Journal of Basic and Applied Engineering Research
Print ISSN: 2350-0077; Online ISSN: 2350-0255; Volume 1, Number 9; October, 2014 pp. 1-5

http://www.krishisanskriti.org/jbaer.html

Synthesis of TiO_2 Nanoparticles by Sol-gel Method and Their Characterization

Ajay Sharma[1], R.K. Karn[2], S.K. Pandiyan[3]

[1,2,3]School of EEE, Department of ECE, Sastra University, Thirumalai Samudram, Thanjavur, Tamilnadu, INDIA

Abstract: **Nano-structured TiO_2 has been synthesized by following Sol-gel method in the present investigation. TiO_2 gel has been obtained and then dried at a temperature of 300 ^{0}C for 2 hrs in a muffle to get the powder. The as synthesized powder was then crushed using mortar for 3 hrs thus TiO_2 nano-structured powder has been obtained. After the successful synthesis thin film has been deposited on titanium substrate for solar cell application using dip coating method. Nano-structured TiO_2 has been characterized using various techniques like XRD, SEM, UV-vis spectroscopy and DSC-TGA and analysed through. XRD confirms the phase SEM confirms the particle size in the range of nano-meter. Optical spectra confirm the enhancement of absorption which is because of its nano size. DSC-TGA analysis was used to investigate the thermal properties of the material. I-V characteristic for TiO_2 efficiency has achieved 1.77 % from pre TiO_2 cell.**

1. INTRODUCTION

The TiO_2 nano-particles are area of interest due to their unique technological properties and applications such as memory devices, sensors, photo catalysis and solar cells [1-3]. Nano-structure TiO_2 has been investigated as a prospective material for dye-sensitized solar cell (DSSC) [4, 5]. In this manuscript, we reported only efficiency of the TiO_2 thin film based solar cell.

The nanostructures TiO_2 exists in three polymorphic phase viz. rutile, anatase and brookite. Amongst these three, anatase & rutile are most thermally stable phases of TiO_2. Anatase structure of TiO_2 belongs to $D^{14}{}_{4h}$-$P4_2$/mnm space group (lattice constant a = 0.4584 nm, c = 0.2953 nm, c/a = 0.664), while rutile structure belongs to $D^{19}{}_{4h}$-$I4_1$/amd space group (lattice constant a = 0.3733 nm, c = 0.937 nm, c/a = 2.51) [6]. These two structures have great importance in the preparation of dssc, due to its high surface area.

TiO_2 nanoparticles adsorb more amounts of dye molecules, which results into the increase photon to current conversion efficiency, because a TiO_2 nanoparticles-coated photoelectrode usually has higher transparency, which cause to transmission of a significant amount of visible light, the smaller particle size of the TiO_2 nanoparticles only permits negligible amount of light scattering [7].

The several method for preparation of nanocrystallite titania are well reported, most of them belonging to wet chemical method. The benefits of the wet chemical method are well studied [9, 10].The best choices of wet chemical methods are hydrothermal [11, 12] and sol–gel [10, 13]. The Sol–gel method is the simple, economical, and accomplished and most frequently used methods of synthesizing TiO_2 nanoparticles. The sol–gel method gives accessibility for synthesizing TiO_2 nanoparticles with different morphologies like sheets, tubes, particles, wires, rods, mesoporous and aerogels.

The main aim of present study is to synthesize the TiO_2 nano-particles through hydrolysis process of Titanium (IV) iso-propoxide and examine photon to current conversion efficiency of the prepared film. In our present work, we synthesized TiO_2 nanoparticles through the hydrolysis process of Titanium (IV) iso-propoxide, which was followed by [15]. Self-hydrolysis of Titanium (IV) iso-propoxide is one of the effective processes to synthesize TiO_2 crystalline powders by one step. The Synthesized TiO_2 nanoparticles properties were studied through XRD, FE-SEM, and UV-Visible spectroscopy and DSC-TGA characerization techniques.

2. EXPERIMENTAL SECTION

Titanium tetra iso propoxide [$Ti(OCH(CH_3)_2)]_4$, Sigma-Aldrich, 97%], iso-propanol [$(CH_3)_2CHOH$, Sigma-Aldrich, 99.7%] and nitric acid [HNO_3] were used as received without any further purification. A 20 ml of solution Titanium tetra iso propoxide was added drop by drop into the 22 ml of solution containing 10 ml of iso-propanol and 12 ml deionised water under constant stirring at 80º C into the round bottom beaker. After 1 h, concentrated HNO_3 (.8 ml) mixed with deionised water was added into the TTIP solution and keep it under constant stirring at 60 ºC for 6 h highly viscous sol gel was obtained. The prepared sol-gel was heated at 300 ºC for 2 h in the open atmosphere. After annealing, the TiO_2 nanocrystalline 2 g powder was obtained. Further preparation of TiO_2 film, the prepared powder was added in the ratio of 1:10 of the solution of iso-propanol. The TiO_2 nanoparticles deposited on titanium substrate (0.5 cm^2) using the dip coating method. Further optical studies, The TiO_2 film were prepared on the two glass substrates. The crystallite structure of the TiO_2 powder were evaluated by an X-ray diffractometery (XRD, XPERT-PRO, PW 3071/xx Bracket) using Cu Kα radiation, furthermore the grain size of TiO_2 was calculated by Scherrer's formula. The particle shape and nanostructure of particles were studied by a field emission scanning electron microscopy (FE-SEM, Jeol, jsm 6701 F). The absorbance and transmittance spectrum was obtained for the nanocomposite coatings in the wavelength range of 200–1200 nm through a UV–Visible spectrophotometer by employing PerkinElmer lambda-35. DSC-TGA studies were examined through TG-DTA SDT Q600 instrument employed by TA instruments (U.S.). DSC-TGA studies were examined from 0 °C to 1000 °C with a heating rate 10 °C/min in the nitrogen (100 ml/min) atmosphere.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization

The structural analysis of TiO_2 particles was carried out using XRD instrument. The diffractograms were recorded in the 2θ range of 10-80º. Figure 1 shows representative XRD patterns taken from Sol residues heated at 300º C for 2 h.

The crystalline nature was observed in the powder XRD of TiO_2 and diffraction peaks belong to rutile and anatase phase of TiO_2. The broad lines were comparatively broad representing nano size crystal. The XRD patterns exhibited diffraction peaks at 25.44º, 36.16º, 47.91º and 54.43º, 63.4º indicating TiO_2 in anatase phase with the corresponding (101), (103), (200) and (105), (204) planes respectively. The peaks observed at 27.47º, 41.20º, 56.62º, 69.35º indicating TiO_2 in rutile phase with the corresponding (110), (111), (220) and (301) planes respectively.

All observed peaks are in good agreement with the standard spectrum (JCPDS no.: 21-1272 and 21-1276). Average particle size was estimated by using scherrer equation.

Grain size $D = \frac{.89\lambda}{\beta \cos\theta}$

Where λ = Cu Kα radiation Wavelength 1.549 Aº

K = Shape factor

The Avg. particle size was calculated to be around 15-20 nm.

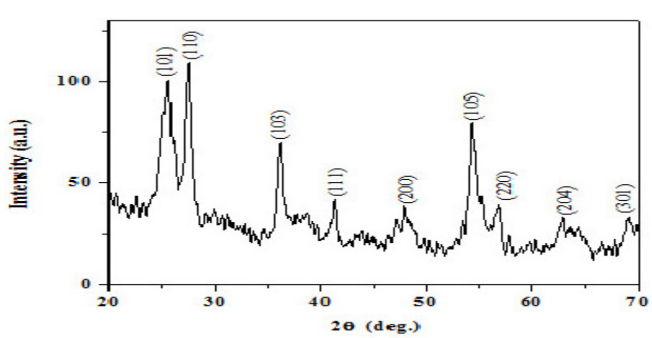
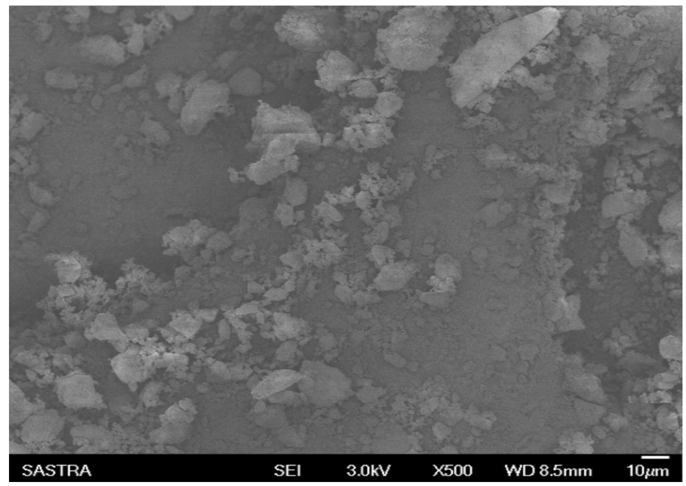
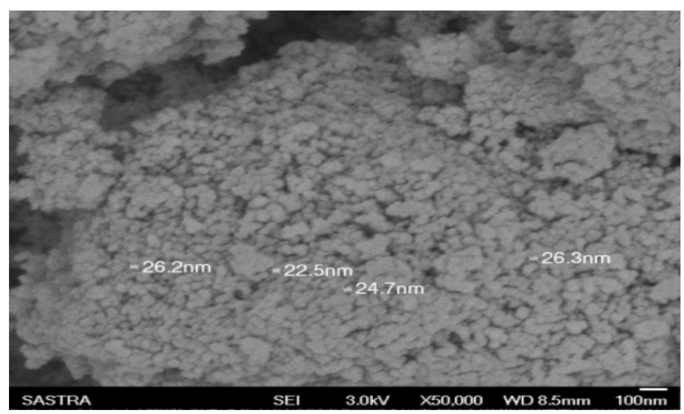


Fig. 1. XRD Graph for TiO_2 powder (300 ºC).

Further structural study of the prepared TiO_2 powder was studied using FE-SEM image analysis. The fig. 2 (a) and 2 (b) shows the FE-SEM images of synthesized TiO_2 powder, which is heated at 300 ºC. From FE-SEM images aggregated spherical TiO_2 particle size was obtained ~25 nm. The size obtained in FE-SEM is significantly higher than that calculated using the Sherrer formula. The FE-SEM images show the high degree of crystallinity of the TiO_2 nanoparticles. The FE-SEM image as shown in fig. 2 (b), Particle was found spherical in shape and surface morphology was found homogenous in specific regions. The agglomeration of the particles was seen in the FE-SEM images.



(a)

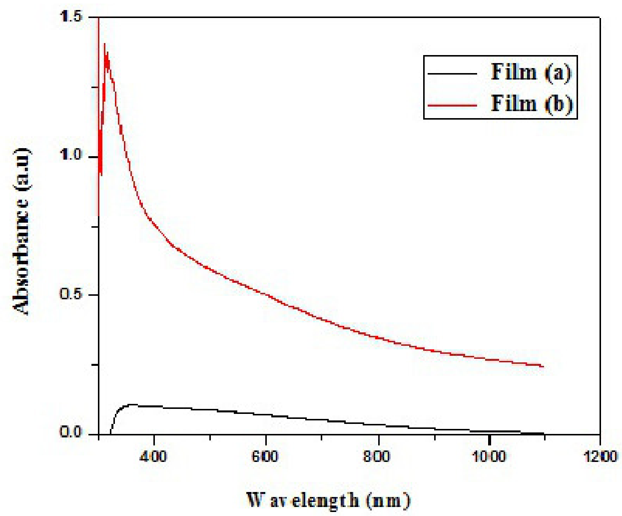


(b)

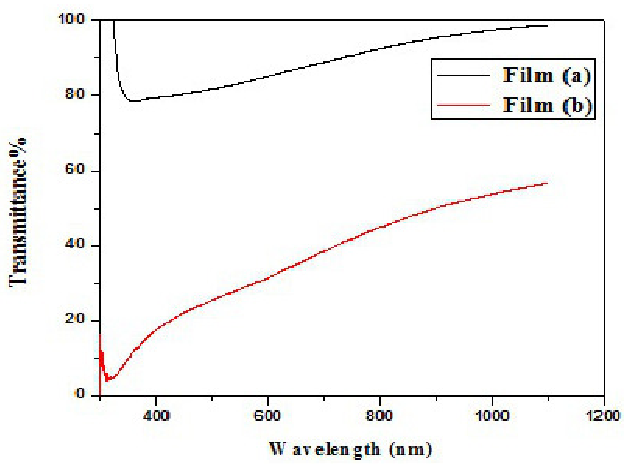
Fig. 2. FE-SEM images of TiO_2 Powder (300 ºC).

3.2 Optical Study

For the comparative optical study, two thin films were prepared on the glass substrate. In order to prepare TiO_2 nanocrystalline film, first the low viscous TiO_2 sol gel was prepared by the incremental adding of 20 ml 2-propanol to 2 g of TiO_2 powder into the mortar under vigorous grinding by the crusher and the prepared homogeneous slurry was layered onto the normal glass substrate (~ 2.1 cm^2) by dip coating technique. Film (a) was prepared by the one dip coating cycle and Film (b) using the three dip coating cycle. The Fig. 3 (a) shows absorbance is slightly shifting towards the lower wavelength with the increasing of film thickness. The shift is ascribed to the difference in crystallite size according to study [16]. Absorption graph confirms that TiO_2 particle responds the UV region may be attributed to TiO_2 particle band gap which is nearly equal 3.32 eV. Transmittance is inversely proportional to the thickness of the film, for Film (a) transmittance was obtained more than 80%, for Film (b) was 10% as shown in fig. 3 (b).



(a)



(b)

Fig. 3. UV-Visible spectrum (a) Absorbance spectrum (b) Transmittance Spectrum.

3.3 DSC-TGA Analysis

Further study of thermal property of the prepared material, DSC–TGA characterization was carried out using TA instrument. The fig. 4 shows the DSC–TGA curves for a synthesized TiO_2 powder sample. In the TGA analysis three weight loss regions were observed. Through TGA analysis the about 18% weight loss observed was. The weight loss was obtained 6%, 3%, 9% in the first, second and third regions respectively. The first weight loss occurred at 125 ºC may be correspond to the desorption of the adsorbed water from the titania surface, The second weight loss at 170 ºC may be correspond to the dehydrogenation of $–CH_2–CH_2–CH_2–CH_3$ in the as-synthesized TiO_2 and desorption of the crystal water, the third weight loss occurred at 615 ºC can be corresponded to the thermal decomposition of residual organic groups in the as-synthesized TiO_2 [17]. The endothermic peak at about 720 ºC is assigned to anatase to rutile phase transformation [18].

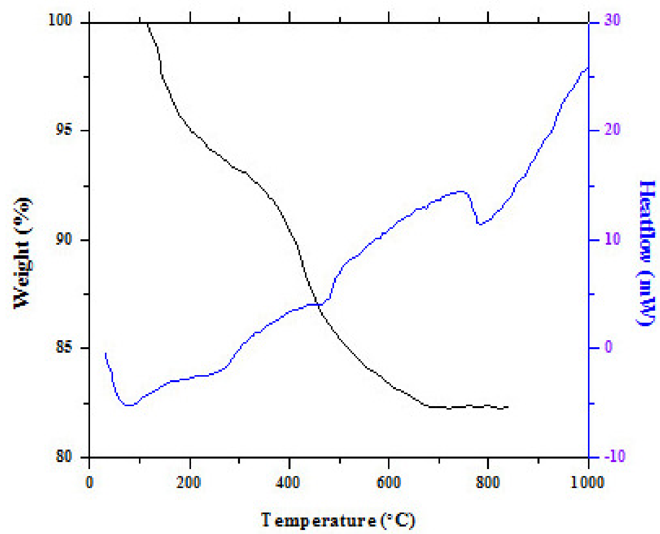


Fig. 4. DSC-TGA graph for synthesized TiO_2 powder.

3.4 I-V Characteristics

The I-V characteristics of the electrodes under dark and illuminated conditions were recorded with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR 179 I/E converter, a PAR Model 175 universal programmer and a Houston (2000) X-Y recorder. The illumination source was a 300 W Xe-Hg lamp was adjusted to give incident intensity 100 mW cm^{-2}. The I-V characteristics of TiO_2 film tested at 25 ºC as shown in fig. 5. From I-V curves photo current and photo voltage obtained 3.6 mA and 330 mV and average factor calculated to be around 0.748. Overall maximum conversion efficiency (η) 1.77 % was measured for the nano-structured TiO_2 films used as anodes. The small differences in the prepared anodes can be ascribed to the nature of the assembly method.

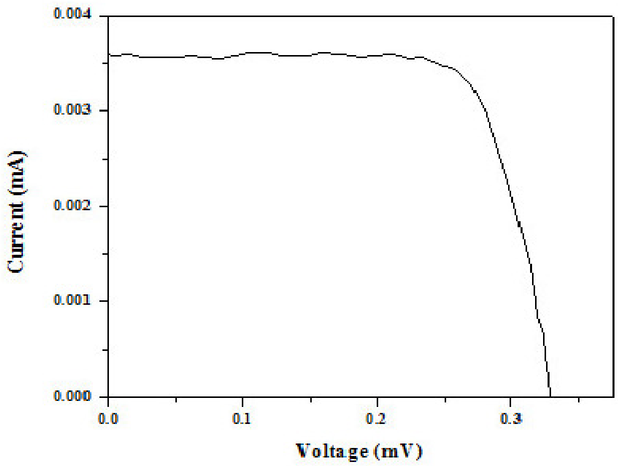


Fig. 5. I-V graph of prepared TiO_2 cell.

4. CONCLUSION

The nano-structured TiO_2 has been synthesized by the hydrolysis process of Titanium (IV) Isopropoxide. The thin films were prepared by dip coating method. The crystallite size of as prepared TiO_2 nanoparticles was obtained approximately 20 nm and anatase and rutile phases confirmed by XRD graph. FE-SEM was employed to further study of the crystallite/particle size and morphology of the as-synthesized TiO_2 particles. The particles of TiO_2 in anatase phase have a mostly spherical morphology. The optical absorbance of the prepared films were found between 360 nm to 310 nm which is correspond to the band gap of TiO_2 (~3.2 ev). From the DSC-TGA analysis phase transformation of TiO_2 obtained at 720 ºC. From I-V graph efficiency was achieved about 1.77 %.

REFERENCES

[1] W. Li, S. Ismat Shah, C. P. Huang, O. Jung and C. Ni, "Metallorganic chemical vapor deposition and characterization of TiO_2 nanoparticles", *Materials Science and Engineering: B*, 96, 3, July 2002, pp. 247-253.

[2] J. T. Remillard, J. R. McBride, K. E. Nietering, A. R. Drews and X. Zhang, "Real time in situ spectroscopic ellipsometry studies of the photocatalytic oxidation of stearic acid on titania films," *The Journal of Physical Chemistry B*, vol. 104, 18, April 2000, p.p. 4440-4447.

[3] E. Traversa, "Design of ceramic materials for chemical sensors with novel properties," *Journal of the American Ceramic Society*, vol.78, 10, October 1995, p.p. 2625-2632.

[4] B. O'Regan, M. Grätzel, "A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO_2 films," *Nature*, vol. 353, 6346, October 1991, p.p. 737–740.

[5] A. Kay, M. Grätzel, "Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder," *Solar Energy Materials and Solar Cells*, vol. 44, 1, October 1996, p.p.99–117.

[6] U. Diebold, "The surface science of titanium dioxide," Tulane University, New Orleans, LA 70118, USA, *Surface Science*, 2003.

[7] S. Hore, C. Vetter, R. Kern, H. Smit, A. Hinsch, "Influence of scattering layers on efficiency of dye-sensitized solar cells *Solar Energy Materials and Solar Cells*, vol. 90, 9, May 2006, p.p. 1176-1188.

[8] H. Zhang and J. F. Banfield, "New kinetic model for the nanocrystalline anatase-to-rutile transformation revealing rate dependence on number of particles," *American Mineralogist*, vol. 84, 4, April 1999, p.p. 528-535.

[9] A. Chemsiddine, H. Jungblut, S. Boulmaaz, "Investigation of the Nanocluster Self-Assembly Process by Scanning Tunneling Microscopy and Optical Spectroscopy," *The Journal of Physical Chemistry B*, vol. 100, 30, July 1996, p.p. 12546-12551.

[10] A. Muramastu, T. Sugimoto, X. Zhou, "Synthesis of uniform anatase TiO_2 nanoparticles by gel–sol method, Formation process and size control," *Journal of Colloid and Interface Science*, vol. 259, 1, p.p. 43-52, March 2003.

[11] H. Mori, H. Yin, S. Kambe, S. Murasawa, Y. Wada, S.Yanagida, T. Kitamura, T. Sakata, "Hydrothermal synthesis of nanosized anatase and rutile TiO_2 using amorphous phase TiO_2," *Journal of Materials Chemistry*, vol. 11, 6, March 2001, p.p. 1694-1703.

[12] A. Kornowski, H. Weller, P.D. Cozzoli, "Low-Temperature Synthesis of Soluble and Processable Organic-Capped Anatase TiO_2 Nanorods," *Journal of the American Chemical Society*, vol. 125, 47, October 2003, p.p. 14539-14548.

[13] C.J. Barbe, F. Arendse, F. Lenzmann, M. Gratzel, P. Comte, M. Jirousek, V. Shklover, "Nanocrystalline titanium oxide electrodes for photovoltaic applications," *Journal of the American Ceramic Society*, vol. 80, 12, December 1997, p.p. 3157-3171.

[14] D.S. Xu, G.L. Guo, J.H. Ouyang, X. S. Zhao, Y. Tang, Z. Miao, "Electrochemically Induced Sol–Gel Preparation of Single-Crystalline TiO_2 Nanowires," *Nano Letters*, vol. 2, 7, May 2002, p.p. 717-720.

[15] R. K. Karn & O. N. Shrivastav, "On the structural and photochemical studies of In_2O_3-admixed nanostructured TiO_2 with regard to hydrogen production through photoelectrolysis," *International Journal of Hydrogen Energy*, vol. 23, 6, June 1998, p.p. 439-444.

[16] Hwan T., Young U., Sung H, Eui J., "Variation of structural and optical properties of sol-gel TiO_2 thin films with catalyst concentration and calcination temperature," *Materials Letters*, vol. 57, 30, December 2003, p.p. 4660-4666.

[17] E.C. Muniz, J. J. Silva, M.S. Goes, "Synthesis and characterization of mesoporous TiO_2 nanostructured films prepared by a modified sol-gel method for application in dye solar cells," *Ceramics International*, vol. 37, 3, April 2011, p.p. 1017-1024.

[18] Bhinyo Panijpan, Chaiyuth Sae-Kung, Supan Yodyingyong, "Physicochemical properties of nanoparticles titania from alcohol burner calcinations," *Bulletin of the Chemical Society of Ethiopia*, vol. 25, 2, January 2011, p.p. 263-272.

[19] A. Fujishima, K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode," *Nature*, vol. 238, July 1972, p.p. 37-38.

[20] D. W. Bahnemann, M. R. Hoffmann, S. T. Martin, W. Choi, "Environmental Applications of Semiconductor Photocatalysis," *Chemical Reviews*, vol. 95, 1, January 1995, p.p.69-96.

[21] H. Z. Zhang and J. F. Banfield, "Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO_2," *The Journal of Physical Chemistry B*, vol. 104, 15, February 2000, p.p. 3481-3487.

[22] A. Chemsiddine, D. Su, T. Moritz, J. Reiss, K. Diesner, "Nanostructured Crystalline TiO_2 through Growth Control and Stabilization of Intermediate Structural Building Units," *The Journal of Physical Chemistry B*, vol. 101, 41, p.p. 8052-8053, Oct. 1997.

[23] A.S. Attar, F. Hajesmaeilbaigi, M.S. Ghamsari, S. Mirdamadi, "Modifier ligands effect on the synthesized TiO_2 nanoctystals," *Journal of Materials Science*, vol. 43, 5, March 2008, p.p. 1723-1729.

[24] M.K. Park, S.K. Kim, S.K. Lee, S.Y. Chae, T.Y. Kim, W.I. Lee, "Preparation of Size-Controlled TiO_2 Nanoparticles and Derivation of Optically Transparent Photocatalytic Films," *Chemistry of Materials,* vol. 15, 17, July 2003, p.p. 3326-3331.

[25] L. Gao, Q. Zhang, "Preparation of oxide nanocrystals with tunable morphologies by the moderate hydrothermal method: Insights from rutile TiO_2," *Langmuir*, vol. 19, 3, January 2003, p.p. 967-971.

[26] H. Arakawa, H. Sugihara, H. Zhou, M.D. Wei, Y. Konishi, "Utilization of titanate nanotubes as an electrode material in dye-sensitized solar cells," *Journal of The Electrochemical Society*, vol. 153, 6, May 2006, p.p. 1232-1236.