THE COMPARISON OF OPAQUE TiO₂ AND TRANSPARENT TiO₂ ON THE PERFORMANCE OF AgSbS₂-SENSITIZED SOLAR CELL PREPARED BY SOLUTION PROCESSING

**Kerista Sebayang¹, Siti Utari Rahayu^{1,2*}, Ming-Way Lee³, Saharman Gea^{2,4},
Herli Ginting¹ and Aditya Warman¹**

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan 20155, Indonesia

²Cellulosic and Functional Materials Research Centre, Universitas Sumatera Utara, Medan 20155, Sumatera Utara, Indonesia

³Institute of Nanoscience and Department of Physics, National Chung Hsing University, Taichung, 402, Taiwan

⁴Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan 20155, Indonesia

*E-mail: siti.utari@usu.ac.id

ABSTRACT

This study reported the investigation of the use of opaque and transparent TiO₂ paste as metal oxide on AgSbS₂ quantum dots (QDs)-sensitized solar cell. Doctor blade method was employed to coat TiO₂ paste onto FTO glass, whereas successive ionic layer adsorption and reaction (SILAR) was applied to grow AgSbS₂ into the TiO₂ layer. The SILAR process consisted of 3 cycles for depositing Ag-S and 6 cycles for obtaining Sb-S. AgSbS₂ was yielded after annealing process at 350°C for 10 minutes under nitrogen condition. The best photovoltaic performance was achieved from transparent TiO₂ paste, which gave the efficiency of 0.317 % with V_{oc} of 0.24 V, J_{sc} of 3.51 mA/cm², and FF of 37.62%. Opaque TiO₂ paste showed lower photovoltaic performance, which gave an efficiency of 0.110% due to the difficulty of electrolyte to penetrate the matrix of the TiO₂ layer and the existence of the cracks at the TiO₂ layer. These results showed that in the case of AgSbS₂ semiconductor, the utilization of transparent TiO₂ paste would give better photovoltaic performance than that of opaque TiO₂ paste.

Keywords: Titanium Dioxide Paste, Quantum Dots Sensitized Solar Cells, SILAR Method, Silver Antimony Sulfide.

© RASĀYAN. All rights reserved

INTRODUCTION

Quantum dots-sensitized solar cells (QDSSCs) are non-silicon solar cells that provide a large chance to result in high efficiency with low-cost production. Theoretically, QDSSCs can achieve an efficiency of 44.4% due to the occurrence of carrier multiplication¹. The study to improve QDSSCs' performance, which has the same structure as DSSCs, is not limited to the variation of semiconductor used as sensitizer; as for DSSCs, there are more recent studies reported the use of different sensitizers.²⁻⁴ As known, QDSSCs consist of three main components, namely, photo-anode, electrolyte, and counter-electrode. The first mentioned component uses metal oxides having a large band gap, such as TiO₂, SnO₂, and ZnO, which are sensitized with semiconductor materials.

Regarding metal oxides, TiO₂ gives a more preferable structure for the reaction of photo-induced, obtaining an increased light absorption rate and higher surface photo-activity.⁵ As reported, the first DSSCs were produced by applying mesoporous TiO₂ as the photo-anode.⁶ Later, an efficiency of 10% was achieved by using TiO₂ nanosized particles as the large gap semiconductor on DSSCs.⁷ Besides, titanium is one of the most abundant elements, thus the use of TiO₂ on solar cells should provide low-cost production. Several studies have been done to examine the effect of the different structures of TiO₂ on the efficiency of solar cells; for instance, Ito et al. investigated the TiO₂ screen printing techniques and their

relation to efficiency. They found that different preparation technique resulted in different particle size of TiO_2 , which gave different efficiency. Larger efficiency was obtained from smaller TiO_2 particle size.⁸ There are two types of commercial TiO_2 pastes, in particular, transparent TiO_2 paste (having roughly uniform particle sizes) and opaque TiO_2 paste (having non-uniform particle sizes). These two different particle sizes give a distinct surface to volume ratio. As studied by Rahayu et al., 30 nm transparent TiO_2 particle size resulted in higher efficiency than that of 30 nm opaque for Cu_3BiS_3 -semiconductor sensitized solar cells.⁹ Also, TiO_2 has three major structures, namely, rutile, anatase, and brookite, which provide a distinction on the performance of solar cells due to different band gaps.¹⁰

Based on that, this study aimed to investigate the comparison of different types of TiO_2 paste, in particular, the transparent paste (20 nm of particle size) and the opaque paste (the particle size varied from 20 nm to larger sizes), on the performance of Silver Antimony Sulfide (AgSbS_2)-QDSSCs. AgSbS_2 as solar absorbers were chosen due to its promising electrical and optical properties, namely, the absorption coefficient of 10^5 cm^{-1} and an energy gap of 1.73 eV.^{11,12} Also, its bandgap matches appropriately with TiO_2 . The method used to obtain AgSbS_2 in this study was successive ionic layer adsorption and reaction (SILAR), which allows the formation of quantum dots to be adaptive to its cycle,^{13,14} providing tunable band gap.

EXPERIMENTAL

Materials

The materials used in this study were TiO_2 paste (20-T and 20-AO, Greatcell Solar), antimony trichloride (99.9%, Alfa Aesar), methanol (99.5%, Macron Fine Chemicals), sodium sulfide nonahydrate (98%, Acros Organics), ethanol (99.5%, Echo), Acetone (99.5%, Merck), Silver nitrate (99.9%, Merck), Potassium chloride (>98%, Choneye Pure Chemicals), Sodium hydroxide (>95%, Shimakyu's Pure Chemicals), Potassium Iodide (99.5%, Shimakyu's Pure Chemicals), hexachloroplatinic acid (99%, Merck), FTO Glass ($15 \Omega/\text{sq}$, Nippon Sheet Glass, GreatCell Solar), Parafilm Sheet ($130 \mu\text{m}$, Pechiney).

Preparation of Photoanode

FTO glass and object glass were cleaned by sonicating for 3 minutes in acetone and for 3 min in methanol, followed by rinsing with DI water and drying by using a hotplate. After the cleaning process, the TiO_2 was pasted on top of FTO-glass by using a doctor blade method, the thickness is defined by the thermoplastic sealant $50 \mu\text{m}$ thick. The samples were annealed by tube furnace under the atmospheric condition for 90 min at 500°C gradually.¹⁵ The process to grow the quantum dots is SILAR (as shown in Fig.-1).¹⁶

Fig.-1: SILAR Method of Growing The Quantum Dots of AgSbS_2

Briefly, the samples were dipped into the solution of silver nitrate and ethanol for 1 min, followed by rinsing, then dipped into the solution of sodium sulfide and methanol for 4 min, followed by rinsing. This

process is called 1-cycle. The process was repeated until 3-cycles. After that, the samples were dipped again into the solution of antimony chloride and ethanol for 15 s, followed by rinsing, then dipped into the solution of sodium sulfide and methanol for 1 min, followed by rinsing. This process is called 1-cycle. The process was repeated until 6-cycles. The samples were then annealed in nitrogen for 10 min at 350° C.

Preparation of AgSbS₂-QDSSCs

The photoanode obtained were assembled with Pt-counter electrode by using parafilm spacer. The polysulfide electrolyte¹⁷ was inserted into the solar cells before measuring the efficiency.

Characterization

PANalytical X'Pert Pro MRD diffractometer was used to obtain the XRD pattern of the samples. Keithley 2400 source meter was for recording the performances of the solar cell. Scanning electron microscope (SEM) EVO MA 10 Zeiss Bruker was used to analyze the surface morphological of AgSbS₂ coated into TiO₂ layer. And, atomic force microscope (AFM) Park System XE-70 was employed to probe the topography of the surface.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

As given in Fig.-2, the AgSbS₂ semiconductor was grown successfully into the TiO₂ layer without any impurities (JCPDS 17-0456). As can be seen, there is a larger intensity of AgSbS₂ peaks on transparent TiO₂ film than that of opaque TiO₂ film. It shows that there are more AgSbS₂ loaded into the layer of transparent TiO₂. This is caused by different surface to volume ratios on each type of paste; the uniform sizes of particles that exist in the paste of transparent TiO₂ gives a small surface to volume ratio, whereas the opaque TiO₂ consists of small and large particles, obtaining larger surface to volume ratio. Eventually, the small surface to volume ratio leads to more ions reacts to each other during the SILAR process, giving larger loading of AgSbS₂ semiconductor.

Fig.-2: XRD Pattern of AgSbS₂ coated into Transparent TiO₂ and Opaque TiO₂

The crystalline form of TiO₂ is different for each paste; the transparent TiO₂ film shows less anatase structure than the opaque one. This will lead to different band gaps, thus affect the performance of cells. As mentioned, the higher photocatalytic activity can be achieved by the anatase structure since it has a larger band gap than that of rutile structure.¹⁸ Basically, the anatase structure is yielded by annealing the paste at 400-500°C and the rutile structure is obtained at 600°C¹⁹; however, on this occasion, the rutile and anatase phase arise at the annealing temperature of 500°C.

Photovoltaic Measurement Analysis

Zhang et al., which investigated the photocatalytic performance of TiO₂ with three different structures, in particular anatase, rutile and brookite, found that the anatase structure could improve the photovoltaic

performance of the cells since it can reduce the carrier, thank its wider indirect band gap.^{18,20} Related to this, AgSbS₂-SSCs using different TiO₂ paste also undergo different photovoltaic performance, as seen in Figure 2, the transparent TiO₂ film shows less anatase structure, yet the intensity of AgSbS₂ on it is larger, resulting in larger loading of semiconductor and larger efficiency (given in Table-1). It shows that the combination of anatase structure and rutile structure at the same TiO₂ crystal gives different photocatalytic performance from either pure rutile structure or pure anatase structure.

Table-1: Measurement Result from AgSbS₂ QDSSCs under Different TiO₂ Paste Types

TiO ₂ Paste Types	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	Efficiency (%)
Transparent TiO ₂	3.51	0.24	37.62	0.317
Opaque TiO ₂	1.42	0.25	31.01	0.110

Transparent TiO₂ results in larger FF than that of opaque TiO₂, showing that the resistance on the AgSbS₂-QDSSC using transparent TiO₂ is relatively small.²¹ As explained earlier that the transparent one lets the AgSbS₂ semiconductor fill in the matrix of TiO₂ very well, thus the electrolyte can penetrate the matrix easier, obtaining more preferable photovoltaic performance.

Atomic Force Microscopy (AFM) Analysis

Figure-3 shows the topography images of AgSbS₂ coated into TiO₂ layer, it can be seen that opaque TiO₂ (Figure 3(b)) gives a rougher surface than transparent (Fig.-3a), the surface difference of opaque TiO₂ is 2.89% and 1.46% for transparent TiO₂. The rough surface comes from different particle sizes that exist in the opaque TiO₂ paste, yet this situation does not improve the loading and reaction of ions during the SILAR process in the case of AgSbS₂ semiconductor. The combination of small and large particles results in the formation of aggregates, thus forming the crack in the obtained TiO₂ film (Fig.-3b).

Fig.-3: Topography Images of of AgSbS₂ coated into (a) Transparent TiO₂, (b) Opaque TiO₂

Scanning Electron Microscopy (SEM) Analysis

As shown in Fig.-4, there are more flakes formed in the opaque TiO₂; however, based on the XRD results, these flakes do not lead to the improved crystal structure of AgSbS₂. A study conducted by Ito *et al.* discovered that some kind of TiO₂ paste gives aggregation when it comes to forming the film. And, the same as this case, those aggregations give small cracks in the porous TiO₂ layer⁸, as also proved by AFM results. Transparent TiO₂, however, shows a smoother surface even though the flakes seem to distribute

non-uniformly. There are fewer cracks compare to those of opaque TiO_2 due to larger particles which results in larger aggregates, thus the performance of AgSbS_2 -QDSSCs is better (as given in Table-1).

Fig.-4: The Photograph of AgSbS_2 coated into (a) Opaque TiO_2 (magnification of 20 times), (b) Opaque TiO_2 (magnification of 100 times), (c) Transparent TiO_2 (magnification of 20 times), and (d) Transparent TiO_2 (magnification of 100 times)

CONCLUSION

In summary, based on the investigation of the different use of TiO_2 layer paste on the AgSbS_2 -QDSSCs, it was found that the transparent TiO_2 paste that consists of uniform 20 nm of particle size performed better than opaque TiO_2 paste, which has particle sizes of 20 nm and larger ones. The lower performance of opaque TiO_2 paste occurred because of the cracks that exist at the TiO_2 layer and the difficulty of electrolyte to penetrate the matrix of the TiO_2 layer.

ACKNOWLEDGMENT

This research was supported by Universitas Sumatera Utara through the Talenta Scheme of Penelitian Unggulan Universitas (PUU) in 2017 with grant number: 5338/UN5.1.R/PPM/2017. The authors would like to thank Electro-Optics Laboratory in National Chung Hsing University Taiwan for the facilities to conduct the experiment.

REFERENCES

1. K. Tanabe, K. Watanabe and Y. Arakawa, *Applied Physics Letters*, **100**(19), 192102 (2012), DOI:10.1063/1.4712597
2. H. Darmokoesoemo, H. Setyawati, A. T. A. Ningtyas, H. S. Kusuma, *Results in Physics*, **7**, 54 (2017), DOI:10.7324/RJC.2017.1021561
3. S. Mohan Kumar, T. Kannaian, and V. Sathyanarayanamoorthi, *Rasayan Journal of Chemistry*, **10**(2), 613(2017), DOI:10.7324/RJC.2017.1021598
4. Hasby, Nurhafidhah, G. Pamungkas, and S. A. Akbar, *Rasayan Journal of Chemistry*, **13**, 38(2020), DOI:10.31788/RJC.2020.1315576
5. Y. Lan, Y. Lu and Z. Ren, *Nano Energy*, **2**, 1031(2013), DOI:10.1016/j.nanoen.2013.04.002
6. B. O'Regan and M. Grätzel, *Nature*, **353**(6346), 737(1991), DOI:10.1038/353737a0
7. M. Grätzel, *Current Opinion in Colloid and Interface Science*, **4**(4), 314(1999), DOI:10.1016/S1359-0294(99)90013-4

8. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy, M. Grätzel, *Progress in Photovoltaics: Research and Applications*, **15**, 603(2007), DOI:10.1002/pip.768
9. L. Sang, Z. Yixin & B. Clemens, *Chemical Reviews*, **114**, 9283(2014), DOI:10.1021/cr400629p
10. S.U. Rahayu, M.W.Lee, *AIP Conference Proceedings*, **2221(1)**, 030005 (2020), DOI: 10.1063/5.0003105
11. S.I. Boldish, and W.B. White, *American Mineralogist*, **83(7-8)**, 865(1998), DOI:10.2138/am-1998-7-818
12. P. K. Santra, and P.V. Kamat, *Journal of the American Chemical Society*, **134(5)**, 2508(2012), DOI:10.1021/ja211224s
13. H. M. Pathan and C. D. Lokhande, *Bulletin of Materials Science*, **27**, 85(2004), DOI: 10.1007/BF02708491
14. N. M. Noer, S. U. Rahayu, K. Sebayang, H. A. Sianturi, and M.-W. Lee, in *TALENTA-International Conference on Science and Technology*, 2019 012041 (IOP Publishing, 2020), DOI: 10.1088/1742-6596/1542/1/012041
15. P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker, and M. Grätzel, *The Journal of Physical Chemistry B*, **107(51)**, 14336(2003), DOI:10.1021/jp0365965
16. W. C. Yang and M. W. Lee, *Journal of the Electrochemical Society*, **161**, 92(2014), DOI: 10.1149/2.035403jes
17. J. Zhao, B. Jiang, B., S. Zhang, H. Niu, B. Jin, and Y. Tian, *Science in China Series B Chemistry*, **52(12)**, 2213(2009), DOI:10.1007/s11426-009-0143-7
18. Y. Luan, L. Jing, Q. Meng, H. Nan, P. Luan, M. Xie, and Y. Feng, *The Journal of Physical Chemistry C*, **116(32)**, 17094(2012), DOI:10.1021/jp305142j
19. J. Ovenstone, and K. Yanagisawa, *Chemistry of Materials*, **11(10)**, 2770(1999), DOI:10.1021/cm990172z
20. J. Zhang, P. Zhou, J. Liu & J. Yu, *Physical Chemistry Chemical Physics*, **16**, 20382(2014), DOI: 10.1039/C4CP02201G
21. S.S. Hegedus, and W. N. Shafarman, *Progress in Photovoltaics: Research and Applications*, **12(2-3)**, 155(2004), DOI:10.1002/pip.518

[RJC-5982/2020]