

Preparation of anatase TiO₂ nanoparticles using low hydrothermal temperature for dye-sensitized solar cell

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Abstract. One device being developed as an alternative source of renewable energy by utilizing solar energy source is dye-sensitized solar cells (DSSC). This device works using simple photosynthetic-electrochemical principle in the molecular level. In this device, the inorganic oxide semiconductor of titanium dioxide (TiO₂) has a great potential for the absorption of the photon energy from the solar energy source, especially in the form of TiO₂ nanoparticle structure. This nanoparticle structure is expected to improve the performance of DSSC because the surface area to weight ratio of this nanostructures is very large. In this study, the synthesis of TiO₂ nanoparticle from its precursors has been performed along with the fabrication of the DSSC device. Effort to improve the size of nanocrystalline anatase TiO₂ was accomplished by low hydrothermal treatment at various temperatures whereas the crystallinity of the anatase phase in the structure was performed by calcination process. Characterization of the materials was performed using X-ray Diffraction (XRD) and scanning electron microscope (SEM), while the DSSC performance was examined through a high precision current versus voltage (I-V) curve analyzer. The results showed that pure anatase TiO₂ nanoparticles could be obtained at low hydrothermal of 100, 125, and 150 °C followed by calcination at 450 °C. The best performance of photocurrent-voltage characteristic was given by TiO₂ hydrothermally synthesized at 150 °C with power conversion efficiency (PCE) of 4.40 %, whereas the standard TiO₂ nanoparticles has PCE only 4.02 %. This result is very promising in terms low temperature and thus low cost of anatase TiO₂ semiconductor preparation for DSSC application.

1. Introduction

Titanium dioxide (TiO₂) has long been the subject of in-depth research because of its wide range applications such as sensors [1], optical emission, photonic crystals, catalysts, photocatalysts [2], purification of environment [3], photovoltaic cells, batteries and electrochemical devices [4-6]. This material is one of the inorganic oxide metals known as transitional metal oxides (TMO) [7]. The discovery that crystalline TiO₂ can be used as electrode in the dye-sensitized solar cell (DSSC) has driven even more intensive research due to its high efficiency and low fabrication cost [6].

The presence of oxide semiconductor layer plays a very important role in the DSSC for converting light energy into electrical energy. Moreover, the interaction between the dye and semiconductor oxide



particles will be very instrumental in determining the process of converting light energy into electrical energy [8].

In the field of nanomaterials, it has been well known that with the small size down to the nanometer scale, the ratio between the surface area to volume ratio (surface-area-to-volume-ratio) of the material will be greater [9]. In this aspect, the possibility of surface interactions with the environment will be higher, and hence, the use of TiO_2 nanomaterial in the form of nanoparticles, nanotubes and or mesoporous as semiconductor oxide layers in a DSSC is expected to improve the system performance [10].

There are many routes for synthesizing TiO_2 nanoparticle, one of which through the hydrolysis of titanium alkoxide followed by a sol-gel reaction in acidic environments and hydrothermal growth [11]. However, the hydrothermal temperature treatment for this method is usually above 190°C , which is still quite high. Because of that, in this paper, preparation of TiO_2 nanoparticles was optimized at relatively low hydrothermal temperature that can be applied for DSSC using titanium tetra isopropoxide precursor by the sol-gel technique in a tetra methyl ammonium hydroxide basic environment. Monodisperse TiO_2 nanoparticles of homogeneous morphology were obtained by optimizing the synthesis method. The results obtained are reported and discussed.

2. Experimental Setup

2.1. Preparation of TiO_2

The precursors were titanium tetra isopropoxide (TTIP) with chemical formula $\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4$ and tetra methyl ammonium hydroxide (TMAH) with chemical formula $\text{N}(\text{CH}_3)_4^+\text{OH}^-$, both were purchased from Sigma Aldrich. These precursors were used during the sol-gel followed by hydrothermal process. The preparation of TiO_2 is in according to the literature [11] with a slight modification to lower the hydrothermal temperature process and the method is explained as the following: A total of 40.5 mL TTIP was added into 112.5 ml of distilled water with a ratio of 1: 50 at 15°C under a magnetic stirrer for 1 hour. White precipitates resulting from the mixing process were filtered and washed three times using 50 ml of distilled water. The precipitates were transferred into a solution of TMAH and were refluxed at 100°C for 4 hours. TiO_2 content was set at 10 % by mass. The colloids produced from peptizing were then treated hydrothermally at three different low temperature variations 100, 125, and 150°C for 12 hours in a Teflon autoclave. The colloidal suspension was then centrifuged at 5,000 rpm and the obtained precipitates were washed with dry ethanol (Merck KGaA, Germany). At the last stage, TiO_2 nanoparticles were calcined at 450°C for two hours before being characterized using X-ray diffraction (XRD, ARL OPTX-2050) and scanning electron microscope (SEM, FEI Quanta-650).

2.2. DSSC Fabrication

The TiO_2 nanoparticle paste was prepared by adding an amount of methanol into TiO_2 nanoparticle powder along with two drops of TRITON X-100 (Sigma Aldrich). The blend was mixed until a homogeneous phase was obtained. Two fluorine-doped tin oxide (FTO, Solaronix) conductive glass substrates were prepared. One of the glass substrates was drilled to create two tiny perforations at one side and dry cleaned by using methanol. The other FTO glass was also dry cleaned by using methanol and attached to a flat layer. This substrate was tape masked and coated with TiO_2 nanoparticle paste using a doctor-blade method under an area of about 1 cm^2 . The paste was dried at 450°C for an hour and allowed to cool down before soaking it in the commercial organic dye solution (RK1, Solaronix) and air dried. As a comparison, the commercial TiO_2 nanoparticle (Degussa P25) was also prepared under the same condition. The other perforated FTO glass substrate was coated with a platinum paste (Platisol, Solaronix) and dried at 400°C for an hour. Both the coated glass substrates were then attached to one another separated by a spacer and sealed to avoid electrolyte leakage. Once dried, the electrolyte (Iodolyte, Solaronix) was then injected through the two tiny holes drilled at one side of the substrate. The holes were then sealed and the cell was ready for characterization. Cell activity was measured by

using a simple ammeter, while the cell performance was tested by using a Semiconductor Parameter Analyzer (SPA, Agilent 4155A) with a standard illumination of about 100 mW/cm².

The power conversion efficiency (PCE) of the device was calculated in accordance with the following equation [12]:

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{I_{in}} \times 100 \quad (1)$$

where J_{sc} is the short-circuit photocurrent density (mA cm⁻²), V_{oc} is the open-circuit voltage (volts), I_{in} is the intensity of the incident light (mW cm⁻²) and FF is the fill factor defined as:

$$FF = \frac{i_{max} V_{max}}{i_{oc} V_{oc}} \quad (2)$$

where i_{max} is the maximum photocurrent, V_{max} is the maximum voltage, respectively, and i_{oc} is the open-circuit current (mA). The values of i_{max} and V_{max} can be extracted from the maximum power of the I-V characteristics.

3. Results and Discussion

The samples prepared from three different hydrothermal temperature variations and calcined at 450 °C were characterized by using X-ray diffraction. As a comparison, diffraction pattern from the commercially available TiO₂ nanoparticle (Degussa P25) was also taken. The diffraction patterns are shown in figure 1.

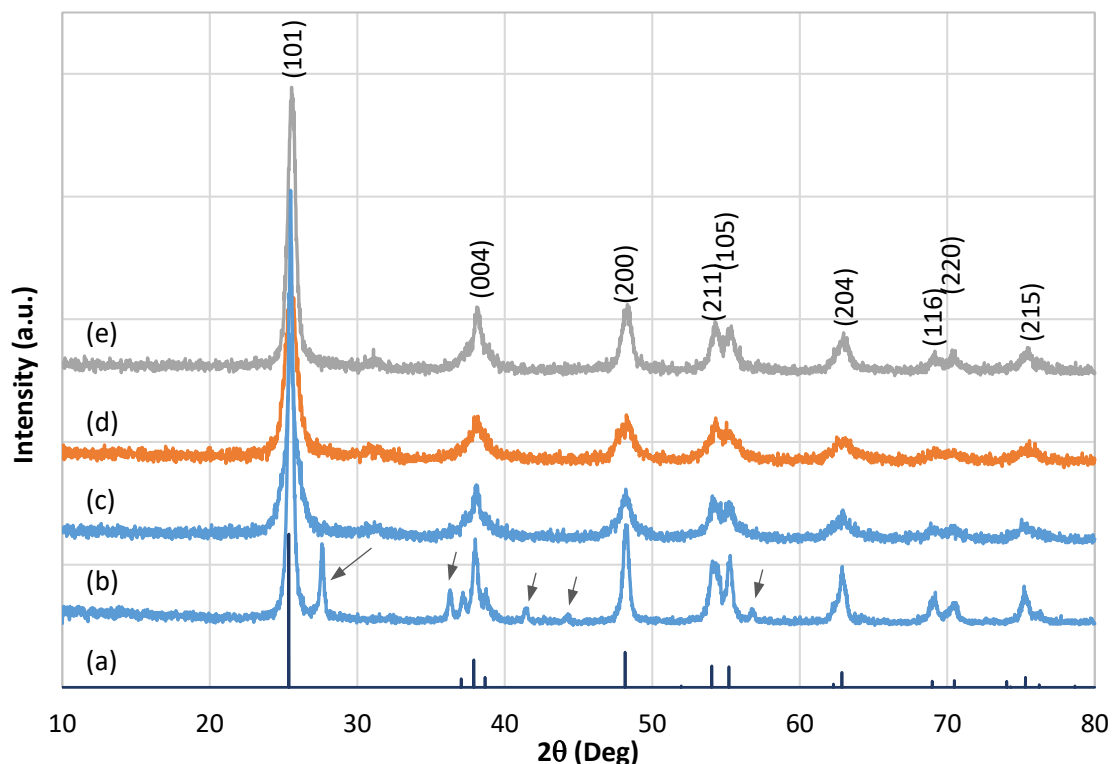


Figure 1. X-Ray diffraction patterns of TiO₂ (a) reference (JCPDS No. 73-1764), (b) Degussa P25, and hydrothermally synthesized at (c) 100 °C, (d) 125 °C, and (e) at 150 °C.

As seen from figure 1, all of the samples show the same trend and confirmed the pure anatase crystal structure (JCPDS file No. 73-1764). The three distinct diffraction peaks observed at 2θ value of 25.31°,

37.79°, and 48.04° are corresponding to (101), (004), and (200) anatase crystal planes, respectively [13]. No other characteristic peaks of rutile phase are detected in the diffractograms of the as-synthesized TiO₂. Other peaks of rutile, however, are observed in the commercial TiO₂ nanoparticles (Degussa P25) as indicated by the arrows in figure 1(b).

Based on the diffractograms, the crystallite size of the as-synthesized TiO₂ nanoparticles was calculated from the Debye–Scherrer’s equation using the XRD line broadening [14]:

$$c_s = \frac{k\lambda}{B \cos \theta} \quad (3)$$

where c_s is the crystallite size, λ is the wavelength of the X-ray radiation with Cu K α = 0.15406 nm, k is a constant taken as 0.94, θ is the diffraction angle, and B is the full width at half maximum (FWHM) peak in radians.

All of the diffraction peaks were taken into account from which the average crystallite size of each temperature variation was obtained, i.e. 5.9 nm, 6.3 nm, and 8.6 nm at temperature variation 100 °C, 125 °C, and 150 °C, respectively. It seems that with the increase of hydrothermal temperature resulted in increase of crystallite size. This can be understood since increasing the hydrothermal temperature will result in more energy for the crystal to grow.

Scanning electron microscope was used to study the surface morphological features of the TiO₂ nanoparticle and the results are given in figure 2. Figure 2(a) is the secondary electron image of the commercial TiO₂ nanoparticle (Degussa P25), whereas the hydrothermally synthesized TiO₂ at 100, 125, and 150 °C is given in figure 2(b), 2(c), and 2(d), respectively.

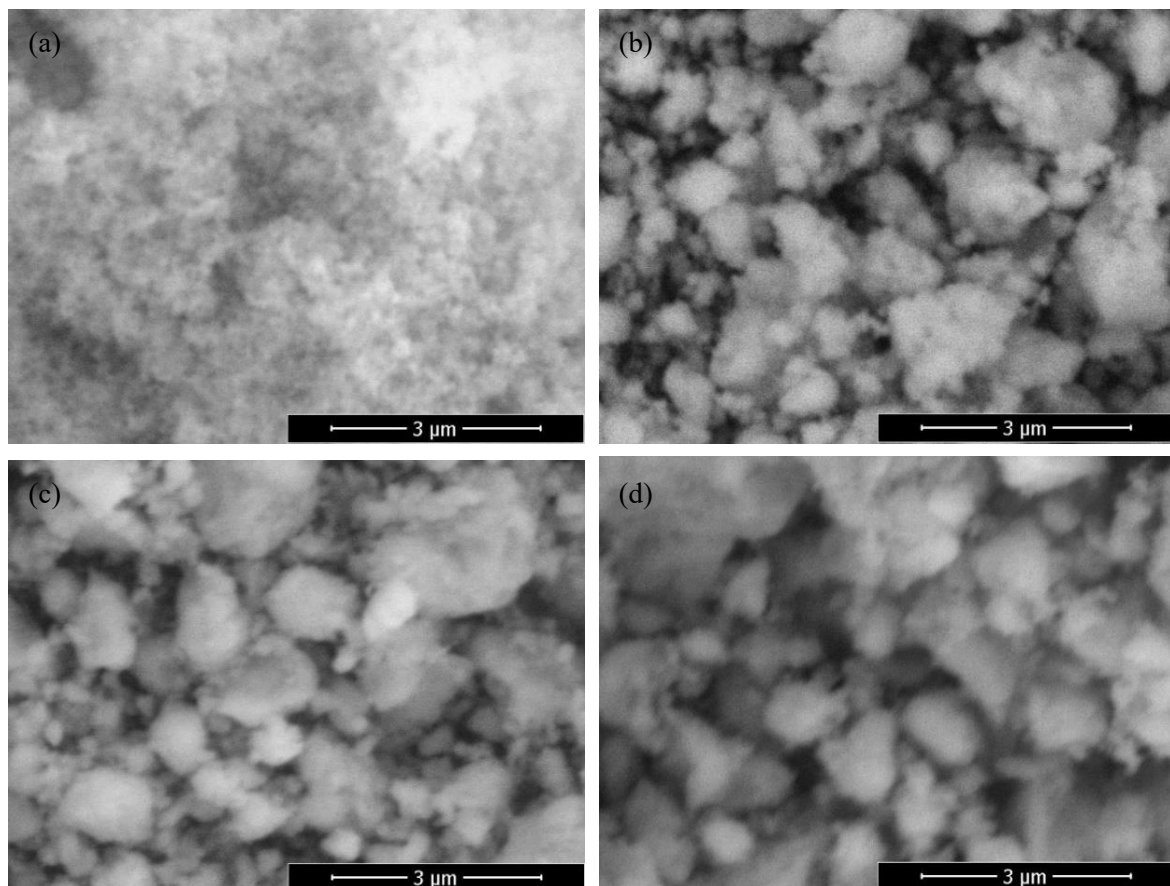


Figure 2. Secondary electron images of (a) commercial TiO₂ nanoparticle and hydrothermally synthesized TiO₂ at (b) 100 °C, (c) 125 °C, and (d) at 150 °C.

As seen in figure 2, the as-synthesized TiO_2 nanoparticles are still quite diverse in size and some of them are still clumped and agglomerated as compared to those of commercial nanoparticles TiO_2 . Nonetheless, image processing shows that the average particle size is 450, 500, and 590 nm for temperature variation 100, 125, and 150 °C, respectively. This result is in agreement with that of the crystallite size confirmed in the X-ray diffraction analysis mentioned previously. Compared to the commercial TiO_2 nanoparticles with an average particle size < 80 nm, the obtained particle sizes from the as-synthesized TiO_2 nanoparticles are still quite large. Nonetheless, since all of the as-synthesized TiO_2 nanoparticles have shown the characteristics of pure anatase, the material thus could be used as semiconductor photoactive layer in dye-sensitized solar cell (DSSC).

Photocurrent-voltage characteristics of the DSSC from commercial TiO_2 (Degussa P25) and as-synthesized TiO_2 at various hydrothermal temperature are given in figure 3. As seen in figure 3, photocurrent-voltage characteristic of both as-synthesized TiO_2 nanoparticle hydrothermally synthesized at various temperatures and commercial TiO_2 nanoparticle show a current density of around 10 mA/cm². Power conversion efficiency (PCE) of the DSSC are given in table 1.

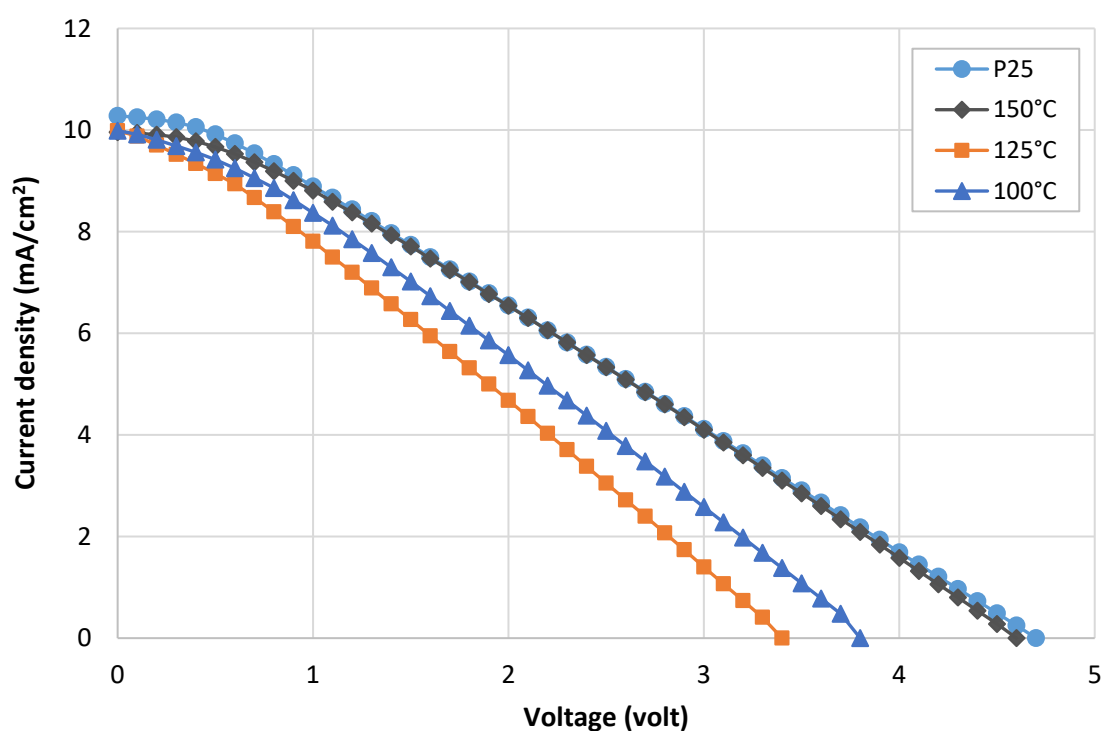


Figure 3. Photocurrent-voltage characteristics of the DSSC from the as-synthesized TiO_2 at various hydrothermal temperatures and commercial TiO_2 nanoparticle.

As seen in table 1, the PCE from all of the samples are above 4 %. For the as-synthesized TiO_2 nanoparticle, it seems that there is an anomaly on the PCE of hydrothermal at 125 °C. In according to the crystallite and particle size, the increase in hydrothermal should also increase the PCE, which is not the case. This could result from particle inhomogeneity and or agglomeration; however, the exact reason has yet to be confirmed. The interesting point is that PCE from the as-synthesized TiO_2 hydrothermally treated at various temperatures is larger than that of commercial TiO_2 . This can be understood since the commercial TiO_2 nanoparticle contains rutile phase. This rutile phase can reduce the power efficiency due to different interparticle connectivity associated with the particle packing density results in a slow electron transport [15, 16].

Table 1. Power conversion efficiency of the DSSC from the as-synthesized TiO_2 at various hydrothermal temperatures and commercial TiO_2 nanoparticle.

	100 °C	125 °C	150 °C	P25
V_{oc} (volt)	3.90	3.60	4.70	4.80
I_{oc} (mA)	9.99	9.99	9.96	10.28
V_{max} (volt)	0.45	0.45	0.45	0.40
I_{max} (mA)	9.42	9.14	9.78	10.06
FF	0.11	0.11	0.09	0.08
PCE (%)	4.24	4.11	4.40	4.02

4. Conclusion

In this work, low hydrothermal temperature method for synthesizing TiO_2 nanoparticles has been successfully carried out at 100, 125, and 150 °C followed by a calcination at 450 °C. The method was able to produce a pure anatase crystalline structure. The smallest crystallite size was achieved at hydrothermal temperature of 125 °C, however, the best performance for DSSC application was achieved at hydrothermal temperature of 150 °C with power conversion efficiency 4.40 %. This result is very promising in terms low temperature and thus low cost of anatase TiO_2 semiconductor preparation for DSSC application

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