process is much faster than those in the two other processes, which demonstrates the synergistic effect between the EC and PC processes. The synergistic factor between these two processes was quantified by the following equation [39]:

$$F = k_{\text{PEC}} / (k_{\text{PC}} + k_{\text{EC}}), \quad (1)$$

where, k_{PEC} , k_{PC} , and k_{EC} are the rate constants of PC, EC, and PEC, respectively. Using Eq. (1), F was calculated to be 6.9, which indicates there is a strong synergistic effect between the EC and PC processes.

3.3. Mechanism of oxidation

Fig. 5. (a) Changes in chlorate concentration over time during electrochemical, photocatalytic, and photoelectrocatalytic oxidation on the BiVO₄ photoelectrode. (b) Variation of $\ln(C_0/C)$ with electrolysis time for the same conditions as in (a). Cell volume 30 mL, light intensity 200 mW/cm².

The exact mechanism of EC, PC, and PEC of chlorate over the BiVO₄ photoelectrode and the chemical identity of the products are difficult to determine and beyond the scope of this study. However, as shown schematically in Fig. 6, under illumination, the photons absorbed by the BiVO₄ photocatalyst layer generated e⁻-h⁺ pairs (Reaction (2)). In the absence of bias potential (PC process), the recombination of electrons and holes is the predominant reaction and oxidation of chlorate is negligible. However, applying an anodic bias to the electrode provides a potential gradient within the film to drive the photogenerated holes and electrons in different directions. Photoexcited electrons will transfer via the external circuit to the Pt counter electrode and reduce water to hydrogen. At the same time, highly oxidative photogenerated holes (oxidative energy) will transfer toward the surface of BiVO₄ and oxidize chlorate ions (Reaction (3)).

The following simple reactions are involved in the oxidation process under light irradiation.

Another possible oxidation process involves production of

Fig. 6. Schematic representation of photoelectrochemical oxidation of chlorate on BiVO_4 under light illumination.

hydroxyl radicals and their subsequent reaction with chlorate ions. It has been reported that oxidation of ClO_3^- can be accomplished through discharge of water molecules at relatively high potentials to give adsorbed hydroxyl radicals [40]. This method has been studied extensively using lead oxide substrates [41]. However, in the case of BiVO_4 , hydroxyl radicals can be generated through photocatalytic reaction of water (or hydroxyl anions) with highly reactive holes in a one-electron transfer step (Reaction (4)). The photogenerated hydroxyl radicals can subsequently oxidize chlorate according to Reactions (5)–(7).

It should be mentioned that oxidation of water to oxygen could compete with chlorate oxidation and perchlorate production. To provide evidence for the mechanism of chlorate oxidation, the solution after PEC oxidation of chlorate for 1 h was analyzed using ion chromatography. Fig. 7 shows that after the photocatalytic reactions on the BiVO_4 film, the chromatogram contains three observable peaks consistent with SO_4^{2-} , ClO_3^- , and ClO_4^- . The strongest peak is attributed to SO_4^{2-} , which was used as a supporting electrolyte for the PEC reaction. The broad peak at long retention time was related to ClO_4^- , implying that perchlorate was the main product obtained from the oxidation of chlorate. These results are in good agreement with our proposed mechanism for chlorate oxidation.

Fig. 7. Ion chromatogram of the reaction solution after 60 min of photoelectrochemical reaction under a light intensity of 200 mW/cm^2 in a cell containing $0.05 \text{ mol/L Na}_2\text{SO}_4$ and 1.0 g/L NaClO_3 .

4. Conclusions

A BiVO_4 photoelectrode was synthesized by a simple EC method. The electrode was characterized using various techniques and subsequently used for oxidation of chlorate by EC, PC, and PEC processes. The results showed that EC and PC processes could not effectively oxidize chlorate over the BiVO_4 photoelectrode. However, their synergistic effect led to high PEC oxidation efficiency, with about 76% chlorate oxidation achieved after 150 min. Chlorate was oxidized by highly oxidizing holes in the VB produced from light irradiation on the BiVO_4 surface. The bias potential extended the lifetime of e^- – h^+ pairs. Using experimental data, a first-order rate constant and synergetic factor for chlorate oxidation over the BiVO_4 photoelectrode were obtained.

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Graphical Abstract

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Synthesis, characterization and application of BiVO₄ photoanode for photoelectrochemical oxidation of chlorate

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We have synthesized and fully characterized BiVO₄ on FTO substrate. Electrochemical, photochemical and photoelectrochemical oxidation of chlorate was investigated. High rate constant of chlorate oxidation was obtained by photoelectrochemical method, as compared to other two methods.

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用于光电化学氧化氯酸盐的钒酸铋光电阳极的合成与表征

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摘要: 采用便捷的涉及电沉积和退火过程的两步法在F掺杂的氧化锡基体上制备了高品质的多晶钒酸铋(BiVO₄)薄膜, 并运用扫描电镜、透射电镜、X射线衍射(XRD)、傅里叶变换红外光谱、紫外-可见光吸收光谱和拉曼光谱表征了所制薄膜的

形貌和结构特征. XRD和光学分析结果表明, BiVO_4 薄膜为纯相的单斜白钨矿晶相结构. 将该薄膜通过电化学(EC), 光化学(PC)和光电化学(PEC)过程用于水溶液中氯酸离子的多相氧化反应中. 采用紫外-可见吸附光谱仪监测氯酸盐浓度的降低. 结果发现, 在光的照射下采用PEC法时, BiVO_4 可有效催化氯酸盐的氧化. 氯酸盐氧化反应级数为1级, PEC过程的反应速率常数明显高于EC和PC过程的. 同时, 提出了基于形成了高氯酸离子的催化氧化氯酸盐的反应机理.

关键词: 钒酸铋; 光催化; 电子-空穴对; 氯酸盐氧化; 光化学反应

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