

The Characteristics of Thin Film Bismuth Vanadium Oxide (BiVO₄) Semiconductor Material as Anode for Electrolysis of Water

Achmad Walid¹, Sudjito Soeparman², Slamet Wahyudi³, Mega Nur Sasongko⁴

¹State Polytechnics of Malang

^{2,3,4}Brawijaya University

Corresponding author: walidachmad@gmail.com

Article Info

Volume 82

Page Number: 7524 - 7532

Publication Issue:

January-February 2020

Abstract

The characteristics of bismuth vanadium oxide BiVO₄ with monoclinic crystal structures were studied. The anode is made by coating indium tin oxide with BiVO₄ powder. Indium tin oxides were spin-coated with BiVO₄ powder. Anode characteristics tested by morphological tests (SEM, XRD). The technique used in making anodes is the spin coating. The analysis shows the peak position in the crystal plane of BiVO₄ at 2 Theta = 28,8986 degrees, 18,8724 degrees, 53,3284 degrees, which is related to the reflection of BiVO₄ with reference number JCPDS 083-1699. Thus the Bismuth Vanadium Oxide crystal structure is monoclinic. Following the shape of the small peak, crystal structure is observed and shows a good crystal shape. Scanning Electron Microscopy determined the morphology of BiVO₄ samples. SEM photos shown in the figure show that the particle size is mostly spherical and slightly plate-shaped. From the photo, it can be seen that the surface of the particles has many cavities. The largest cavity showed in the figure, namely at 800 rpm, 7 seconds deposition time. With the presence of a small cavity increases the possibility of electron jumps between particles forming particles and enlarging currents.

Keywords: Bismuth vanadium Oxide (BiVO₄), crystal structure, x-ray diffraction, scanning electron microscopy, spin coating

Article History

Article Received: 18 May 2019

Revised: 14 July 2019

Accepted: 22 December 2019

Publication: 03 February 2020

1. INTRODUCTION

The renewable energy source was gotten by solar energy using the photoelectrochemical water splitting (PEC) technology, which is such a promising technology to produce the hydrogen since the TiO₂ studied for increasing efficiency intensively[1]. It was reported, that Fe₂O₃, WO₃, BiVO₄, and SrTiO₃: Rh from active metal oxide electrode toward visible light. Recently, some nitride ingredients (oxy) are like TaON, Ta₃N₅, SrNbO₂N, and Ta_{0.9}Co_{0.1}N_x also have been found responsively toward visible light for water splitting. On the water-splitting process and degradation of dangerous pollutants which involving photocatalyst activity, ionic conductivity, and ferroelasticity, BiVO₄ has become a vital semiconductor photocatalyst based on non-titania solar. The crystal shape and

morphology significantly affect the BiVO₄ photocatalyst activity for increasing the system PEC efficiency needs improvement in circumscision, splitting, and load transfer of charge to the electrode. There are three structures of BiVO₄ crystals, namely scheelite monoclinic structure, tetragonal (s-t), and zirconia structure with tetragonal (z-t). Several of the BiVO₄ characteristics are low bandgap with 2,4 eV bandgap according to sunlight spectrum with 520 nm wavelength. Position of the valence band is quite around 2.4 vs. RHE according to water oxidation, and conduction band 0 V vs. RHE which is thermodynamically appropriate to produce H₂ and hole-electron effective mass lower than similar semiconductors are like TiO₂ in principle increasing the splitting and extraction of hole-electron pair and material compositions

are not expensive and nontoxic[2]. BiVO₄ electrode powder that has made with BiVO₄ nanoparticle casts plus H₂SO₄ on the FTO substrate can split the water by applying external bias < 1.23 V vs. electrode counter using sunlight simulator[3]. Semiconductor electrode material for water splitting has developed since Honda and Fujishima did the research, although electrode powder has an appropriate potential band with water splitting (conduction band under < 0 V and valence band above > 1.23 V vs. NHE at PH = 0, water splitting by applying electrode powder still applying external bias[4]. The solar energy source for increasing the production of hydrogen from water electrolysis use semiconductor as electrode material. Other solar sources like laser diode and white light are involving to learn more about collimated solar influence or parallel in water electrolysis. For determining voltage and strain like transportation and ion mobility effect field, electric influence determined from surface tension and electrical conductivity measurement[4].

Semiconductor material and photocatalyst systems have developed for more than several decades for water molecule solving reaction (water splitting) under the UV radiation and visible light. It observed that separation of electric charges, avoiding water splitting feedback, and the using of reaction and energy fraction are essential requirements to reach high photon efficiency. Improvement of hydrogen production has seen with hole adding can feedback and inhibit charge recombination. Synthesis procedure variety like loading, metal doping, or oxide metal particle in photocatalyst and has succeeded in developing for increasing water-splitting photocatalyst performance [5]. Among several elements and compound combination, metal oxide has been known as the best photoanode material because the price is cheap, non-toxic, stable, and not expensive. Those metal oxides are like CuO, TiO₂, and BiVO₄. Although, some limitations, especially about efficiency problems, material absorption ability toward solar and structure influence. However, electricity conductivity from the semiconductor electrode is urgently required. Photoelectrode material development by involving solar light had studied for more efficient use of solar energy [4]. BiVO₄ has a narrow bandgap and

can break water molecules under visible light radiation. BiVO₄ has four crystalline phases, namely monoclinic, orthogonol, tetragonal-1 and tetragonal 2. The absence of Bi, V, O vacancies in the structural, electronic, and optical properties at 2x2x2 BiVO₄ influences that the lattice parameter changes slightly[6].

In this study, we conducted a study of the characteristics of BiVO₄, which was applied as an anode for applications in electrolysis systems, where BiVO₄ was deposited on the surface of the ITO substrate (Indium Tin Oxide). Discussions about the structure of BiVO₄ are reviewed in terms of the characteristics of X-ray diffraction and Scanning Electron Microscopy on their surfaces.

2. MATERIAL AND METHOD

In this experiment, the material used was Bismuth Vanadium Oxide (BiVO₄). Bismuth Vanadium Oxide (BiVO₄) is a semiconductor material used as an anode in electrolysis systems, and the material is in the form of powder. The use of BiVO₄ is done by making a BiVO₄ coating on the conductive glass Indium Thin Oxide (ITO). However, before making a layer on conductive glass, BiVO₄ powder is dissolved first in a water solvent. BiVO₄ coating process uses spin coater, arranged in several settings including spin 2000 rotation per minute (rpm) for 4 seconds and 7 seconds, 1400 rpm for 4 seconds, and 800 rpm for 7 seconds. After the coating sample is carried out on the conductive glass, then the X-Ray diffractometer and Scanning Electron Microscopy data are taken.

2.1 BiVO₄ Powder and the specification

The powder that uses on the experiment is Bismuth Vanadium Oxide powder, or also call yellow Bismuth Vanadate by BiVO₄ chemical formula with the 99.9% purity. The powder dissolved into the water before the coating process. Based on the information from the supplier, BiVO₄ powder has 260°C heat resistance, level 5 light resistance, level 5 acid resistance, level 5 alkali resistance, 600 mesh particle size, 0.05 water content, 17-25g/100 g oil absorption, and PH around 7-7.5.

2.2 Main Tools

The tools that use for coating the ITO (Indium Thin Oxide) are spin coater 6800 type series, and the maker is Specialty Coating Systems 7645 Woodland Drive Indianapolis IN 46278, USA. X-Ray characteristics used X-Ray Diffractometer (MPD Expert type) and Scanning Electron Microscopy SEM PAN Analytical type.

3. RESULTS AND DISCUSSIONS

Below are the results of the experiments that have been carried out. The results obtained consisted of X-Ray Diffraction patterns and Scanning Electron Microscopy results of BiVO₄ (thin-film BiVO₄) powder coating on ITO Indium thin oxide conductive glass. X-ray diffraction is used to enter the crystalline phase of the BiVO₄ material and provide information about the unit dimensions of the BiVO₄ material cell. In this experiment, X-Ray Diffraction is used to determine the Crystal phase, which is marked by the diffraction peaks and determine the Crystal size of BiVO₄ material and several other parameters.

3.1 X-Ray diffraction

Figure 1 shows the diffraction pattern of BiVO₄ coating on ITO with a spin of 2000 rpm and a time of 4 seconds with several diffraction peaks at

an intensity of $2\theta = 28.8986^\circ$; 18.8724° ; 30.5434° ; 53.3284° and the highest peak is at $2\theta = 28.8986^\circ$. The XRD diffraction pattern of figure 1 also shows the presence of peaks so that the BiVO₄ powder layer at ITO has a crystalline structure.

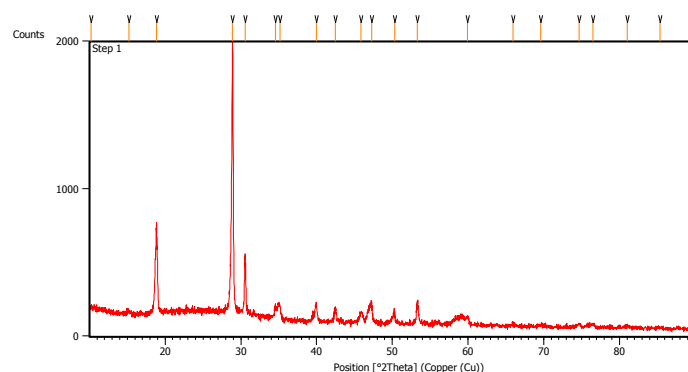


Figure 1. BiVO₄ coating diffraction pattern with a spin coating of 2000 rpm and time of 4 seconds

Table 1 shows the full-width half-maximum, the distance between the atomic crystal lattice (*d*), and the diffraction peak (heights). From the data in table 1, we can calculate the crystal size from some of the highest peaks. The farthest distance between the atomic crystal lattices is obtained at a distance of 8.65013 Å (angstrom). While at the highest peak obtained the distance between the atomic crystal lattice of 3.08964 Å.

Table 1: Value of height (peaks), full width half maximum, *d*-spacing, and BiVO₄ position parameters

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	<i>d</i> -spacing [Å]	Rel. Int. [%]
10.2265	17.28	0.6691	8.65013	0.97
15.2022	25.37	0.5353	5.82827	1.42
18.8724	608.29	0.1004	4.70230	34.00
28.8986	1789.30	0.1506	3.08964	100.00
30.5434	406.36	0.1338	2.92691	22.71
34.5390	74.82	0.2007	2.59691	4.18
35.1661	94.97	0.1673	2.55203	5.31
39.9600	127.11	0.2342	2.25623	7.10
42.4662	96.76	0.2007	2.12870	5.41

45.8610	64.46	0.4684	1.97872	3.60
47.2471	128.04	0.1673	1.92385	7.16
50.3022	60.28	0.2676	1.81394	3.37
53.3284	149.87	0.2676	1.71792	8.38
59.9377	41.53	0.3346	1.54333	2.32
65.9596	13.57	0.5353	1.41627	0.76
69.5811	11.64	0.8029	1.35115	0.65
74.6864	24.07	0.4015	1.27094	1.34
76.4811	18.91	0.8029	1.24553	1.06
81.0194	12.40	0.8029	1.18683	0.69
85.3402	5.22	0.6691	1.13745	0.29

Table 2 shows the crystal sizes obtained from the X-Ray Diffraction test from some of the highest peaks in the X-ray Diffraction pattern on a thin BiVO₄ coating with a 2000 rpm spin coating in 4 seconds.

Table 2: crystal size of BiVO₄ thin film

2 θ	Peaks	Crystal size (Å ^o)
28,8986	1789.30	9,2938
18,8724	608.29	13,9995
30.5434	406.36	0,6000
53,3284	149.87	5,7979

Figure 2 shows the diffraction pattern of the BiVO₄ coating on ITO with a spin of 2000 rpm and a time of 4 seconds with several diffraction peaks at an intensity of 2 θ = 28.9349^o; 30.6424^o; 30.1355^o; 35,2387^o and the highest peak is at 2 θ = 28,9349^o. The XRD diffraction pattern of Figure 2 shows the presence of peaks in the

diffraction pattern so that the BiVO₄ powder layer at ITO shows the existence of a crystal structure.

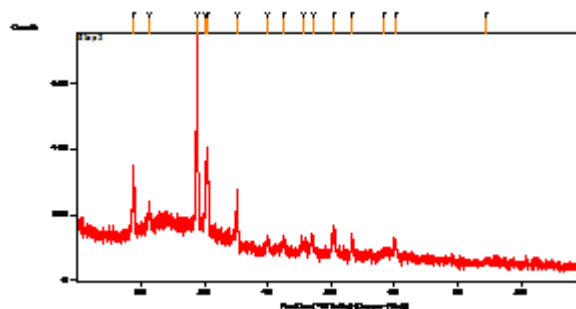


Figure 2. BiVO₄ coating diffraction pattern with 2000 rpm spin coating and 7 seconds

Table 3 shows the full width half maximum, the distance between the atomic crystal lattice (d), and the diffraction peaks (heights). From the data in table 3, we can calculate the crystal size from some of the highest peaks. The farthest distance between the atomic crystal lattices is obtained at a distance of 4.69710 Å. While at the highest peak obtained the distance between the atomic crystal lattice of 3.08584 Å.

Table 3: Value of height (peaks), full width half maximum, d-spacing, and BiVO₄ position parameters

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
18.8935	171.84	0.1004	4.69710	29.25
21.2953	59.35	0.2676	4.17244	10.10
28.9349	587.42	0.1673	3.08584	100.00
30.1355	182.38	0.2007	2.96559	31.05
30.6424	206.90	0.1004	2.91768	35.22
35.2387	153.65	0.3011	2.54693	26.16
39.9839	27.02	0.4015	2.25494	4.60
42.5626	32.30	0.2676	2.12410	5.50
45.5777	19.64	0.8029	1.99035	3.34
47.2584	42.96	0.4015	1.92342	7.31
50.5476	72.17	0.2676	1.80571	12.29
53.3355	48.91	0.2676	1.71771	8.33
58.4163	17.45	0.8029	1.57984	2.97
60.2926	42.04	0.2342	1.53509	7.16
74.5194	9.20	0.4684	1.27337	1.57

Table 4 shows the crystal sizes obtained from the X-Ray Diffraction test of some of the highest peaks of the X-Ray Diffraction pattern on a 2000 rpm BiVO₄ thin film in 7 seconds.

Table 4: crystal size of BiVO₄ thin film

2θ	Peaks	Crystal size (Å)
28,9349	587,42	8,4475
30,6424	206,90	14,3078
30,1355	182,38	7.1579
35,2387	153,65	4,8315

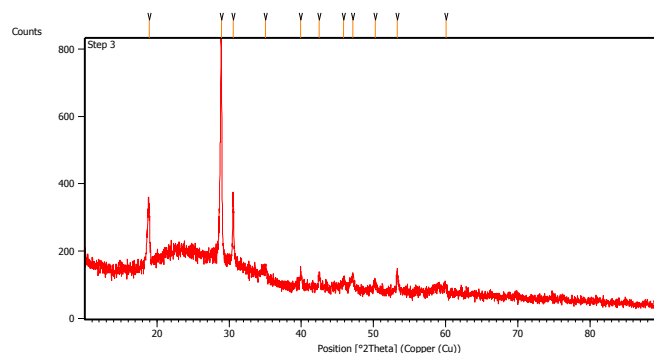


Figure 3. BiVO₄ coating diffraction pattern with a spin coating of 1400 rpm and time of 4 seconds

Figure 3 shows the diffraction pattern of BiVO₄ coating on ITO with a spin of 2000 rpm and a time of 4 seconds with several diffraction peaks at an intensity of $2\theta = 28.9228^\circ$; 30.65639° ; 18.9080° ; 53.3213° and the highest peak is at $2\theta = 28.9228^\circ$. XRD diffraction pattern Figure 3 shows the diffraction peaks so that the BiVO₄ powder layer at ITO shows the crystal structure.

Table 5 shows the full-width half-maximum, the distance between the atomic crystal lattice (d) and the diffraction peaks (heights). From the data in table 5, we can calculate the crystal size from some of the highest peaks. The farthest distance

between the atomic crystal lattices is obtained at a distance of 4.69353Å. While at the highest peak obtained the distance between the atomic crystal lattice of 3.08711 Å.

Table 5: Value of height (peaks), full-width half-maximum, d-spacing, and BiVO₄ position parameters

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
18.9080	168.20	0.2342	4.69353	26.41
28.9228	636.92	0.1673	3.08711	100.00
30.5639	173.15	0.1338	2.92499	27.19
35.0085	28.15	0.8029	2.56316	4.42
39.9232	48.88	0.2676	2.25823	7.67
42.5106	37.95	0.2676	2.12658	5.96
45.8667	24.24	0.4015	1.97849	3.81
47.1783	46.61	0.2007	1.92650	7.32
50.2445	23.25	0.4015	1.81589	3.65
53.3213	55.18	0.2007	1.71814	8.66
60.0397	14.46	0.4684	1.54095	2.27

Table 6 shows the crystal sizes obtained from the X-Ray Diffraction test from some of the highest peaks of the X-Ray Diffraction pattern on the BiVO₄ 1400 rpm thin film in 4 seconds.

Table 6: crystal size of BiVO₄ thin film

2θ	Peaks	Crystal size (Å)
28,9228	636,92	8,5639
30,5639	173,15	10,7480
18,9080	168,20	6,0021
53,3213	55,18	7,7285

Figure 4 shows the diffraction pattern of the BiVO₄ coating on ITO with a spin of 2000 rpm and a time of 4 seconds with several diffraction

peaks at an intensity of 2θ = 28.8016°; 18.7140°; 30,4077°; 47.5382° and the highest peak is at 2θ = 28.8016°. The XRD diffraction pattern of Figure 4 shows the diffraction peaks so that the BiVO₄ powder layer at ITO shows the crystal structure.

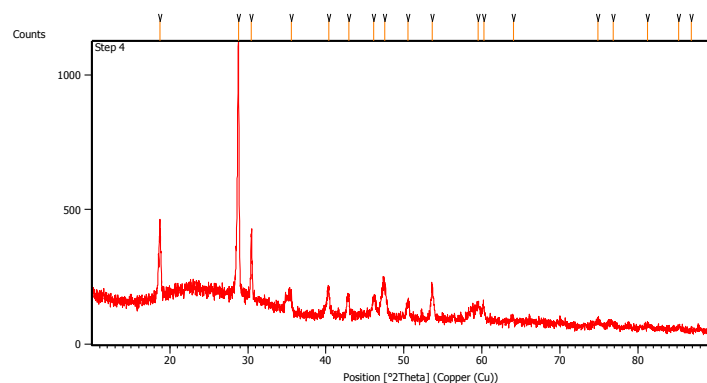


Figure 4. BiVO₄ coating diffraction pattern with 800 rpm spin coating and 7 seconds

Table 7 shows the full width half maximum, the distance between the atomic crystal lattice (d), and the diffraction peak (heights). From the data in Table 7, we can calculate the crystal size from some of the highest peaks. The furthest distance

between the atomic crystal lattice is obtained at a distance of 4.74174 Å. While at the highest peak obtained the distance between the atomic crystal lattice of 3.09983 Å.

Table 7: Value of height (peaks), full-width half-maximum, d-spacing, and BiVO₄ position parameters

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
18.7140	249.15	0.2007	4.74174	26.43
28.8016	942.81	0.1673	3.09983	100.00
30.4077	224.77	0.1004	2.93966	23.84
35.5536	56.64	0.4015	2.52510	6.01
40.3892	97.14	0.1338	2.23324	10.30
42.9641	72.97	0.1004	2.10518	7.74
46.1367	66.65	0.4015	1.96753	7.07
47.5382	117.43	0.6691	1.91275	12.46
50.5542	65.35	0.4015	1.80549	6.93
53.6293	115.05	0.1673	1.70900	12.20
59.5148	62.99	0.2676	1.55328	6.68
60.2414	52.11	0.2676	1.53627	5.53
64.0250	13.12	0.4015	1.45431	1.39
74.8606	21.03	0.4015	1.26841	2.23
76.8101	13.89	0.8029	1.24101	1.47
81.2656	9.41	0.8029	1.18386	1.00
85.2486	8.53	0.8029	1.13844	0.90
86.8815	10.87	0.1673	1.12119	1.15

Table 8 shows the crystal size obtained from the X-Ray Diffraction test of some of the highest peaks of the X-Ray Diffraction pattern on the 800 rpm BiVO₄ thin film in 7 seconds.

Table 8: crystal size of BiVO₄ thin film

2θ	Peaks	Crystal size(Å)
----	-------	-----------------

28,8016	942,81	8,5586
18,7140	249,15	7,0060
30,4077	224,77	14.3233
47,5382	117,43	2,2251

3.2 Scanning Electron Microscopy

Figure 6 shows the results of Scanning Electron Microscopy on a thin layer of Bismuth Vanadium Oxide with a spin coating of 2000 rpm for 4 seconds and magnification of 1500 times.

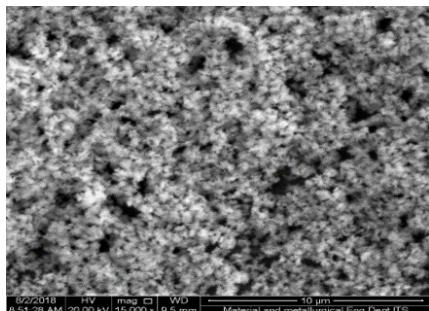


Figure 6. SEM photo results for a sample with 2000 rpm with a 4 second deposition time

Figure 7 shows the results of Scanning Electron Microscopy with a spin coating of 2000 rpm with a deposition time of 7 seconds.

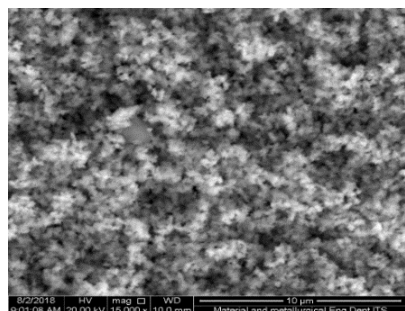


Figure 7. Photographs of SEM for samples with sample 2000 rpm with 7 seconds deposition time

Figure 8 shows the results of Scanning Electron Microscopy with a spin coating of 2000 rpm with a deposition time of 4 seconds.

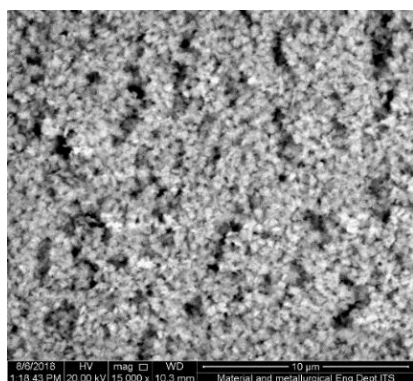


Figure 8. SEM photo results with sample 1400 rpm magnification with 4 seconds deposition time

Figure 9 shows the results of Scanning Electron Microscopy with a spin coating of 800 rpm and a deposition time of 7 seconds

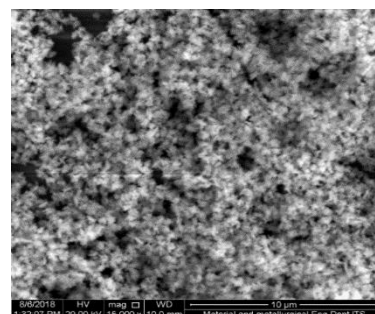


Figure 9. SEMphoto results with samples 800 rpm with 7 seconds deposition time

From the figures, it appears BiVO_4 that on the coating in the ITO glass, the shape of BiVO_4 nanomaterial is sphere or 0-D, it is distributed evenly with a particle size around 0.1-0.3 µm. Several spheres gather together to make groups.

By the high spin round, 2000 rpm and quick deposition time 4 seconds are causing the swelling to enlarge although the different size is not very clear slightly. BiVO_4 with a 0-D sphere structure usually has photocatalytic performance better because it has solar harvester ability and occurs better chemical reaction.

The figure can be seen that the particle surface has many cavities. The most significant cavity showed in Figure 9 is in 800 rpm round deposition time 7 seconds. In the presence of a small cavity, enlarge the possibility of electron jumps between atoms particle forming and enlarge the current.

Conclusion

The result can conclude that Bismuth Vanadium Oxide has crystal structure form, which is made with monoclinic shape. It was signed there are some peaks in the X-Ray diffraction pattern. The largest crystal size is at 14.3233 Å with an 800 rpm spin-coating deposition time of 7 seconds. On the Scanning Electron Microscopy, it is obtained good crystal shape on 2000 rpm round with deposition time 4 seconds because there is little cavity and particle are shaped sphere or 0-D. However, the most appropriate to be made as a photoanode at the photoelectrochemical

system is on 2000 rpm round and deposition time 4 seconds.

REFERENCES

- [1] Z. Zhu, L. Zhang, J. Li, J. Du, Y. Zhang, and J. Zhou, "Synthesis and photocatalytic behavior of BiVO₄ with decahedral structure," *Ceram. Int.*, vol. 39, no. 7, pp. 7461–7465, 2013.
- [2] H. R. Kim, G. Kim, S. Il In, and Y. Park, "Optimization of porous BiVO₄ photoanode from electrodeposited Bi electrode: Structural factors affecting photoelectrochemical performance," *Electrochim. Acta*, vol. 189, pp. 252–258, 2016.
- [3] Q. Jia, K. Iwashina, and A. Kudo, "Facile fabrication of an efficient BiVO₄ thin film electrode for water splitting under visible light irradiation," 2012.
- [4] N. Bidin *et al.*, "The effect of sunlight in hydrogen production from water electrolysis," *Int. J. Hydrogen Energy*, vol. 42, no. 1, pp. 133–142, 2017.
- [5] C.-H. Liao, C.-W. Huang, and J. C. S. Wu, "Hydrogen Production from Semiconductor-based Photocatalysis via Water Splitting," *Catalysts*, vol. 2, no. 4, pp. 490–516, 2012.
- [6] X. Zhang, Y. Huang, F. Ma, Z. Zhang, and X. Wei, "Influences of vacancies on the structural, electronic and optical properties of monoclinic BiVO₄," *J. Phys. Chem. Solids*, vol. 121, no. April, pp. 85–92, 2018.