THE COMPARISON OF OPAQUE TiO$_2$ AND TRANSPARENT TiO$_2$ ON THE PERFORMANCE OF AgSbS$_2$–SENSITIZED SOLAR CELL PREPARED BY SOLUTION PROCESSING

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ABSTRACT

This study reported the investigation of the use of opaque and transparent TiO$_2$ paste as metal oxide on AgSbS$_2$ quantum dots (QDs)-sensitized solar cell. Doctor blade method was employed to coat TiO$_2$ paste onto FTO glass, whereas successive ionic layer adsorption and reaction (SILAR) was applied to grow AgSbS$_2$ into the TiO$_2$ layer. The SILAR process consisted of 3 cycles for depositing Ag-S and 6 cycles for obtaining Sb-S. AgSbS$_2$ was yielded after annealing process at 350°C for 10 minutes under nitrogen condition. The best photovoltaic performance was achieved from transparent TiO$_2$ paste, which gave the efficiency of 0.317 % with $V_{oc}$ of 0.24 V, $J_{sc}$ of 3.51 mA/cm$^2$, and FF of 37.62%. Opaque TiO$_2$ paste showed lower photovoltaic performance, which gave an efficiency of 0.110% due to the difficulty of electrolyte to penetrate the matrix of the TiO$_2$ layer and the existence of the cracks at the TiO$_2$ layer. These results showed that in the case of AgSbS$_2$ semiconductor, the utilization of transparent TiO$_2$ paste would give better photovoltaic performance than that of opaque TiO$_2$ paste.

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

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 multiplication. 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. 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 TiO$_2$, SnO$_2$, and ZnO, which are sensitized with semiconductor materials.

Regarding metal oxides, TiO$_2$ gives a more preferable structure for the reaction of photo-induced, obtaining an increased light absorption rate and higher surface photo-activity. As reported, the first DSSCs were produced by applying mesoporous TiO$_2$ as the photo-anode. Later, an efficiency of 10% was achieved by using TiO$_2$ nanosized particles as the large gap semiconductor on DSSCs. Besides, titanium is one of the most abundant elements, thus the use of TiO$_2$ on solar cells should provide low-cost production. Several studies have been done to examine the effect of the different structures of TiO$_2$ on the efficiency of solar cells; for instance, Ito et al. investigated the TiO$_2$ screen printing techniques and their
They found that different preparation technique resulted in different particle size of TiO₂, which gave different efficiency. Larger efficiency was obtained from smaller TiO₂ particle size. There are two types of commercial TiO₂ pastes, in particular, transparent TiO₂ paste (having roughly uniform particle sizes) and opaque TiO₂ 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 TiO₂ particle size resulted in higher efficiency than that of 30 nm opaque for Cu₃BiS₃-semiconductor sensitized solar cells. Also, TiO₂ has three major structures, namely, rutile, anatase, and brookite, which provide a distinction on the performance of solar cells due to different band gaps.

Based on that, this study aimed to investigate the comparison of different types of TiO₂ 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 (AgSbS₂) QDSSCs. AgSbS₂ as solar absorbers were chosen due to its promising electrical and optical properties, namely, the absorption coefficient of 10⁵ cm⁻¹ and an energy gap of 1.73 eV. Also, its bandgap matches appropriately with TiO₂. The method used to obtain AgSbS₂ in this study was successive ionic layer adsorption and reaction (SILAR), which allows the formation of quantum dots to be adaptive to its cycle, providing tunable band gap.

**EXPERIMENTAL**

**Materials**

The materials used in this study were TiO₂ 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), Siver nitrate (99.9%, Merck), Potassium chloride (>98%, Choneye Pure Chemicals), Sodium hydroxide (>95%, Shimakyu’s Pure Chemicals), hexachloroplatinic acid (99%, Merck), FTO Glass (15Ω/sq, Nippon Sheet Glass, GreatCell Solar), Parafilm Sheet (130 μm, 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 TiO₂ was pasted on top of FTO-glass by using a doctor blade method, the thickness is defined by the thermoplastic sealant 50 μm thick. The samples were annealed by tube furnace under the atmospheric condition for 90 min at 500° C gradually. The process to grow the quantum dots is SILAR (as shown in Fig.-1).

![SILAR Method of Growing The Quantum Dots of AgSbS₂](image)

Fig.-1: SILAR Method of Growing The Quantum Dots of AgSbS₂

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
The 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 AgSbS$_2$-QDSSCs**

The photoanode obtained were assembled with Pt-counter electrode by using parafilm spacer. The polysulfide electrolyte was inserted into the solar cell 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 AgSbS$_2$ coated into TiO$_2$ 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 AgSbS$_2$ semiconductor was grown successfully into the TiO$_2$ layer without any impurities (JCPDS 17-0456). As can be seen, there is a larger intensity of AgSbS$_2$ peaks on transparent TiO$_2$ film than that of opaque TiO$_2$ film. It shows that there are more AgSbS$_2$ loaded into the layer of transparent TiO$_2$. 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 TiO$_2$ gives a small surface to volume ratio, whereas the opaque TiO$_2$ 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 AgSbS$_2$ semiconductor.

![XRD Pattern of AgSbS$_2$ coated into Transparent TiO$_2$ and Opaque TiO$_2$](image)

The crystalline form of TiO$_2$ is different for each paste; the transparent TiO$_2$ 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. Basically, the anatase structure is yielded by annealing the paste at 400-500°C and the rutile structure is obtained at 600°C; 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 TiO$_2$ 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.\textsuperscript{18,20} Related to this, AgSbS\textsubscript{2}-SSCs using different TiO\textsubscript{2} paste also undergo different photovoltaic performance, as seen in Figure 2, the transparent TiO\textsubscript{2} film shows less anatase structure, yet the intensity of AgSbS\textsubscript{2} 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 TiO\textsubscript{2} crystal gives different photocatalytic performance from either pure rutile structure or pure anatase structure.

Table-1: Measurement Result from AgSbS\textsubscript{2} QDSSCs under Different TiO\textsubscript{2} Paste Types

<table>
<thead>
<tr>
<th>TiO\textsubscript{2} Paste Types</th>
<th>J\textsubscript{sc} (mA/cm\textsuperscript{2})</th>
<th>V\textsubscript{oc} (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparent TiO\textsubscript{2}</td>
<td>3.51</td>
<td>0.24</td>
<td>37.62</td>
<td>0.317</td>
</tr>
<tr>
<td>Opaque TiO\textsubscript{2}</td>
<td>1.42</td>
<td>0.25</td>
<td>31.01</td>
<td>0.110</td>
</tr>
</tbody>
</table>

Transparent TiO\textsubscript{2} results in larger FF than that of opaque TiO\textsubscript{2}, showing that the resistance on the AgSbS\textsubscript{2}-QDSSC using transparent TiO\textsubscript{2} is relatively small.\textsuperscript{21} As explained earlier that the transparent one lets the AgSbS\textsubscript{2} semiconductor fill in the matrix of TiO\textsubscript{2} 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 AgSbS\textsubscript{2} coated into TiO\textsubscript{2} layer, it can be seen that opaque TiO\textsubscript{2} (Figure 3(b)) gives a rougher surface than transparent (Fig.-3a), the surface difference of opaque TiO\textsubscript{2} is 2.89\% and 1.46\% for transparent TiO\textsubscript{2}. The rough surface comes from different particle sizes that exist in the opaque TiO\textsubscript{2} paste, yet this situation does not improve the loading and reaction of ions during the SILAR process in the case of AgSbS\textsubscript{2} semiconductor. The combination of small and large particles results in the formation of aggregates, thus forming the crack in the obtained TiO\textsubscript{2} film (Fig.-3b).

![Fig.-3: Topography Images of of AgSbS\textsubscript{2} coated into (a) Transparent TiO\textsubscript{2}, (b) Opaque TiO\textsubscript{2}](image)

** Scanning Electron Microscopy (SEM) Analysis**

As shown in Fig.-4, there are more flakes formed in the opaque TiO\textsubscript{2}; however, based on the XRD results, these flakes do not lead to the improved crystal structure of AgSbS\textsubscript{2}. A study conducted by Ito et al. discovered that some kind of TiO\textsubscript{2} paste gives aggregation when it comes to forming the film. And, the same as this case, those aggregations give small cracks in the porous TiO\textsubscript{2} layer, as also proved by AFM results. Transparent TiO\textsubscript{2}, however, shows a smoother surface even though the flakes seem to distribute.
non-uniformly. There are fewer cracks compared 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).

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.

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REFERENCES


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