A Brief Study of the Carbon Counter Electrode for Photosensor based on DSSC

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Abstract. We investigate the fabrication of photosensor devices based on dye sensitized solar cells (DSSC). DSSC photovoltaic cells use solar light energy to trigger chemical reactions as a source of electrical energy. DSSC has several advantages, namely low production costs, environmental friendliness, easy fabrication, and high-power conversion efficiency. Therefore, DSSC is ideal for use as a photosensor. Most DSSCs use a wet electrolyte to provide ionic conductivity to the photoanode. However, long-term use of liquid electrolyte causes corrosion which can reduce the stability of the resulting current. In this research, yttria stabilized zirconia (YSZ) solid electrolyte was used to prevent corrosion of the photoanode. Samples were characterized using XRD, SEM, UV-Vis and photoresponse. The XRD results show the crystallinity of nanoporous TiO2 and YSZ. SEM results show that the average particle size distribution of TiO2/YSZ DSSC cells is 315 nm. The sensitivity, rise and fall times of the photosensor have been calculated by varying the counter electrode when testing the photoresponse. Finally, Graphene as a counter showed higher voltage and current compared to AC which is 0.2 V and 0.05 µA.

1 Introduction

DSSC is a dye-based solar cell that is capable of converting photons into electrical energy by utilizing semiconductor materials that have wide band gap energy [1]. TiO2 mesoporous material is used as a photoanode because it effectively increases light absorbance, has good chemical stability, high refractive index and low level of toxicity. [2]. Therefore, DSSC is ideal for use as a photosensor platform [3]. Most DSSC fabrications use liquid electrolyte, but using liquid electrolyte for a long time can cause the photoanode and counter electrode to easily corrode. [4], so it affects lifetime in the long term [5]. Another alternative is to replace the liquid electrolyte with solid electrolyte in order to increase the stability of the DSSC device [6]. One of the solid electrolytes, namely Yttria Stabilized Zirconia (YSZ), has

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high ionic and electrical conductivity, low thermal conductivity and good corrosion resistance at high temperatures to avoid degradation. [7][8].

The counter electrode uses molybdenum (Mo) which is deposited on a glass preparation as a substrate. Mo materials have been considered as promising electrode materials due to their unique structural and performance advantages. Mo is inexpensive and abundant in the earth's crust [9]. Mo thin films have been widely used as back electrodes in solar cells. Sputter deposition has become the most popular choice for growth of Mo thin films in solar cell applications [10]. To maximize the performance of the counter electrode on the photosensor, carbon materials such as activated carbon (AC) and graphene are added. AC is a processed amorphous carbon which has stable chemical properties and high mechanical strength, acid resistance, alkali resistance, heat resistance, and insolubility in water and organic solvents [11]. Graphene has good conductivity and electrocatalytic action has been demonstrated as a potential material for counter electrode [12]. The development of photosensors is expected to function with a measurable photovoltaic response presented using a sandwich structure.

2 Experimental Method

The FTO substrate with a size of 2 x 2 cm² was washed alternately with acetone and deionized water for 15 minutes at 50°C and dried at room temperature. TiO₂ seed layer deposition using the sputtering method on the FTO substrate (Figure 1). TiO₂ nanoporous was synthesized from 0.25 gr PEG added with 1 gr TiO₂ dissolved in 1 ml HNO₃ and triton X-100. TiO₂ nanoporous deposition was carried out using the screen-printing method. The samples were heated with temperature increases of 100°C (15 minutes), 300°C (15 minutes), and 500°C (30 minutes). Post treatment was carried out on the samples by immersing the samples in a solution of 100 µL TTAIP and 20 ml IPA heated at 100°C for 30 minutes. The sample was cleaned with ethanol solution p.a. and heated again at 500°C. Next, TiO₂ sputtering was carried out on the film using the Direct Current method with a power of 150 W for 60 minutes.

A total of 2 grams of YSZ powder which had been activated at a temperature of 1200°C was added with 300 µL of IPA and 180 µL of HNO₃ p.a. Deposition on a TiO₂ nanoporous film using a doctor blade with a thickness of 5 µm. The sample was heated at 100°C for 1 hour. The counter electrode was made by deposition of activated carbon and graphene on a Mo substrate. Next, the counter electrode and FTO/TiO₂/YSZ photoanode were fabricated as shown in Figure 1. The microstructure of the photosensor film was tested through XRD, SEM-EDX, and UV-Vis characterization. Furthermore, solar simulator testing was also carried out to determine the response of the photosensor when exposed to light.

3 Result and Discussion

3.1 X-Ray Diffraction (XRD)

Figure 2 shows the diffraction patterns of nanoporous TiO₂ and nanoporous TiO₂/YSZ films using the screen printing and doctor blade method. Figure 2(a) that TiO₂ is in the anatase phase confirmed by AMCSD No. 0019093. XRD analysis shows that the diffraction pattern
of nanoporous TiO$_2$ is detected at the 2θ: 25.37°, 37.04°, 37.88°, 52.1°, 54.02°, 55.22°, 62.28°, 70.5°, 75.26°, 78.88°, and 82.93° with consecutive hkl fields (011), (013), (004), (200), (022), (015), (121), (123), (220), (125), (026), and (224). Figure 2(b) shows the YSZ diffraction pattern detected at the 2θ: 30.2°, 31.51°, 35.1°, 50.2°, 59.9°, 62.79°, and 74.29° with consecutive hkl fields (111), (002), (200), (202), (311), (222), and (400) [13]. The highest peak of YSZ is at an angle of 30.2°. Figure 2(c) shows the XRD results of TiO$_2$ nanoporous/YSZ with the highest peak of TiO$_2$ detected at an angle of 62.28° with hkl (123).

3.2 Spektrofotometer Ultraviolet-Visibel (UV-Vis)

UV-Vis characterization was carried out to determine the optical properties and bandgap of the resulting film. The absorbance graph and fitting tauc plot are shown in figure 3. Figure 3(a) shows the UV-Vis absorbance graph of TiO$_2$ and TiO$_2$/YSZ measured in the wavelength range of 200 nm to 1100 nm. The nanoporous TiO$_2$ sample shows absorbance at 250 nm, while the nanoporous TiO$_2$/YSZ sample shows absorbance at 225 nm and 300 nm. Based on the frequency of the light spectrum, the wavelength range that can be absorbed by the film is 225 nm to 350 nm. This shows that the film is only able to absorb UV rays.

To determine the bandgap of TiO$_2$ nanoporous and TiO$_2$ nanoporous/YSZ tauc plots were constructed using direct methods. The direct bandgap value of TiO$_2$ is 3.62 eV (Fig. 3(b)) which is higher than the corresponding indirect band gap values and to the standard band-gap range of TiO$_2$ (3.2 eV–3.35 eV). The bandgap value is more related to the absorption edge value of the UV-visible spectrum, which is why the direct band gap is assigned to the synthesized sample [14]. Bandgap dari TiO$_2$ nanoporous/YSZ adalah 3.28
This was confirmed by Costantini, et al (2022) that the YSZ bandgap is around 3.0 eV and 3.8 eV [15].

3.3 Morphology

SEM image of TiO$_2$ nanoporous and TiO$_2$ nanoporous/YSZ are shown in Figure 4. The average particle distribution of TiO$_2$ nanoporous is 297.2 nm, while the thickness of TiO$_2$ nanoporous layer is 40.4 µm. After YSZ deposition, the thickness of nanoporous TiO$_2$ decreased to 10.93 µm, while the thickness of YSZ was measured to be 10.07 µm, just like the thickness setting when deposition using the doctor blade method, namely 10 µm. The average particle distribution of TiO$_2$ nanoporous/YSZ is 315 µm.

3.4 Photoresponse

Figure 5 shows a graph of the voltage and current photoresponse as a function of time for photosensor based on DSSC with different counter electrode which is AC and graphene. The photosensor with graphene counter has a high voltage response of 0.51 V and high current response of 0.425 µA, while, for the photosensor with AC counter has a voltage response of 0.38 V and current response at 0.37 uA. Therefore, the photoresponse of photosensor with graphene counter is better than photosensor with AC counter. The parameters of the photoresponse test results are summarized in Table 1.
In this study, the synthesis of TiO$_2$ mesoporous as the fotoanode for making photosensor based on DDSC was carried out using YSZ solid electrolyte and different counter electrode, (a) (b)  

**Fig. 4.** Morphology of SEM on (a) TiO$_2$ nanoporous film and (b) TiO$_2$ nanoporous/YSZ film.  

(a) (b)  

**Fig. 5.** Graph of photoresponse of (a) current and (b) voltage, and fitting current photoresponse (c) AC and (d) graphene counter electrode.  

(c) (d)  

4 **Summary**  

In this study, the synthesis of TiO$_2$ mesoporous as the fotoanode for making photosensor based on DDSC was carried out using YSZ solid electrolyte and different counter electrode,
which is AC and graphene. Based on the result of XRD, UV-Vis, SEM and photoresponse can be concluded that graphene counter electrode on molybdenum substrate produces large values of voltage, current and fast light response. Finally, photodetector with graphene as counter electrode showed higher performance compared to photodetector with AC counter electrode.

**Table 1.** Parameters for photosensor based on DSSC photoresponse.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2$/YSZ/AC/Mo</th>
<th>TiO$_2$/YSZ/Graphene/Mo</th>
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</thead>
<tbody>
<tr>
<td>Voltage (V)</td>
<td>0.38</td>
<td>0.51</td>
</tr>
<tr>
<td>Current (μA)</td>
<td>0.377</td>
<td>0.425</td>
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<td>t rise (s)</td>
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<td>1.92</td>
</tr>
<tr>
<td>t decay (s)</td>
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<td>3.09</td>
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</tbody>
</table>

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**References**


