

# Photoelectrochemical properties of thin $\text{Bi}_2\text{WO}_6$ films

Xu Zhao<sup>a,b</sup>, Yan Wu<sup>a</sup>, Wenqing Yao<sup>a</sup>, Yongfa Zhu<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

<sup>b</sup> State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Science, Chinese Academy of Science, Beijing 100085, P.R. China

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## Abstract

Thin  $\text{Bi}_2\text{WO}_6$  film prepared from an amorphous heteronuclear complex via dip-coating method is investigated as a visible light-driven photoelectrode material. Photoelectrochemical properties of the resultant film are investigated on the basis of linear sweep voltammetry and current–time curves, and conduction and valence band edges of the film electrode are determined from the photocurrent voltage response. Anodic photocurrent associated with the oxidation of water is obtained under visible light irradiation. Furthermore, the film as a photoanode can degrade rhodamine B (RhB) and methylene blue (MB) in aqueous solution under visible light irradiation slowly. The application of bias potential further improves the photodegradation efficiency of RhB and MB. Based on the analytic result of current–time curve, the stability of the film electrode is confirmed.

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**Keywords:**  $\text{Bi}_2\text{WO}_6$ ; Visible light; Photoelectrocatalysis; Thin film

## 1. Introduction

Semiconductor photocatalysis has gained more attention due to its potential application in environmental purification [1], solar energy [2], and splitting water for  $\text{H}_2$  production [3]. To obtain a more efficient utilization of solar irradiation, many photocatalysts responsive to visible light have been developed [4–6].

$\text{Bi}_2\text{WO}_6$  is the simplest members of the aurivillius family of structurally related oxides with the layer structure and interesting physical properties [7]. Kudo and Hiji firstly found that  $\text{Bi}_2\text{WO}_6$  had photocatalytic activities for  $\text{O}_2$  evolution under visible light irradiation [8]. Zou et al. revealed that  $\text{Bi}_2\text{WO}_6$  could degrade the organic compound under visible light [9]. Our recent work revealed that  $\text{Bi}_2\text{WO}_6$  prepared by amorphous complex method/hydrothermal method exhibited high photocatalytic activities towards degrading rhodamine B (RhB) compared with that of solid samples [10]. On the other hand, there has been an increasing interest in thin films of these semiconductor materials because they are suitable for optical, electrochemical, and electronic studies, as well as their potential electrochemical or

catalytic application [11–13]. As the electrochemical and photoelectrochemical properties of  $\text{Bi}_2\text{WO}_6$  film have not yet been examined in detail, those properties are investigated for the  $\text{Bi}_2\text{WO}_6$  film prepared from amorphous complex precursor via dip-coating method in the present study. Furthermore, the  $\text{Bi}_2\text{WO}_6$  film exhibited photocatalytic activities towards degrading of RhB and methylene blue (MB). Application of bias potentials to the  $\text{Bi}_2\text{WO}_6$  film efficiently improved the photodegradation efficiency of RhB/MB.

## 2. Experimental section

### 2.1. Fabrication and characterization of $\text{Bi}_2\text{WO}_6$ films

Indium-tin oxide (ITO) glass was employed as a substrate, which was purchased from China Southern Glass Co. Ltd., with a thickness of 1.1 mm and a sheet resistance of  $15 \Omega/\square$ . All other chemicals were analytical grade reagents and used without further purification. Deionized water was used throughout the experiment. Given amounts of  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$  were dissolved in deionized water and then were mixed with certain amounts of  $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Following, given amounts of Diethylenetriaminepent acetic acid (DTPA) was added into

\* Corresponding author. Tel.: +86 10 62783586; fax: +86 10 62787601.

E-mail address: [zhuyf@mail.tsinghua.edu.cn](mailto:zhuyf@mail.tsinghua.edu.cn) (Y. Zhu).

above suspension as a chelating agent for the metal ions. The molar ratio of metal ions to DTPA was 1:2. The solution was stirred for 2 h. A precursor was obtained by drying the above solution at 80 °C for 3 days. The precursor dissolved in aqueous solution was deposited onto an ITO glass via dip-coating method, and fired at 500 °C in air for 4 h.

Morphology of the resulting film was characterized by a JSM 6301 scanning microscope (SEM). Its crystal phase was determined using Laser Raman spectra (LRS) and X-ray diffraction (XRD). LRS was conducted on a Renishaw RM 1000 spectroscopy. The wavelength of the laser light was 514 nm. XRD was performed on the X-ray diffractometer (Japan, Rigaku, D/max-RB).

## 2.2. Photoelectrochemical experiments

The photoelectrochemical experiment was carried out using a PARSTAT 2273 Advanced electrochemical system (Princeton Applied Research) with a Lock-In amplifier (Model SR830 DSP, Stanford research systems). A collimated light beam from a 300 W xenon lamp was used for excitation of the electrode. A Bausch and Lomb high-intensity grating monochromator was introduced in the path of the excitation to carry out wavelength-dependent photocurrent measurements. For photoelectrochemical measurement, a Cu wire was attached to the Bi<sub>2</sub>WO<sub>6</sub> film with ITO substrate with epoxy resin to prevent current leakage. A quartz electrolytic cell was employed, filled with 20 mL of 0.5 mol/L Na<sub>2</sub>SO<sub>4</sub> solution. A Pt wire and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. Electrochemical impedance spectra (EIS) were recorded in the potentiostatic mode. Amplitude of the sinusoidal wave was 10 mV, and frequency range of the sinusoidal was from 100 kHz to 0.05 Hz. Photoelectrochemical degradation of RhB/MB was performed in a photoelectrochemical system as described by our previous work [14]. A 400 nm filter was used to filter the light from a 300 W xenon lamp (wavelength < 400 nm). Photoelectrochemical reaction employed the advance electrochemical system connected with a counter-electrode (Pt wire, 70 nm in length with a 0.4 mm diameter), a working electrode (the Bi<sub>2</sub>WO<sub>6</sub> film, active area of 14 cm<sup>2</sup>), and a SCE reference electrode. 0.5 mol/L Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as electrolyte solution. RhB/MB solution (100 mL) with an initial concentration of 5 mg/L was sampled periodically during the reaction to check the degree of decoloration, which was done by measuring the absorbance at 550/663 nm as a function of reaction time using a Shimadzu S 2600 UV spectrophotometer.

## 3. Results and discussion

### 3.1. Characterization of Bi<sub>2</sub>WO<sub>6</sub> film

Fig. 1(A) shows the LRS of Bi<sub>2</sub>WO<sub>6</sub> film coated for one, two and three times, respectively. All Raman spectra of the film were assigned to those of Bi<sub>2</sub>WO<sub>6</sub> in addition to the ITO substrate material. The Raman peak intensity increases with the coating time. Furthermore, the film coated for three times was analyzed by XRD. As shown in Fig. 1(B), all of the XRD diffraction peaks of

the film were assigned to those of Bi<sub>2</sub>WO<sub>6</sub> in addition to the ITO substrate material, which further confirmed the formation of Bi<sub>2</sub>WO<sub>6</sub> crystal phase. Fig. 2 shows the SEM images of the surface of the Bi<sub>2</sub>WO<sub>6</sub> films coated for various times. The film surface looked porous. The grain size tended to increase with the coating time, from ca. 40 to 70 nm, which, however, is the size of the secondary particles. The thicknesses of the films are estimated to be 14–30 nm for the film coated for one time by SEM observation. Thus, the thickness of the films prepared with three-times coating is estimated to be 42–90 nm. The Bi<sub>2</sub>WO<sub>6</sub> film was not removed by hard scratch with a Teflon plate, suggesting a good adhesion property of the film due to the strong connection between particles.

### 3.2. Photoelectrochemical studies of the thin films

Incident photo-to-current conversion efficiency (IPCE) defined as the number of electrons collected per incident photon, was evaluated from short circuit photocurrent ( $I_{sc}$ ) measurements at different wavelengths ( $\lambda$ ) and using the following expression (Eq. (1)) [15]:

$$IPCE\% = \frac{[1240 \times I_{sc}(\text{mA}/\text{cm}^2)]}{[\lambda(\text{nm}) \times I_{inc}(\text{mW}/\text{cm}^2)]} \times 100 \quad (1)$$

where  $I_{inc}$  is the incident light intensity. The constant “1240” is the conversion rate of photon energy to electrochemical current

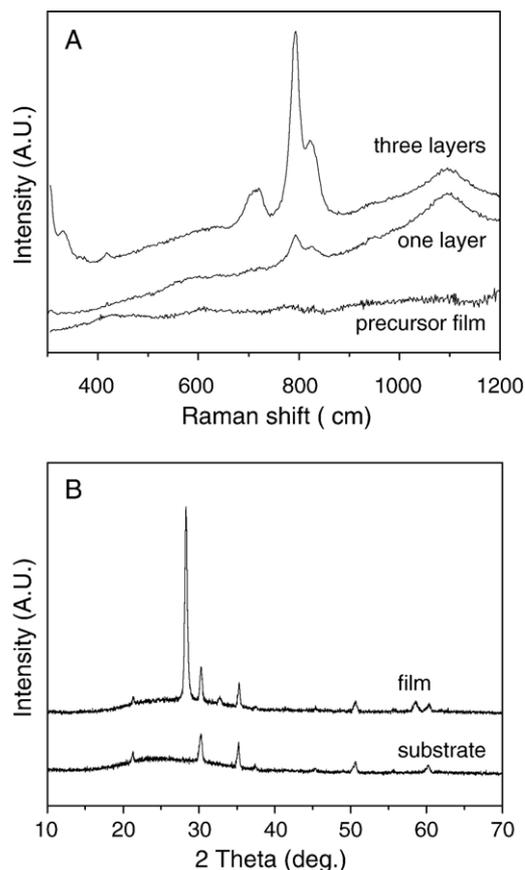


Fig. 1. (A) LRS of Bi<sub>2</sub>WO<sub>6</sub> film coated for one, two, and three times. (B) XRD patterns of Bi<sub>2</sub>WO<sub>6</sub> film coated for three times and Bi<sub>2</sub>WO<sub>6</sub> powder.

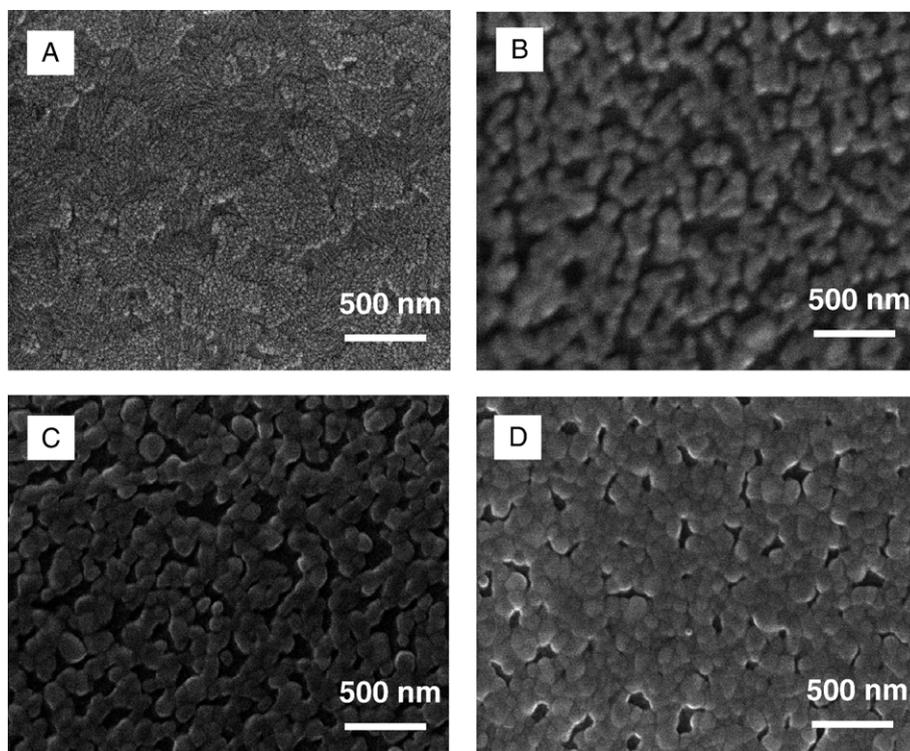


Fig. 2. SEM images of precursor film (A) and film calcined at 500 °C via one (B), two (C), and three times (D) coating, scale bar=1  $\mu\text{m}$ .

used to determine the IPCE value. As shown in Fig. 3, IPCE value of  $\text{Bi}_2\text{WO}_6$  film was in the following order: two times > three times > one time. Moreover, the IPCE value of  $\text{Bi}_2\text{WO}_6$  film coated for two times starts to increase near 420 nm. It can reach 1.2% at 330 nm.

As shown in Fig. 4, the overall charge-transfer resistance of the film coated for two times appears to be smaller compared with that of the film samples coated for three or one time. On one hand, with the increase in coating times for the  $\text{Bi}_2\text{WO}_6$  film, the large amount of  $\text{Bi}_2\text{WO}_6$  particles may lead to the high photocurrent generation. On the other hand, the size of the particles increased with the coating time as observed by the SEM results. The relatively large grain size and the nature of the

interparticle contacts can lead to the decrease of the photocurrent.

Fig. 5 shows the current–potential curves of the  $\text{Bi}_2\text{WO}_6$  film coated for two times in the 0.5 M  $\text{Na}_2\text{SO}_4$  solutions where the difference in current measured in light (the solid line) and dark (the broken line) is regarded as the photocurrent. The dark current density at  $V=1.0$  V (vs. SCE) is c.a. 0.0010  $\text{mA}/\text{cm}^2$ , and the photocurrent density at  $V=1.0$  V (vs. SCE) is ca. 0.0025  $\text{mA}/\text{cm}^2$ . The curve of the dark current density intersects with that of the photocurrent density at  $V=-0.11$  V. It is known that the contact between ITO conductive electrode and the oxide semiconductor film is generally ohmic [15]. Thus, from Fig. 3,

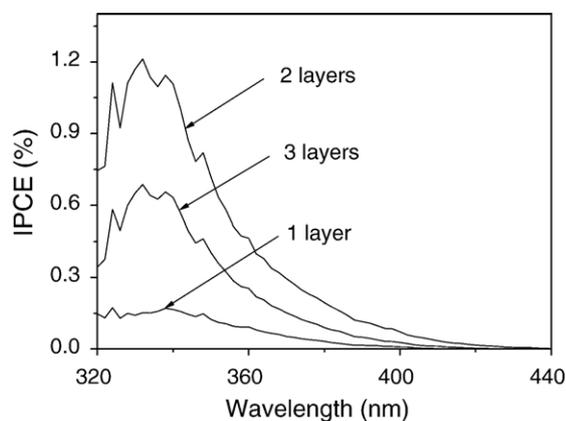


Fig. 3. Action spectra of photocurrent generated on the  $\text{Bi}_2\text{WO}_6$  film coated one, two, and three times in 0.5 M  $\text{Na}_2\text{SO}_4$  solution at various potentials under monochromatic light irradiation.

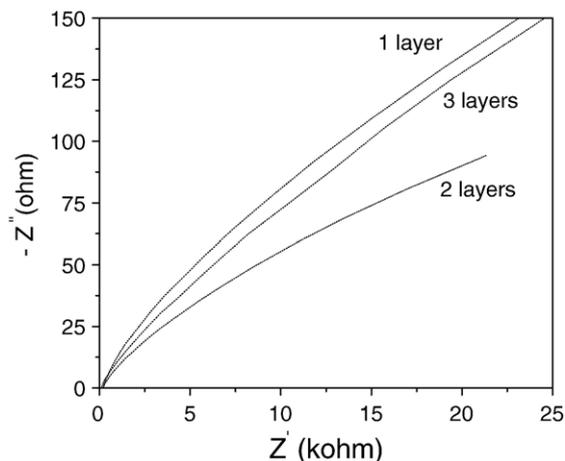


Fig. 4. EIS plane display of the  $\text{Bi}_2\text{WO}_6$  film samples coated one, two and three times (the counter electrode was a Pt wire, and the electrolyte was a 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution.)

the flat-band potential of the  $\text{Bi}_2\text{WO}_6$  film can be roughly estimated as  $-0.11$  V vs. SCE. It was found that the potential at the bottom of most n-type oxide semiconductors is ca.  $0.10$ – $0.30$  eV more negative than the Fermi level [16–18]. For the  $\text{Bi}_2\text{WO}_6$  film, the difference between the potential at the bottom of conduction band and the Fermi level is ca.  $-0.20$  eV. So, it is reasonably suggested that the bottom of conduction band was ca.  $-0.31$  V. The band gap of  $\text{Bi}_2\text{WO}_6$  powder prepared from the amorphous heteronuclear complex calcined at  $500$  °C for 4 h was ca.  $2.75$  eV as described in the literature [16]. Thus, the potential at the top of the valence band should be ca.  $2.44$  V.

### 3.3. Electrochemically assisted photocatalytic degradation of RhB/MB

It is confirmed that  $\text{Bi}_2\text{WO}_6$  powder can photocatalytically degrade RhB in aqueous solution in our previous study [19,20]. Thus, the  $\text{Bi}_2\text{WO}_6$  film was tested to photocatalytically degrade RhB. Because the  $\text{Bi}_2\text{WO}_6$  film coated for two times exhibits high photocurrent response, it was selected to photocatalytically degrade RhB. As shown in Fig. 6, there was no change in the solution concentration of RhB due to the specific adsorption on the surface of the reactor,  $\text{Bi}_2\text{WO}_6$  film during a 12-h period. This does not imply that RhB is not adsorbed by these surfaces, but rather that there is no sufficient surface area to produce any change in RhB concentrations over this time period. Furthermore, under visible light irradiation, degradation of RhB occurs slightly in the absence of  $\text{Bi}_2\text{WO}_6$  film within 12 h. In contrast, 53% RhB was degraded in the presence of  $\text{Bi}_2\text{WO}_6$  film after reaction for 12 h. These results indicate the photocatalytic activities of  $\text{Bi}_2\text{WO}_6$  film towards degrading RhB in aqueous solution.

To improve the photodegradation efficiency of RhB, the applied bias potentials with values of 0, 0.3, and 0.6 V were applied. The amount of degradation increased when an external potential was applied to the electrode. We believe this to be due mostly to a decrease in the electron-hole recombination rate. When various potentials (from 0 to 0.3 and 0.6 V vs. SCE) are applied to the  $\text{Bi}_2\text{WO}_6$  film, the amount of increase in degradation for each applied potential was not significant. These results suggest that a 0 V potential (vs. SCE) provides

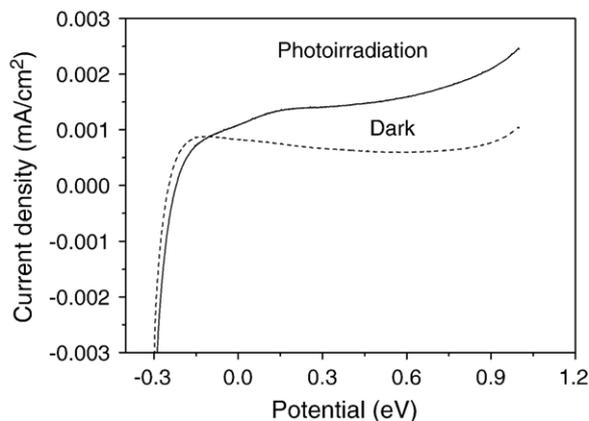


Fig. 5. Current–potential curves of the  $\text{Bi}_2\text{WO}_6$  film coated two times ( $0.5$  M  $\text{Na}_2\text{SO}_4$  solution, scan rate =  $10$  mV  $\text{s}^{-1}$ ,  $\lambda > 400$  nm).

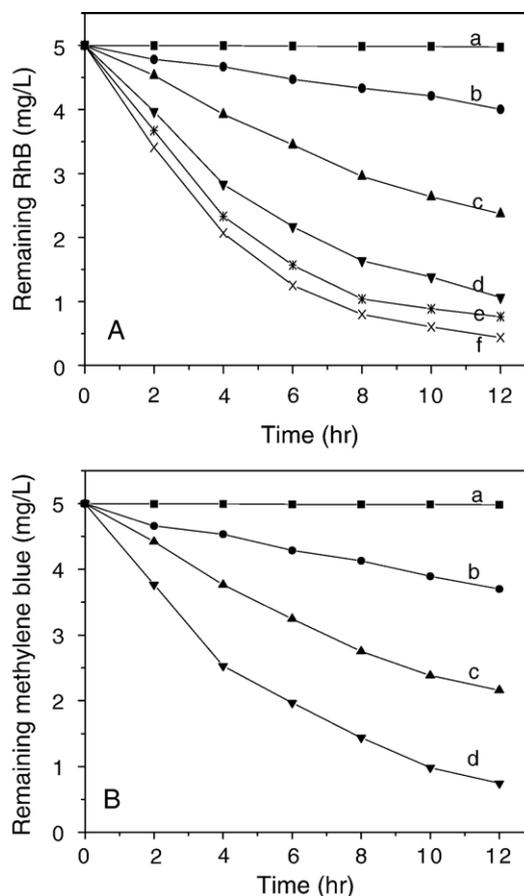


Fig. 6. Concentration variation of RhB (A) and methylene blue (B) under various conditions. (a) no light and no  $\text{Bi}_2\text{WO}_6$  film; (b) direct photolysis; (c) photocatalysis ( $\text{Bi}_2\text{WO}_6$  film); (d) electrochemically assisted photocatalysis (0 V); (e) electrochemically assisted photocatalysis (0.3 V); electrochemically assisted photocatalysis (0.6 V) ( $0.5$  M  $\text{Na}_2\text{SO}_4$  solution,  $\lambda > 400$  nm).

enough band bending to withdraw electrons to the counter electrode and implies that the flat-band potential of the  $\text{Bi}_2\text{WO}_6$  film in this experimental condition is below 0 V (SCE). This behavior is similar to the results of others [21,22], which indicated that the effect of applying an electrical bias between

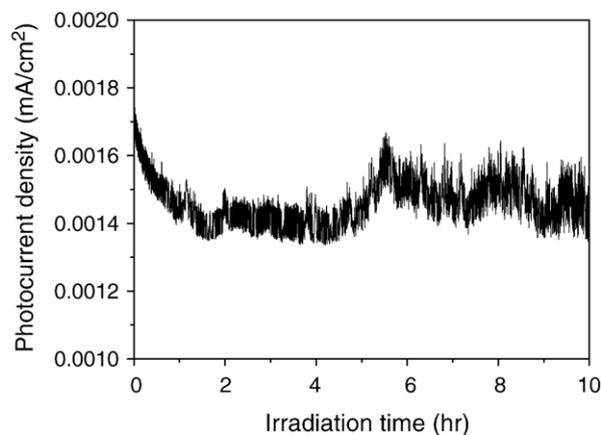


Fig. 7. Current–time curve of the  $\text{Bi}_2\text{WO}_6$  film coated two times with an applied bias potential of 0.5 V under visible light irradiation ( $\lambda > 400$  nm).

the electrodes is more important than the difference of the voltage applied. In order to further confirm the photocatalytic activities of the  $\text{Bi}_2\text{WO}_6$  film, degradation of MB is also studied. As shown in Fig. 6(B), degradation rate of MB in the presence of  $\text{Bi}_2\text{WO}_6$  film is higher than that in the absence of  $\text{Bi}_2\text{WO}_6$  film under visible light irradiation. Moreover, the applied bias potential (0 V) increases the degradation rate of MB.

In photoelectrocatalytic reactions, the reduction reaction on the counter electrode may be the reduction of oxygen. Further studies to detect the intermediates and reaction mechanisms of RhB/MB degradation by photoelectrocatalysis are currently in progress. In addition, it can be seen from Fig. 7 that nearly unchanged photocurrent density generated from the  $\text{Bi}_2\text{WO}_6$  film under visible light irradiation for 10 h in the 0.5 M  $\text{Na}_2\text{SO}_4$  solution without the presence of RhB, which confirmed the stability of the  $\text{Bi}_2\text{WO}_6$  film electrode.

#### 4. Conclusions

The electrochemical behavior of thin  $\text{Bi}_2\text{WO}_6$  films was investigated as an n-type semiconductor electrode. An anodic photoinduced ( $\lambda > 400$  nm) current associated with oxidation of water appeared under the application of a potential bias. Action spectra suggested that the observed photocurrent occurred via a band gap transition. The thin  $\text{Bi}_2\text{WO}_6$  films exhibit photocatalytic activities towards degradation of RhB/MB under visible light irradiation ( $\lambda > 400$  nm). Furthermore, application of bias potential can enhance the photocatalytic degradation of RhB/MB efficiently. Moreover, the thin  $\text{Bi}_2\text{WO}_6$  films were stable. Thus,  $\text{Bi}_2\text{WO}_6$  film has been demonstrated to be a suitable electrode material for visible light-driven photochemical cells. Many parts of the fabrication have not yet been optimized and therefore we expect that the efficiency can be improved.

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