Fabrication and photoelectrocatalytic properties of nanocrystalline monoclinic BiVO$_4$ thin-film electrode

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Abstract

Monoclinic bismuth vanadate (BiVO$_4$) thin film was fabricated on indium-tin oxide glass from an amorphous heteronuclear complex via dip-coating. After annealation at 400, 500, and 600$^\circ$C, the thin films were characterized by X-ray diffraction, field emission scanning electron microscopy, X-ray photoelectron spectroscopy, and UV-Vis spectrophotometry. The BiVO$_4$ particles on the ITO glass surface had a monoclinic structure. The UV-Visible diffuse reflection spectra showed the BiVO$_4$ thin film had photoabsorption properties, with a band gap around 2.5 eV. In addition, the thin film showed high visible photocatalytic activities towards 2,4-dichlorophenol and Bisphenol A degradation under visible light irradiation ($\lambda > 420$ nm). Over 90% of the two organic pollutants were removed in 5 hr. A possible degradation mechanism of 2,4-dichlorophenol were also studied.

Key words: BiVO$_4$ thin film; degradation of pollutants; photoelectrochemical process

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Introduction

Photoelectrochemical degradation of organic water pollutants using solar energy has received increasing attention over the past decade. To date, several semiconductors have been found to exhibit high organic substance degradation under light irradiation. Traditional photocatalysts like TiO$_2$ (Carneiro et al., 2004; Li et al., 2007; Yang et al., 2005) and ZnO (Sakthivel et al., 2003; Daneshvar et al., 2004) have been widely studied and work well under UV light. When the wavelength extends to the visible light region, however, photoelectrochemical system efficiency decreases significantly. Additionally, other catalysts such as CdS (Reutergardh and Iangphasuk, 1997) are unstable in aqueous solutions and severe catalytic photocorrosion can occur. The development of visible light responsive catalysts is of significant interest as they utilize abundant solar energy. A great number of the transitional metal complex oxides have been synthesized and studied, with some of these compounds showing absorption ability and photocatalytic activities in the visible light range (Uno et al., 2006; Zhao and Zhu, 2006).

Transitional metal complex oxides that contain bismuth, such as bismuth titanate (Thanabodeekij et al., 2005), bismuth molybdate (Zhou et al., 2007a) and bismuth tungstate (Zhang and Zhu, 2005), have been found to have good response to visible light irradiation. In those composites, Bi 6s orbit normally hybrids with O 2p to form an up-shift valence band and results in a smaller band gap (Oshikiri and Boero, 2006) and this specific structure makes bismuth oxides better photoresponse to visible light. Bismuth vanadate is also a mixed oxide that has a high photocatalytic activity (Kohtani et al., 2002; Jiang et al., 2008; Long and Cai, 2008). The band gap of the BiVO$_4$ photocatalyst is around 2.4 eV, much smaller than that of TiO$_2$ photocatalysts (3.2 eV) (Sayama et al., 2003; Tokunagu et al., 2001), which indicates that BiVO$_4$ can absorb a wider spectrum of visible light. Research has shown that BiVO$_4$ photocatalytic properties strongly depend on crystal structure and morphology. Three BiVO$_4$ crystal forms exist, monoclinic scheelite structure, tetragonal zircon structure, and tetragonal scheelite structure (Tokunagu et al., 2001), with monoclinic structure possessing the highest photocatalytic activity for water splitting and organic pollutant photodegradation under visible light irradiation (Tokunagu et al., 2001; Kudo et al., 1999). The three phases can also be transformed by treatments such as heating or crushing. Several methods have been reported for BiVO$_4$ synthesis, including solid-state reaction (Kudo et al., 1998), solution coprecipitation (Tokunagu et al., 2001), hydrothermal treatment (Zhang et
Most previous studies on BiVO$_4$ have focused on photocatalytic activity (Kohtani et al., 2002; Zhang et al., 2006; Sayama et al., 2006). Fabricating BiVO$_4$ thin film allows for the study of photoelectrochemical properties and its ability to degrade organic substances under visible light irradiation. Photoelectrochemical techniques have several advantages, such as enabling estimation of band gaps and band edge positions and in situ investigation of charge transfer details (Long et al., 2008). Importantly, the gaps and band edge positions in situ allow for the study of photoelectrochemical properties of photoelectrocatalytic systems (Kohtani et al., 2002; Zhang et al., 2006). Fabricating BiVO$_4$ thin film annealed at 500°C degraded 95% of phenol in 8 hr by PEC system. They also fabricated Ag doped BiVO$_4$ using the same method (Zhang et al., 2009a) and found that photodegradation efficiency increased dramatically. Additionally, Chatchai et al. (2009) prepared WO$_3$/BiVO$_4$/FTO thin film by spin coating for water oxidation, which promoted photoelectrochemical performance.

Porous thin film on conducting oxide electrodes deposited by amorphous heteronuclear complex has been tried via the addition of polyethylene glycol, which induced the formation of porous structures during the annealing process (Zha et al., 2007). It is much easier, however, to produce homogeneous fine coating at the surface of substrates, which increases surface area.

Porous BiVO$_4$ film was prepared from amorphous heteronuclear complex with addition of polyethylene glycol to maximize the formation area of BiVO$_4$ particles and aqueous solution (Zhang et al., 2001). For the BiVO$_4$ thin film studies mentioned above, however, none investigated the influence of annealing temperature or other factors that might affect photoelectrocatalytic system efficiency, such as applied bias potential and light irradiation. In the present article, we studied the influence of heat treatment on the formation of monoclinic scheelite BiVO$_4$ and optimized PEC experimental conditions. As a result, the prepared film exhibited excellent photocurrent response and high photoelectrocatalytic activities towards 2,4-dichlorophenol degradation under visible light irradiation. The mechanism of photoelectrochemical 2,4-dichlorophenol oxidation was also discussed and proposed.

1 Materials and methods

1.1 Preparation of BiVO$_4$ thin film

All reagents were of analytical grade and were used without further purification. The BiVO$_4$ thin films on ITO glass were prepared from an amorphous heteronuclear complex via dip-coating by adding PEG400. A certain amount of commercial Bi$_2$O$_3$ and NH$_4$VO$_3$ were mixed in the mole ratio of 1:2, which made the two metal elements bismuth and vanadium in a ratio of 1:1. A certain amount of deionized water was added into a beaker with continuous magnetic stirring. Diethylene triamine pentaacetic acid (DTPA), a chelating agent for metal ions, was added into the suspension such that the mole ratio of Bi, V, and DTPA was 1:1:3. The pH value was adjusted to basic condition (pH = 10) with ammonia. The mixed solution was continuously stirred at 80°C until the solids were completely dissolved and a transparent dark blue and homogeneous solution was obtained. The solution was then transferred to an oven and dried at 80°C for 48 hr to ensure that all water was evaporated off. The remaining gel was dissolved in deionized water to a concentration of 20 g (dry weight)/100 mL DI water. Finally, 4 mL of polyethylene glycol 400 (PEG 400, HO(CH$_2$CH$_2$O)$_{400}$(H)) was added. Pretreated indium-tin oxide (ITO) glasses (thickness, 1.1 mm; sheet resistance, 15 Ohm/sq; China Southern Glass Co., Ltd.) were dipped into the precursor solution and slowly lifted at a constant speed (1 mm/sec) so the solution fully covered the surface. The glasses were dried at 80°C in a baking oven and then coated with the precursor annealed at 400, 500, and 600°C, respectively in air. The ramping rate was 3°C/min. This dip-coating and annealing process was repeated three times to ensure sufficient coating of BiVO$_4$ onto the ITO glass.

1.2 Sample characterization

The BiVO$_4$ thin film crystalline structure on the surface of the ITO glass was examined by X-ray diffraction (XRD) performed on a D/Max RB diffractometer (Rigaku, Japan) with Cu Ka radiation (λ = 1.54056 Å) at 30 kV, 30 mA, and a 20 scan rate of 0.3°/min between 15° and 80°. X-ray photoelectron spectroscopy (XPS) was conducted to identify elemental composition and chemical state. Spectra were recorded in a PHI 5600 spectrometer using a monochromatic Al Ka X-ray (beam energy 1486.6 eV) and hemispherical electron energy analyzer. Pass energies of 58.7 eV for regional spectra were used. To study surface morphology and texture, the thin films were examined by a field emission scanning microscope (JSM-6700F, JEOL, Japan). The UV-Vis diffuse adsorption spectra of the BiVO$_4$ coatings deposited on the ITO class were recorded on a UV-Vis spectrophotometer with an integrating sphere attachment, using BaSO$_4$ as a reference (UV-3010, Hitachi, Japan).

1.3 Photoelectrochemical experiment

To examine the photoelectrocatalytic property of the prepared BiVO$_4$ thin film, a series of degradation experiments of 2,4-dichlorophenol and Bisphenol A aqueous solutions under different conditions were performed. The initial concentration of phenol used was 10 mg/L, with 0.5 mol/L Na$_2$SO$_4$ used as the supporting electrolyte. The total volume of the solution was 75 mL. Experiments were carried out in an optical quality quartz cell equipped with a three-electrode system. A saturated calomel electrode was employed as the reference electrode and a platinum wire was used as the counter electrode. The working electrode was irradiated from the front side by a 150-W Xe lamp (Osram, German) through a glass filter that allowed only light with a wavelength of more than 420 nm to pass through. Light intensity measured at a point...
4 cm from the filter was ca. 25 mW/cm². Potentiostatic control was maintained with a potentiostat. Concentrations of 2,4-dichlorophenol and Bisphenol A were analyzed by reversed-phase HPLC with HPLC apparatus (Diode Array Detector L-2450, Column Oven L-2300, and Pump L-2130, Hitachi, Japan). An all sphere ODS-25u column (Alltech, USA) was used. The mobile phase employed was a mixture of 70:30 methanol/water containing 1% acetic acid with a flow rate of 1.0 mL/min. The detector wavelength was set to 280 nm. Samples were also examined by GC-MS (7890GC/5975MSD, Agilent, USA) to detect the degradation products. Analysis was carried out on an Agilent 7890GC/5975MSD with a HP-5 MS capillary column.

2 Results and discussion

2.1 Characteristics of BiVO₄ thin film

The crystal structures of the BiVO₄ coating obtained under different annealing conditions were investigated by XRD. As shown in Fig. 1, when the heating temperatures were set at 500 and 600°C, characteristic diffraction peaks with 2θ at 18.5°, 28.6°, 30.3°, 35.2°, 39.7°, and 53.1° were observed. All peaks coincided with the monoclinic scheelite BiVO₄ structure (JCPDS file No.: 14-0688), which is the only structure that shows photocatalytic activity under visible light irradiation. The monoclinic phase has a different crystal structure in which the Bi-O polyhedron is more distorted by a 6s² lone pair of Bi³⁺ (Tokunaga et al., 2001). The angle of monoclinic crystal is 90.4°, whereas tetragonal crystal is 90° (Zhou et al., 2007b). As shown in Fig. 1, the peaks at 2θ = 35°, 46°, and 59° were obviously split and differentiated between monoclinic and tetragonal phases. The peak patterns for 500 and 600°C were very similar in relation to both position of the peaks and the intensity. The product obtained after annealing at 400°C contained some impurities, however.

Other phase diffraction peaks were detected in addition to the characteristic peaks of monoclinic BiVO₄. These results indicate that calcination is an important process for crystallization. Results also showed that phase transition occurred when the heating temperature increased to 400°C, with the XRD data demonstrating that pure monoclinic BiVO₄ thin film could be fabricated when annealing temperature was above 500°C.

The ITO glass film substrate was fully and evenly
covered by vivid yellow nanocrystallized BiVO₄ particles after the preparation process. The morphology of the BiVO₄ thin films were revealed by FE-SEM. Surface micrographs are shown in Fig. 2, which show that BiVO₄ particles at the surface of three samples were adherent to the glass surfaces. However, morphologies changed with annealing temperature. The sample annealed at 400°C had many holes at the film surface. As the heating temperature increased to 500°C, the holes changed to pores and smooth network agglomerations of individual BiVO₄ crystallites were observed. When the temperature increased to 600°C, the BiVO₄ catalyst particles became more scattered. The formation of these holes and pores was assigned to the burning of organic materials in the precursor complex, such as PEG and chelating agent DTPA which turned to gases at around 400°C and were fully burned-out at 500°C. The distance among particles continued to increase with higher temperatures. The SEM of BiVO₄ thin film showed that the obtained BiVO₄ particles were homogeneous, mainly elliptical, and increased in size with increasing temperature. Most particles were around 100 to 200 nm at 500°C and increased to 200 to 300 nm at 600°C.

The diffuse reflectance spectra of the BiVO₄ thin films annealed under different temperatures are shown in Fig. 3a. The steep curves reflect the optical absorption property of the prepared semiconductor catalyst. The correspondent onset adsorption edges for the three BiVO₄ samples were 501, 510, and 513 nm, respectively. This indicates that all thin films had a good response to visible light in addition to that in the UV light region. The absorption threshold was comparable to previously reported values (Sayama et al., 2003; Tokunag et al., 2001). In addition, an obvious red shift was observed when the heating temperature increased, indicating that calcination temperature affected visible light absorption efficiency. From the XRD images, it is clear that calcinations promoted the crystallization of BiVO₄ composite oxide and affected the phase transition. A 10 nm red shift was observed when heating temperature changed from 400 to 500°C, demonstrating that higher temperature was beneficial to crystallization. Another 3 nm red shift occurred for samples heated at 500 and 600°C. From the UV-Vis test, greater photoelectrochemical activity was expected by the sample obtained at higher temperatures. For semiconductor catalysts, optical band gap can be estimated by the Kubelka-Munk function as follows (Xu et al., 2008):

\[ A\hbar = c (\hbar\nu - E_g)^n \]  

where, \( A \) is the absorption coefficient; \( \hbar\nu \) is the photon energy; \( c \) is the constant (\( c = 1 \)); \( E_g \) is the band gap energy; and \( n \) is a constant determined by the semiconductor, that is, a direct band gap for \( n = 1/2 \) and an indirect band gap for \( n = 2 \).

The \((A\hbar)^2 - \hbar\nu\) plot was drawn according to the data and function above. The \( E_g \) for BiVO₄ prepared at 400, 500 and 600°C were 2.53, 2.49, and 2.47 eV, respectively (Fig. 3b). Heating treatment at high temperatures narrowed the catalyst’s band gap, which facilitated electron excitation from the valence to conduction band in the transitional metal complex oxides, and thus increased photocatalytic activity of the material. The steep shape of the spectra indicated that visible light absorption was not due to the impurity level transition but to band-gap transition (Tang et al., 2004). Two shoulders appeared in the curve of the BiVO₄ test, and were ascribed to the charge-transfer transition involving the V-O component and Bi and V centers (Luo et al., 2008).

The XPS spectra identified the chemical states of bismuth, vanadium, and oxygen in the oxide composite. Figure 4a exhibits the characteristic spin-orbit split of Biδ 5/2 and Biδ 7/2 signals at approximately 159.2 and 164.6 eV respectively, corresponding to Bi^{3+} in the sample. The V₂p peak at ca. 516.5 eV was assigned to V⁵⁺ and the O₁s signal at 530.0 eV was attributed to the lattice oxygen in BiVO₄ (Fig. 4b).

### 2.2 Photoelectrocatalytic decomposition of 2,4-dichlorophenol by BiVO₄ thin films

Figure 5 shows photocurrent density as a function of the applied potential for BiVO₄ thin film electrodes annealed at 400, 500 and 600°C with a ramping rate of 3°C/min under dark and visible light irradiation. The sample was
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Fig. 4 X-ray photoelectron spectroscopy (XPS) analysis of Bi_{4f} (a) and V_{2p} and O_{1s} (b).

Fig. 5 Current-potential plots for prepared BiVO₄ thin films in Na₂SO₄ solution (pH = 5.5).

Fig. 6 Degradation of 2,4-dichlorophenol by BiVO₄ thin films annealed at 400, 500 and 600°C with a ramping rate of 3°C/min (E_{bias} = 2.0 V vs. SCE; λ > 420 nm).

evaluated in 0.5 mol/L Na₂SO₄ electrolyte and the pH value was adjusted to 5.5. External potential was set to sweep from −0.5 to 2.5 V (vs. SCE). An increase of the photocurrent by all films was observed as sweeping potential increased, with the BiVO₄ at 600°C having the highest photocurrent and 400°C having the lowest (Fig. 5). The BiVO₄ treated at higher temperatures also had a narrower band gap. Light with a greater scale of wavelength can be utilized. In addition, oxygen defects exist in the molecules of BiVO₄, a kind of single-phase mixed oxide, which makes photoelectron transfer much easier (Hoffart et al., 1995). The SEM image (Fig. 2) shows that the higher the annealing temperature, the better the porous structure formed at the surface of BiVO₄ film and more scattered the BiVO₄ particles dispersed at the surface of ITO glass. More active sites were offered to adsorb water and hydroxyl groups, which captured photogenerated holes under irradiation and produced active hydroxyl radicals.

Photoelectrocatalytic activity of the prepared BiVO₄ thin films was also examined by measuring the degradation efficiency of 2,4-dichlorophenol in aqueous solution under visible light irradiation. Initial concentration was 10 mg/L and a cut-off filter was used to ensure that only light with a wavelength of more than 420 nm could pass through.

The degradation data are shown in Fig. 6. The film heated at 600°C had the highest degradation efficiency and over 90% of the targeted pollutant was removed within 3 hr. For the film prepared at 500°C, efficiency was over 85% during the same period. This sequence was consistent with that in the current voltammetry test. Considering the minor differences in the efficiency of the films obtained at 500 and 600°C, the film heated at 500°C was selected for the following test.

Photoelectrocatalytic oxidation (PEC) combines the advantages of both photocatalytic (PC) and electrocatalytic (EC) oxidation. Figure 7 shows that 2,4-dichlorophenol can be degraded by all three systems (PEC, PC, and EC). The degradation efficiency of BiVO₄ thin film in the PEC system was highest among the three systems under the same conditions, nearly 100% after 5 hr. Only 10% of the target pollutant was decomposed when the film was irradiated by visible light only without applying external bias potential. For the EC system, degradation efficiency was around 70% in 5 hr. It has been reported that pure BiVO₄ has relatively low photocatalytic efficiency because of its poor adsorptive performance and difficult migration of electro-hole pairs (Long et al., 2006). When the bias...
potential was applied in addition to visible light illumination, photogenerated electrons were forced towards the system cathode through the circuit and the photogenerated holes left at the surface of anode for oxidizing organic materials. Thus, the recombination of electrons and holes was effectively prevented. A schematic diagram of the PEC system is shown in Fig. 8. As potential continued to increase, electric energy was not merely utilized to separate the electron-hole pairs; electrochemical oxidation also occurred. The sum of the PC and EC system degradation rates were less than that of PEC at the same point. This indicates that a photochemical and electrochemical oxidation synergistic effect occurred in the PEC system. Pelegrini et al. (1999) reported the same synergistic effect related to photoelectrochemical degradation of C.I. Reactive Blue 19 using TiO$_2$ as the photoanode. They found that removal efficiencies of both color and TOC from the solution containing C.I. Reactive Blue 19 with photoelectrochemical technology were higher than the sum of those by a single application of electrochemical and photocatalytic process. External voltage is a key factor in a PEC system. The application of positive potentials across the photoelectrode establishes a potential gradient within the BiVO$_4$ film, which produces the same effect as band bending in single-crystal photoelectrodes (Candal et al., 2000). To evaluate the influence of external voltage on degradation, six different conditions were chosen for testing. When no electrical bias was applied between a Pt wire and BiVO$_4$ thin film, the PEC system was equal to a PC system. As positive potential was applied and increased, the resulting electrical gradient separated holes and electrons, decreasing their rate of recombination. When bias potential was lower than the redox potential of the organic pollutant, the electric energy was mainly used to drive photogenerated electrons away from the holes. The higher the bias potential, the greater the electric force applied and the more electrons transferred. As a result, degradation efficiency increased with potential. When potential was higher than the redox potential of the organic pollutant, electrochemical oxidation and photochemical oxidation occurred. From Fig. 9, it can be seen clearly that the 2,4-dichlorophenol degradation rate had a positive correlation to voltage. The rate had a linear relationship to voltage under 0.5 V, and 1.0 V vs. SCE and no bias potential applied. When potential increased to 1.5 V vs. SCE, the rate increased significantly. This result may be explained by the synergistic effect of both electrochemical and photochemical oxidation. The decomposition rates at 2.0 V and 2.5 V VS. SCE showed little difference. Most photogenerated electrons either reacted at the surface of the photoelectrode with dissolved oxygen or were transferred to the cathode under the influence of the electric field. The generation of holes reached maximum. Increasing the potential beyond this value (2.0 V vs. SCE) did not greatly influence degradation efficiency and bias potential was no longer the limiting factor.

To utilize the photoelectrochemical technique on a large scale, sunlight can be used as the best light source for energy input. As such, the cut-filter placed in front of the Xe lamp was removed and the BiVO$_4$ thin film was exposed directly to the full spectrum of the Xe lamp, used to simulate the sun. Figure 10a displays the results of the

![Fig. 8 Schematic diagram of BiVO$_4$ PEC system.](image)

![Fig. 9 Degradation of 2,4-dichlorophenol using BiVO$_4$ thin film (500°C) as electrode illuminated by visible light ($\lambda > 420$ nm) under different bias potentials (vs. SCE) and without bias potential.](image)
different illustration conditions. When the film was directly irradiated by the Xe lamp, over 90% of 2,4-dichlorophenol was removed from the solution after 2 hr. Almost 100% of the pollutant was degraded after 3 hr, while the system with the film illuminated by visible light only removed 85% of 2,4-dichlorophenol in 3 hr. Additionally, degradation efficiency of the film under dark conditions was about 50%. According to the Kubelka-Munk calculation, the band gap for BiVO₄ annealed at 500°C was 2.49 eV. Theoretically, light with a wavelength shorter than 510 nm can be absorbed by the film. Under the irradiation of the unfiltered Xe lamp, more holes and electrons were generated and degradation efficiency increased. From the whole Xe lamp spectra (Fig. 10b), only a small portion of light was shorter than 420 nm. Although this part of light has energy that can be utilized to excite BiVO₄ molecule electrons to move from valence bands to conduct bands, degradation efficiency did not show a dramatic improvement.

GC-MS was employed to detect intermediates generated in the PEC degradation process of 2,4-dichlorophenol. The organic substances in Table 1 are the intermediate products after 2 and 5 hr using BiVO₄ thin film as the photoelectrode. 2,4-Dichlorophenol is difficult to degrade as its highly electronegative chlorine atoms make the benzene ring electrophobic, which is difficult to oxidize. From Table 1, it can be seen that dechlorination was the main reaction during the first 2 hr. The two chlorine atoms in 2,4-dichlorophenol were substituted and two alkanes containing chlorine were detected. The stable structure of 2,4-dichlorophenol was destroyed after dechlorination. Pandiyan et al. (2002) investigated photolysis of 2,4-dichlorophenol using GC-MS and identified monochlorophenol as the main product, which differs from our results. Hirvonen et al. (2000) investigated photooxidation reactions using UV/H₂O₂ methods and observed the formation of numerous hydroxylated intermediates, which is consistent with our results. The materials detected in 5 hr demonstrate that the opening of the benzene ring was the next step in the mineralization process of 2,4-dichlorophenol after dechlorination. Several kinds of small molecular acids were detected in the sample taken at 5 hr.

### 2.3 Photoelectrocatalytic decomposition of Bisphenol A by BiVO₄ thin films

To demonstrate that BiVO₄ thin film photoelectrochemical oxidation was not specifically effective to 2,4-dichlorophenol, another organic endocrine disruptor substance, Bisphenol A, was employed as the target pollutant. Bisphenol A has two benzene rings and two phenolic hydroxyl groups, but contains no chlorine atoms in the molecule. All experimental conditions were the same as that of 2,4-dichlorophenol and the applied bias potential was 2.0 V vs. SCE. Results show that almost all Bisphenol A was degraded at the end point of 5 hr (Fig. 11). It is clear that BiVO₄ thin film can be used to remove Bisphenol A in a photoelectrocatalytic system under visible light, which confirms the high photoelectrocatalytic activity of the prepared BiVO₄ thin film. The intensity of the characteristic Bisphenol A peak at 4.9 min decreased and another signal at 2.0 min was strengthened. It was assumed that Bisphenol A was transformed during the PEC reaction. Compared with the degradation curve of 2,4-dichlorophenol, the degradation efficiency of Bisphenol A was higher. Photogenerated holes at the surface of the anode acted as decomposing agents or combined with hydroxyl species hydrolyzed from water to form hydroxyl radicals. Free radical OH is a very strong activator in...
Table 1  Intermediates detected in the photoelectrochemical oxidation process of 2,4-dichlorophenol using BiVO₄ thin film irradiated by visible light with the applied bias potential of 2.0 V vs. SCE

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electrophilic aromatic substitution. Halogen substations are suspected to be accomplished by the effect of photo-generated OH and holes directly (Sivalingam et al., 2004). The reactive group O₂ then attacks the dechlorinated intermediates with OH and holes by photooxidation to form oxygenated intermediates.

3 Conclusions

Monoclinic BiVO₄ thin film was successfully prepared through amorphous heteronuclear complex and dip-coating. The BiVO₄ particles attached to ITO glass retained a monoclinic scheelite structure, removed impurities after annealation above 400°C for 4 hr, and evenly covered the substrate surface. Particle size increased with annealing temperature. UV-Vis spectra indicated that the absorption edge of BiVO₄ films started from 501 to 513 nm, with a corresponding band gap from 2.47 to 2.53 eV. High temperature treatment narrowed the band gap of the catalyst. The composite photocatalyst exhibited high photoelectrocatalytic activity under visible light irradiation and effectively degraded 2,4-dichlorophenol and Bisphe- nol A when bias potential was applied and irradiated by visible light. A synergistic effect was observed in the PEC system, which enhanced degradation efficiency of organic contaminants in aqueous solution. According to the analysis of intermediates, dechlorination was the first step in 2,4-dichlorophenol degradation. The prepared composite photocatalyst is a promising application for water purification due to its good photoelectrocatalytic performance and stability. It is believed that activity can be further improved by reducing the dimension of BiVO₄ and hybrid BiVO₄ by adding other elements.

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References


No. 1 Fabrication and photoelectrocatalytic properties of nanocrystalline monoclinic BiVO₄ thin-film electrode


