

STRUCTURAL AND MORPHOLOGICAL STUDIES OF CNT/TiO₂ NANOCOMPOSITE FOR DYE-SENSITIZED SOLAR CELL APPLICATION

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Keywords: TiO₂, CNT, doctor-blade technique and nanocomposite.

Abstract

In this study, CNT/TiO₂ nanocomposite solution was obtained by modified acid treatment sol-gel method and CNT/TiO₂ thin film produce using doctor-blade technique. The preparation was performed as follows. Firstly, certain amounts of carbon nanotubes – 0.03 g, 0.06 g and 0.09 g were acid treatment with 30 ml of concentrated nitric acid for 1 hour. The CNTs were filtered and washed for several time with distill water to rinsed out excess acid nitric and subsequently put into oven about 5 hour to dry. The acid treatment CNTs were sonicated in 100 ml 2-propanol to disperse them well. Then the measured quantity of titanium tetraisopropoxide (TTIP) 50 ml was introduced into the CNT/2-propanol solution. The mixture of TTIP and CNTs was sonicated for 120 min to improve the interaction between the two materials. Then, the solution was stirred magnetically for 30 min and added slowly into 100 ml of distilled deionized water and stirring vigorously. The mixture was then heated at 60 °C for 1 hour. The characterization of the CNT/TiO₂ paste was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis.

1 Introduction

Titanium oxide - TiO₂ is a widely used photocatalyst for the decontamination of organic pollutants for its easy availability, strong oxidizing power, non-toxicity, and excellent photo-stability [1]. To avoid the use of TiO₂ powders, which are difficult to be separated from the aqueous systems after the photocatalytic (PC) treatment of organic pollutants, various ways have been developed to prepare PC TiO₂ coatings on solid substrates, including chemical vapor deposition, spray pyrolysis, electro deposition, sputtering and sol-gel methods [2]. Dye-sensitized solar cells (DSSCs) based on dye-sensitized nanocrystalline titanium dioxide and [Ru(4,40-dicarboxylic acid 2,20-bipyridine)2(NCS)2] have been reported by Regan and Grätzel

in 1991 [3]. The transport of photoinduced electrons across a TiO₂ nanoparticle network is the major concern in attaining higher overall light to electricity efficiency in such nanostructure working electrodes. Rapid photoinduced electron transport in a DSSC electrode is necessary to ensure the efficient collection by the conducting substrate when it competes with the charge recombination processes. In general, photogenerated electrons injected onto the mesoscopic film of a TiO₂ electrode must travel through the TiO₂ nanoparticle network and encounter many grain boundaries. This random transit path of the photoinduced electron enhances the probability of recombination with oxidizing species or the tri-iodide ions in the electrolyte, thus inhibiting the photocurrent and the photoconversion efficiency [4]. DSSC is composed of dye molecules, nanocrystalline titanium dioxide, and electrolytes containing a redox couple and counter electrode. The PtCl₄-treated electrode as a catalyst is used as the counter electrode in DSSC because of its high electrochemical activity even though this electrode is expensive. A low cost electrode with high electrochemical activity is an important requirement to enhance the practical utility of DSSC. However, compared with a silicon solar cell, its conversion efficiency was still unsatisfied. Therefore, there have been many studies to obtain high efficiency DSSC such as the increasing porosity and crystallizing TiO₂ electrode [5]. CNTs could offer a potential route to provide high area, interpenetrating electrodes in DSSCs. The introduction of carbon nanotubes into the electrode of organic solar cells and dye-sensitized solar cells had been performed, and it has been concluded that carbon nanotubes would efficiently increase the electronic conductivity of the electrode, increasing the photo conversion efficiency of the photovoltaic device. Furthermore, prior research indicates that introducing carbon nanotubes decreases the TiO₂ crystalline grain and particle size [6-7]. The objectives of this study are to synthesis CNT/TiO₂ nanocomposite by modified acid treatment sol-gel method and analyzing the morphological structure of CNT/TiO₂ thin film using SEM, XRD and TEM analysis.

2 Experimental Methodology

The CNT/TiO₂ nanocomposite was prepared by modified acid-catalyzed sol-gel method. The preparation was performed as follows, certain amounts of carbon nanotubes – 0.03 g, 0.06 g and 0.09 g were acid treatment with 30 ml of concentrated nitric acid for 1 hour. The CNTs were filtered and washed for several time with distill water to rinsed out excess acid nitric and subsequently put into oven about 5 hour to dry. The acid treatment CNTs were sonicated in 100 ml anhydrate 2-propanol to disperse them well. Then the measured quantity of TTIP 50 ml was introduced into the CNT/2-propanol solution. The mixture of TTIP and CNTs was sonicated for 120 minutes to improve the interaction between the two materials. Subsequently, the solution was stirred magnetically for 30 minutes and added slowly into 100 ml of distilled water, stirring vigorously. The mixture was then heated at 60 °C for 1 hour after adding nitric acid (69%). The 2-propanol and water was allowed to evaporate during this time. The CNT/TiO₂ solution transferred into an oven 100 °C for 24 hours. The 3 different quantities of CNT/TiO₂ powders were mix with small amount of polyethylene glycol to produce CNT/TiO₂ paste and put on an electric conducting glass plate. Indium-doped tin oxide (ITO) was used as an electric conducting plate. This mixture was doctor-bladed onto the support to generate a fine active area, and dried at room temperature for 1 hour. Subsequently, the electrodes were sintered in the air at 450 °C for 30 minutes, generating a crack-free, high surface area CNT/TiO₂ nanocomposite electrode. The flow chart for this method was illustrated by Figure 1 below.

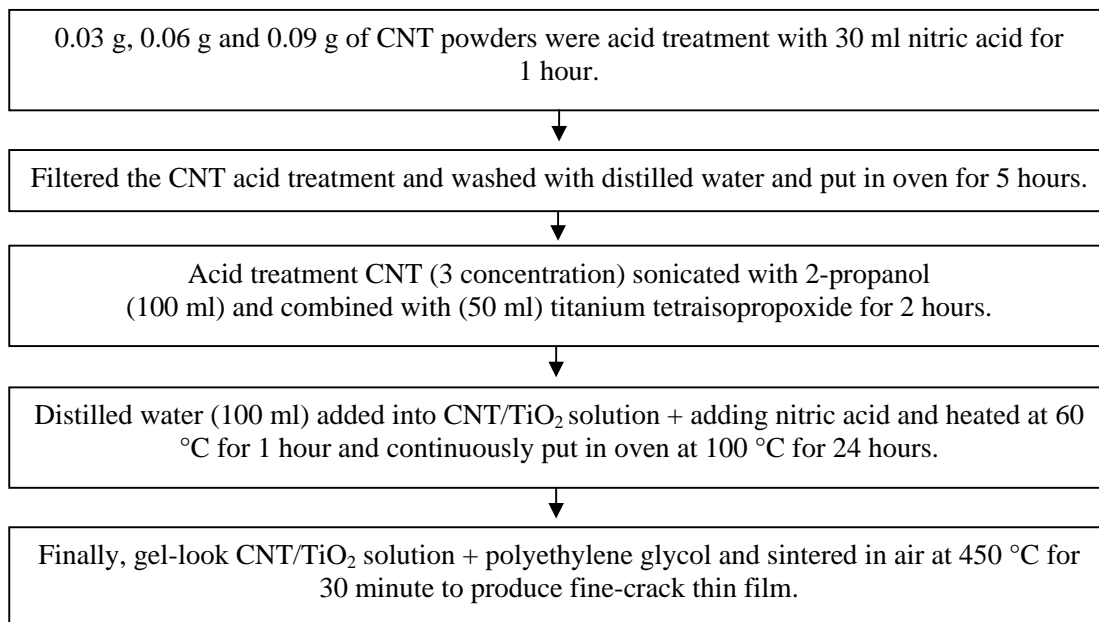
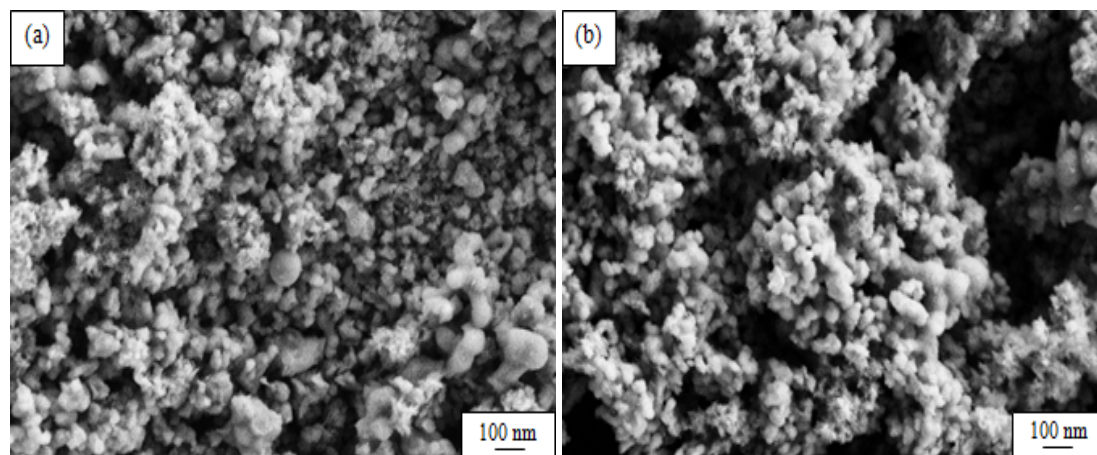


Figure 1. Synthesis method for CNT/TiO₂ thin film.

3 Discussion

3.1 Scanning Electron Microscopy, SEM

Carbon nanotube and titanium tetraisopropoxide as precursor for TiO₂ nanoparticles were used to synthesis CNT/TiO₂ thin film in this study. Due to the favorable electrical conductivity of CNT on the metal oxide nanocomposite, we expected that the presence of the CNT should enhance the electron transport rate and extend the electron lifetime in the TiO₂ electrode hence improve the dye-sensitized solar cell efficiency. In addition, from the other literature view, it was showed that the oxidation of CNT in concentrated acid treatment could produce CNT with terminal -COOH group that will have better contact around TiO₂ nanoparticles to improve the absorption of electrons [8]. The scanning electron microscopy (SEM) images of CNT/TiO₂ nanocomposite containing (a) 0.03 g, (b) 0.06 g and (c) 0.09 g added CNT are shown in Figure 2.



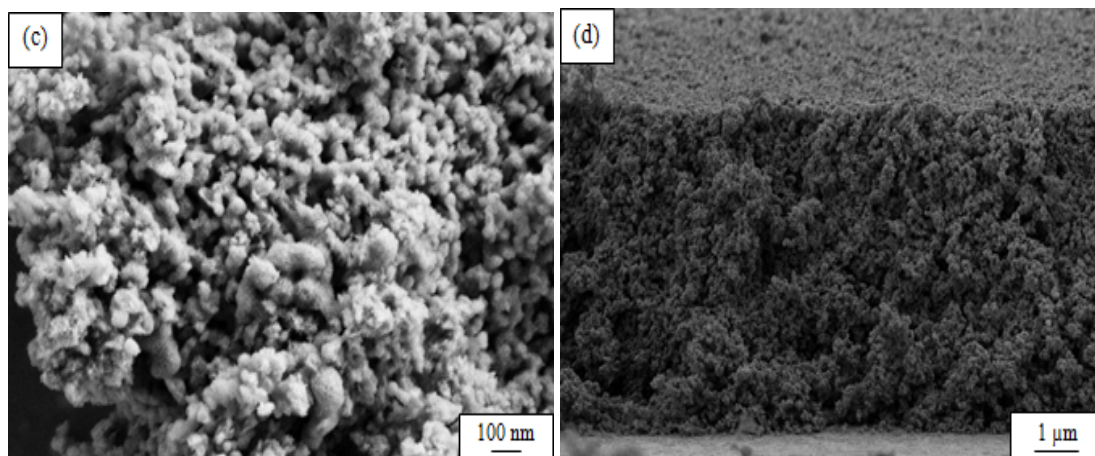


Figure 2. SEM micrographs of CNT/TiO₂ thin film annealed at 450 °C for (a) 0.03 g, (b) 0.06 g and (c) 0.09 g added CNT.

From the SEM images, we found that the CNT were well-dispersed among the TiO₂ nanoparticles and the bonding and contact between the CNT and TiO₂ nanoparticles was in a good shape. To see the change in porosity and structural design of CNT with respect to TiO₂ nanoparticles powder for thin film preparation, the amount of CNT powder added in the CNT/TiO₂ paste has been investigated. The average thickness for all samples are almost 18.19 μm. Comparing from all images, the 0.03 g CNT showing the least porous structure compare to 0.06 g and 0.09 g of CNT whereas the 0.09 g CNT added have the highest porosity due to the small CNT/TiO₂ nanoparticles size.

Energy Dispersion X-ray spectroscopy analysis using the same instrument with SEM showed that the weight percentage for carbon nanotube, titanium dioxide and oxygen increase with each time CNT powder added to the solution [9]. From EDX analysis, we can see that the weight percentage of oxygen decrease slowly from 40.14% to 37.70% while percentage weight for carbon increased initially from 4.15% to 14.00% but decreased at the end from 14.00% to 12.39% with 0.03 g, 0.06 g and 0.09 g added CNT. In the hand, the weight percentage trend for titanium slightly different with carbon with starting to decreased from 55.71% to 47.79% and finally increased with 0.09 g added CNT from 47.79% to 49.91%. These results reveal that the concentration of carbon nanotube in 0.06 g added CNT is the highest compared to other concentrations 0.03 g and 0.09 g.

Sample	Weight %			Atomic %		
	Carbon (C)	Oxygen (O)	Titanium (Ti)	Carbon (C)	Oxygen (O)	Titanium (Ti)
0.03 g	4.15	40.14	55.71	8.60	62.44	28.95
0.06 g	14.00	38.21	47.79	3.37	68.16	28.48
0.09 g	12.39	37.70	49.91	2.98	67.27	29.75

Table 1. Table show weight and atomic percentage for at 450 °C for (a) 0.03 g, (b) 0.06 g and (c) 0.09 g added CNT.

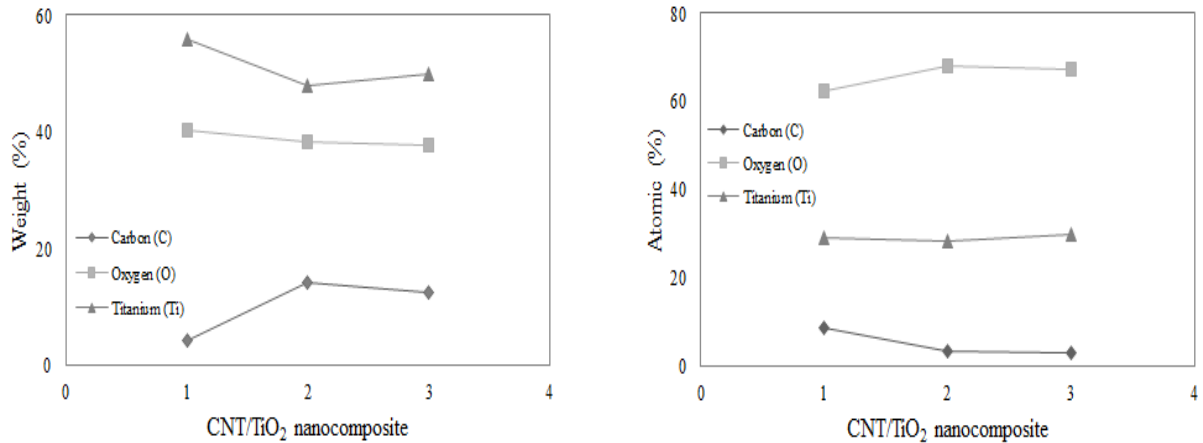
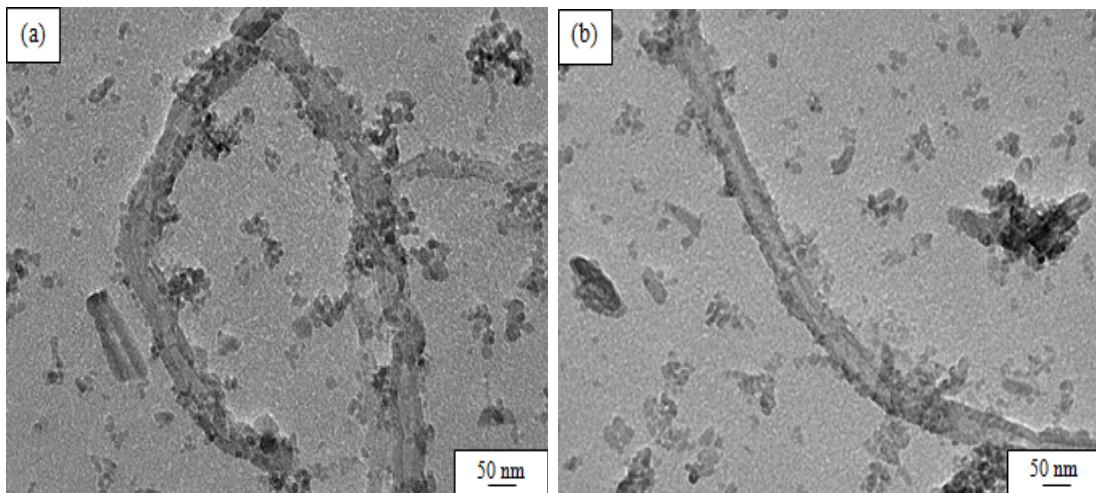


Figure 2. Energy dispersive x-ray spectroscopy graph for weight and atomic percentage of all samples.

3.2 Transmission Electron Microscopy, TEM

Transmission electron microscopy (TEM) studies confirmed the successful deposition of TiO₂ nanoparticles and CNT onto the surface on all crystalline samples. When the TEM micrographs of the samples were compared, the diameter and the length of the carbon nanotube have no obvious difference in size. In addition, in case of the amorphous titanium sample no metal particles were found on the surface of the nanotubes. TEM also confirmed that the nanotube tubular morphology in all samples was still preserved after the annealing process. The carbon nanotubes possessed a uniform diameter and had lengths of several micrometers [10].

Moreover, some small clusters of titanium dioxide were absorbed around the carbon nanotube surface area as shown in Figure 3 sample (a) and (b). Sample (c) shows the titanium dioxide nanoparticles without additional carbon nanotube particles and was used to differentiate between the CNT/TiO₂ nanoparticles and titanium dioxide nanoparticles sample.



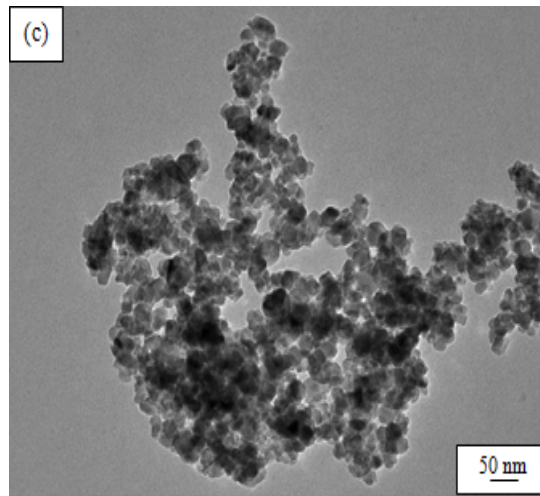


Figure 3. TEM micrograph show (a) and (b) CNT/TiO₂ sample and (c) TiO₂ sample.

3.3 X-ray Diffraction, XRD

X-ray diffraction pattern analysis has been conducted using x-ray diffractometer at diffraction angle of 20°–60° theta for (a) 0.03 g, (b) 0.06 g and (c) 0.09 g added CNT into CNT/TiO₂ nanocomposite. Figure 3 shows that the annealed thin film is identified as titanium dioxide (TiO₂) by PDF No. JCP2.2CA: 01-086-1156 and PDF No. JCP2.2CA: 01-078-2486 reference. The annealed CNT/TiO₂ thin film from figure 4 below composed of three peaks (101), (004) and (200) planes and the dominant peak is at (101) plane with 25.12° at 2θ position. It clearly reveals that the crystalline phase of the immobilized CNT/TiO₂ nanocomposite is in anatase phase while rutile and brookite phase does not appear in the graph. The XRD result suggests that there is no significant phase-preferred deposition in spite of the CNT addition, however there is any carbon nanotube peak appearing in the 2θ region which should be due to low CNT incorporation on the CNT/TiO₂ thin film [11].

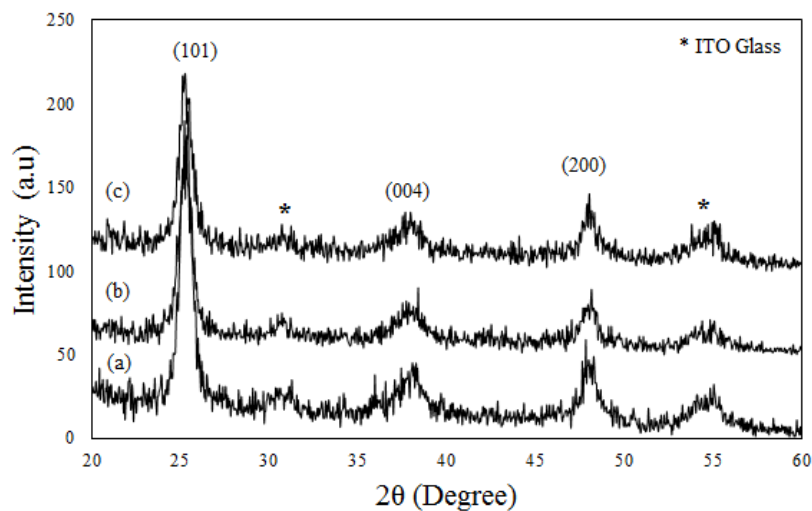


Figure 4. X-ray diffraction pattern of (a) 0.03 g, (b) 0.06 g and (c) 0.09 g added CNT annealed at 450 °C.

The average crystalline size of the particles was calculated from the XRD (101) peaks of anatase TiO₂ by applying the Scherrer's formula [12-13]:

$$D = \frac{k \lambda}{B \cos \theta} \quad (1)$$

From the equation above, the average of crystalline size composes of Scherrer's constant (k), the X-ray wavelength (λ), the broadening of the diffraction line measured as the full width at half maximum intensity (FWHM) (B), the corresponding diffraction angle and the main peak position (θ). The crystalline sizes of anatase TiO₂ are found to be (a) 7.74 nm, (b) 12.50 nm and (c) 16.85 nm in diameter when calcination temperature is at 450 °C and was indicated in table 1 parameter. Figure 5 shows that the crystalline sizes of the samples are increase with adding the CNT particle for each sample respectively.

Table 1. Crystalline size parameter

CNT/TiO ₂ Sample	Crystalline size
0.03 g	7.74 nm
0.06 g	12.50 nm
0.09 g	16.85 nm

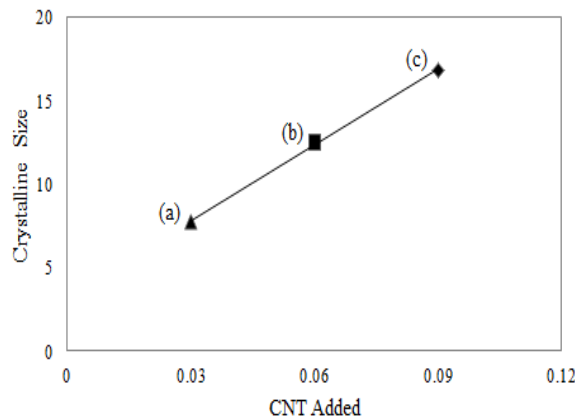


Figure 5. XRD Crystalline size analysis graph for all three samples.

Conclusion

From the above experimental results and discussion, this study can be conclude as follow; the SEM analysis show that the CNT were well-dispersed among the TiO₂ nanoparticles and the bonding and contact between the CNT and TiO₂ nanoparticles was in a good shape and the average thickness for all samples are 18.19 μ m. The XRD analysis confirmed that the thin films composed of titanium dioxide with dominant peak is at (101) plane with 25.12° at 2 θ degree position. From XRD also found that the sample is in anatase phase and the crystalline size increase with the amount of CNT particle added for the samples from 7.74 nm to 16.85 nm. Last but not least, TEM analysis also confirmed that the nanotube tubular morphology in all samples was still preserved after the annealing process.

Acknowledgements

The author would like to thank the laboratory of photonics institute of microengineering and nanoelectronic (IMEN), Universiti Kebangsaan Malaysia for providing the facilities.

Reference

- [1] X. Chen, S.S. Mao, Synthesis properties modifications and applications. Titanium dioxide nanomaterials: Chem Rev, **107**, pp. 2891–2959 (2007).
- [2] A.L. Pénard, T. Gacoin, J.P. Boilot, Functionalized sol–gel coatings for optical applications. Acc Chem Res, **40**, pp. 895–902 (2007).
- [3] B.O'Regan, M.Gratzel, A low-cost, High efficiency solar cell based on dye- sensitized colloidal TiO₂ films, Nature **353**, 737–740 (1991).
- [4] Heimer T A, Heilweil E J, Bignozzi C A and Meyer G J, J. Phys. Chem. A **104** 4256 (2000).
- [5] S.Kambe, S.Nakade, Y.Wada, T.Kitamura, S.Yanagida, Effects of crystal structure, size, shape and surface structural differences on photo-induced electron transport in TiO₂ mesoporous electrodes, J.MaterChem. pp. 723–728 (2002).
- [6] Miller A. J, Hatton R. A, Chen G. Y. and Silva. S. R. P. Appl. Phys. Lett. 90023105 (2007).
- [7] Jang S. R, Vittal R. and Kim K. J. Langmuir **20** 9807 (2004).
- [8] J. Liu. A.G. Rinzler, H.J. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias et al. Fullerenes pipes, Science **280** 1253-1256 (1998).
- [9] N. P. Ariyanto, H. Abdullah, N. S. A. Ghani. Materials Research Innovations. Volume **13** No 3 (2009).
- [10] D. Eder, M.S. Motta, I.A. Kinloch, A.H.Windle, Physica E **37** 245-249 (2007).
- [11] Wirat J, Samuk P, Santi M, Ekaphan S, Vittaya A. Journal of Alloys and Compounds **476**, 840-846 (2009).
- [12] Cullity, B. D., and S. R. Stock, Elements of X-ray Diffraction. 3rd Ed. Prentice-Hall (2001).
- [13] H. Abdullah, N. P. Ariyanto, S. Shaari, B. Yulianto, S. Junaidi. American J. of Engineering and Applied Science **2** (1): 236-240 (2009).