Material analysis and characterization of working electrodes of dye-sensitized solar cells

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Abstract. The aim of this paper is to demonstrate the influence of the TiO₂ with different sintered time regarding the performance of photovoltaic characteristics of DSSCs. A layer of TiO₂ with a thickness of ~8-10 μm and an area of 0.25 cm² was prepared by depositing TiO₂ nanoparticles paste onto a fluorine-doped tin oxide (FTO) substrate by doctor blade technique, followed by sintering at 450°C with 4 different sintering times: 10 min, 20 min, 30 min, and 40 min. The Pt solution was dripped on FTO substrate works as counter electrode. SEM, XRD and I-V curve were conducted for the material analysis. The photovoltaic characteristics were measured under AM 1.5 sunlight simulator. The results reveal that the different sintered time of TiO₂ working electrode did affect the photovoltaic conversion efficiency. In conclusion, TiO₂ sintered for 30 min yields the highest power conversion efficiency of 6.273%.

1 Introduction

The needs for alternative energy has become a great concern due to the growing energy demand. Solar energy resource is a rich and clean renewable energy and has attracted great attention of researchers in the world. According to the BP Statistical Review of World Energy, it revealed that the reserves/production ratio for oil, natural gas and coal was 50.6 years, 52.5 years, and 153 years, respectively in 2017. [1-2]. Among all of these materials, dye-sensitized solar cells (DSSCs) is one of the most prospective materials for photovoltaic solar cell devices [1,3]. The advantages of DSSCs including easy fabrication, cost-effectiveness, excellent low light performance, highly flexible, and lightweight[1,3]. A conventional DSSCs consists three main components: a mesoporous nanocrystalline TiO₂ anode which sensitized with light-absorbing dye molecules, a counter electrode (CE) which collects electrons and catalyze the redox couple regeneration, and a liquid electrolyte which comprising an iodide/triiodide (I⁻/I³⁻) redox couple between two electrodes[3-4].

A layer of TiO₂ with a thickness of ~8–10 μm and area of 0.25 cm² was usually prepared by depositing TiO₂ nanoparticles paste onto FTO by doctor blade technique,
followed by sintering at 450°C for 30 min. The sintered TiO₂ FTO was then immersing into N719 dye solution for dye absorption[5-6].

This paper discusses the effects on different annealing times of TiO₂ nanoparticles, in order to find out the best quality of working electrode.

2 Experimental

The main components of DSSCs are fluorine-doped tin oxide (FTO) conductive glass substrate, a TiO₂ film as photoanode, and a dye electrolyte and a counter electrode. The three components were stacked like a sandwich which is shown in Figure 1.

2.1 Fabrication of photoanode

A layer of TiO₂ with a thickness of ~8-10 μm and area of 0.25 cm² was prepared by depositing TiO₂ nanoparticles paste onto FTO substrate by doctor blade technique, shown in Figure 2.

Fig. 1. The configuration of DSSCs.

Fig. 2. Depositing TiO₂ nanoparticles paste onto FTO substrate.

A piece of transparent tape with 1 cm of adiameter area was cut off and pasted on the FTO substrate. The TiO₂ film was then depositing on the FTO substrate by doctor blade technique, followed by sintering at 450°C. These four different sintering time samples were indicated by A, B, C, and D, which correspond to four different sintering time conditions, 10 min, 20 min, 30 min, and 40 min, respectively. The fabricated TiO₂ working
electrode is shown in Figure 3. It was then soaked in the dye solution for 24 hours at room temperature and subsequently carefully rinsed with ethanol to remove unadsorbed dye.

2.2 Fabrication of counter electrode

The main material for the fabrication of counter electrode (CE) was platinum (Pt) by using spin coating method.

The Pt solution was dripped on FTO substrate and then placed on a spin coater machine with a spin speed of 500 rpm for 90 s in order to be evenly coated on FTO substrate. The fabricated Pt counter electrode is demonstrated in Figure 4.

2.3 Preparation of dyes

Acetonitrile, tert-Butyl alcohol (TBA) and N719 dye powder were the materials to prepare for the dye. Acetonitrile and TBA were mixed with the proportion of 1:1 and the dye concentration was $5 \times 10^{-4}$ mol/L. The prepared TiO$_2$ photoanode was then soaked in the dye solution for 24 hours at room temperature.

2.4 Preparation of electrolyte

The chemicals used to prepare the electrolyte including 0.5 M tert-butylypyridine, 0.005 M iodine (I$_2$), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, and 0.1 M lithium iodide (LiI). The above chemicals were all mixed with acetonitrile.

![Fig. 3. Fabricated TiO$_2$ film working electrode.](image3)

![Fig. 4. Fabricated Pt counter electrode.](image4)
2.5 Assembly of DSSCs

The DSSCs components were assembled started with applying a membrane (Surlyn) with an area of 1.5 cm × 1.5 cm and a thickness of 60 μm on TiO₂ working electrode. A area with idiameter of 1cm was cut off in order to expose the TiO₂ layer. The counter electrode was aligned and assembled with the membrane. The components were sealed together by heat press sealing maching with temperature of 145°C and 1.5 kg/mm² pressure. The electrolyte was injected to the drilled hole of counter electrode and sealed with a 3M transparent tape. An assembled DSSCs device was shown in Figure 5.

![Fabricated DSSCs](image)

3 Results and Discussion

3.1 SEM analysis

Figure 6 shows the SEM (Scanning Electron Microscopy) images of surface morphology of TiO₂ sintered at 450°C with different time (a) 10 min (b) 20 min (c) 30 min (d) 40 min. The uniformity, thickness, porosity, and grain size of TiO₂ were observed through SEM. The result indicates that the adhesion of TiO₂ on FTO does not change with different sintered times. In addition, the surfaces of TiO₂ were coral shape and without serious cracking which helps dye absorption.

3.2 XRD analysis

XRD analysis was conducted and shown in Figure 7. It was found that TiO₂ appears to be anatase phase crystals with different sintered time. However, the diffraction peak did not increase significantly as sintered time increased. It results in the best anatase phase crystals and diffraction peak under 20 and 30 min of sintered time.
2.5 Assembly of DSSCs

The DSSCs components were assembled started with applying a membrane (Surlyn) with an area of 1.5 cm × 1.5 cm and a thickness of 60 μm on TiO2 working electrode. A area with idameter of 1cm was cut off in order to expose the TiO2 layer. The counter electrode was aligned and assembled with the membrane. The components were sealed together by heat press sealing machine with temperature of 145 oC and 1.5 kg/mm2 pressure. The electrolyte was injected to the drilled hole of counter electrode and sealed with a 3M transparent tape. An assembled DSSCs device was shown in Figure 5.

Fig. 5. Fabricated DSSCs.

3 Results and Discussion

3.1 SEM analysis

Figure 6 shows the SEM (Scanning Electron Microscopy) images of surface morphology of TiO2 sintered at 450°C with different time (a) 10 min (b) 20 min (c) 30 min (d) 40 min. The uniformity, thickness, porosity, and grain size of TiO2 were observed through SEM. The result indicates that the adhesion of TiO2 on FTO does not change with different sintered times. In addition, the surfaces of TiO2 were coral shape and without serious cracking which helps dye absorption.

3.2 XRD analysis

XRD analysis was conducted and shown in Figure 7. It was found that TiO2 appears to be anatase phase crystals with different sintered time. However, the diffraction peak did not increase significantly as sintered time increased. It results in the best anatase phase crystals and diffraction peak under 20 and 30 min of sintered time.

(a) 10 min (30.0 kV, ×60k)
(b) 20 min (30.0 kV, ×60k)
(c) 30 min (30.0 kV, ×60k)
(d) 40 min (30.0 kV, ×60k)

Fig. 6. Top SEM images of TiO2 sintered at 450°C with different time (a) 10 min (b) 20 min (c) 30 min (d) 40 min.

Fig. 7. XRD pattern of TiO2 with different sintered times.
3.3 Measurement of photovoltaic characteristics of the DSSCs

The photovoltaic characteristics of the DSSCs were measured and shown in Figure 8. The characteristics including open-circuited voltage ($V_{oc}$), short-circuited current density ($J_{sc}$), fill factor (FF), and photovoltaic conversion efficiency. The results with different parameters are listed in Table 1. The $J_{sc}$ of the DSSCs with the TiO$_2$ working electrode fabricated under condition A, B, C, and D is 16.182, 16.284, 16.734, 16.423 mA/cm$^2$, respectively. The photoelectric conversion efficiency is 5.885%, 6.010%, 6.273%, and 5.634%, respectively.

![Graphs showing photovoltaic characteristics](image)

**Fig. 8.** The measurement of photovoltaic characteristics of the DSSCs with the TiO$_2$ working electrodes. (a) 450°C, 10 min (b) 450°C, 20 min (c) 450°C, 30 min (d) 450°C, 40 min.
3.3 Measurement of photovoltaic characteristics of the DSSCs

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![Fig. 8. The measurement of photovoltaic characteristics of the DSSCs with the TiO$_2$ working electrodes.](image)

Table 1. The photovoltaic characteristics of the DSSCs with the TiO$_2$ working electrodes.

| Time  | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF (%)  | Efficiency (%) |
|-------|-------------|----------------------|---------|----------------|
| 10min | 0.761       | 16.182               | 47.750  | 5.885          |
| 20min | 0.768       | 16.284               | 48.006  | 6.010          |
| 30min | 0.767       | 16.734               | 48.870  | 6.273          |
| 40min | 0.769       | 16.423               | 44.574  | 5.634          |

![Fig. 9. The I-V curves of the DSSCs with the TiO$_2$ working electrodes under different sintered times.](image)

As we input all of the characteristics results into Origin software, the I-V curves figure was yield as Figure 9. The I-V curves indicates that different parameter has an effect on the photovoltaic characteristics of DSSCs. It also reveals that the photocurrent increases as the TiO$_2$ sinter time increases. Based on Table 1, we also found that as the TiO$_2$ sintered time increases, it improves $J_{sc}$ and FF. It explains the result of XRD in Figure 7. When TiO$_2$ sintered at 450°C with enough time, anatase phase crystals and diffraction peak will be increased. In addition, TiO$_2$ sintered for 30 min will yield the highest power conversion efficiency of 6.273%.

4 Conclusions

In summary, we have demonstrated the influence of the TiO$_2$ with different sintered time (10 min, 20 min, 30 min, 40 min) of the working electrode on the DSSCs performance. It includes $V_{oc}$, $J_{sc}$, fill factor, and power conversion efficiency. SEM, XRD and I-V curve were conducted for the material analysis of the TiO$_2$ photoanode. The photovoltaic characteristics were measured under AM 1.5 sunlight simulator. Different sintered time of TiO$_2$ working electrode has an influence on the photovoltaic conversion efficiency. TiO$_2$ sintered for 30 min will yield the highest power conversion efficiency of 6.273%.
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