Electrospinning Titanium Dioxide (TiO$_2$) nanofiber for dye sensitized solar cells based on Bryophyta as a sensitizer

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Abstract. From an engineering and economic perspective, immobilized TiO$_2$ nanocatalysts are preferred in a variety of applications. In this study, TiO$_2$ polymer solution was synthesized using ethanol, acetic acid, polyvinylpyrrolidone (PVP), and titanium tetra isopropoxide (TTIP). TiO$_2$ solution was deposited on the FTO substrate by electrospinning method to obtain nano-sized layer. Capillary of syringes given a positive DC voltage of 6 kV to produce nanofiber, then annealed at 450 $^\circ$C for 3 hours. Chlorophyll has obtained from extracted moss through a chromatographic process to used for dye. TiO$_2$ nanofiber layer manufactured with varied by time and characterized by UV-Vis and IV-meter. The result exhibited a maximum efficiency of 0.0036% and significant absorption at 350 nm-500 nm wavelength.

1. Introduction
Currently, power conversion efficiencies of up to 24% was achieved by silicon-based solar cells, although this high efficiency was offset by the high cost.[1] DSSC is promising alternative to silicon analogues because of inherent advantages such a simple manufacturing processing, low cost, and ease of large-scale of production.[2] DSSC have high conversion efficiencies up to 12% have been reported.[3-6]

Key factor to achieve DSSC high performance is to choose of mesoporous TiO$_2$ working electrode and light scattering layer. The concept is to incorporated light scattering layer so that the lower conversion of photon due to thin mesoporous TiO$_2$ layer can be compensated.[7] The charge carrier mobility, electron transfer efficiency and the rate of recombination of charge carriers are performance related size-dependent an improvement of the performance with respect to micrometric-size materials as a result of the increased specific surface area and surface reactivity.[8] The nanofibers showed increase light absorbed in the visible of region. This is partly derived optical path length extending from the wavelength of incident light caused by scattering of light in a layer of TiO$_2$ nanofibers.[9]

The sol-gel electrospinning derived TiO$_2$ nanofibers provide the unique advantage of high specific surface area with enhanced catalytic property.[10] A comparative among nanoparticles and sol-gel derived nanofibers suggested that enhanced catalytic property of nanofibers is often attributed to the higher specific surface area, for mesoporosity and particle alignment.[11-12] The method of electrospinning has been drawing attentions in the field of research TiO$_2$ nanofibers in preparation for
the DSSC application for a careful selections of raw materials with different ratios can produce in TiO$_2$ desired shape with a uniform control diameter of the fiber.[9]

In this research, we success to fabricated and synthesize TiO$_2$ nanofibers by electrospinning method as the working electrode and DSSC scattered layer. The rate of time of electrospinning to fabricated TiO$_2$ nanofibers was varied from 10, 15, 30, and 45 min.

2. Experimental details

2.1. Materials

The materials used in manufacturing of polymer solution was made by using absolute ethanol (C$_2$H$_5$OH, Merck, Jerman), acetic acid (CH$_3$CO$_2$H, 99.7% Aldrich) was obtained from Sigma-Aldrich, USA. Powder polyvinylpyrrolidone (PVP, Mw ~29000 Aldrich) and titanium tetra isopropoxide (TTIP, 97% purity, Aldrich, USA) were used as a precursor in the electrospinning procedure.

2.2. Preparation of photocatalysts

Flourine doped tin oxide (FTO) glass was prepare as follow: FTO glass was cutted into 2.5 cm × 2 cm pieces, successively rinsed with soap, alcohol 90% in an ultrasonicator for 15 min, and dried at temperature of room.

2.2.1. Preparation of electrospinning solution. First, TiO$_2$ nanofiber solution was made by mixed 3.5 mL absolute ethanol with 1 mL acetic acid under stirring for 10 minutes. Subsequently, 2.5 g of PVP were successively added to a stirred solution and dissolved under magnetic stirring for 1 hour. Finally, 0.5 mL TTIP was mixed in solution to obtain a homogeneous solution after the PVP was completely dissolve and stirred at room temperature for 24 hours.

2.2.2. Preparation of TiO$_2$ nanofiber. Electrospinning consist of a high-voltage DC power supply positive, infusion pumps and syringe with a needle tip diameter in 0.45 mm and collector. Figure 1 shows an electrospinning illustration for preparation TiO$_2$ nanofibers.

![Electrospinning illustration for preparation of TiO$_2$ nanofiber](image)

**Figure 1.** Electrospinning illustration for preparation of TiO$_2$ nanofiber

The syringe was connected to high-voltage power supply and the solution was loaded into the syringe. Electrospinning was performed at a voltage of 6 kV with a high-voltage supply. The flow rate was controlled at 3.0 mL/h by the syringe pump, and aluminum foil collector was set at a distance 25 cm. In this experiment, the rate of time of the electrospinning solution was varied from 10, 15, 30, and 45 minutes. The nanofibers electrode obtained was consequently subjected to calcinated in a furnace at 450 °C for 3 hours with healing rate 10 °C/min for removal of residual solvent and allow further condensation of the structure. Table 1 shows list the conditions of experimental for the TiO$_2$ nanofiber preparation.
Table 1
The Condition for the TiO$_2$ nanofiber preparation

| Code | Acetic acid (ml) | Ethanol (ml) | PVP (g) | TTIP (ml) | Time (min) |
|------|-----------------|--------------|---------|-----------|------------|
| C-1  | 1.0             | 3.5          | 2.5     | 0.5       | 10         |
| C-2  | 1.0             | 3.5          | 2.5     | 0.5       | 15         |
| C-3  | 1.0             | 3.5          | 2.5     | 0.5       | 30         |
| C-4  | 1.0             | 3.5          | 2.5     | 0.5       | 45         |

2.3. Characterization of the photocatalysts

Before characterization of photocatalysts, TiO$_2$ nanofiber was submerged in dye solution for 24 hours. Dye solution made from the moss (Bryophyta) extracted by chromatography process to obtain purified chlorophyll. The solution of dye was a mixture from bryophyta and acetone with a weight ratio of 1:5, and stirring for 1 h.

For efficiency tests, the finished DSSC was cut into 2 cm × 1 cm pieces, and their $I-V$ curves were measure using 1000 w/m$^2$ xenon lamp with Keithley 2602A $I-V$ meter. The light absorption edges of photocatalysts was observed by UV-vis Lambda 25 spectrophotometer.

3. Results and discussion

3.1 Photocatalytic activity

Absorbance spectrum measurement of photocatalysts layer was measured using a UV-Visible Lambda 25 spectrophotometer with a determined wavelength in the range 300-700 nm. Based on the result of these measurements, obtained the following results:

Figure 2. Comparison of absorbance and wavelength of TiO$_2$ nanofibers, and dye + TiO$_2$ nanofiber with rate of time electrospinning (a) 10 min, (b) 15 min, (c) 30 min, (d) 45 min; Comparison of
absorbance and wavelength dye + TiO$_2$ nanofiber for electrospinning (e) 10 and 15 min, (f) 30 and 45 min.

Figure 2 shows that the Bryophyta dye has the highest absorbance in range of the wavelength 350-500 nm and the second absorbance peaks appeared in range of the wavelength 650-700 nm. It shows that the absorbance of Bryophyta dye has sizeable in the wavelength range of visible light. It also shows that there was a displacement in the maximum absorbance of the mixture dye titanium dioxide nanofiber. Bryophyta dye has significant effect to enlarge absorbance and expand wavelength range of TiO$_2$ nanofibers.

In this study, the absorbance of TiO$_2$ nanofibers been obtained are small. However, all the data showed an increased in range of the wavelength 300-350 nm. So it can be seen that the maximum absorbance of TiO$_2$ nanofiber occurs in range of the wavelength 300-350 nm, with a maximum absorbance of 0.12 Au. The significant result was obtained from displacement wavelength of the TiO$_2$ nanofiber to dye TiO$_2$ nanofibers absorbance. The ability to absorb the light of dye TiO$_2$ nanofibers expand to the wavelength range of 300-500 nm and 650-700 nm. This displacement indicates that TiO$_2$ requires dye as a photosensitizer to extend the light absorption range, because when dye and TiO$_2$ mixed the dye molecules will firmly anchor to the surface of TiO$_2$.[13]

Maximum absorbance at the dye TiO$_2$ nanofibers layer is obtained at the rate of time TiO$_2$ nanofiber 15 min, of 0.85 Au. The result of a significant increase in absorbance shown in Table 2.

| Code | Rate of time (min) | Absorbance of TiO$_2$ nanofibers (Au) | Absorbance of Dye TiO$_2$ nanofibers (Au) | Beginning wavelength range (nm) | Final wavelength range (nm) |
|------|-------------------|--------------------------------------|------------------------------------------|-------------------------------|--------------------------|
| C-1  | 10                | 0.06                                 | 0.80                                     | 300-350                       | 300-500                  |
| C-2  | 15                | 0.12                                 | 0.85                                     | 300-350                       | 300-500                  |
| C-3  | 30                | 0.02                                 | 0.56                                     | 300-350                       | 300-500                  |
| C-4  | 45                | 0.03                                 | 0.72                                     | 300-350                       | 300-500                  |

Although there was a decrease of absorbance at 30 min electrospinning variety, increased return on variations within 45 min. As for yield reduction absorbance of 30 min and 45 min can be caused by many factors, such as the thickness, the evaporation of TiO$_2$ nanofibers layer, the effects of temperature, and the degree of homogeneity of the solution. Thus, it can be concluded that the higher the TiO$_2$ nanofibers electrospinning rate of time, the absorbance layer will tend to increase.

3.2 Performance of photocatalytic

The ability of DSSC was determined by converting the light into electrical energy by using characterizing current-voltage (I-V) method. Characterization performed by using a Keithley 2602A in dark and light condition under irradiation intensity of halogen lamps 1000 W/m$^2$, this intensity is the highest intensity radiation standards in Indonesia. The resulting test of current and voltage on photovoltaics with a rate of time variation electrospinning nanofibers as the working electrode is shown in Figure 3.
Figure 3. Efficiency graph of the photovoltaics TiO$_2$ nanofibers based on bryophyta dye as a sensitizer with a variation of the rate of time electrospinning (a) 10 min, (b) 15 min, (c) 30 min, (d) 45 min.

Based on Figure 3 can be seen that there were an not significant increase and a decrease in the efficiency of DSSC at a variation of time of TiO$_2$ nanofiber layer. The graph in Figure 3 is obtained from the data shown in Table 3. Determination of the efficiency equation follows:

$$\eta = \frac{P_{\text{max}}}{P_{\text{light}}} \times 100$$  \[14\]

Table 3
### Efficiency of Photovoltaics

| Rate of time | 10 min | 15 min | 30 min | 45 min |
|--------------|--------|--------|--------|--------|
| $I_{sc}$     | 2.7 mA | 5.2 mA | 9.2 mA | 2.2 mA |
| $V_{oc}$     | 0.3 mV | 0.3 mV | 0.3 mV | 0.2 mV |
| $P_{max}$    | 5.5 Watt | 6.5 Watt | 5.3 Watt | 4.0 Watt |
| Efficiency   | 0.0028% | 0.0036% | 0.0027% | 0.002% |

In this work, it can be determined that the efficiencies generated stable and did not increase significantly. This can be caused by many factors, including the influence of immersion layer in dye time, a low level of homogeneity in the mixed layer, layer thickness, the electrolyte used quick-drying, saturation levels of Bryophyta dye was very quickly, and sandwich system dssc that not working optimally.

Maximum efficiency photovoltaic layer obtained on dye TiO$_2$ nanofiber 15 min of 0.0036%. While the efficiency for variation electrospinning layer of 10 min, 30 min, and 45 min respectively 0.0028%, 0.0027%, and 0.002%.

### 4. Conclusion

The alteration from the rate of time of electrospinning nanofibers TiO$_2$ layer affects the absorbance value and efficiency DSSC. Bryophyta dye has a maximum absorbance in the wavelength range of 350-500 nm and 650-700 nm. After TiO$_2$ nanofibers layer dissolve in bryophyta dye, the absorbance of TiO$_2$ nanofibers layer displaced from range 300-350 nm to 300-500 nm.

The efficiency obtained on the variation rate of time electrospinning 10 min of 0.0028%, the variation rate of time electrospinning 15 min of 0.0036%, the variation rate of time electrospinning 30 min of 0.0027%, and the variation rate of time electrospinning 45 min of 0.002%. It means, the greater rate of time electrospinning TiO$_2$ nanofibers layer then the absorbance and the efficiency of DSSC will tend to increase.

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