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Effect of Physical Properties upon Hydrothermal Treatments on Titanium Dioxide Films

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Titanium dioxide is used extensively as semiconductor since more than five decades. Hydrothermal method is one the method which widely used for the synthesis of TiO_2 have been widely developed. The effect of hydrothermal temperatures on the titanium dioxide films is investigated. The TiO_2 films were prepared by hydrothermally layering a mixture of aquadest, HCl and titanium(IV) isopropoxide over indium tin oxide glass, at 110, 150, 180 and 200 ºC for 10 h. The film on the surface of indium tin oxide glass was calcined at 500 ºC and characterized by X-ray diffraction, UV-visible spectroscopy and scanning electron microscopy-energy dispersive X-ray (SEM-EDX) methods. The study shows that the TiO_2 has a spherical morphology with the size between 0.5 to 2 µm. The TiO_2 consits of rutile and anatase with the particle size ranging from 16.97 to 24.10 nm and from 18.09 to 26.75 nm, respectively. The band gap energy of TiO_2 is between 3.17 to 3.48 eV.

Keywords: Hydrothermal, Anatase, Solar cell, TiO_2.

INTRODUCTION

Now a days the use of renewable energy sources such as solar and wind as an alternative to overcome the energy crisis needs attentions. Photovoltaics is a promising renewable energy technology that can directly convert sunlight into electrical energy. The photovoltaic technology has vast potential to make a significant contribution in solving future energy problems [1]. The discovery of dye sensitized solar cell (DSSC) in 1991 was reported by O'Regan and Grätzel. DSSC has become a very interesting study for scientists and researchers because of its simple fabrication technology, low cost and environmentally friendly production, with energy conversion efficiency capable of reaching 11 % [2].

Titanium dioxide (TiO_2) becomes the most studied semiconductor material because it is very promising in photovoltaic technology. The most basic TiO_2 fabrication or fabrication for such applications is in the form of thin films. The fabrication of thin films at the present time allows for a wide range of applications, given the properties of materials from thin films can be modified according to the desired variation. Therefore, TiO_2 thin film fabrication is continuously conducted to obtain better film characteristics. Several methods used in the synthesis of TiO_2 are sol gel methods [3,4], solvotermal [5], thermal decomposition [6] and hydrothermal [7-9]. The hydrothermal method has the advantage of simple preparation, relatively low reaction temperature, uniform dispersion for metal ion doping, as well as stoichiometric control and provides good homogeneity [10-12] although method usually proceeds for a relatively long time (~ 10 h). The synthesis of spherical particles TiO_2 by hydrothermal method for 5 h at 110 ºC has been undertaken [13,14]. In this study, titanium tetra isopropoxide was used as a titanium precursor and hydrochloric acid as structural directing agent to obtain TiO_2 nanosphere particle. This hydrothermal reaction was carried out at 110, 150, 180, and 200 ºC for 10 h.

EXPERIMENTAL

Titanium tetraisopropoxide (TTIP) (Merck 98 %), tin-doped indium oxide-coated (ITO) glass slide (Merck 1,200-1,600 Å) and HCl p.a. (Merck 36 %) were used as received without any further purification.

Synthesis: To a mixture of 8 mL of aquadest and 8 mL of HCl 36 %, 0.4 mL TTIP was added, followed by stiring for 30 min. The mixture was put into Teflon tube where ITO slides were then inserted. Furthermore, the tube was tightly closed, and heated at 110 °C for 10 h. The ITO slides were then taken out from the teflon tube, and calcined at 500 °C for 3 h. These works were repeated at hydrothermal temperature of 150, 180, and 200 °C.

Thin layer on the surface of ITO sildes were then characterized by using powder X-ray diffraction CuKα (λ = 1.5405981 Å) (XRD Rigaku Multiflex) in 2θ range between 20°-80°, UV-Vis UV 1700 Pharmaspec spectrophotometer specular reflectance scanning electron microscopy (SEM Jeol JCM-6000) and EDX methods.

RESULTS AND DISCUSSION

The XRD patterns of thin layer of TiO_2 nanoparticles on the surface of ITO are shown in Fig. 1. The patterns indicate that the samples consist of two crystalline phases ie. rutile and anatase noted by peaks at (110), (101), (200), (111), (210), (211) and (220) (JCPDS no. 75-1755) and (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) (JCPDS no. 21-1272), respectively. The rutile phase crystallinity dominates the sample hydrothermally synthesized at low temperature (110 °C), while anatase at higher temperature (180 °C). In general, the increasing hydrothermal temperature leads the producing of the higher crystallinity of anatase. However, the mean of the rutile to anatase quantitative ratio in all samples determined by applying Spurr-Myers's equation remain the same, *i.e.* about 0.70:0.30 [15]. The ratios are listed in Table-1. The majority of rutile in the sample is clearly not as result of hydrothermal treatment, but the calcination temperatuture *i.e.* 500 °C. This is in agreement with Chen *et al.* [16] described that rutile phase exists at samples calcined at above 500 °C.

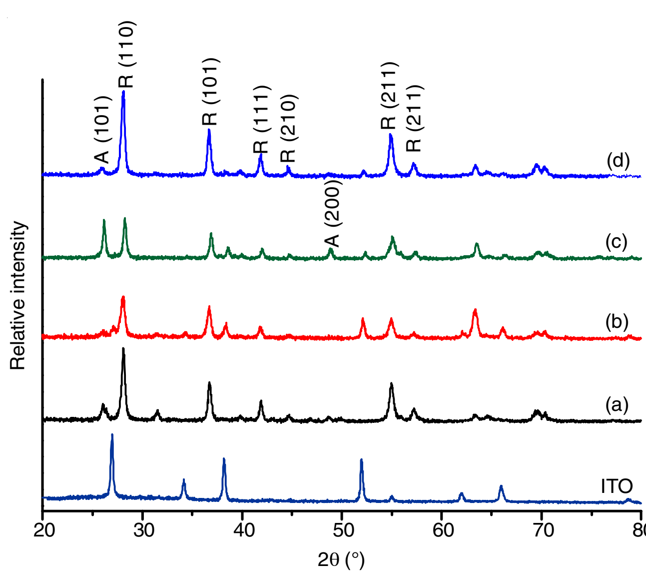

Fig. 1. Powder XRD difractogram of ITO and thin layer over the ITO treated at hydrothermal temperature of (a) 110, (b) 150, (c) 180, and (d) 200 °C

The crystallite size of TiO_2 was calculated using the Scherrer equation [17]:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

TABLE-1
RUTILE TO ANATASE QUANTITATIVE RATIO IN SAMPLES

Hydrothermal temperature (°C)	Rutile fraction	Anatase fraction
110	0.70	0.30
150	0.71	0.29
180	0.68	0.32
200	0.71	0.29

where λ is the wavelength of CuK_α radiation source, β is the FWHM of the diffraction peak, and θ is the angle of diffraction. The crystallite size of rutile and anatase are listed in Table-2. There is no indications that hydrothermal temperature affecting the crystallyte size of rutile and anatase. The rutile and anatase crystallites have similar average sizes of 21.0 and 23.5 nm, respectively.

TABLE-2
CRYSTALLITE SIZE OF RUTILE AND ANATASE IN SAMPLES

Hydrothermal temperature (°C)	Rutile phase (nm)	Anatase phase (nm)
110	19.87	22.78
150	24.10	26.75
180	16.97	18.09
200	23.09	25.68

The synthesized material was also characterized using UV-Vis UV 1700 Pharmaspec spectrophotometer specular reflectance methods to determine the absorption activity of TiO_2 thin layer hydrothermally synthesized at 110, 150, 180 and 200 °C. The absorption spectra of TiO_2 can be seen in Fig. 2.

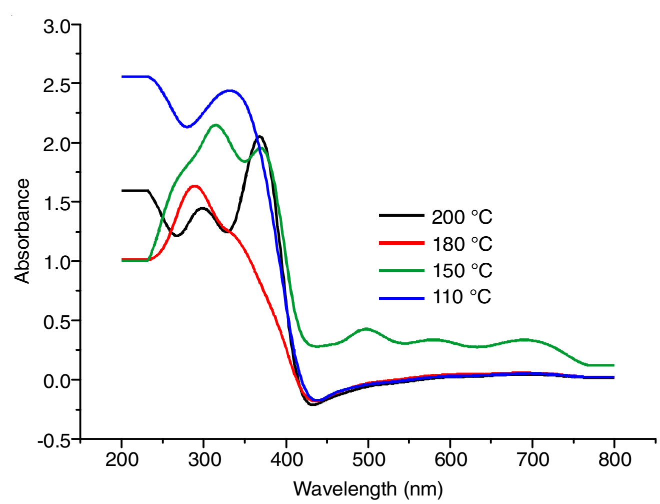

Fig. 2. UV-visible spectra of thin layer over the ITO treated at hydrothermal temperature of 110, 150, 180, and 200 °C

The band gap energy (E_g) of the samples was determined using the Kubelka-Munk equation [18]:

$$F(R'_\infty) = \frac{(1-R'_\infty)^2}{2R'_\infty}$$

From Kubelka-Munk equation, the value of E_g can be obtained by correlating hν (eV) with $[F(R'_\infty)h\nu]^{1/2}$ and extrapolating the linear part of its intersection with the energy axis

(Fig. 3). The calculated values of E_g are listed in Table-3. The hydrothermal treatment affects the E_g of TiO_2. The hydrothermal temperature is linear to E_g, but not to E_g of the sample hydrothermally synthesized at 200 ºC. This phenomenon is in agreement with the finding that anatase phase of TiO_2 is formed at low temperature treatment and the rutile is obtained at relatively higher temperature. The clear transition of anatase to the rutile occurs at temperatures between 600-700 ºC [19]. According to Bak *et al*. [20] the higher E_g will result in wider active surface area resulting in more effective photoactivity. When the anatase and rutile phases are mixed, the resulting E_g is within the range of E_g of rutile and anatase [21].

TABLE-3
E_g VALUES OF TITANIUM DIOXIDE FILMS

Hydrothermal temperature (°C)	E_g (eV)
110	3.12
150	3.39
180	3.53
200	3.30

SEM: The SEM micrographs of a selective sample hydrothermal synthesized at 150 ºC are shown in Fig. 4. The TiO_2 is observed as about 58 µm thick of layer on ITO (Fig. 4a). Based on SEM micrograph, TiO_2 synthesized at 150 ºC has spherical

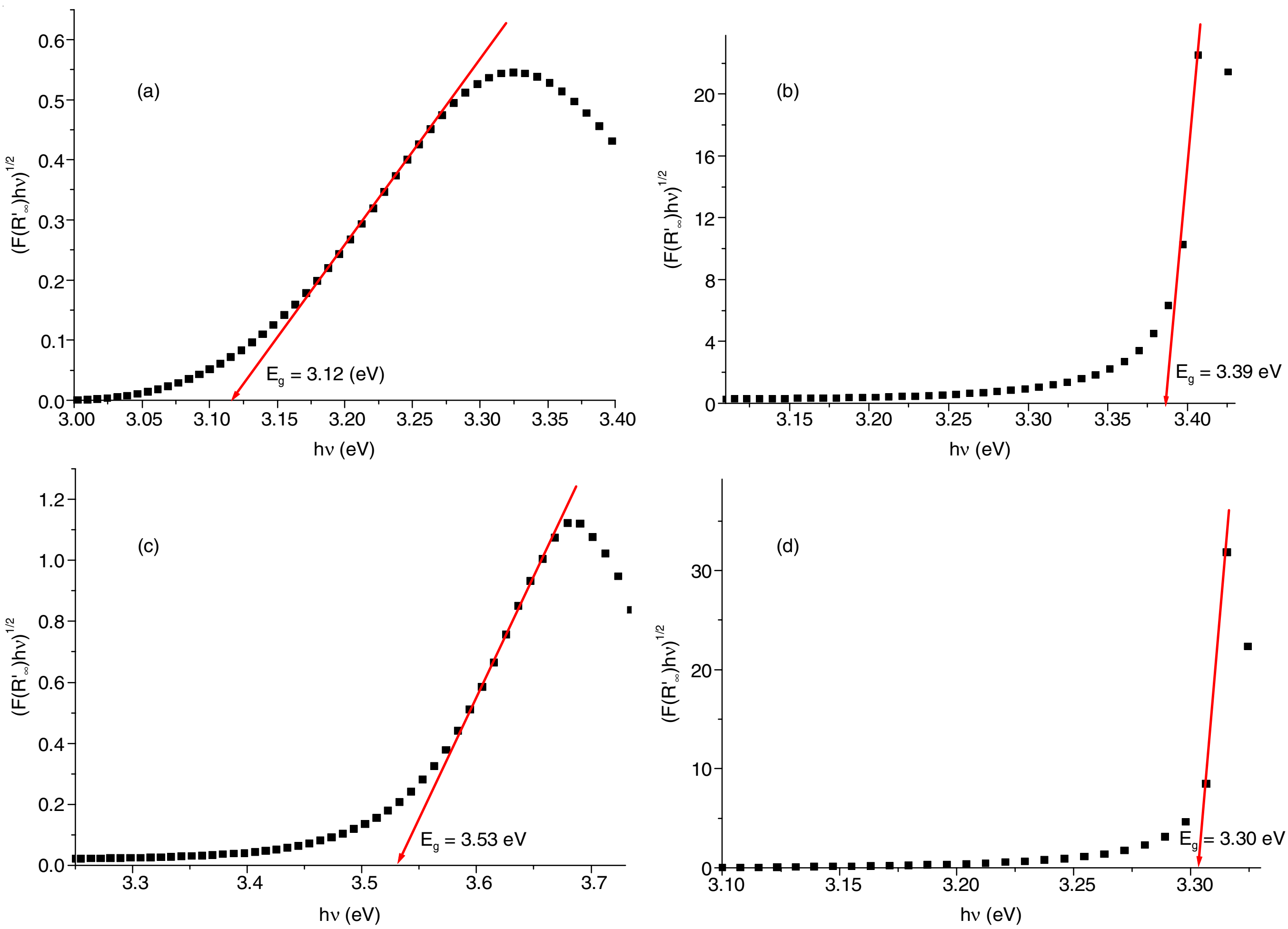

Fig. 3. Band gap energies (E_g) of thin layer over the ITO treated at hydrothermal temperature of (a) 110, (b) 150, (c) 180, and (d) 200 °C

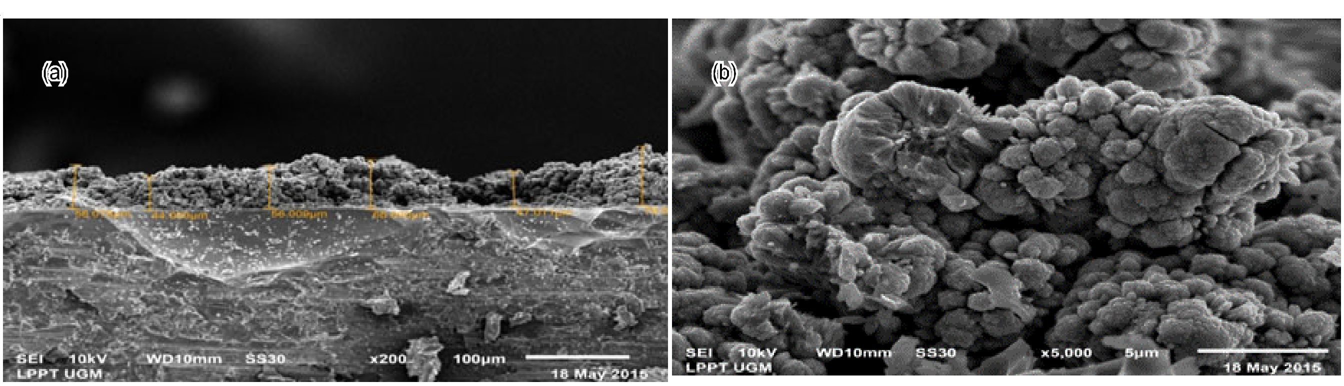

Fig. 4. SEM micrographs of a selective sample hydrothermally sinthesized at 150 °C; (a) 200x and (b) 5000x magnifications

in shape with the size between 0.5-2 µm and indicates rough surface.

Conclusion

This study revealed that hydrothermally synthesized TiO_2 consits of rutile and anatase with the particle size ranging from 16.97 to 24.10 nm and from 18.09 to 26.75 nm, respectively. The band gap energy of TiO_2 increases with the increasing temperature used in the hydrothermal treatment, except for treatment at 200 ºC. The TiO_2 has a spherical morphology with the size between 0.5 to 2 µm.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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