

Photoelectrocatalytic degradation of 4-chlorophenol at Bi_2WO_6 nanoflake film electrode under visible light irradiation

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Abstract

To efficiently utilize the solar light and improve the photooxidation technique for wastewater purification, a new type of photoelectrode, visible light responsive Bi_2WO_6 nanoflake film, was covered onto the indium–tin oxide glass substrate via the electrostatic self-assembly deposition. The photocatalytic oxidation, electro-oxidation, and photoelectrocatalytic (PEC) oxidation of 4-chlorophenol (4-CP) in aqueous solution using the film electrode were investigated and compared under visible light irradiation ($\lambda > 400$ nm). The experimental results demonstrated that 4-CP could be degraded by the nanoflake film under visible light irradiation or by applying a bias potential greater than 0.8 V. Based on X-ray photoelectron spectra (XPS) analysis of the electrode after electrochemical reaction, the electropolymerization was suggested to occur in the electro-oxidation process. Furthermore, degradation efficiency of 4-CP was largely increased by combined electro-oxidation and photocatalysis. And, it is the largest at the bias potential of 2.0 V. The characteristics of the PEC degradation of 4-CP were also investigated by electrochemical impedance spectroscopy (EIS). It is shown from the EIS that the PEC degradation appears to be a simple reaction on the electrode surface, suggesting that only one step of charge transfer is involved in the electrode process. The total organic carbon analysis indicated that 4-CP could be efficiently mineralized during the PEC process.

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Keywords: Bi_2WO_6 ; Nanoflake film; Photoelectrocatalytic degradation; 4-CP; Visible light

1. Introduction

Photoelectrocatalytic (PEC) oxidation has proven to be an efficient method in degrading organic contaminants in aqueous solution using the TiO_2 based film electrode [1–5]. However, the wide band gap of TiO_2 can only capture less than 5% of solar irradiance at the Earth's surface. To obtain a more efficient utilization of solar irradiation, many attempts were made to shift its photocatalytic activity to the visible region [6,7]. In another way, some novel photocatalyst with can absorb visible light and degrade organic pollutants are developed [8,9].

Bi_2WO_6 is the simplest members of the aurivillius family of structurally related oxides with the layer structure and interesting physical properties [10]. Kudo found Bi_2WO_6 had photocatalytic activities for O_2 evolution [11], and Zou and

coworkers revealed the Bi_2WO_6 could degrade CHCl_3 and CH_3CHO under visible light irradiation [12]. Our recent work reveals that nanoflake Bi_2WO_6 have high photocatalytic activity in degrading rhodamine B compared with that of solid samples [13]. Bi_2WO_6 with nanoflake structure has exhibited novel or enhanced physical properties such as large blue shift of the absorption edge and high specific surface areas [14–16]. These specific properties are beneficial for the photocatalytic degradation of organic contaminants.

Herein, Bi_2WO_6 nanoflake film electrode was prepared onto indium–tin oxide (ITO) glass via electrostatic self-assembly deposition (ESD) according to the method described in the literature [17]. The resultant Bi_2WO_6 nanoflake film exhibits photocatalytic activities towards degrading 4-CP under visible light irradiation. The removal efficiency of 4-CP was increased by applying a bias potential to the Bi_2WO_6 nanoflake film electrode. Moreover, a synergetic effect was observed in the degradation of 4-CP by the combined electro-oxidation and photocatalysis. The synergetic mechanism was further investigated.

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2. Experimental section

2.1. Materials

ITO glass employed as a substrate was purchased from China Southern Glass Co. Ltd., with a thickness of 1.1 mm and a sheet resistance of $15 \Omega/\square$. It was cleaned by sonication in acetone, ethanol, and ultrapure water for 30 min each and stored in water until use. All other chemicals are analytical grade reagents and used without further purification. Deionized water was used throughout the experiment.

2.2. Preparation and characterization of the Bi_2WO_6 nanoflake film

Bi_2WO_6 nanoflake powder was synthesized through hydrothermal process according to previously reported procedure [13]. The Bi_2WO_6 nanoflake films were prepared via the electrostatic self-assembly deposition (ESD) according to the procedure [18]. Briefly, poly(sodium-*p*-styrenesulfonate) (PSS) and polyethyleneimine (PEI) was dissolved in deionized water with a concentration of 2 mg/mL. Bi_2WO_6 nanoflake was suspended in deionized water with a concentration of ca. 2 mg/L, and the pH value was adjusted to about 10 with dilute NaOH solution. The ITO substrate (40 mm \times 40 mm) was immersed firstly in 0.2 mg/mL PSS aqueous solution for 20 min, then rinsed with deionized water and dried at room temperature, followed by immersion in the PEI solution for another 20 min, and rinsed with deionized water and dried again. Then the film were immersed in the PSS aqueous solution for 20 min, rinsed and dried again. Then, the substrate was immersed in the PEI solution for 20 min followed by the immersion in the Bi_2WO_6 nanoflake suspension for another 20 min. In each cycle for the last two steps, a layer of Bi_2WO_6 nanoflake was deposited on the substrate. Finally, the obtained film was calcinated at 450 °C for 6 h. The morphology and crystal phase of the Bi_2WO_6 film was characterized by a JSM 6301 electron-scanning microscope (SEM) and a Renishaw RM1000 spectroscopy, respectively. Diffuse reflect spectroscopy (DRS) of Bi_2WO_6 nanoflake film is measured by a Shimadzu S 2600 UV spectrophotometer with a solid attachment.

2.3. Degradation experiments

The PEC degradation experiments were performed in a rectangular (50 mm \times 50 mm \times 140 mm) reactor which is made from quartz glass. The reactor, which contained a 100 mL sample solution allowing 7 cm of the supported film electrode to be immersed into the solution, was placed 3 cm in front of a 500 W Xe lamp (CHF-XIU-500 W) purchased from the Beijing Broadview Technology Co. Ltd. The intensity of light, as measured by a visible-irradiance meter (Instruments of Beijing Normal University) was 150 mW/cm² at 4 cm into the reactor, the position where the film electrode was placed. The PEC reaction employed a CHI660B electrochemical system (Shanghai, China) connected with a counter-electrode (Pt wire, 70 mm in length with a 0.4 mm diameter), a working electrode (the Bi_2WO_6 film), and a reference electrode (a saturated calomel electrode (SCE)). A 0.5 mol/L Na_2SO_4 (pH 6.6) was used as electrolyte solution. Initial concentration of 4-CP solution was 10 mg/L, and its concentration variation was examined by a high performance liquid chromatography (HPLC) (PU-1580, UV-1575, Jasco Corporation, Japan) with a Kromasil ODS (5 μm , 4.6 mm \times 250 mm) reverse-phase column. The mobile phase was 1.0 mL min⁻¹ of methanol and water (*V:V* = 4:1) and was determined at 280 nm. Total organic carbon analyzer (TOC-*V*_{wp}, Shimadzu, Japan) was employed for mineralization degree analysis of 4-CP solution. Prior to injection into the TOC analyzer, the samples were filtrated with 0.45 μm Millipore filter to remove any particles. All experiments were carried out at least in duplicate. The reported values are within the experimental error of $\pm 3\%$. Electrochemical impedance spectra (EIS) were recorded in the potentiostatic mode. The amplitude of the sinusoidal wave was 10 mV, and the frequency range of the sinusoidal was 100 kHz to 0.01 Hz.

3. Results and discussion

3.1. Characterization of the Bi_2WO_6 nanoflake film electrode

Fig. 1(A) shows the Raman patterns of the Bi_2WO_6 nanoflake film as well as the ITO substrate. The Raman analysis shows that

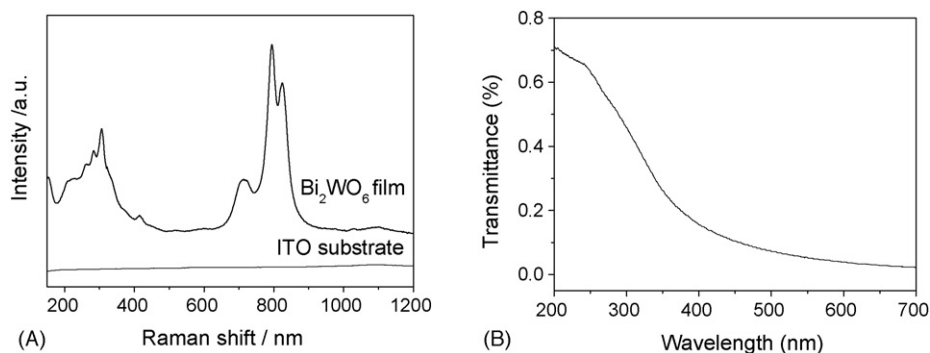


Fig. 1. (A) Raman spectra of Bi_2WO_6 nanoflake film coated on ITO glass as well as ITO substrate; (B) transmittance spectroscopy of Bi_2WO_6 nanoflake film coated on quartz glass.

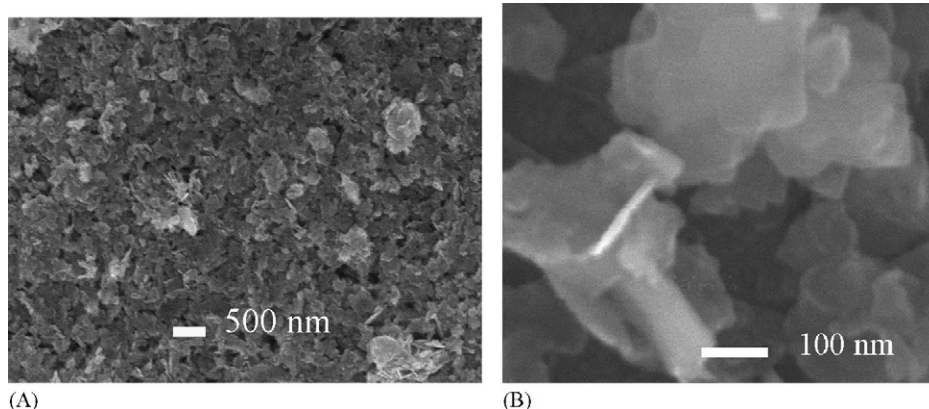


Fig. 2. SEM of Bi_2WO_6 nanoflake film coated on ITO glass.

the Bi_2WO_6 is well crystallized with the orthorhombic structure. Fig. 1(B) represents the UV–vis diffuse transmittance spectra of the Bi_2WO_6 nanoflake film coated on quartz glass. The steep shape of the spectra indicated that the visible light absorption was not due to the band-gap transition. The band gap of the Bi_2WO_6 film is estimated to be 2.80 eV from the onset of the absorption edge. The color of the film is yellowy, as can be expected from its absorption spectrum. Fig. 2 shows SEM images of the deposited layer of Bi_2WO_6 nanoflake on the ITO glass. Although there are small uncovered areas and some overlapped patches, the surface is covered with regularly flakelike crystallites, and the dimensions of which range from 50 to several hundreds of nanometers. A section analysis reveals their nanoflake nature, showing an average thickness of ca. 10 nm.

3.2. Synergetic degradation of 4-CP

Photocatalysis, electrochemical degradation, and PEC degradation of 4-CP at the bias potential of 2.0 V were performed, respectively. The variation of relative concentration of 4-CP (C_t/C_0) as a function of reaction time is shown in Fig. 3.

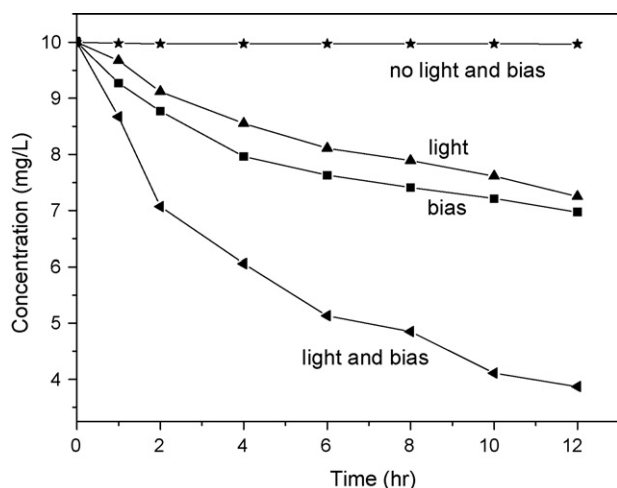


Fig. 3. Variation of 4-CP concentration under various conditions with initial concentration = 10 mg/L, applied bias potential = 2 V, and light intensity = 150 mW/cm².

It is clear that 4-CP can be photocatalytically degraded using the Bi_2WO_6 nanoflake film electrode; it can also be degraded via the electro-oxidation process at the bias potential of 2 V. Clearly, the degradation rate of 4-CP was the largest under PEC process with same bias potential. It is well recognized that the PEC degradation of organic pollutants follows pseudo-first-order kinetics [19]. Herein, pseudo-first-order kinetics was also confirmed in the electrochemical, photocatalytic, and PEC process by the linear transform of $\ln(4\text{-CP}_0/4\text{-CP}_t) = Kt$ (K is the kinetic constant). As shown in Table 1, the pseudo-first kinetic constant of 4-CP for PEC process is larger than the sum of the electrochemical or photocatalytic process individually. A similar conclusion can be drawn by considering the reduction of TOC content (Table 2). At the potential of 2 V, after reaction of 12 h, the individual electrochemical degradation and photocatalysis permit TOC reduction of 25% and 20%, respectively, while the combined PEC process leads to a TOC reduction of 65%. Thus, it is reasonable to conclude that a sort of synergetic effect occurs during the PEC degradation of 4-CP.

Fig. 4 shows the EIS response of the Bi_2WO_6 nanoflake film electrode under dark, photoirradiation, the applied bias potential, and combined photoirradiation and the applied bias

Table 1
Pseudo-first-order rates of 4-CP degradation (k'_{obs}) (100 mL, 10 mg/L) under various conditions (visible light intensity = 150 mW/cm²)

Method	k'_{obs} (h ⁻¹)	R^2
Photocatalysis	0.0259	0.967
Electro-oxidation	0.0282	0.910
Photoelectrocatalysis	0.0765	0.947

Table 2
Reduction of the total organic carbon content

Process	TOC reduction (%)
Photocatalysis	20
Electro-oxidation	25
Photoelectrocatalysis	65

4-CP concentration of 10 mg/L; bias potential of 2.0 V; treatment time of 12 h.

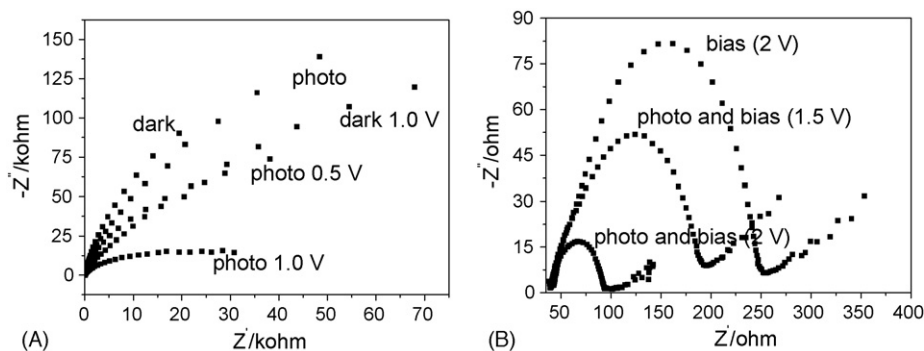


Fig. 4. Effects of photoirradiation and the bias potential on the EIS plane display of the degradation of 4-CP at Bi_2WO_6 nanoflake film electrode.

potential. It is clear that the size of the arc radius on the EIS Nyquist plot is reduced due to the photoirradiation. Furthermore, the sizes of the arc radius are reduced by applying the applied potential of 0.5 or 1.0 V. The size of the arc radius on the EIS Nyquist plot means the reaction rate occurring at electrode surface as suggested by Liu and Leng et al. [20,21]. These results confirmed that the applied bias potential increased the degradation rate of 4-CP. In addition, only one arc can be observed on the Nyquist plot, which suggested that the electro-oxidation, photocatalysis, and PEC reaction appears to be a simple electrode process [20].

However, as shown in Fig. 4, the sizes of the arc radius are largely reduced under application of 1.5 and 2.0 V bias potential or under photoirradiation and applied bias potential of 1.5/2.0 V simultaneously. It is the smallest when the applied potential is 2.0 V under photoirradiation, which means an effective separation of photogenerated electron–hole pair and fast interfacial charge transfer to the electron donor/electron acceptor as suggested by Leng et al. [21]. Thus, 4-CP can be effectively degraded. Moreover, the Nyquist plot shapes are largely changed, which suggests that different reaction mechanisms are involved.

The cyclic voltammetry scan of the Bi_2WO_6 film in the 0.5 M Na_2SO_4 solution without 4-CP and with various concentration of 4-CP are presented in Fig. 5. At the bias

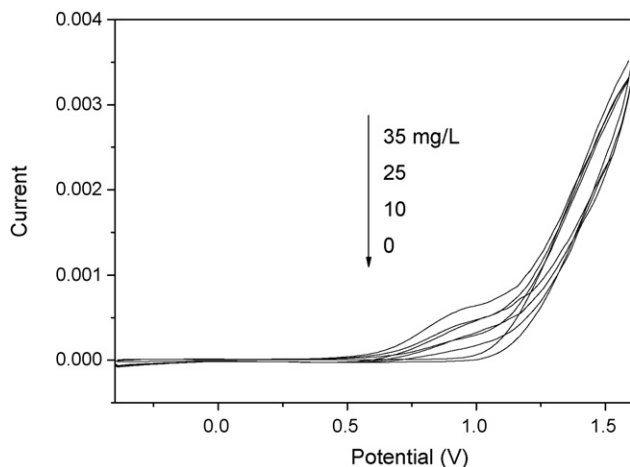


Fig. 5. Cyclic voltammetry scan curves of Bi_2WO_6 film electrode with various concentration of 4-CP in 0.5 M Na_2SO_4 solution.

potential of around 1.5 V, the current densities increase with the concentration of 4-CP, which was attributed to the electro-oxidation of 4-CP. It can also be seen that the oxygen evolution occurs at the anode. With the evolution of oxygen, the active species can be formed, which are responsible for the electro-oxidation of 4-CP. Moreover, the O_2 generated at the electrode surface by electro-oxidation of water acts as an acceptor of electrons, and promotes 4-CP photocatalysis.

Furthermore, XPS analysis as shown in Fig. 6 indicated that the intensity of Bi and W for the film sample used in the PEC process (2.0 V) for 12 h decreased slightly. However, their intensities greatly decrease for the film sample used in electrochemical process at the same condition. The binding energy of O largely changed in comparison with that during the PEC process. Moreover, a certain amount of Cl is clearly observed. The electro-oxidation of phenol and chlorinated phenols can involve direct and indirect (e.g., OH mediated) pathway, which result in the formation of quinines, carboxylic acids, and polymeric reaction products. The first step in the electro-oxidation of phenol or chlorinated phenols is phenoxy radical formation: a species that can be further oxidized to form soluble products or can undergo radical–radical or radical–substrate coupling to form polymeric products [22]. The polymeric products tend to have low solubility in aqueous media and adsorb on electrode surfaces, passivating electrode from further reaction [23]. Thus, the electro-oxidation process was prohibited. For the PEC process, the photogenerated activate species could activate the surface of the electrode and promote the electro-oxidation of 4-CP. All of these factors are responsible for the synergetic effect in the PEC degradation of 4-CP.

3.3. Effect of external potential on the synergetic effect

The redox potential of 4-CP ($E_{4\text{-CP}}$) at the Bi_2WO_6 film electrode is determined as ca. 0.8 V in the present system as shown in Fig. 6. It is known that limited electrochemical degradation of 4-CP could take place when the applied potential is well below the redox of 4-CP. When the bias potential is higher than $E_{4\text{-CP}}$, electro-oxidation reaction may take place.

The effect of the bias potential on the PEC degradation rate of 4-CP was further investigated. As shown in Fig. 7, with the increase of external potential, degradation rate of 4-CP

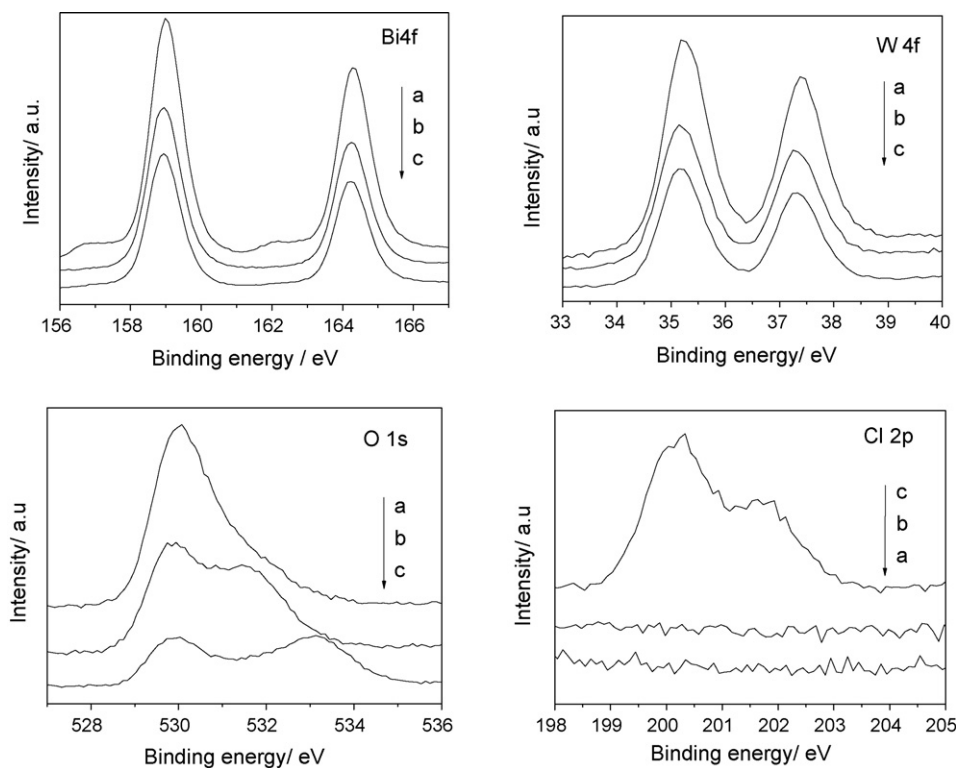


Fig. 6. XPS of Bi_2WO_6 nanoflake film (a) before and after (b) PEC reaction (2.0 V), and (c) electro-oxidation (2.0 V) in 0.5 M NaSO_4 solution with 10 mg/L 4-CP (12 h reaction, light intensity of 150 mW/cm^2).

increases gradually. The influence of applied bias potential on 4-CP degradation was more significant at higher potential than at lower potential. The application of potentials greater than the Bi_2WO_6 flat band potential across a photoelectrode increases the concentration of photogenerated holes or hydroxyl radicals on the surface by decreasing the rate of recombination of photogenerated holes and electrons. As a result, as the potential increases, the rate of 4-CP degradation increases, until most of the photogenerated electrons are

removed either by the electric field or by reaction with dissolved oxygen. Further increase of the applied potential beyond the redox potential of 4-CP improves the degradation largely. In this case, the degradation of 4-CP was carried out by the combined electro-oxidation and photocatalysis simultaneously. However, at the bias potential greater than 2.0 V, the synergetic effect decreases gradually. The similar phenomenon was observed in our previous work [24], and the explanation has been presented in details.

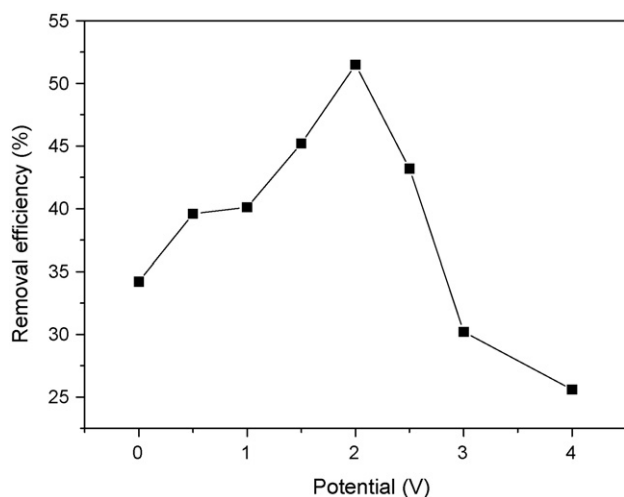


Fig. 7. The effect of the bias potential on 4-CP removal efficiency with initial concentration of 10 mg/L, reaction time = 8 h.

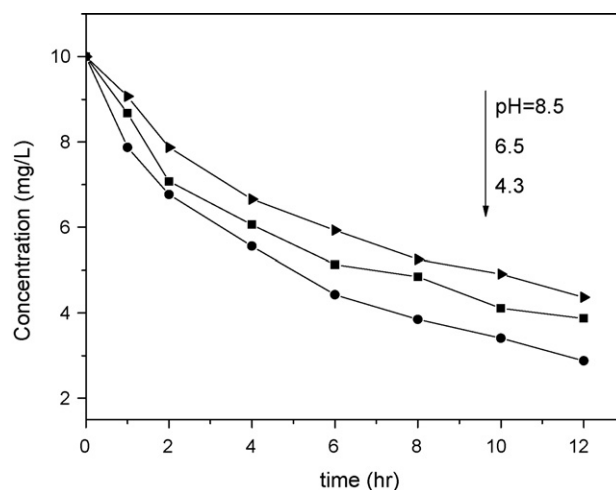


Fig. 8. The effect of pH on 4-CP removal efficiency with initial concentration of 10 mg/L.

3.4. Effect of pH on the synergetic degradation of 4-CP

The dependence of 4-CP PEC degradation rate on the pH values of the solution was examined with the constant bias potential of 2.0 V. As shown in Fig. 8, 4-CP is degraded faster in acidic solution than that in alkaline solution. Li et al. observed similar phenomenon from the electrochemical assisted photocatalytic degradation of humic acid [25]. However, Hepel and Luo reported reversed pH dependence for a diazo degradation [26]. As Hepel stated that the pH of solutions can influence the process through the following process: (a) the semiconductor flat-band potential variation, (b) adsorption isotherm of electroactive species (the adsorption of electroactive species is governed by Langmuir adsorption equilibrium equation), and (c) photoelectrochemical oxidation of water and OH⁻ ion competing with other reactants able to form powerful oxidants on irradiation. It indicated that the PEC degradation was highly affected by physical and chemical properties of the tested compound. At alkaline condition, 4-CP is ionized with negative charges, and becomes more water-soluble. However, at acidic condition, 4-CP remains in molecular form with more hydrophobic property. Thus, large amount of 4-CP will absorb onto the surface of Bi₂WO₆ film, which is beneficial to its PEC degradation.

3.5. Stability of the Bi₂WO₆ nanoflake film electrode

The surface texture of the Bi₂WO₆ film after PEC reaction for 12 h was shown in Fig. S1 (shown in supporting information), no noticeable change is observed in comparison with that of the original film (Fig. 2(A)). Furthermore, the film was analyzed by the Raman spectroscopy. As shown in Fig. S2, no noticeable difference is observed compared with the film before the PEC reaction, indicating the stability of the Bi₂WO₆ film during the PEC process. The stability of the Bi₂WO₆ film electrode was further investigated by repeating the 4-CP PEC degradation experiments at the bias potential of 2.0 V for 8 h for five times. The degradation efficiencies were ca. 59% in all the cases with the relative standard deviation of 4.2%, indicating the stability of the Bi₂WO₆ nanoflake film. It is considered that the observed chemical stability led to the stable catalytic activities of the Bi₂WO₆ film electrode.

4. Conclusions

The experimental results demonstrated that 4-CP could be degraded by the Bi₂WO₆ nanoflake film under visible light irradiation. The bias potential with various values applied to the Bi₂WO₆ film electrode increase the degradation efficiency of 4-CP. The bias potential below 0.8 V promotes the separation of electron and holes, leading to the increase of degradation rate of 4-CP. At the potential higher than 0.8 V, combined electro-oxidation and photocatalysis lead to the synergetic degradation of 4-CP. Moreover, it reaches the largest at the bias potential of 2 V. In this PEC process, 4-CP can also be efficiently mineralized. The produced active species produced in the

photocatalytic process activate the electrode surface and promote the electro-oxidation of 4-CP; the applied bias potential promote the separation of electrons and holes; the O₂ generated during the electro-oxidation process can act as electron scavengers. All of these factors are responsible for the synergetic effect.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2006.01.006.

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