



SACT 2016

# Improved the charge transfer for highly efficient photoelectrochemical water oxidation: the case of $\text{WO}_3$ and $\text{BiVO}_4$

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## Abstract

The tungsten oxide ( $\text{WO}_3$ ) and bismuth vanadate ( $\text{BiVO}_4$ ) thin films were successfully deposited on indium doped tin oxide (ITO) by dc reactive magnetron sputtering and spin coating technique, respectively. The physical structural were characterized by field-emission scanning electron microscopy (FE-SEM) and X-ray diffractometry (XRD). The photoelectrocatalytic water oxidation of ITO/ $\text{WO}_3$  and ITO/ $\text{WO}_3$ / $\text{BiVO}_4$  electrodes were compared under visible light irradiation. The double layer of  $\text{WO}_3$ / $\text{BiVO}_4$  thin film are present the enhancing efficiency of water oxidation comparing with single  $\text{WO}_3$  layer. The results showed the improvement of charge transfer by using heterojunction nanostructure semiconductor electrode in order to suppress the recombination effect and enhance an efficient of water splitting.

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Selection and/or Peer-review under responsibility of SACT 2016.

*Keywords:* Charge transfer; Photoelectrochemical; Water oxidation; Tungsten oxide; Bismuth vanadate

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## 1. Introduction

A photoelectrocatalytic water splitting has been usually used by semiconductors as a photoelectrode. Therefore, a selections of semiconductors considering is very important for improve the photoelectrocatalytic activity. A tungsten oxide ( $\text{WO}_3$ ) has been investigated for water oxidation from water splitting under visible light irradiation [1-3]. To enhance the efficiency, which that designs of nanostructured  $\text{WO}_3$  [4-6] combined with the suitable

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semiconductor for used to enhance of charge transfer process [7-9]. Especially the combination of nanostructured morphology and suitable semiconductors as is interfacial heterojunction are an interesting topics to improve the high efficiency of water splitting.

This article describe the nanostructured  $\text{WO}_3$  by dc reactive deposition of sputtering technique [10] and combine with  $\text{BiVO}_4$  spin-coated [11] on indium doped tin oxide (ITO) substrate. The film morphology and crystalline structure of the film composition were studied by field-emission scanning electron microscopy (FE-SEM), X-ray diffractometry (XRD), respectively. The photoelectrocatalytic activity for water oxidation of fabricated electrode was studied by amperometry method under visible light irradiation. The comparison between pure and couple semiconductors were studied in order to confirm the charge transfer enhancement of heterojunction semiconductor.

## 2. Experiment

The 250 nm-thick tungsten oxide ( $\text{WO}_3$ ) thin films were deposited on silicon wafers and indium doped tin oxide (ITO) coated glass substrates ( $12\Omega/\square$ ) by dc reactive sputtering technique with a 3 inch-diameter tungsten (W) target (purity 99.995%). The distance from substrate to target and substrate rotation speed were fixed at 7 cm and 10 rpm, respectively. The substrate normal was positioned at an angle of 45 with respect to the vapor incident flux in order to obtain the optimal film uniformity. The discharge was generated at a constant dc power of 150 W. The chamber obtained a vacuum state by mechanical pump and a turbo pump vacuum with a base pressure of  $8.5 \times 10^{-6}$  mbar. After a based pressure, the W target were reactively sputtered in a mixture of 99.999% argon and 99.999% oxygen. The flow rate of the oxygen and argon were controlled with mass flow controller at 24 and 8 sccm, respectively. The bismuth vanadate ( $\text{BiVO}_4$ ) were prepared by spin coating technique which the condition of 1,000 rpm for 60 second after that repeated until the 5 layers. Fig. 1 shows schematic diagram of preparation double layer  $\text{WO}_3/\text{BiVO}_4$  thin film.

The physical morphology and film thickness of the  $\text{WO}_3$  and  $\text{BiVO}_4$  thin film were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700). The crystalline structure of the fabricated thin films were confirmed by X-ray diffractometer (TTRAX III-RIGAKU) with  $\text{Cu-K}\alpha_1$ , TTRAX III-RIGAKU. The  $\text{Cu-K}\alpha$  radiation was operated at 50 kV, 300 mA with a scanning speed of 2 $\theta$  per minute at a 2 $\theta$  step of 0.02°. The photoelectrocatalytic activity for water oxidation of fabricated electrodes were studied by amperometry in solution of 0.5 M sodium sulfate under visible light irradiation.

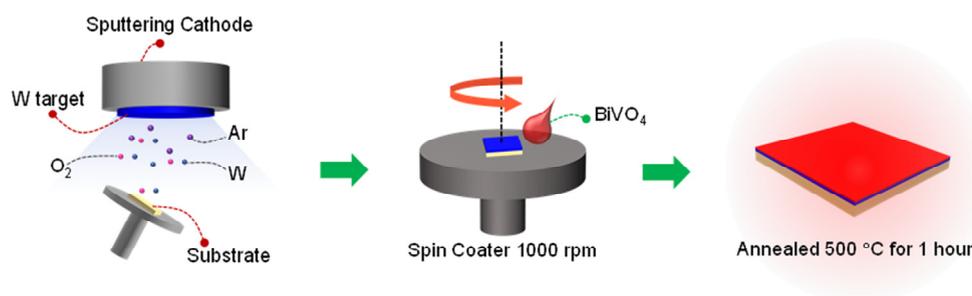


Fig. 1. schematic diagram of develop multilayer  $\text{WO}_3/\text{BiVO}_4$  thin film.

## 3. Results and discussion

### 3.1. Thin films morphology

The cross sections and surface to pology from the FESEM micrographs (Fig. 2(a)-(b)) showed dense morphology of  $\text{WO}_3$  film with the thickness layer of 250 nm prepared by the dc reactive magnetron sputtering technique. The total thickness of multilayer was increased to 330 nm after spin coated  $\text{BiVO}_4$  on  $\text{WO}_3$  thin film which showed the particles dispersed on the dense film of  $\text{WO}_3$  (Fig. 2(c)). Fig. 2(d) showed the surface roughness morphology of

WO<sub>3</sub> thin films was increased by the present of BiVO<sub>4</sub>. The results from the coated film demonstrated morphology improvement of dense WO<sub>3</sub> film by BiVO<sub>4</sub>, that would be suitable for water adsorption.

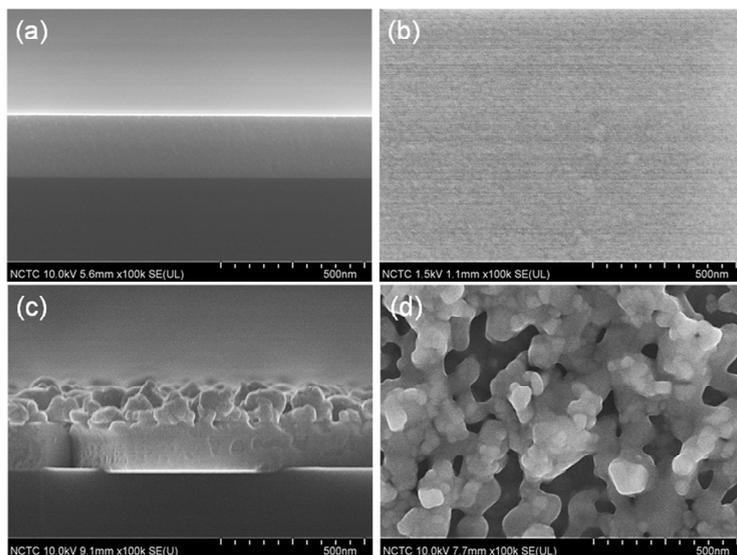


Fig. 2. Morphology of (a) cross sectional of WO<sub>3</sub>, (b) top view of WO<sub>3</sub>, (c) cross sectional of WO<sub>3</sub>/BiVO<sub>4</sub> after annealed and (d) top view of WO<sub>3</sub>/BiVO<sub>4</sub> after annealed on silicon wafers.

### 3.2. Crystalline structure

The XRD patterns of the annealed WO<sub>3</sub> and BiVO<sub>4</sub> deposited on silicon wafers were shown in Fig. 3. The results showed that the as-deposited WO<sub>3</sub> film were amorphous without observable crystallinity (Fig. 3(b)). After the sample was annealed at 500°C, the XRD patterns monoclinic (Fig. 3(c),(d)) [12]. Therefore, the XRD results confirmed the formation of the WO<sub>3</sub> and BiVO<sub>4</sub> materials on the substrates based on the proposed preparation process.

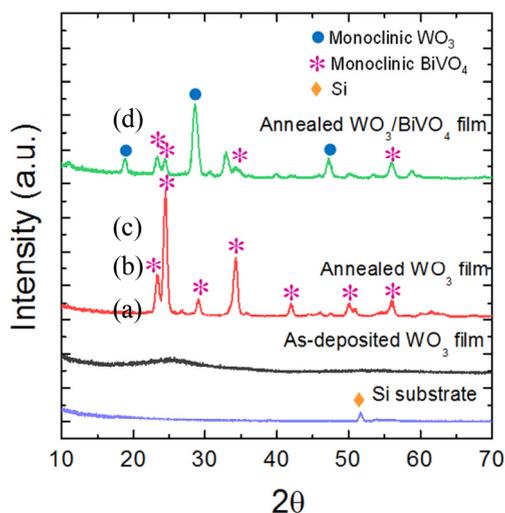


Fig. 3. The XRD patterns of (a) Silicon wafer, (b) WO<sub>3</sub> as-deposition, (c) WO<sub>3</sub> after annealed and (d) WO<sub>3</sub>/BiVO<sub>4</sub> after annealed at 500°C.

### 3.3. Photoelectrocatalytic properties

The amperometric method was used to study the photocurrent activities from water oxidation of ITO/WO<sub>3</sub>/BiVO<sub>4</sub> electrode in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution under visible light irradiation ( $\lambda > 420$  nm). Fig. 4 showed the photocurrent results of the prepared ITO/WO<sub>3</sub>/BiVO<sub>4</sub> sample in comparison with the ITO/WO<sub>3</sub> sample as a referent. The amperographs showed significant enhancement of the anodic photocurrent from the ITO/WO<sub>3</sub>/BiVO<sub>4</sub> electrodes. The results indicated that the combination of the BiVO<sub>4</sub> structures with the WO<sub>3</sub> thin films could greatly improve the photoelectrocatalytic activity for water oxidation of pure WO<sub>3</sub> due to the function of charge separation and roughness surface morphology improvement.

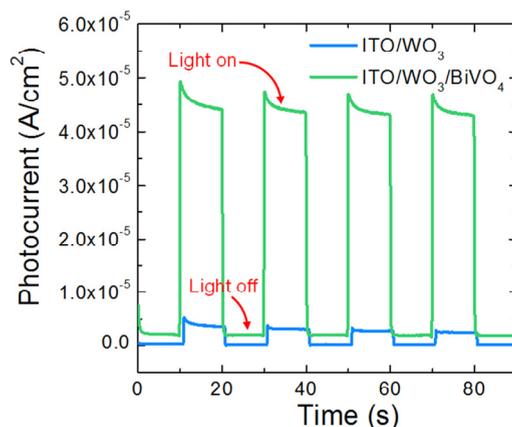


Fig. 4. Amperographs of ITO/WO<sub>3</sub> and ITO/WO<sub>3</sub>/BiVO<sub>4</sub> electrodes at 1.0 V vs. Ag/AgCl in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution under visible light irradiation.

We could demonstrate the fundamental technique to improve the photoelectrocatalytic activity for water oxidation by use the heterojunction of suitable couple semiconductor. Fig. 5 showed the schematic diagram of the charge transfer process at the heterojunction semiconductor ITO/WO<sub>3</sub>/BiVO<sub>4</sub> electrode under visible light irradiation. A combination of the composited WO<sub>3</sub> and BiVO<sub>4</sub> semiconductors would readily yield corresponding band energy level which helped generate electron transfer from the conduction band of WO<sub>3</sub> and BiVO<sub>4</sub> into the electrode. At the same time, the generated hole transfer from the valence band of WO<sub>3</sub> to that of BiVO<sub>4</sub> caused a number of holes occurred at electrode surface that high efficiency to oxidize the water to O<sub>2</sub> in solution [13].

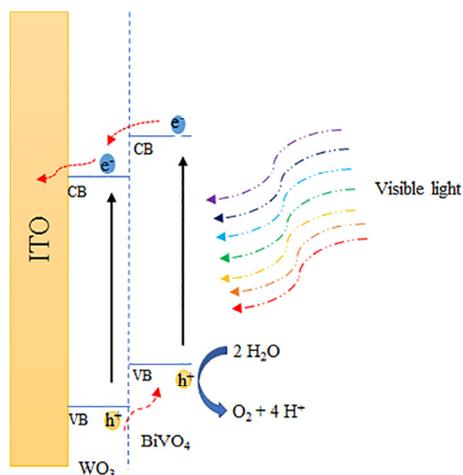


Fig. 5. Schematic diagram of charge transfer process of ITO/WO<sub>3</sub>/BiVO<sub>4</sub> electrode for water oxidation under visible light irradiation.

#### 4. Conclusion

In summary, the ITO/WO<sub>3</sub>/BiVO<sub>4</sub> composited electrodes were fabricated by the GLAD sputtering and spin coating technique. The SEM images confirmed the roughness morphology improvement of dense WO<sub>3</sub> film by BiVO<sub>4</sub> at the outward direction for water adsorption. The crystalline structure of the composited WO<sub>3</sub> and BiVO<sub>4</sub> on the substrate were confirmed by the XRD results. The BiVO<sub>4</sub> at the outer side of composited WO<sub>3</sub>/BiVO<sub>4</sub> electrode could had enhance the photocurrent activities from water oxidation by the function of the charge separation and surface roughness improvements. There are suitable for applied with other couple semiconductor in order to enhance the photoelectrocatalytic activity under visible light irradiation.

#### Acknowledgments

This work was carried out with the help of Optical Thin-Film Technology Laboratory (OLT): Thin films group, the National Electronics and Computer Technology Center (NECTEC) for supporting their facilities. Researcher would like to thank to department of chemistry, faculty of science and technology, Rajamangala University of Technology Thanyaburi (RMUTT) for facility and especially thank to Research and Researchers for Industries-RRI (MSD5810038) for financial support.

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