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IMPROVEMENT THE $BiVO_4$ PHOTOANODE FABRICATED FOR WATER OXIDATION BY ELECTRODEPOSITION TECHNIQUE

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ABSTRACT: Photoelectrocatalytic (PEC) technique for water oxidation technologies could become important components in the renewable energy sector. $BiVO_4$ has been receiving attention for applications in PEC cell for O_2 evolution with high photoelectrocatalytic activity and the advantage of visible radiation absorption. The simple and high efficiency $BiVO_4$ thin film fabrication for large scale is essential for scaling up to the industrial application. This research describes the $BiVO_4$ thin films fabrication on fluorine doped tin oxide (FTO) by electrodeposition technique as simple, fast and suitable for scaling up of electrode preparation. Cyclic voltammetry deposition was developed by studying the effect of potential range, scan rate, number of scan, temperature, and pH of the solution to enhance the photoelectrocatalytic activity of water oxidation under visible light irradiation. The fabricated FTO/$BiVO_4$ thin films were characterized by scanning electron microscope (SEM), X-ray diffractometer (XRD) and UV-Vis spectrophotometer. The developed FTO/$BiVO_4$ present the photocatalytic activities for water oxidation improvement more than 10 times when compared with the previous spin coating techniques. Therefore, this developing method shows that the high efficiency, fast, simple and suitable for scaling up able to approach for water oxidation in the industrial application.

Keywords: Photoelectrocatalytic properties, Water oxidation, $BiVO_4$, Electrodeposition

1. INTRODUCTION

Photoelectrochemical (PEC) water splitting is an alternative way to produce hydrogen and oxygen supporting the hydrogen fuel cell which an important choice in the renewable energy and green technology sector [1, 2]. The development of photoelectrocatalytic activity based on semiconductor materials with appropriate narrow band-gap energy is the key factor to energy conversion efficiency driven by sunlight. Recently, many metal oxide semiconductor materials such as Co_3O_4, Fe_2O_3, WO_3, and $BiVO_4$ have been employed as photocatalysts for visible light has driven water splitting [3-6]. Among them, $BiVO_4$ has recently been extensively investigated as a photoanode for the generation of oxygen from water due to its favorable optical band gap (~2.4 eV), non-toxicity, and stability [7-9]. Especially in the last few years, the PEC performance of $BiVO_4$ photoanode has been significantly improved via the building of nanostructures [10, 11]. One of the most selected $BiVO_4$ thin film fabrication is electrodeposition method due to the advantages of highly efficient, simple, rapid method and practicable to scaling up.

In this work, the FTO/$BiVO_4$ fabricated thin films using cyclic voltammetry electrodeposition method (CVD) was developed by the study of the effects of an applied potential range, scan rate, number of cycle scan, temperature, and pH of the solution. The developed $BiVO_4$ prepared by CVD method was compared with the other electrodeposition technique and classical spin coating method.

2. EXPERIMENTAL

2.1 Materials

Fluorine doped tin oxide (FTO, ~7 Ω/sq, Sigma-Aldrich) was used as a bare electrode substrate. The chemicals used in this study was $Bi(NO_3)_3 \cdot 5H_2O$ (≥ 98.0%, Sigma-Aldrich), $VOSO_4 \cdot xH_2O$ (97%, Sigma-Aldrich), HNO_3 (70.0%, Sigma-Aldrich) CH_3COONa (≥ 99.0%, Sigma-Aldrich), and Na_2SO_4 (Univar).

2.2 Preparation of $BiVO_4$ thin films

The $BiVO_4$ thin films were fabricated on FTO substrate by electrodeposition technique. A precursor solution was prepared by mixing solution of 10 mM $Bi(NO_3)_3$ and 35 mM $VOSO_4$ and adjusted pH < 0.5 with HNO_3[7]. Then 2 M of sodium acetate was added for adjusting pH of the solution to study the effect of pH on various values of 3.0, 4.0, 4.5, and 5.0. Cyclic voltammetry was introduced for $BiVO_4$ thin film fabrication by using potentiostat (Metrohm 663VA Stand). A typical three-electrode system was comprised of the FTO as working electrode, the Ag/AgCl (3 M KCl) as a reference electrode and a platinum wire as a counter electrode. The amorphous Bi-V-O film deposition was studied with the effect of several parameters; the apply potentials of +1.5 to +2.5 V, the precursor solution temperatures of RT (25°C), 40°C, 50°C, 60°C, and 70 °C, the scan rate of 25, 50, 100, and 250 mV/s and the number of cycle scan of 1, 3, 5, and 7 cycles. The crystalline $BiVO_4$ thin film was carried out by annealing the amorphous Bi-V-O at the temperatures of 500°C. The optimum condition was considered with the highest photocurrent from the photoelectrocatalytic water oxidation depending on the FTO/$BiVO_4$ photoanode from each condition. The photocurrent was measured at a fixed potential of 1.0 V vs. Ag/AgCl in 0.5 M Na_2SO_4 aqueous solution under chopped visible light illumination.

2.3 Characteristic and photoelectrocatalytic properties of $BiVO_4$ thin films

The morphologies of the $BiVO_4$ thin films on FTO were investigated by using scanning electron microscopy (SEM, JEOL, JSM -5410LV). X-ray diffraction (XRD, JEOL, JDX-3530) analysis was carried out (Cu Kα radiation) to confirm the crystallinity of the prepared $BiVO_4$ electrodes. The optical absorption spectra of the electrodes were measured by using a UV/Vis spectrophotometer (Shimadzu, UV-1601). The photoelectrocatalytic activity and the electrochemical impedance spectroscopy (EIS) were performed with a VersaSTAT3 (Princeton Applied Research, Inc.) at the potential of 1.0 V vs. Ag/AgCl under visible light illuminated and frequencies ranging from 100 kHz to 0.1 Hz. The characteristic and photoelctrocatalytic activities of $BiVO_4$ thin films electrode prepared by CVD method were compared with the other $BiVO_4$ thin films fabrication by the amperometry (keep the potential of 1.9 V) [7] and spin coating methods (5 layers of $BiVO_4$) [12].

3. RESULTS AND DISCUSSION

3.1 Evaluation of the optimum condition for $BiVO_4$ thin films fabricated by CVD method

3.1.1 Effect of pH

After dissolving $Bi(NO_3)_3 \cdot 6H_2O$ with concentrated HNO_3, $VOSO_4$ was added in the chemical bath solution and adjusted pH again by sodium acetate to study the effect of pH value of 3.0, 4.0, 4.5 and 5.0. At pH 3.0 the precursor solution was turbid and presented reddish-brown peeling out occurring of $BiVO_4$ film from FTO substrate because Bi(III) is soluble at a very low pH value, there is no film formation on the substrate. When pH of the electrolyte solution increases to the middle acidity rank, the $BiVO_4$ film could be completely deposited on the FTO substrate which improved the photoelectrocatalytic activity at pH 4.5. At the pH 5.0, the $BiVO_4$ was also deposited on the FTO substrate, but the photoelectrocatalytic activity was decreased due to the V(IV) precipitates from the solution at the pH above 5 [7]. This result indicates that the specific pH value of a precursor solution is very important to control the quality of $BiVO_4$ thin film fabrication at FTO substrate.

3.1.2 Effect of precursor solution temperature

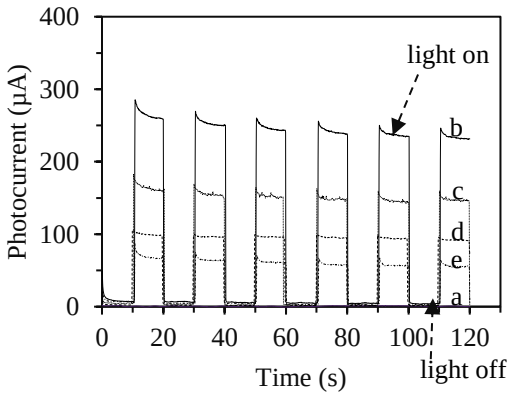

Fig. 1. Amperograms of FTO/$BiVO_4$ prepared with the different precursor solution temperatures of (a) Room Temperature (b) 40 °C (c) 50 °C (d) 60 °C and (e) 70 °C

The photoelectrocatalytic water oxidation of the $BiVO_4$ photo anode obtained at the different precursor solution temperatures during cyclic voltammetry electrodeposition process is shown in Fig. 1. It was

found that at room temperature $BiVO_4$ film could not be deposited on FTO substrate and did not present the photoelectrocatalytic activity. When the temperature was increased to 40°C, a $BiVO_4$ film was completely immobilized onto the substrate cause to the increasing photocurrent from the water oxidation. However, the $BiVO_4$ was agglomerated on the substrate surface and decreased photocurrent when the temperature is higher than 40°C. This effect due to the increasing temperature would create many ions on the surface that may be resulted in the agglomerated and peeled $BiVO_4$ [13] . Therefore, the temperature of a precursor solution for $BiVO_4$ electrodeposition was selected at 40°C.

3.1.3 Effect of scan rate

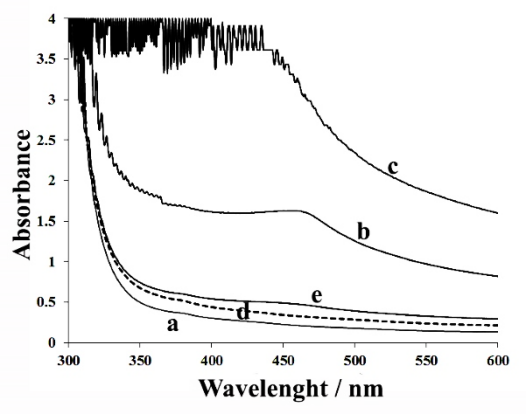

Fig. **2**. The UV-visible spectra of (a) bare FTO and FTO/$BiVO_4$ prepared by the different scan rates of (b) 25 (c) 50 (d) 100 and (e) 250 mV/s

The absorption edge of electrodes were used to calculate a band gap energy with equation 1 .

$$E_g = \frac{1240}{\lambda} \quad (1)$$

Where Eg is band gap energy and λ is absorption edge (nm)

Figure 2 shows that the absorption spectra of FTO/$BiVO_4$ with the difference of scan rate fabrication condition. The band gap energy of $BiVO_4$ with the scan rate of 25 and 50 mV/s were calculated of 2.20 eV and significantly higher absorption ability than that the scan rate of 100 and 250 mV/s. The results indicate that $BiVO_4$ prepared by lower scan rate have a narrower band gap energy and present the good absorbance properties than that higher scan rate condition. Figure 3 shows that the effect of scanning rate on CVD technique for $BiVO_4$ thin film fabrication related with the photocurrent from water oxidation. As a result, the low scan rate values of 25 and 50 mV/s presented high photoelectrocatalytic water oxidation of FTO/$BiVO_4$ electrode. The increasing scan rate to 100 and 250 mV/s were performed the decreasing of photoelectrocatalytic activity. It indicates that faster scan rate affects the speed of a precursor deposition to incompletely grow the $BiVO_4$ on FTO while slower scan rate with more diffusion time of a $BiVO_4$ precursor to deposit completely on the substrate. Based on this experiment, the scanning rate of 50 mV/s was selected with the highest photocurrent from water oxidation.

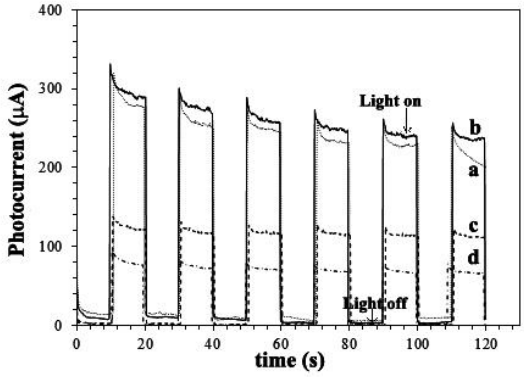

Fig. **3**. Amperograms of FTO/$BiVO_4$ prepared by the different scan rates of (a) 25 (b) 50 (c) 100 and (d) 250 mV/s

Figure 4 shows the narrowest semi-circle of the Nyquist plot of $BiVO_4$ electrode prepared by lower scan rate condition represents the lowest charge transfer resistant or highest electron transfer rate at the electrode surface. The result can support the highest photoelectrocatalytic activity of the developed $BiVO_4$ electrode.

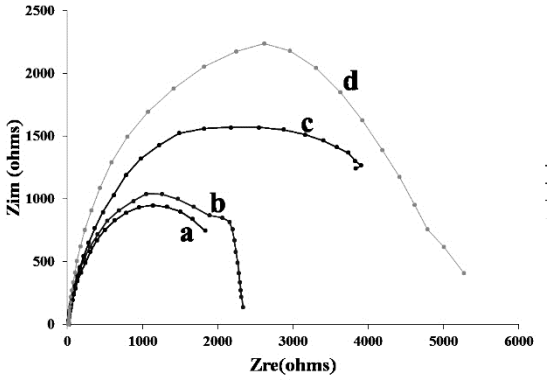

Fig. **4**. Nyquist plot of FTO/$BiVO_4$ prepared by the different scan rates of (a) 25 (b) 50 (c) 100 and (d) 250 mV/s

3.1.4 Effect of scanning cycle number

The experiment shows that the photocurrent enhances with the increasing number of scans from

1-5 cycles and decrease when the cycle is more than 5 cycles (Fig. 5) . Moreover, the photocurrent was related to the EIS results which the charge transfer resistance decreased at the cycle scan 1 to 5 and increased at 7 cycles. This result indicates that the photocurrent of $BiVO_4$ depended on the film thickness that related to the number of the scan. However, the high film thickness may affect the charge transfer rate resistance at the electrode surface.

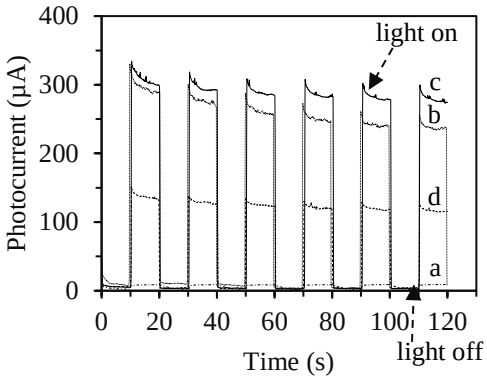

Fig. **5.** Amperograms of FTO/ $BiVO_4$ electrode prepared by CVD method with the study of scanning cycle number (a) 1 (b) 3 (c) 5 and (d) 7 cycles

3.2 Comparison $BiVO_4$ electrode with different deposition method

The characteristic properties and photoelectrocatalytic water oxidation of different $BiVO_4$ electrode fabrication methods were studied. The $BiVO_4$ electrode prepared by CVD (applied potential of 1.5-2.5 V) method was compared with the previous research of the amperometry method (keep the potential of 1.9 V) [7] and spin coating method (5 layers of $BiVO_4$) [12]

3.2.1 Absorption properties

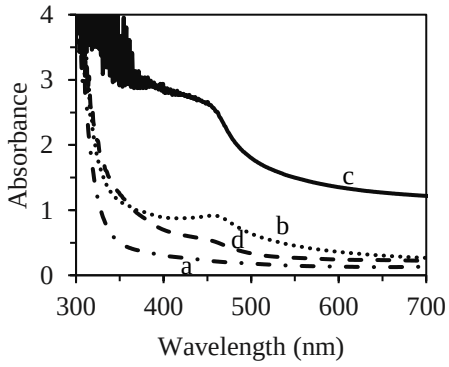

Fig. 6. The UV-visible spectra of (a) FTO and FTO/$BiVO_4$ electrodes prepared by different method of (b) Cyclic voltammetry (c) Amperometry and (d) spin coating

The band gap energy of $BiVO_4$ from CVD, spin coating, and amperometric method were calculated of 2.21, 2.38 and 2.29 eV, respectively (Fig.6). The results show that $BiVO_4$ prepared by CVD have a narrower band gap energy than that other technique indicates that higher visible light absorption property.

3.2.2 Photoelectrocatalytic properties

The photoelectrocatalytic properties were studied by measure the photocurrent from water oxidation reaction at the FTO/ $BiVO_4$ electrode surface. The photocurrent from FTO/ $BiVO_4$ prepared by CVD technique shows the significantly higher photocurrent than that the amperometry and spin coating technique about 2 and 15 times, respectively (Fig. 7) . The result can use to confirm the photoelectrocatalytic improvement of the introduced CVD method for $BiVO_4$ film fabrication. There are related to high absorption property of the electrode could produce high photo hole(h^+) at valent band efficient to oxidize water to oxygen cause present high photocurrent from this reaction.

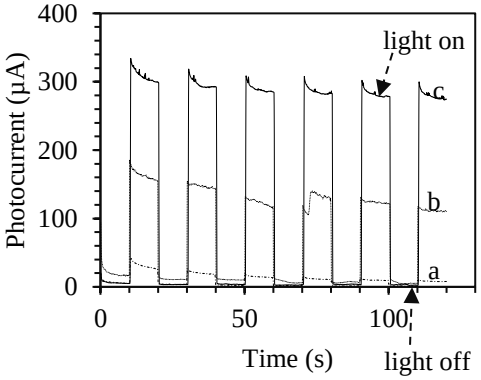

Fig. **7**. Photocurrent of $BiVO_4$ electrode prepared by different methods (a) spin coating (b) amperometry and (c) cyclic voltammetry

3.2.3 Charge transfer resistant properties

An EIS measurement was applied to characterize electrochemical interfacial reaction of FTO/ $BiVO_4$ electrode for water oxidation under visible light irradiation that shows in Fig. 8. The narrowest semi-circle of the Nyquist plot of $BiVO_4$ electrode prepared by CVD method represents the lowest charge transfer resistant or highest electron transfer rate at the electrode surface. The result can support the highest photocurrent of the electrode due to the reason of high photo e^-- h^+ generation and low e^--h^+ recombination effective with the highest photoelectrocatalytic activity of the developed $BiVO_4$ electrode.

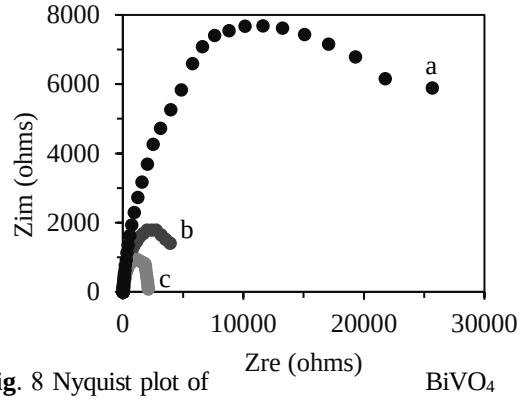

Fig. 8 Nyquist plot of $BiVO_4$ electrode prepared by different methods of (a) spin coating (b) amperometry (c) Cyclic voltammetry

3.2.4 Morphology and crystalline structure

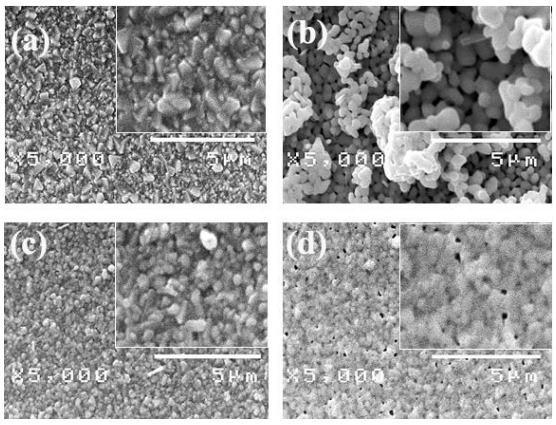

Fig. **9**. SEM images of (a) bare FTO substrate and FTO/$BiVO_4$ electrode prepared by the different methods of (b) Amperometry (c) Cyclic voltammetry and (d) Spin coating

Figure 9 shows the morphology of bare FTO was changed by the covered $BiVO_4$ and different characteristic depended on the deposition method. The morphologies of $BiVO_4$ electrodes prepared by CVD method presented the small particle size and well distribution. The particles are clustered together, and the size is different when $BiVO_4$ was prepared by the amperometry method. While the spin coating method shows flat surface by the fused together of $BiVO_4$. As a result, it can support that the uniform morphology is given a good photoelectrocatalytic properties. Figure 10 shows the XRD patterns of $BiVO_4$ film fabricated with applied potentials after annealing at 500 °C for 1 h**.** The XRD peaks observed at $2\theta = 18.8°$, 28**.**9° and 30**.**6° were indicated to the diffractions monoclinic $BiVO_4$ plane of **(**011**)**, **(**121**)** and **(**040**)**, respectively**.** As the results show that the monoclinic $BiVO_4$ crystalline structure can be performed by all methods preparation after annealed at 500ºC.

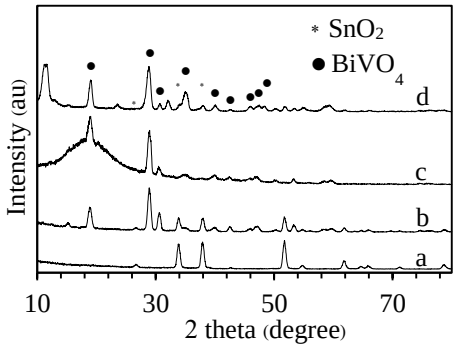

Fig.10. X-Ray diffraction patterns of **(**a**)** FTO and the FTO/$BiVO_4$ prepared by the different methods of **(**b**)** Cyclic voltammetry, **(**c**)** Amperometry **(**d**)** Spin coating

4. CONCLUSIONS

The $BiVO_4$ thin film deposited on FTO using cyclic voltammetry method were successful optimized and presented the photoelectrocatalytic for water oxidation improvement under the good characteristic of films properties. This developed CVD method for FTO/$BiVO_4$ fabrication shows the high efficiency, fast, simple method and suitable for scaling up able to approach for water oxidation in the industrial application.

5. ACKNOWLEDGEMENTS

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