Electrical Conductivity Characteristic of TiO2 Nanowires From Hydrothermal Method

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Abstract. One dimensional nanostructures of titanium dioxide (TiO2) were synthesized via hydrothermal method by mixing TiO2 as precursor in aqueous solution of NaOH as solvent. Then, heat and washing treatment was applied. Thus obtained wires had diameter ~15nm. TiO2 nanowires will be used as a network in solar cell such dye-sensitized solar cell in order to improve the performance of electron movement in the device. To improve the performance of electron movement, the characteristics of TiO2 nanowires have been analyses using field emission scanning electron microscopy (FESEM) analysis, x-ray diffractometer (XRD) analysis and brunauer emmett teller (BET) analysis. Finally, electrical conductivity of TiO2 nanowires was determined by measuring the resistance of the TiO2 nanowires paste on microscope glass.

1. Introduction
One dimensional nanostructure become interest field to investigate in order to enhance the performance of electron movement in the dye sensitized solar cell (DSSC). Then, it will be increase the efficiency of DSSC which is new type of solar cell technology that offer low-cost material. In DSSC, light is absorbed by wide band gap of metal oxide semiconductor nanoparticle such as TiO2, ZnO, Nb2O5 and SnO [1], [2], [3] which is coating with dye-sensitive light onto the semiconductor nanoparticle surface to absorb the light. the effective surface area for dye adsorption can be greatly enhanced and efficient light absorption[4]. Figure 1 illustrate during the illumination, electrons are injected into the conduction band of semiconductor nanoparticle by excited dye molecules adsorbed on the semiconductor nanoparticle surface, which is in contact with an electrolyte. In electrolyte, triiodide will react with electron at cathode to produce iodide, then iodide will react with oxidized dye molecule to regenerate dye sensitized molecule. But there are two undesirable reactions will be occurring toward the injected electron. First, the injected electron will be recombining with the oxidized dye molecules and dye sensitized molecule will be regenerate. Second reaction is the injected electron reacts with triiodide to produce iodide. Unfortunately, from both reactions, the injected...
electron travels through the semiconductor to back electrode decrease, consequence the efficiency of DSSC is low.

To solve the recombination problem, the one dimensional nanostructure is the best solution to form a semiconductor network in the DSSC. The nanowires will provide direct path for electron that bring the electricity move after injected from dye in the excited state. The direct path for electron movement can avoid the electron from the recombination situation. A dense network of nanowires can provide both high surface area and direct connectivity for electron movement [4], [5], [6]. In this paper, we choose TiO2 as a material of metal oxide semiconductor to synthesis TiO2 nanowires. TiO2 has been the mostly preferred as the semiconductor compare to other semiconductor [3] because it has good mechanical flexibility, non toxic, easily available, environmental stability, low cost characteristics and its conductivity could be controlled with acid/base (doping/undoping) [3], [7]. Characteristics of TiO2 nanowires by analyzing with FESEM, BET and XRD have been reported. The electrical conductivity of TiO2 nanowires also been discussed.

![Figure 1. Primary reaction steps in dye-sensitized solar cells[8]](image)

2. Experimental Procedure
This section is discussed all process involves to figure out the characteristics of TiO2 nanowires which is synthesizing via hydrothermal method. All the process includes procedure to synthesis TiO2 nanowires, after obtained white precipitation of TiO2 nanowires, send sample to FESEM analysis, BET analysis and XRD analysis. Next, the electrical conductivity of TiO2 nanowires have been determines by applying a formula of conductivity.

2.1. Synthesis of TiO2 Nanowires
The TiO2 nanowires were synthesized from a commercial powder of TiO2 (Degussa, P25) as a main material. A total of 2g of TiO2 powder and 50mL of 10M NaOH in aqueous solution were stirred together at room temperature until the TiO2 powder fully dissolves in the NaOH aqueous solution. The mixture was put into a Teflon-lined stainless autoclave which was heated at 150°C for 5 days. After that, it was naturally cooled down to room temperature. The solution was washed with 0.1M of HCl aqueous solution by stirring the mixture for 24h. The function of HCl treatment is to remove or eliminate the Na ions in the solution [9], [10], [11], [12]. HCl solution as acid treatment that it can decrease the Na:H ratio in the solution by replacing Na+ with H- [11]. After 24h, the solution was centrifuged and white precipitation was obtained. After HCl treatment, the white precipitation was washed by deionized water until the pH value 9. Then, the white precipitation was dried at 70°C to obtain TiO2 nanowires powder.
2.2. Process of coating TiO2 Paste

In order to put TiO2 nanowires onto the glass substrate, there are involved 2 methods that include preparation of TiO2 nanowires paste and the process of coating TiO2 nanowires paste onto the glass substrate.

2.2.1. Preparation of TiO2 Paste

TiO2 nanowires paste was prepared by mixing a different weight of TiO2 nanowires powder, such 5mg, 10mg, 20mg, and 40mg with a few drops of NMP in a mortar. NMP is used as a binder to bind the nanowires with each other. The mixture was mixed well until the paste became viscous paste. The ratio of mixture to prepare TiO2 nanowires paste as shown in the table below.

| Weight of TiO2, mg | Drop of NMP |
|-------------------|-------------|
| 5                 | 1           |
| 10                | 2           |
| 20                | 3           |
| 40                | 4           |

2.2.2. Coating TiO2 Paste

The TiO2 nanowires paste were pasted onto glass substrate in small area by using doctor blade technique. The area of TiO2 paste onto the glass substrate is in µm. Firstly, the glass substrate was cut into small pieces and continued with cleaning process by washing it with acetone and heating and sonicating it with deionized water for 30 minutes and washed again with ethanol. After that, the small pieces of glass were dried at 70°C for 10 minutes.

Figure 2. TiO2 nanowires paste onto the glass substrate a) 5mg, b) 10mg and c) 20mg.

2.3. Characterization Method

Finally, the TiO2 nanowires were characterized by FESEM analysis to figure out the nanostructure of TiO2, XRD analysis, BET analysis to determine the surface area and lastly, electrical conductivity. The electrical conductivity were observed by using resistance measurement by using digital multimeter equipment and by applying the resistance measurement, the conductivity of TiO2 nanowires based on different weight will be calculated. The equation below is a formula to calculate
the conductivity where $R$ is resistance (Ω), $l$ is length between 2 points (mm), and $A$ is area of TiO$_2$ nanowires paste onto glass substrate (µm), $\rho$ is resistivity (Ωmm) and $\sigma$ is conductivity (Ω$^{-1}$m$^{-1}$m).

$$\rho = \frac{RA}{l} \quad \text{Eq (1)}$$

$$\sigma = \frac{1}{\rho} \quad \text{Eq (2)}$$

3. Result and Discussion

Figure 3 shows the FESEM analysis image of TiO$_2$ nanowires after synthesis using hydrothermal method at 150°C for 5 days. The nanowires are close-packed with each other and make a network too dense. Although, the network of nanowires is dense, the surface area of TiO$_2$ nanowires is high which is 258.2911 m$^2$/g. From figure 4, the XRD pattern shown that TiO$_2$ nanowires has same as XRD pattern of TiO$_2$ (P25) but slightly different. In TiO$_2$ nanowires, the nanostructure is less crystalline compare to TiO$_2$ (P25).

![Figure 3. FESEM images of TiO$_2$ nanowires](image-url)
Figure 4. XRD pattern of TiO2 nanowires compared with TiO2 commercial, Degussa P25.

TiO2 nanowires also were characterized in terms of electrical conductivity. In order to improve the performance of electron movement in nanowires structures, the electrical conductivity testing is important to determine whether the nanowires has high conductivity or not by measuring the resistance values using digital multimeter. In the band theory of solids, the conduction process is whether or not there are electrons in the conduction band; more electrons on conduction band more conductive a material is [13]. Conductivity is increased when electrons in valence band supplied with external energy so that the electrons have enough energy to excite into conduction band. By applying below formula, the conductivity values will be determined as shown in figure 5. Increase the amount of TiO2 nanowires will be affected on the conductivity.

Table 2. The average values of resistance, resistivity and conductivity of TiO2 nanowires

| Weight of TiO2 Nanowires, mg | Resistance, Ω | Resistivity, Ωm | Conductivity, Ω⁻¹m⁻¹ |
|-----------------------------|----------------|-----------------|----------------------|
| 5                           | 8.26M          | 16.51k          | 6.279E-5             |
| 10                          | 7.85M          | 15.70k          | 6.67E-5              |
| 20                          | 2.06M          | 4.12k           | 2.2103E-4            |
| 40                          | 2.23M          | 4.47k           | 2.2438E-4            |
Figure 5. The graph of electrical of conductivity with different weight of TiO2 nanowires.

4. Conclusion
TiO2 nanowires were successfully synthesis by using hydrothermal method. TiO2 nanowires also have a high surface area that will be affect the performance of TiO2 nanowires especially in electrical conductivity. By analyzing the characteristics of TiO2 nanowires such XRD analysis, BET analysis, and FESEM analysis, TiO2 nanowires were successfully synthesis via hydrothermal method with high surface area. As conclusion, the electrical conductivity will be increasing as the weight of TiO2 nanowires in making paste. We achieved to show that, TiO2 nanowires have high conductivity.

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