Structural, morphological, optical, and electrical properties of TiO$_2$/ZnO rods multilayer films as photoanode on dye-sensitized solar cells

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Abstract. TiO$_2$ nanoparticles have been widely studied as photoanode materials in DSSC due to the high surface area. Still, TiO$_2$ nanoparticles exhibit weak light scattering which limiting red light absorption. On the other hand, one-dimensional structures such as rods demonstrate an increase in the light scattering. ZnO has undergone many structural modifications and exhibits higher mobility than TiO$_2$. The combining characteristics of TiO$_2$ nanoparticles and ZnO rods can improve photoanode performance. Therefore, the efficiency of DSSC can be increased. The TiO$_2$/ZnO rods photoanodes were fabricated in the following steps. First, TiO$_2$ nanoparticles were deposited on the conductive surface of ITO-Glass to form a double layer using the spin-coating method. Meanwhile, we prepare ZnO rods grown on the TiO$_2$ nanoparticles layer using the hydrothermal method by varying Zinc Nitrate Tetrahydrate precursors (20; 30; 50; and 100 mM). Several physical characterizations have been carried out, including XRD, SEM, FTIR, UV-VIS, and Keithley SourceMeter 2400 equipped with a solar simulator 100 mW/cm$^2$. Based on the results, the increasing concentration of Zinc Nitrate Tetrahydrate precursor affects the structural, morphological, optical, and electrical properties of TiO$_2$/ZnO rods multilayer photoanode and reaches the optimum point at 50 mM.

1. Introduction
Solar energy is considered as the most efficient sustainable energy resource due to the abundance in nature and low negative environmental impact. At present, the most extensively developed as solar energy technology is solar cells. Dye-sensitized solar cells (DSSC) belong to the group of thin-film solar cells which convert the visible light into electricity based on the photo-electrochemical processes [1]. Generally, DSSC structure consists of several components, among others, a conductive substrate such as Fluorine Tin Oxide (FTO) or Indium Tin Oxide (ITO) coated with semiconductor materials, dye molecules as sensitizers, redox mediator, and counter electrode [2]. The semiconductor materials play a significant role in electron transport performance [3]. Titanium dioxide (TiO$_2$) is one of the...
semiconductor materials which has been widely studied and implemented as photoanode on DSSC. TiO₂ nanoparticles have a high surface area for the higher dye loading [4]. However, the high surface area inhibits the absorption of red light through light scattering [5, 6]. Moreover, a large number of grain boundaries indicate low electron mobility (\( \sim 10^{-5} \) cm²/Vs). Hence, the possibility of electron recombination from TiO₂ nanoparticles and triiodide in redox mediator is higher [7,8]. Therefore, TiO₂ nanoparticles need to be incorporated with different types of materials, including polymer [9,10], carbon [11, 12], metal [13, 14], or metal oxide [15, 16]. The incorporation of TiO₂ nanoparticles with other metal oxides has shown superior physical properties. Zinc Oxide (ZnO) is one of the metal oxides which has attracted a great deal of attention as alternative photoanode materials on DSSC. ZnO offers high electron mobility (\( \sim 115-155 \) cm²/Vs) which can inhibit the process of electron recombination [17]. Nevertheless, DSSC based on TiO₂/ZnO nanocomposite photoanode produced a relatively low efficiency of 0.08% due to the weak light scattering ability.

On the other hand, ZnO with a 1D micro-nano structure such as rods demonstrates an increase in light scattering due to the low surface area. Electrons can travel through ZnO rods tens to hundreds of times faster than that through ZnO nanoparticles [18]. The TiO₂/ZnO rods photoanode can be fabricated using the hydrothermal method. Normally, the chemical reaction process takes place at high temperatures (\( \sim 200 \) °C) in a Teflon-lined stainless-steel autoclave which is heated using a vacuum furnace [19]. DSSC based on TiO₂/ZnO rods photoanode allowed to enhance the power conversion efficiency up to 0.46% [20]. Improvement of the efficiency can be attributed to the higher light-harvesting efficiency, lower charge recombination, and longer electron lifetime [21,22]. However, the components for the manufacture of Teflon-lined stainless-steel autoclave are relatively expensive and the crystal growth process is also difficult to observe [23].

So far, no comprehensive study has been found concerning the growth of ZnO rods on TiO₂ photoanode using the hydrothermal method at low temperatures (\( \sim 100 \) °C). The hydrothermal method at low temperature shows an effortless procedure due to the chemical reaction process takes place in a beaker glass which is heated using an oven [24, 25]. The low hydrothermal temperature will not damage the flexibility of the materials [26]. Furthermore, the low hydrothermal temperature is an environment-friendly method because the conditions can be controlled easily [27]. Therefore, in this research, we report a comprehensive study related to Structural, Morphological, Optical, and Electrical Properties of TiO₂/ZnO rods Multilayer Films as Photoanode on Dye-Sensitized Solar Cells. This research is expected to provide information related to the easy fabrication and detailed characterization of TiO₂/ZnO rods as photoanode on DSSC.

2. Method

2.1. Materials
Titanium dioxide (TiO₂) (particle size <25 nm; Sigma Aldrich; 99.7%), zinc nitrate tetrahydrate (Zn(NO₃)₂·4H₂O) (Merck KGaA), hexamethylenetetramine (C₆H₁₂N₄) (Merck KGaA), ITO-Glass conductive substrate, nitric acid (HNO₃) (Merck KGaA), deionized water (Waterone Onemed).

2.2. Fabrication of Double Layer TiO₂ Photoanode
0.5 g TiO₂ nanoparticles crushed using an agate mortar and added gradually 2 mL of 0.1 M HNO₃ until the solution was homogenous. The TiO₂ solution was deposited on the active area of the ITO-Glass conductive substrate using the spin-coating method 1000 rpm for 15 seconds. TiO₂ photoanode was dried using a hotplate at 90 °C for 30 minutes. The TiO₂ photoanode was fabricated twice using the same steps. The TiO₂ photoanode was calcined at 450 °C for 30 minutes.

2.3. Fabrication of TiO₂/ZnO rods Multilayer Photoanode
The growth of ZnO rods on the TiO₂ photoanode was accomplished by the hydrothermal method at low temperature (\( \sim 100 \) °C) using two main materials, namely Zinc Nitrate Tetrahydrate (Zn(NO₃)₂·4H₂O) as a precursor and Hexamethylenetetramine (C₆H₁₂N₄) as a buffer. Zinc Nitrate
Tetrahydrate solution (20; 30; 50; and 100 mM) and 50 mM Hexamethylenetetramine were stirred at 500 rpm for 30 minutes. The TiO₂ photoanode was immersed in a hydrothermal solution at 100 °C for 4 hours using an oven. The TiO₂/ZnO rods photoanode was washed using deionized water and then dried using a hotplate at 100 °C for 1 hour.

2.4. DSSC Assembly Based on TiO₂/ZnO rods Multilayer Photoanode

The TiO₂/ZnO rods multilayer photoanode was immersed in a mixed dye solution of N719/β-carotene for 24 hours, then dripped with iodine solution and stacked with a polyaniline (PANI) emeraldine salt-based counter electrode. DSSC was assembled to form a sandwich arrangement as shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** The illustration design of TiO₂/ZnO rods multilayer photoanode based DSSC.

Based on Figure 1, when DSSC is directed at sunlight, the dye molecule of N719/β-carotene will absorb the sunlight. Then the electrons from the dye molecule will be excited from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) followed by the injection of electrons from the dye molecule to the TiO₂/ZnO rods multilayer photoanode. The electrons collected from the TiO₂/ZnO rods multilayer photoanode are directed towards the counter electrode of PANI emeraldine salt. The electrons on the counter electrode reduce the triiodide to the iodide ion which is contained in the electrolyte solution and it leads to the regeneration of the dye molecule. The iodide/triiodide redox also flows towards the counter electrode to regenerate the lost electrons.

2.5. Characterization and Measurement

Fourier Transform Infrared (FTIR) Shimadzu IR-Prestige 21 was carried out to determine the functional groups of the TiO₂/ZnO rods multilayer photoanode. X-Ray Diffractometer (XRD) PanAnalytical E’xpert Pro with Cu anode was conducted to find out the unit cell volume and crystal size. The surface morphology and grain size were identified through the Scanning Electron Microscopy (SEM) FEI Inspect-S50. The light absorbance and energy gap were obtained based on the Ultraviolet and Visible (UV-Vis) Pharmaspec Shimadzu 1700. Keithley SourceMeter 2400 equipped with a solar simulator 100 mW/cm² was carried out to study the performance of DSSC based on the TiO₂/ZnO rods multilayer photoanode.

3. Results and Discussion

3.1. Functional Group of TiO₂/ZnO rods Multilayer Photoanode

The functional group of TiO₂/ZnO rods multilayer photoanode can be obtained based on FTIR characterization in the wavenumber range of 4000-400 cm⁻¹ or mid-IR. Figure 2 shows the functional group characteristic spectrum of TiO₂/ZnO rods multilayer photoanodes (20; 30; 50; dan 100 mM). The broad absorption peak at 3287 cm⁻¹ can be assigned to the O-H stretching vibrations [28]. The absorption peak at 1708 cm⁻¹ relates to the C=O stretching carboxyl [29]. The absorption peak at 1649 cm⁻¹ corresponds to the C=C ring stretching or H-O-H bending vibrations of adsorbed molecular water. The absorption peak at 1531 cm⁻¹ correlates to the C-OH stretching [30]. The absorption peaks at 1413 and 1236 cm⁻¹ can be assigned to the C-O stretching carboxyl and epoxy, respectively [31]. The absorption peak at 1124 cm⁻¹ relates to the Ti-OH vibrations [32]. The absorption peak at 1066 cm⁻¹ corresponds to the C-O stretching alkox [33]. In the low frequency or fingerprint region, the
absorption peaks at 909, 764, and 495 cm\(^{-1}\) correlate to the Ti-O, O-Ti-O, and Ti-O-Ti, respectively [34], while the absorption peak of ZnO metal oxide can be observed at 548 cm\(^{-1}\) [35]. The increasing concentration of Zinc Nitrate Tetrahydrate precursor in TiO\(_2\)/ZnO rods photoanode is shifted to the Ti-O-Ti absorption peak towards the higher wavenumber due to the crystal size of TiO\(_2\) nanoparticles decrease [36]. On the other hand, a broad absorption band and shifted of Zn-O towards the lower wavenumber can be attributed to stress and changes in the morphology of ZnO [37].

\[\text{Figure 2. The functional group of TiO}_2/ZnO rods multilayer photoanode.}\]

3.2. Diffraction Pattern of TiO\(_2\)/ZnO rods Multilayer Photoanode
The diffraction pattern of TiO\(_2\)/ZnO rods multilayer photoanode can be obtained based on the XRD characterization in the 2\(\theta\) range of 10-80\(^\circ\). Figure 3 shows the diffraction pattern of ITO-Glass conductive substrate and TiO\(_2\)/ZnO rods multilayer photoanodes (20; 30; 50; and 100 mM). The diffraction pattern of TiO\(_2\) nanoparticles can be indexed well to the anatase crystal structure of COD-2310710. The main peaks of TiO\(_2\) anatase are found at 2\(\theta\) of 25,37\(^\circ\); 37,88\(^\circ\); 48,03\(^\circ\); 53,98\(^\circ\); 55,12\(^\circ\); 62,46\(^\circ\); and 75,06\(^\circ\) corresponding to the hkl (101), (004), (200), (105), (211), (204), and (215), respectively. The diffraction pattern of ZnO rods can be indexed well to the wurtzite crystal structure of COD-9008877. The main peaks of ZnO wurtzite are found at 2\(\theta\) of 31,75\(^\circ\); 34,40\(^\circ\); 36,28\(^\circ\); and 56,56\(^\circ\) corresponding to the hkl (100), (002), (101), and (110), respectively. Based on the diffraction pattern of TiO\(_2\)/ZnO rods multilayer photoanode, the information concerning the unit cell volume can be estimated by the Rietveld refinement using the Rietica software. In detail, the unit cell volume of the TiO\(_2\)/ZnO rods photoanodes (20; 30; 50; and 100 mM) refinement are listed in Table 1, respectively.
Figure 3. The diffraction pattern of TiO$_2$/ZnO rods multilayer photoanode.

Table 1. Rietveld refinement of TiO$_2$ nanoparticles and ZnO rods.

| Unit cell volume (Å$^3$) | Model     | Results     |
|-------------------------|-----------|-------------|
|                         | 20 mM     | 30 mM       | 50 mM       | 100 mM      |
| TiO$_2$                 | COD-2310710 | 136.330     | 136.325     | 136.036     | 136.247     |
| ZnO                     | COD-9008877 | 47.643      | 46.888      | 47.813      | 48.479      |

The TiO$_2$/ZnO rods multilayer photoanode 50 mM shows the decreasing unit cell volume of TiO$_2$ nanoparticles up to 136.036 Å$^3$ and equally to the TiO$_2$/ZnO rods multilayer photoanode 30 mM which shows the decreasing unit cell volume of ZnO rods up to 46.888 Å$^3$. The decreasing unit cell volume is closely related to the reduction in crystal defects caused by oxygen vacancy [39]. Moreover, the decreasing unit cell volume also indicated the reduction in crystal size which can lead to the increasing electrostatic force [40]. On the other hand, the crystal size is obtained through the Debye-Scherrer Equation. In detail, the relationship between FWHM in hkl (011) and the crystal size of TiO$_2$ nanoparticles are presented in Table 2.

Table 2. The crystal size of TiO$_2$ nanoparticles.

| Photoanode (mM) | 20 | 30 | 50 | 100 |
|----------------|----|----|----|-----|
| 2θ (rad)       | 0.220 | 0.220 | 0.221 | 0.221 |
| FWHM (rad)     | 0.009 | 0.010 | 0.010 | 0.009 |
| Crystal size (nm) | 14.701 | 14.026 | 13.767 | 14.517 |

Based on Table 2, the increasing concentration of Zinc Nitrate Tetrahydrate precursor in TiO$_2$/ZnO rods multilayer photoanode is relatively decreased the crystal size of TiO$_2$ nanoparticles. However, the crystal size of TiO$_2$/ZnO rods multilayer photoanode 100 mM increase up to 14.517 nm. It can be indicated that the crystal size of TiO$_2$ nanoparticles decreases [41]. The crystal size of TiO$_2$/ZnO rods multilayer photoanode 50 mM can be attributed to the an increase in microstrain. [42].

3.3. Surface Micrographs of TiO$_2$/ZnO rods Multilayer Photoanode
The surface micrographs of TiO$_2$/ZnO rods multilayer photoanode can be obtained based on SEM characterization. Figure 4 shows the surface micrograph of TiO$_2$/ZnO rods multilayer photoanodes (20; 30; 50; dan 100 mM) at 10,000x magnification, where the first layer is TiO$_2$ nanoparticles and the second layer is ZnO rods. The TiO$_2$ nanoparticles are spherical, porous, and agglomeration. Nanoparticles have a strong tendency to agglomerate. The increasing of agglomeration is closely related to the increasing of the surface area [43]. Generally, agglomeration is caused by the presence...
of Van der Waals attractions between the nanoparticles and can be re-balanced through electrostatic and steric stabilization [44]. On the other hand, the ZnO rods on the top of the TiO$_2$ nanoparticles layer can also be observed. ZnO rods look like rods with randomly scattered hexagonal structures. The increasing concentration of Zinc Nitrate Tetrahydrate precursor in TiO$_2$/ZnO rods multilayer photoanode relatively increased the diameter size of the ZnO rods, as confirmed by the unit cell volume refinement of ZnO in Table 1 [45]. Figure 4 (a) shows the surface micrograph of TiO$_2$/ZnO rods multilayer photoanode 20 mM which has the diameter and width of the ZnO rods up to 829.876 and 897.648 nm, respectively. A different characteristic is also illustrated, where the ZnO rods which are on top of the TiO$_2$ nanoparticles layer look like non-uniform flowers. The structure is composed of tens of nanometers of ZnO emitted through the center [46]. In the TiO$_2$/ZnO rods multilayer photoanode 20 mM, the hydrothermal solution has a high pH, resulting in a slow nucleation rate (homogeneous nucleation) and relatively fast crystal growth. The nucleation process and crystal growth on the TiO$_2$/ZnO rods multilayer photoanode 20 mM are influenced by the presence of a high nucleation barrier (ΔG *) on the surface [47]. Therefore, the TiO$_2$/ZnO rods multilayer photoanode 20 mM has a relatively higher diameter and width. On the other hand, Figure 4 (b) shows a different structure, where the ZnO formed possess rods structure. The TiO$_2$/ZnO rods multilayer photoanode 30 mM has the diameter, width, and length of the ZnO rods, namely 705.394; 788.382; and 2556.502 nm, respectively. In Figure 4 (c), the TiO$_2$/ZnO rods multilayer photoanode 50 mM shows the diameter, width, and length of the ZnO rods, namely 1659.751; 1907.360; and 3779.352 nm. In Figure 4 (d), the TiO$_2$/ZnO rods multilayer photoanode 100 mM also shows the higher diameter, width, and length of the ZnO rods, namely 2067.206; 2785.033; and 4398.340 nm.

**Figure 4.** The surface micrographs of TiO$_2$/ZnO rods multilayer photoanode.

Two factors which can lead to an increase in the size of ZnO rods are the techniques used in photoanode fabrication (composite layer technique) and the method used in the growing process of ZnO rods (hydrothermal method). The morphology of TiO$_2$/ZnO rods multilayer photoanode greatly affects the surface porosity [48]. In detail, the surface porosity of TiO$_2$/ZnO rods multilayer photonodes (0; 30; 50; and 100 mM) are presented in Table 3.
Table 3. The surface porosity of TiO$_2$/ZnO rods multilayer photoanode.

| Photoanode (mM) | 20    | 30    | 50    | 100   |
|----------------|-------|-------|-------|-------|
| Porosity (%)   | 70.665| 66.034| 72.325| 70.510|

Based on Table 3, the TiO$_2$/ZnO rods multilayer photoanode 30 mM has a relatively homogeneous surface, the decreasing crystal size and diameter of ZnO rods is decreased the surface porosity [49]. Furthermore, the TiO$_2$/ZnO rods multilayer photoanode 50 mM is showed a relatively high surface porosity of 72.325% due to the small crystal size of TiO$_2$ nanoparticles (13.767 nm) [48]. The increasing surface porosity of TiO$_2$/ZnO rods multilayer photoanode facilitates optimal absorption of dye molecules and electrolyte diffusion [5].

3.4. Light Absorbance and Energy Gap of TiO$_2$/ZnO rods Multilayer Photoanode

The light absorbance of TiO$_2$/ZnO rods multilayer photoanode can be obtained based on the UV-Vis characterization in the wavelength range of 200-800 nm. Figure 5 shows the light absorbance spectrum of TiO$_2$/ZnO rods multilayer photoanodes (20; 30; 50; and 100 mM). Concretely, the increasing concentration of Zinc Nitrate Tetrahydrate precursors has increased the absorbance peak of TiO$_2$/ZnO rods multilayer photoanode. The weak absorbance peak corresponds to the electronic ZnO transition [50]. However, the TiO$_2$/ZnO rods multilayer photoanode 50 mM shows stronger ZnO absorbance peaks due to the quantum size effect of the ZnO rods [51]. The relatively dominant TiO$_2$ nanoparticles layer resulted in a strong absorbance peak in the wavelength range from ultraviolet to visible light (270-400 nm) [52]. The strong absorbance peak represents the transfer of charge from the valence band (2p orbital) to the conduction band (3d orbital) [53]. Furthermore, the absorbance spectrum of TiO$_2$/ZnO rods multilayer photoanode also shows broad absorbance peaks in the visible light wavelength range (400-600 nm) [54]. The increasing light absorbance of TiO$_2$/ZnO rods multilayer photoanode is increased by the excited electrons from the HOMO to the LUMO state. Therefore, the energy conversion efficiency generated by the DSSC also increases [55]. The light absorbance level of TiO$_2$/ZnO rods multilayer photoanodes (0; 20; 50; and 100 mM) can be determined by considering the maximum absorbance peaks of each photoanode spectrum, as written in Table 4.

Figure 5. The light absorbance spectrum of TiO$_2$/ZnO rods multilayer photoanode.
Table 4. Light absorbance of TiO$_2$/ZnO rods multilayer photoanode.

| Photoanode (mM) | 20  | 30  | 50  | 100 |
|-----------------|-----|-----|-----|-----|
| Wavelength (nm) | 224 | 303 | 312 | 346 |
| Absorbance peak (a.u) | 2.157 | 1.559 | 1.046 | 2.078 |

Based on Table 4, the increasing concentration of Zinc Nitrate Tetrahydrate precursor has relatively decreased the light absorbance of TiO$_2$/ZnO rods multilayer photoanode. However, the TiO$_2$/ZnO rods multilayer photoanode 100 mM is increased the light absorbance. The decreasing light absorbance of TiO$_2$/ZnO rods multilayer photoanode 50 mM can be attributed to the decrease in the crystal size of TiO$_2$ nanoparticles (13.767 nm) [56]. Furthermore, the increasing concentration of Zinc Nitrate Tetrahydrate precursor has relatively increased the energy gap of TiO$_2$ in TiO$_2$/ZnO rods multilayer photoanode as shown in Figure 6. The high energy gap of TiO$_2$ is influenced by the low light absorbance of TiO$_2$ in TiO$_2$/ZnO rods multilayer photoanode [57]. The small crystal size of TiO$_2$ nanoparticles is increased the energy gap of TiO$_2$ in TiO$_2$/ZnO rods multilayer photoanode [58]. The increasing concentration of Zinc Nitrate Tetrahydrate precursor also affects the energy gap of ZnO in TiO$_2$/ZnO rods multilayer photoanode. The energy gap of ZnO is relatively increased due to the quantum size effect (diameter, width, and length) [51]. Electrons can easily be excited from the valence band to the conduction band if the electrons have the same or higher energy than the energy gap of TiO$_2$/ZnO rods multilayer photoanode [59].

![Energy gap of ZnO and TiO$_2$ in TiO$_2$/ZnO rods multilayer photoanode.](image)

Figure 6. The energy gap of ZnO and TiO$_2$ in TiO$_2$/ZnO rods multilayer photoanode.

3.5. DSSC Performance Based on TiO$_2$/ZnO rods Multilayer Photoanode

The characteristics of solar cells can be obtained based on the Keithley SourceMeter 2400 characterization which is equipped with a solar simulator 100 mW/cm$^2$. The characterization data provides a graph of electric current (I) as the vertical axis and voltage (V) as the horizontal axis. Figure 7 shows the I-V curve of DSSC based on TiO$_2$/ZnO rods multilayer photoanode (20; 30; 50; and 100 mM). In detail, the solar cell parameters are presented in Table 5.
Figure 7. The performance of TiO$_2$/ZnO rods multilayer as photoanode on DSSC.

Table 5. Solar cell parameters of DSSC based on TiO$_2$/ZnO rods multilayer photoanode.

| Photoanode (mM) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF | Eff (%) |
|----------------|----------------------|--------------|-----|---------|
| 20 (0.5 cm$^2$)| 0.091                | 0.573        | 0.416 | 0.010 |
| 30 (0.5 cm$^2$)| 0.095                | 0.503        | 0.708 | 0.017 |
| 50 (0.5 cm$^2$)| 0.092                | 0.684        | 0.561 | 0.017 |
| 50 (0.2 cm$^2$)| 0.209                | 0.494        | 1.321 | 0.027 |
| 100 (0.5 cm$^2$)| 0.093               | 0.543        | 0.511 | 0.012 |

Based on Table 5, the increasing concentration of Zinc Nitrate Tetrahydrate precursor in TiO$_2$/ZnO multilayer rods photoanode increase the $J_{sc}$ and $V_{oc}$. However, the DSSC based on TiO$_2$/ZnO rods multilayer photoanode 50 mM with an active area of 0.5 cm$^2$ shows a decrease in $J_{sc}$ (0.092 mA/cm$^2$) and an increase in $V_{oc}$ (0.684 V). In contrast, the DSSC based on TiO$_2$/ZnO rods multilayer photoanode 50 mM with an active area of 0.2 cm$^2$ shows an increase in $J_{sc}$ and a decrease in $V_{oc}$, namely 0.209 mA/cm$^2$ and 0.494 V, respectively. Table 5 also informs that the increasing concentration of Zinc Nitrate Tetrahydrate precursor in TiO$_2$/ZnO multilayer rods photoanode results an increase in FF. However, in the DSSC based on TiO$_2$/ZnO multilayer rods photoanode 50 mM with an active area of 0.5 cm$^2$ shows a relatively high in FF (0.561) and the same thing was also shown by the DSSC based on TiO$_2$/ZnO multilayer rods photoanode 50 mM with an active area of 0.2 cm$^2$ (1.321). The increasing FF is in line with the increase of efficiency generated by the DSSC. The highest efficiency was produced by DSSC based on TiO$_2$/ZnO multilayer rods photoanode 50 mM with an active area of 0.2 cm$^2$, namely 0.027%, followed by the same system but with an active area of 0.5 cm$^2$, namely 0.017%. DSSC based on TiO$_2$/ZnO multilayer rods photoanode with an active area of 0.2 cm$^2$ proves that the small working area of the cell can inhibit the electron recombination process. Therefore, the efficiency generated by the DSSC increased [60].

4. Conclusion

The increasing concentration of Zinc Nitrate Tetrahydrate precursor affects the structure of TiO$_2$/ZnO rods multilayer photoanode and reaches the optimum point at 50 mM. The TiO$_2$/ZnO rods multilayer photoanode has been successfully synthesized as shown by the functional group gained from the FTIR analysis. The increasing concentration of Zinc Nitrate Tetrahydrate precursor causes the absorption peak of TiO$_2$ nanoparticle shifted to the higher wavelength, while ZnO rods shifted to the lower wavelength. The TiO$_2$/ZnO rods multilayer photoanode possess a crystalline structure as shown by the XRD analysis. The diffraction patterns of TiO$_2$/ZnO rods multilayer photoanode shows the TiO$_2$
nanoparticle (anatase) and ZnO rods (wurtzite) phases. The increasing concentration of Zinc Nitrate Tetrahydrate precursor affects the crystal size of TiO2 relatively decreased. The TiO2/ZnO rods multilayer photoanode 50 mM has the crystal size of TiO2 up to 13.767 nm. Moreover, the SEM analysis clearly shows the surface morphology of TiO2/ZnO rods multilayer photoanode. TiO2 nanoparticles are spherical, porous, and undergo agglomeration, while ZnO rods appear to be rod-shaped with a randomly scattered hexagonal structure. The increasing concentration of Zinc Nitrate Tetrahydrate precursor also causes the size (diameter, width, and length) of ZnO rods increased. The TiO2/ZnO rods multilayer photoanode 50 mM has a diameter, width, and length of the ZnO rods up to 1659.751; 1907.360; and 3779.352 nm, respectively. The increasing concentration of Zinc Nitrate Tetrahydrate precursor affects the light absorbance and energy gap of TiO2/ZnO rods multilayer photoanode and reaches the optimum point at 50 mM. The increasing concentration of Zinc Nitrate Tetrahydrate precursor causes the light absorbance of the TiO2/ZnO rods multilayer photoanode relatively decreased. The TiO2/ZnO rods multilayer photoanode 50 mM showed the light absorbance relatively low of 1.046 a.u. On the other hand, the energy gap of TiO2 and ZnO in the TiO2/ZnO rods multilayer photoanode is relatively increased. The energy gaps of TiO2 and ZnO in the TiO2/ZnO rods multilayer photoanode 50 mM are 3.247 eV and 3.274 eV, respectively. The increasing concentration of Zinc Nitrate Tetrahydrate precursor affects the performance of the DSSC based on TiO2/ZnO rods multilayer photoanode and reaches the optimum point at 50 mM. DSSC performance which is expressed by the efficiency relatively increased. The highest efficiency produced by the TiO2/ZnO rods multilayer photoanode 50 mM with an active area of 0.2 cm2, namely 0.027%.

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