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A comparative study between titania and zirconia as material for scattering layer in dye-sensitized solar cells

N M Nursam, J Hidayat, Shobih, E S Rosa L M Pranoto
Research Centre for Electronics and Telecommunication – Indonesian Institute of Science
Kampus LIPI Building 20 level 4 Jl. Sangkuriang, Cisitu, Bandung 40135, Indonesia
Email: natalita.maulani.nursam@lipi.go.id

Abstract. The photoanode of dye-sensitized solar cells (DSSC) is typically composed of nanocrystalline titania (TiO2) layer that has been sensitized with light-absorbing dye molecules. Large portion of the light, however, could not be efficiently absorbed due to some physical reasons, such as TiO2 crystal size (typically 10-25 nm) that makes the photoanode remains partially transparent to the visible region in the solar spectrum. One of the ways to improve the light harvesting efficiency in DSSC could be achieved by employing an additional scattering layer over the TiO2 electron transport material. In this contribution, we evaluate the effect of light scattering properties on the performance of DSSC. Specifically, the light scattering properties provided from two different scattering materials, i.e. additional TiO2 scattering layer and zirconia (ZrO2) scattering layer, were compared. Both layers were deposited using screen printing technique under the same condition on top of 8 µm thick TiO2 photoanode layer. All samples subsequently received the same thermal annealing treatment at 500 °C and sensitized with ruthenium-based synthetic dyes. Our results revealed that the thickness of the scattering layer for both TiO2 and ZrO2 had a significant effect on the solar cell performance. The best photoconversion efficiency was achieved by samples that were coated with one screen-printing cycle, giving an overall efficiency of 3.50 % and 4.02% for TiO2 and ZrO2, respectively.

Keywords: efficiency; hydrothermal; photoelectrode; solar cell; TiO2

1. Introduction
Dye-sensitized solar cell (DSSC) based on porous nanocrystalline films offers low fabrication cost yet with high attainable efficiency. As one of the entities of third generation photovoltaic technology, DSSC was made to achieve high photoconversion efficiency beyond the Shockley-Quisser limit of 31% [1]. The performance of DSSC has been progressing considerably since its breakthrough in 1991 [2].

There have been many efforts reported to increase the performance of DSSC. The DSSC photoelectrode is typically formed by highly porous titanium dioxide with a particle size in the range of 10-50 nm [3, 4]. This specification provides a high surface area that allows an effective monolayer adsorption of the dye molecules at the surface of TiO2. However, according to Rayleigh and Mie scattering theory [5], particle size above 200 nm is typically required to be able to scatter light in the visible light range between 500-700 nm. Consequently, the TiO2 particles are transparent to most of the incident light during the solar cell operation. Hence, additional layer with large particle size could
be employed to reflect the light back into the TiO$_2$ layer, thus increasing the amount of light captured by the cell and minimizing the loss of radiation. Optical enhancement of the porous film has also been shown to improve the performance of TiO$_2$ photocatalyst [6]. Light scattering effect could be achieved by employing different structures or materials, for example using large TiO$_2$ beads [7], rutile TiO$_2$ [8], TiO$_2$ with core-shell [9], or hollow sphere structure [10]. Among the approaches above, the use of large TiO$_2$ and ZrO$_2$ particles have been some of the most frequently implemented techniques. However, the comparison between the effectiveness of those two materials in improving the DSSC performance has not yet been explored. In this contribution, we report the enhancement in photoelectric conversion efficiency of TiO$_2$-based DSSC by applying two different materials the scattering layer, namely anatase TiO$_2$ and monoclinic ZrO$_2$. These two materials were particularly selected as they are abundant, versatile, stable, and can be readily synthesized using relatively simple techniques such as via wet chemistry method. The extent of their roles as scattering layer will be investigated thoroughly by analyzing the optical properties as well as measuring the electrical parameters of the cells.

2. Experimental Section

2.1. Cells preparation

DSSC photoanodes with an active area with a size of 1×1 cm$^2$ was prepared by depositing TiO$_2$ paste (Dyesol, 18NR-AO opaque paste) on top of fluorine-doped tin oxide substrate (Dyesol, 15 Ω/sq, 3.2 mm thick) using the screen-printing technique. The TiO$_2$ layer was printed in two cycles for each sample, giving a total thickness of approximately 8-10 μm. After the deposition, the TiO$_2$ films were subsequently annealed at 500 °C for 15 min (RTC L4-310 conveyer belt furnace) to strengthen the bonding between the TiO$_2$ particles and the substrate.

Before proceeding to the sensitization step, all samples received an additional coating of either TiO$_2$ (Dyesol, TiO$_2$-WER) or ZrO$_2$ (Solaronix) reflective layer. To analyze the effect of thickness, the deposition of each scattering layer was varied to 1, 2 and 4 cycles. The thickness of the scattering layer was approximately 2, 4 and 6 μm after 1, 2 and 4 cycle of printing, respectively. The samples were labeled as TiO$_{2-x}$ or ZrO$_{2-y}$, wherein x and y represent the number of coating cycle for TiO$_2$ and ZrO$_2$, respectively. Meanwhile, a sample without any scattering layer was referred as a control. Another annealing at 500 °C for 15 min was subsequently conducted on all samples. The sensitization process was carried out by soaking all samples in ruthenium-based dye [RuL$_2$(NCS)$_2$]:2 tetranbutylammonium, where L=2,2′-bipyridil-4,4′-dicarboxylic acid (Dyesol, Z907) with a concentration of 20 mg/L in ethanol. Meanwhile, the counter electrodes were prepared by sputtering Pt target using DC sputtering (ARC-12 M) under argon gas with a pressure of 4mTorr for approximately 20 min. After both electrodes were attached together using thermoplastic sealant, an acetonitrile-based liquid electrolyte containing 1/I$_3^-$ redox mediators (Dyesol, EL-HPE) was then injected through the spacer using a syringe. The electrolyte filling holes were then sealed using the two-part hermetic sealing compound to protect the cells from the external environment.

2.2. Characterizations

The morphology of the final films was studied using field emission scanning electron microscopy (FE-SEM, JEOL JB-4610F) operated at 15 kV. All samples were sputter coated with carbon before the analysis. The crystal phase and structure of the films were characterized using X-ray diffraction (XRD) analysis (Shimadzu Maxima XRD-7000 X-ray diffractometer) with Cu Kα source at λ=1.54056 Å. After the construction of the cells, the electrical parameters of the finished samples were immediately measured using current-voltage (I-V) measurement system (National Instrument) under sun simulator with AM1.5 filter and an intensity of 500 W/m$^2$ (Oriel, 91192).
3. Results and Discussion

Figure 1 shows the surface morphology of the TiO$_2$ photoanodes without and with scattering layers. The control sample (Figure 1a) essentially represented the photoactive layer, showing mesoporous TiO$_2$ with average particle size of approximately 30-50 nm. It can be seen that the particle size of the scattering materials (Figure 1b and c) were in the order of hundreds of micrometers, which are much larger compared to the particle size of the TiO$_2$ photoactive layer. It is clear that both TiO$_2$ and ZrO$_2$ reflective layers existed as aggregates. However, it can be qualitatively seen that ZrO$_2$ formed larger agglomerations compared to TiO$_2$. The particle size of TiO$_2$ is estimated at ~200 nm, while the particle size of ZrO$_2$ was larger than 400 nm. In addition, it can be seen that the TiO$_2$ reflective layer was separated by large voids between the particles.

Figure 1. SEM images of TiO$_2$ photoanodes (a) without scattering layer, (b) with TiO$_2$ reflective layer, and (c) with ZrO$_2$ reflective layer.

Figure 2. XRD patterns of photoanodes with TiO$_2$ and ZrO$_2$ scattering layer (both samples were deposited in 1 cycle). The black triangle (▲) symbols represent the crystal planes of the FTO glass, while the A and Z represent the crystal planes of anatase TiO$_2$ and monoclinic ZrO$_2$, respectively.

Note that the patterns were shifted along the y-axis for clarity.

Figure 2 shows the XRD spectra obtained on the photoanodes with reflective layers. The wide-angle XRD was used to determine the crystal phase of the reflective layers. The XRD pattern shows that the TiO$_2$ reflective material consisted of anatase phase based on JCPDS 21-1272. This was confirmed by the presence of strong peaks located at 20~25.4° that can be assigned to (101) plane of anatase titania. Meanwhile, from JC-PDS 37-1484, the XRD pattern of the ZrO$_2$ reflective layer only
showed monoclinic phase, as indicated by the strong peak at 20–28.1° and 31.3°. These results indicated that both TiO$_2$ and ZrO$_2$ only existed as single phase crystal.

The effect of scattering layer was subsequently characterized by the photovoltaic performance of the constructed cells. Figure 3 shows the current-voltage ($I$-$V$) curves for DSSC with and without scattering layer, while the electrical parameters of the cell are summarized in Table 1. For both TiO$_2$ and ZrO$_2$ scattering layer, 1 cycle scattering layer deposition gave the best photoconversion efficiency among all variations, showing almost ten folds enhancement in the efficiency as compared to that of the control sample. The improvement was mainly attributed by the significant rise in the photocurrent density, as indicated by the $I_{SC}$ that increased from 0.817 mA in the control sample to 7.860 mA when TiO$_2$ and ZrO$_2$ scattering layer was respectively added. The increase in the $I_{SC}$ suggested that the additional scattering layer may also serve as the anchoring spots for the dye molecules, thus not only giving enhancement from light scattering but also increasing light absorption through better dye loading. However, the $I_{SC}$ was found to drop when the thickness of the scattering layer was increased further, suggesting a decrease in charge collection efficiency as previously reported by Son et al. [11].

![Figure 3. $I$-$V$ curves of DSSC made with (a) TiO$_2$ and (b) ZrO$_2$ scattering layer with various deposition cycles, compared to the cell without any scattering layers (control).](image)

Table 1. Photovoltaic properties of the DSSC prepared without and with scattering layer with different scattering material and thickness.

|                  | Control | TiO$_2$-1 | TiO$_2$-2 | TiO$_2$-4 | ZrO$_2$-1 | ZrO$_2$-2 | ZrO$_2$-4 |
|------------------|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| $P_{max}$ (mW)   | 0.312   | 2.635     | 1.423     | 0.262     | 3.099     | 0.008     | 0.003     |
| $V_{max}$ (V)    | 0.488   | 0.447     | 0.427     | 0.264     | 0.488     | 0.366     | 0.305     |
| $I_{max}$ (mA)   | 0.640   | 5.887     | 3.332     | 0.995     | 6.348     | 0.022     | 0.010     |
| $I_{SC}$ (mA)    | 0.817   | 7.860     | 4.547     | 1.478     | 7.879     | 0.038     | 0.018     |
| $V_{oc}$ (V)     | 0.631   | 0.672     | 0.611     | 0.407     | 0.713     | 0.611     | 0.488     |
| $FF$             | 0.606   | 0.499     | 0.512     | 0.436     | 0.551     | 0.349     | 0.353     |
| Efficiency (%)   | 0.42    | 3.50      | 1.88      | 0.35      | 4.02      | 0.07      | 0.03      |

Table 1 shows that the best performing sample in this work was achieved by sample ZrO$_2$-1 with an efficiency of 4.02%. The reason for this could be related to the particle size of the reflective layer. As previously confirmed by the SEM analysis, ZrO$_2$ had a bigger particle size (i.e., $>400$ nm) than TiO$_2$, which consequently reflected light in the visible light wavelength ($400 \text{ nm}<\lambda<700$ nm) more.
efficiently according to the Mie wavelength dependent scattering theory. Overall, the deterioration in the performance of the cell with the increase in the scattering layer thickness could be attributed to two plausible factors. First, as previously mentioned, the decrease in the efficiency was associated with the decrease in $I_{SC}$. This trend was especially profound for the ZrO$_2$ samples. It was suspected that the denser nature and larger aggregates in the ZrO$_2$ layer might have affected the infiltration of dye (during the impregnation process) and hindered the electrolyte contact with the photoactive layer. These possibilities were supported by the significant decrease in $I_{SC}$ for ZrO$_2$-2 and ZrO$_2$-4. Secondly, the fill factor ($FF$) also decreased with the addition of scattering layer. Thicker films typically lead to higher series resistance in the cell [12]. Thus it was fairly expected that the increase in the scattering layer thickness would result in lower $FF$, although such decrease was not significantly observed in this work.

4. Conclusions

In this study, we have presented a comparison of the material characteristics and photovoltaic performance between TiO$_2$ and ZrO$_2$ as a scattering layer in DSSC. Both materials were shown to exist as large aggregates, which was an order of magnitude larger than the particle size of the mesoporous TiO$_2$ photoactive layer. Likewise, both materials showed similar characteristics in term of the crystal phase, i.e., both had only single crystal phase that is anatase TiO$_2$ and monoclinic ZrO$_2$. The addition of TiO$_2$ and ZrO$_2$ scattering layer significantly enhanced the cell performance to some extent. The highest improvement was obtained when ZrO$_2$ deposited through 1 printing process was applied. However, the increase in the scattering layer thickness has a negative influence on the cell performance due to incomplete dye and electrolyte penetration as well as the increase in the internal resistance. The results of this study could be used as standard guidelines for applying TiO$_2$ and ZrO$_2$ as a reflective layer in TiO$_2$-based DSSC.

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