

# A New Method of Enhancing Photoelectrochemical Characteristics of Bi/Bi<sub>2</sub>O<sub>3</sub> Electrode for Hydrogen Generation via Water Splitting

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The Bi<sub>2</sub>O<sub>3</sub> film was deposited on FTO substrate by the magnetron sputtering method. Then the Bi/Bi<sub>2</sub>O<sub>3</sub> film was prepared by a simple electrolysis treatment of Bi<sub>2</sub>O<sub>3</sub> film in Na<sub>2</sub>SO<sub>3</sub> aqueous solution. In contrast to Bi<sub>2</sub>O<sub>3</sub> film, Bi/Bi<sub>2</sub>O<sub>3</sub> film showed a stronger visible light absorption. The characterization of photoelectrochemical properties of the Bi/Bi<sub>2</sub>O<sub>3</sub> film showed that, both under UV-vis light and visible light irradiation, the photocurrent density was found to be in milliampere range, which is much higher than that of the Bi<sub>2</sub>O<sub>3</sub> film. Under visible light irradiation, generation of hydrogen was observed in the presence of Bi/Bi<sub>2</sub>O<sub>3</sub> composite electrode with the assist of an external bias voltage, while no hydrogen was produced with Bi<sub>2</sub>O<sub>3</sub> photoelectrode under the same condition. Furthermore, the proposed mechanism of enhancement of hydrogen evolution activity by Bi modification was discussed from the view of the energy band structure.

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**Keywords:** Bi<sub>2</sub>O<sub>3</sub>, Photoelectrocatalysis, Hydrogen generation, Electrolysis, Energy band structure

## 1. INTRODUCTION

There is no doubt that hydrogen, a new source of clean and renewable energy, has the potential to minimize our dependence on fossil fuel and therefore reduce environmental pollution[1]. Photoelectrochemical (PEC) water splitting is a promising and environmentally friendly method for hydrogen generation. Since the debut of this concept in 1972[2], much attention has been paid to exploring suitable and high efficient photoelectrodes[3, 4]. So far, some visible light driven metal-oxides and sulfides[5, 6] have been used for hydrogen evolution from water.

$\text{Bi}_2\text{O}_3$  is an important metal-oxide semiconductor with a band gap of 2.8eV[7], and has attracted much attention for organic degradation[8,9] under visible light irradiation. As to hydrogen evolution material, suitable band edge position to enable reduction of water was required for efficient hydrogen generation[10, 11]. Nevertheless, as the conduction and valence band edges of  $\text{Bi}_2\text{O}_3$  were +0.33eV and +3.13eV[12] (with respect to NHE) respectively, it cannot be used directly as hydrogen evolution materials. One way to generate hydrogen is to raise the conduction band bottom of the photocatalysts by doping other elements in the photocatalyst. For example, Cu(II) ion was doped in  $\gamma\text{-Bi}_2\text{O}_3$ [13]. Alternatively, an external voltage can be applied to assist the reduction reaction, for it can adjust the band edges of the photoelectrode. This method has been applied to a variety of materials to realize the photocatalytic hydrogen production[14, 15].

In this study, the  $\text{Bi}_2\text{O}_3$  film was deposited on FTO substrate by the magnetron sputtering method and the Bi/ $\text{Bi}_2\text{O}_3$  composite film was prepared by electrolysis treatment of  $\text{Bi}_2\text{O}_3$  film. With the assist of an external bias voltage, Bi/ $\text{Bi}_2\text{O}_3$  photoelectrode showed hydrogen evolution ability under visible light irradiation while there was no hydrogen evolution for the  $\text{Bi}_2\text{O}_3$  electrode under the same conditions.

## 2. EXPERIMENTAL

The photocathode substrate is F-doped  $\text{SnO}_2$  (FTO) purchased from Nippon Sheet Glass Co., Ltd., Japan.  $\text{Bi}_2\text{O}_3$  film was sputtered on the substrate using a 60 mm diameter metal Bi target (of purity 99.99%) by a direct current (DC) reactive magnetron sputtering system in a mixture of argon (Ar) and oxygen ( $\text{O}_2$ ) at room temperature. The total pressure was 1 Pa, the Ar and  $\text{O}_2$  flow rates were 80 SCCM (SCCM denotes cubic centimeters per minute) and 20 SCCM respectively and the sputtering power was 50 W. The sputtering time was 3 minutes and the  $\text{Bi}_2\text{O}_3$  deposition rate was about 120nm/min under the preparing conditions above. Then, to obtain good crystallinity, the  $\text{Bi}_2\text{O}_3$  film was annealed in air at 300<sup>o</sup>C for 2 hours. Afterwards, the  $\text{Bi}_2\text{O}_3$  film was treated by electrolyzation process which was accomplished in a three-electrode photoelectrochemical system (CHI660D, Shanghai Chen Hua Instrument Co., Ltd.). The working area is 4.2(3.5cm×1.2cm) cm<sup>2</sup>. A platinum (Pt) sheet (1cm×3cm) served as the counter, a saturated Ag/AgCl as the reference electrode, and the 0.2 M  $\text{Na}_2\text{SO}_3$  aqueous solutions as the electrolyte. The electroreduction reaction was carried out at 4V bias voltage versus Ag/AgCl electrode for 3min at a scan rate of 20mV/s under UV-vis light irradiation. The obtained Bi/ $\text{Bi}_2\text{O}_3$  film was dark grey.

UV-vis spectrophotometer (HITACHI UV-3010) was employed to characterize absorption spectra of the samples. The crystalline structure of the samples was determined by X-ray diffraction (XRD, Panalytical X'pert pro mpd) with a Cu  $K\alpha$  source and the morphologies were investigated by field-emission scanning electron microscope (FESEM, HITACHI S4800).

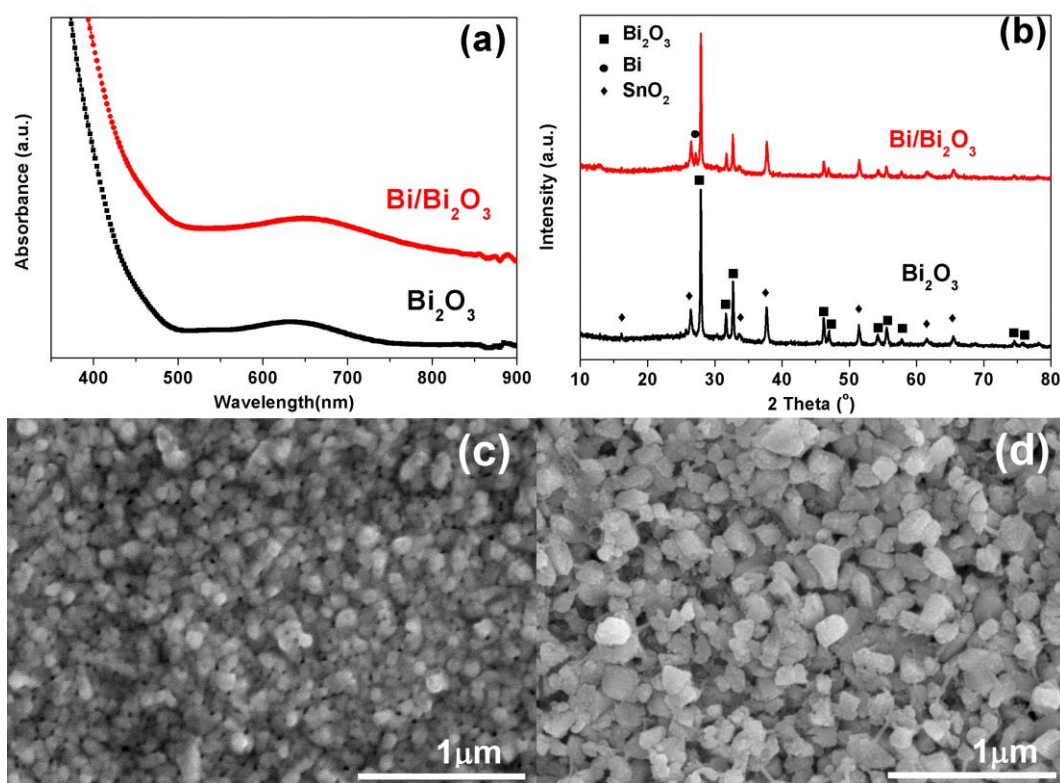
Photocurrent and hydrogen production measurements were carried out with the same system as above, including the same electrolyte, light irradiation, and the three-electrode system. Prior to the hydrogen evolution, the mixture was aerated with Ar for 5 min to remove the air in the water and headspace. A 300 W Xenon (Xe) lamp (PLS-SXE-300, Beijing perfectlight Technology Co., Ltd.),

positioned 50 cm away from the test tube, was used as the UV-visible light irradiation source. The intensity of the incident light was  $100 \text{ mW/cm}^2$ . The solution was kept at room temperature by cooling water. The amount of generated  $\text{H}_2$  was determined by a gas chromatograph (SP6900, Beijing Jingkeruida technology Co., Ltd.).

### 3. RESULTS AND DISCUSSION

The absorption spectra of  $\text{Bi}_2\text{O}_3$  and  $\text{Bi/Bi}_2\text{O}_3$  are presented in Figure 1(a). It can be seen that, in contrast to  $\text{Bi}_2\text{O}_3$  film,  $\text{Bi/Bi}_2\text{O}_3$  has a stronger absorption in the visible region and that electrolysis treatment triggers a redshift. Moreover, a noticeable color change was observed when the  $\text{Bi}_2\text{O}_3$  film turned to  $\text{Bi/Bi}_2\text{O}_3$  film. The former is yellow, while the latter is dark grey. This may indicate the formation of Bi in the  $\text{Bi}_2\text{O}_3$  film during electrolysis process.

Figure 1(b) shows the XRD patterns of  $\text{Bi}_2\text{O}_3$  and  $\text{Bi/Bi}_2\text{O}_3$  films. The two samples both exhibited the typical pattern of the tetragonal structure of  $\beta\text{-Bi}_2\text{O}_3$  (JCPDS 27-0050), which is marked with squares. The peaks associated with  $\text{SnO}_2$  (JCPDS 46-1088), component of FTO substrate, were also observed and marked with diamonds. For the  $\text{Bi/Bi}_2\text{O}_3$  films, the peak centered at  $27.1^\circ$  (marked with circle) is assigned to the metallic Bi (JCPDS 85-1329).



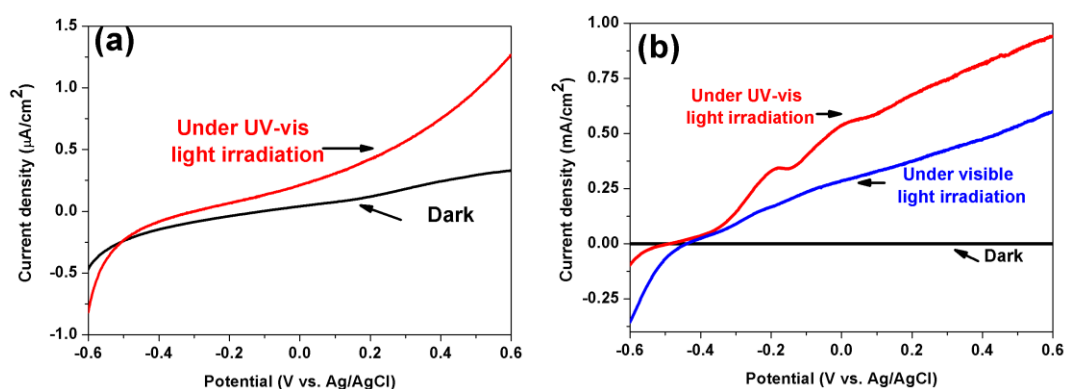
**Figure 1.** Absorption spectra (a), XRD patterns (b) of  $\text{Bi}_2\text{O}_3$  and  $\text{Bi/Bi}_2\text{O}_3$  films, FESEM images of  $\text{Bi}_2\text{O}_3$  film (c) and  $\text{Bi/Bi}_2\text{O}_3$  film (d).

Beyond that, no characteristic peaks of impurities and other phases are observed. As the  $\text{SO}_3^{2-}$  was reducing ion, when an additional bias voltage of 4V versus Ag/AgCl electrode was applied, the  $\text{SO}_3^{2-}$  ions gathered at the surface of the anode and react with  $\text{Bi}_2\text{O}_3$ , generating  $\text{SO}_4^{2-}$  and metallic Bi.

Figure 1(c) shows the morphology of  $\text{Bi}_2\text{O}_3$  film which is uneven, and the grain size of  $\text{Bi}_2\text{O}_3$  is ranged from 50 to 200 nm. The  $\text{Bi}_2\text{O}_3$  grains are peanut-like shaped, which is quite different from ones prepared on the quartz substrate[16]. As presented in Figure 1(d), the surface morphology of the Bi/ $\text{Bi}_2\text{O}_3$  film was loose and rough, which was mainly caused by the electrolysis treatment.

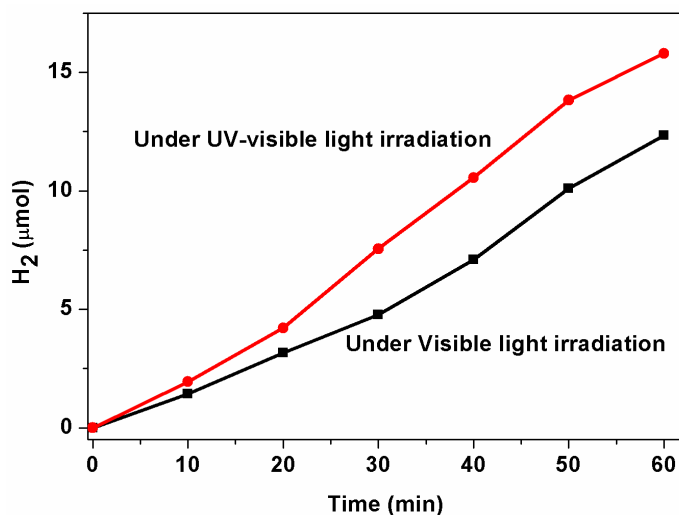
Additionally, it could not be overlooked that the choice of electrolyte is very important. We have conducted experiments with NaOH and  $\text{Na}_2\text{SO}_4$  aqueous solution as electrolyte, and also obtained the Bi/ $\text{Bi}_2\text{O}_3$  samples containing Bi. However, only the sample prepared in  $\text{Na}_2\text{SO}_3$  aqueous solution could produce hydrogen. Further investigation of the details and of the mechanism is ongoing.

The current densities measured as a function of bias voltage ( $I$ - $V$ ) for the  $\text{Bi}_2\text{O}_3$  photocathode in dark conditions and under light irradiation are shown in Figure 2(a). Compared with the current density measured in the dark, it was higher under light irradiation, indicating that the  $\text{Bi}_2\text{O}_3$  electrode can respond to light. The  $I$ - $V$  curves of Bi/ $\text{Bi}_2\text{O}_3$  electrode are shown in Figure 2(b). The current density measured for the Bi/ $\text{Bi}_2\text{O}_3$  electrode in dark is in microampere range, while the current density both under UV-vis light and visible light irradiation is in milliampere range, which is much higher than that of  $\text{Bi}_2\text{O}_3$  film. It implies that the Bi/ $\text{Bi}_2\text{O}_3$  electrode may have a superior ability for hydrogen generation. That the current density of the Bi/ $\text{Bi}_2\text{O}_3$  under visible light irradiation is lower than that of under UV-vis light irradiation, is mainly attributed to the lower light intensity in the presence of the 420 nm cutoff filters.



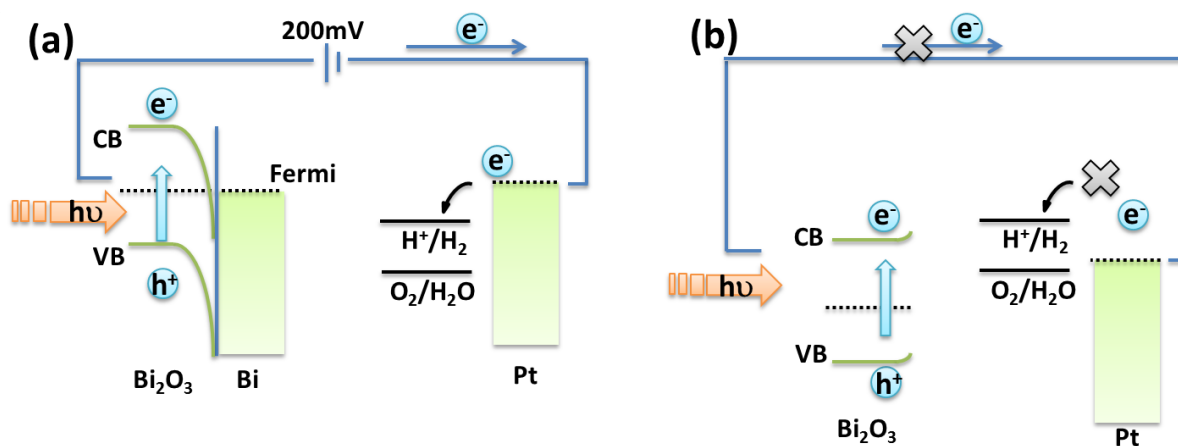
**Figure 2.** Current densities as a function of bias voltage for  $\text{Bi}_2\text{O}_3$  film in dark and under light irradiation (a), and Bi/ $\text{Bi}_2\text{O}_3$  film in dark, under UV-vis and visible light irradiation(b).

Figure 3 shows the variation of hydrogen evolution amount with Bi/ $\text{Bi}_2\text{O}_3$  electrode as a function of time within 1 hour with an additional bias voltage of 200mV versus Ag/AgCl electrode in 0.2M  $\text{Na}_2\text{SO}_3$  aqueous solution under UV-visible light and visible light irradiation. Under UV-vis light irradiation, 15.8 $\mu\text{mol}$  of hydrogen was produced at the reaction time of 60min.



**Figure 3.** Hydrogen production amount of the Bi/Bi<sub>2</sub>O<sub>3</sub> electrode under light irradiation with an additional bias voltage of 200mV.

A schematic representation with energy diagrams of the Bi/Bi<sub>2</sub>O<sub>3</sub> photoelectrode is shown in Figure 4(a). It is well known that the work function of Bi is 4.22eV[17], smaller than that of Bi<sub>2</sub>O<sub>3</sub> (6.23eV) [12], indicating that the electrons will transfer from Bi to the conduction band (CB) of Bi<sub>2</sub>O<sub>3</sub> to achieve the Fermi level balance of the two materials. This means that the surface modification of metallic Bi would make the energy level of Bi<sub>2</sub>O<sub>3</sub> shift upward. When the Bi/Bi<sub>2</sub>O<sub>3</sub> composite film was irradiated by the light, the electrons in the valance band (VB) of Bi/Bi<sub>2</sub>O<sub>3</sub> became excited to the conduction band (CB). In order to keep the Fermi equilibrium, some of these excited electrons migrated to Pt electrode and left holes behind in the valance band of Bi<sub>2</sub>O<sub>3</sub>. Thus the Fermi level of the Pt moved upward and was slightly above the energy level of the proton reduction (H<sup>+</sup>/H<sub>2</sub>). When a 200mV external bias was applied, a further shift upward of the Fermi level of Pt electrode was obtained, which assisted overcoming the over potential. Hence the hydrogen generated continuously.



**Figure 4.** Schematic representation with energy diagrams of the Bi/Bi<sub>2</sub>O<sub>3</sub> electrode (a) and Bi<sub>2</sub>O<sub>3</sub> electrode (b).

On the contrary, there was no hydrogen generated with the Bi<sub>2</sub>O<sub>3</sub> electrode under the same conditions. For the single Bi<sub>2</sub>O<sub>3</sub> film, the proposed energy level schematic is shown in Figure 4(b). It is indicated that the 200mV voltage is too small to elevate the Fermi level of the Pt cathode to be above the energy level of the proton reduction (H<sup>+</sup>/H<sub>2</sub>).

The Bi/Bi<sub>2</sub>O<sub>3</sub> electrode is a potential material for hydrogen production. The H<sub>2</sub> generation rate slightly decreased when UV-light was filtered out, because of the lower light intensity in the presence of the filters.

#### 4. CONCLUSIONS

The Bi<sub>2</sub>O<sub>3</sub> thin film was prepared on FTO substrates by reactive direct current magnetron sputtering and then treated by electrolysis process to obtain the Bi/Bi<sub>2</sub>O<sub>3</sub> composite film. The absorbance to visible light of Bi/Bi<sub>2</sub>O<sub>3</sub> film was significantly higher than that of Bi<sub>2</sub>O<sub>3</sub> film. Under light irradiation, the current density of Bi/Bi<sub>2</sub>O<sub>3</sub> electrode was in milliamperere range, much higher than that of Bi<sub>2</sub>O<sub>3</sub> electrode. When the reaction time was 60min, 15.8μmol of hydrogen was produced under UV-vis light irradiation with a relative small additional bias voltage of 200mV versus Ag/AgCl electrode. On the contrary, there was no hydrogen evolution for the Bi<sub>2</sub>O<sub>3</sub> electrode under the same conditions. It is mainly due to the upward shift of the anodic energy leading to hydrogen evolution in the cathode compartment.

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