



ZIBELINE INTERNATIONAL

ISSN: 2521-0882 (Print)

ISSN: 2521-0483 (Online)

CODEN: EESND2



## STUDY ON OPTICAL PROPERTIES OF GRAPHENE-TiO<sub>2</sub> NANOCOMPOSITE AS PHOTOANODES LAYER IN DYE SENSITIZED SOLAR CELL (DSSC)

M. F. Zulkapli\*, N. M. Rashid , Mohd Nazri Mohd Sokri, Noorshawal Nasri

Department of Energy Engineering, Faculty of Chemical and Energy Engineering Universiti Teknologi, Malaysia, Johor.

\*Corresponding author email: [norhanarashid@utm.my](mailto:norhanarashid@utm.my)

This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited

### ARTICLE DETAILS

#### Article History:

Received 10 May 2018

Accepted 6 Jun 2018

Available online 10 July 2018

### ABSTRACT

Dye Sensitized Solar Cell (DSSC) using titanium dioxide (TiO<sub>2</sub>) has begun to play a significant role in future solar energy since it is known as cost effective and highly efficient. DSSC is the third generation of photovoltaic cells that have been widely investigated as a promising replacement of current commercial solar cell. However, the highest efficiency of DSSC still has not achieved the minimum requirement so that it can be commercialize. Much research has been done to improve DSSC performance by focusing on photoanodes layer. In this study, graphene was employed into TiO<sub>2</sub>photoanode to increase the efficiency and to enhance the performance of dye sensitized solar cell. Four different samples of nanocomposites paste were prepared by varying the graphene composition of 0.00, 0.30, 0.50 and 0.70 wt%. The prepared samples were coated on Fluorine-Doped Tin Oxide (FTO) conductive glass substrates by a doctor blade method and annealed at 450°C for 30 minutes. The morphology and structure of the graphene-TiO<sub>2</sub> nanocomposites layer were characterized by using Field Emission Scanning Electron Microscope (FESEM). The optical properties were studied by using UV-visible spectroscopy. Based on the result show that addition of graphene into TiO<sub>2</sub> have provide larger surface area compared to pure TiO<sub>2</sub>. The optical properties of Graphene-TiO<sub>2</sub> nanocomposites also improved as the fundamental of absorption edge has shifted toward longer wavelength and reduce the optical band gap.

### KEYWORDS

Dye Sensitized Solar Cell, Graphene, TiO<sub>2</sub>, Doctor Blade.

### 1. INTRODUCTION

Wastewater In this era of modern technology, energy has become one of the main parts of our life. Every day, a lot of energy is used among four economic sectors which are residential, commercial, industry and transportation. Increasing population has resulted in increased energy demand, thus accelerating depletion of fossil fuels [1]. It is expected that the world reserves of fossil fuel can only survive about 40 to 60 years for oil and natural gas and 200 years for coal [2]. Hence, to deal with this crisis we need to look for a clean energy source, also well-known as renewable energy sources to cope with the energy supply demand [3,4].

Among all the renewable energy sources such as wind, water and geothermal energy, solar energy is recognized as the potential candidate to meet the future energy source demand [5,6]. The earth's surface receives approximately  $3 \times 10^{24}$  joule/year of solar radiation, which is 10 times higher than energy demand of the entire world. This light intensity from the sun could be harvested by DSSC since this third generation of photovoltaic cell is known to be cost effective and highly efficient [2,7]. DSSC materials like TiO<sub>2</sub> semiconductor are inexpensive and produce no harmful effect to the environment [2,8]. In addition, DSSC device can perform better compared to 1<sup>st</sup> and 2<sup>nd</sup> generation solar cell under low light intensities and even in darker conditions such as in cloudy weather or at dawn [2]. These unique characteristics make DSSC favored in indoor applications such as sunroof and windows because it is effectively utilizing diffused light. To date, the most efficient DSSC consists of polypyridyl ruthenium sensitizers-based solar cells, which have obtained up to 11% conversion efficiency [9].

However, the commercial application of this device is still low due to some system inefficiencies. The major factor that leads to low efficiency of DSSC is recombination of photo-excited electrons from dye to conduction band

of semiconductor with the electrolyte [10,11]. Photoanode which is one of the main components in DSSC plays a significant role in the separation and transportation of electrons [6,12]. Much of research has been done to improve the properties of photoanode, such as modifying the photoanode by adding additive like graphene [13,14]. Graphene is one of the promising carbon materials as it shows some spectacular and unique potential compared to other materials such as activated carbon.

At present, graphene is used to replace high-cost platinum counter electrode in DSSC due to its properties of fast electron transfer, good optoelectronic properties and high visible light transparency [15]. Many methods have been developed to produce graphene. Among them, the two most popular are by reduction of Graphene Oxide (GO) and through Chemical Vapor Deposition (CVD) because these methods are cost effective, easy to handle and suitable for large-scale production [14]. Graphene is known as carbonaceous material with a single layer that provides a faster electron transfer path, reduces the electron-hole recombination rate in TiO<sub>2</sub>layer and produce large surface area [14,16]. These unique characteristics of graphene make it usable as additive in TiO<sub>2</sub>photoanodes to enhance electron mobility and further improve DSSC performance.

This research is focusing on investigating the optical properties of graphene-TiO<sub>2</sub> nanocomposites film for DSSC application. Based on the FESEM result, increasing concentration of graphene has provided larger surface area compared to pure TiO<sub>2</sub> [14,15]. Incorporation of graphene into TiO<sub>2</sub> also enhanced the optical properties of Graphene-TiO<sub>2</sub>nanocomposites by shifting the fundamental absorption edge toward the longer wavelength [13]. Thus, with lower band it is expected can enhance the DSSC performance and efficiency.

### 2. EXPERIMENTAL

## 2.1 Materials

The main components used to produce Graphene-TiO<sub>2</sub> paste are graphene purchased from Platonic Nanotech and the titanium oxide, TiO<sub>2</sub> (T/SP 14451, Solaronix). Other components used are the conductive glass plates (FTO glass, 7Ω/cm<sup>2</sup>, 300 x 300 x 2.2mm) LATECH, thin film solar applicator (for doctor blading), solvents (ethanol and methanol) purchased from VChem.

## 2.2 Preparation of Graphene-TiO<sub>2</sub> paste

1 ml of TiO<sub>2</sub> paste was measured and put in 4 different vials. Then, 1 ml of ethanol was poured into each vial. Calculated amount of graphene is then mixed with TiO<sub>2</sub> in the vials with an exact amount. 4 different samples of Graphene-TiO<sub>2</sub> with different composition of Graphene of 0.00%, 0.30%, 0.50% and 0.70% were prepared. Then, the nanocomposites paste were stirred by using roller mixer for 12 hours. The composite paste then was coated on FTO glass by using doctor blading method. Small amount of Graphene-TiO<sub>2</sub> composite paste was dropped on a FTO glass substrate masked with tape, and was spread with a blade to form a particle film. Then, the sample was annealed at 450°C for 30 minutes.

## 2.3 Characterization of Graphene-TiO<sub>2</sub> photoanode layer

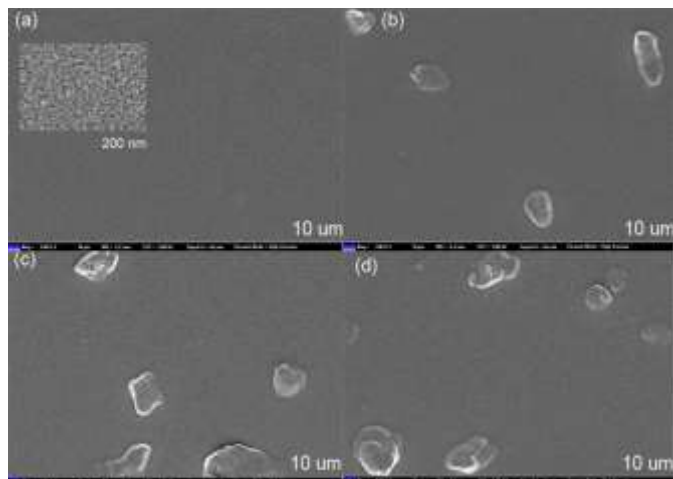
The morphology and structure of Graphene-TiO<sub>2</sub> coated on FTO glass substrate were characterized by using Field Emission Scanning Electron Microscope (FESEM) operating at 5.0 Kv. Before the analysis, the sample was coated by using platinum for 30s. UV- visible Spectroscopy (UV-Vis, Shimadzu, UV-1800) was used to examine the photon absorption efficiency of nanocomposites paste films at glass substrate.

## 3. RESULTS AND DISCUSSION

Based on the experiments, the incorporation of graphene in TiO<sub>2</sub> photoanode enhanced the optical properties of photo anode layer. In this study, different sample compositions of Graphene-TiO<sub>2</sub> from 0.30, 0.50 and 0.70 wt% were prepared to investigate the effect of graphene toward DSSC performance. The effects of graphene compositions towards photoanode layer were observed by using FESEM and UV-Vis analysis.

### 3.1 Field Emission Scanning Electron Microscope (FESEM)

The surface morphologies of the original TiO<sub>2</sub> and Graphene-TiO<sub>2</sub> nanocomposites anodes were investigated by FESEM analysis. Figure 1(a) represents the results for the surface morphology and structure of pure TiO<sub>2</sub> photoanode for scale 10 μm and 200 nm. It is shown that pure TiO<sub>2</sub> displays a uniform morphology of small spherical nanoparticles. Figure 1(b)-(d) represents the surface morphology of the Graphene-TiO<sub>2</sub> nanocomposites. Figure 1(b) showed the presence of graphene sheet that scatter on the TiO<sub>2</sub> nanoparticles compared to pure TiO<sub>2</sub>. The presence of graphene has supplied a larger surface area for the absorption of photon. Figure 1(c) and (d) showed that the amount of graphene sheet is increasing compared with Figure 1(b) as the concentration of graphene is higher, larger surface area is available which favours photon absorption efficiency. This clearly shows that the incorporation of graphene into TiO<sub>2</sub> photoanode at different concentrations will increase the effective surface area compared to pure TiO<sub>2</sub> photoanode.

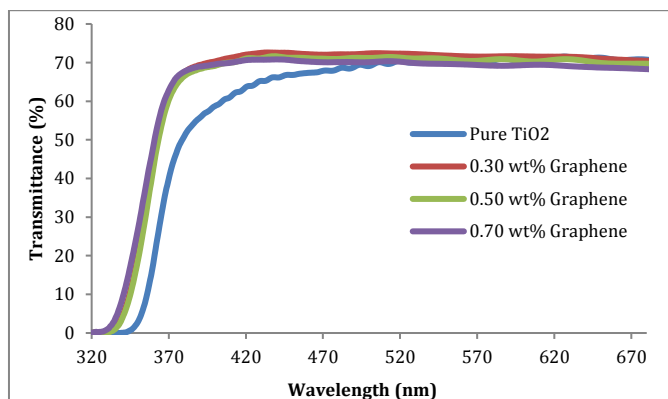


**Figure 1:** Field emission scanning electron microscopy (FESEM): (a) TiO<sub>2</sub>, (b)-(d) Graphene-TiO<sub>2</sub>

## 3.2 Optical Properties Study

### 3.2.1 Transmittance Analysis

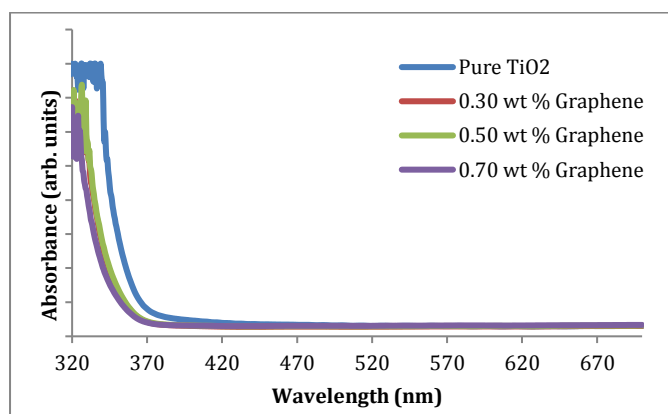
Figure 2 shows the analysis of transmittance for pure TiO<sub>2</sub> and Graphene-TiO<sub>2</sub> nanocomposites. For pure TiO<sub>2</sub>, it can be seen that the transmittance is initially increased with increasing wavelength up to ~500 nm and become constant. For Graphene-TiO<sub>2</sub> nanocomposites, the transmittance is initially increased with increasing wavelength up to ~400 nm before it becomes constant. The average transmittance of Graphene-TiO<sub>2</sub> nanocomposites obtained is within 67-72%. As shown in Figure 2, the concentration of 0.30 wt% Graphene-TiO<sub>2</sub> has the highest transmittance value. This indicates a higher amount of light passes through the samples with lower absorption by the photoanode layer. The concentration of 0.70 wt% Graphene-TiO<sub>2</sub> showed the lowest percentage of transmittances which indicates the highest absorption capability. This can be explained by, if all light passes through a solution without any absorption, the absorbance is zero, and percent transmittance is 100% and vice versa.



**Figure 2:** Transmittance of different Graphene-TiO<sub>2</sub> nanocomposites film

### 3.2.2 Optical Band Gap

UV-Vis Spectroscopy was used to study and understand the optical properties of Graphene-TiO<sub>2</sub> nanocomposites film. The UV-Vis absorption spectrum of pure and Graphene-TiO<sub>2</sub> nanocomposites were studied in order to determine the optical band gap. As shown in Figure 3, the absorption band appeared at approximately 324-340 nm. In the Graphene-TiO<sub>2</sub> spectra, the absorption edge was slightly shifted to a longer wavelength compared to pure TiO<sub>2</sub>.



**Figure 3:** Absorbance of different nanocomposite paste

The optical band gap energies of pure and Graphene-TiO<sub>2</sub> nanocomposites from UV-Vis absorption spectra have been calculated using equation (1) [17].

$$hv = \frac{1240}{\lambda(nm)} \quad (1)$$

A plot of  $(ahv)^{1/2}$  vs  $hv$  of pure TiO<sub>2</sub> and Graphene-TiO<sub>2</sub> nanocomposites are shown in Figure 4. The determination of optical band gap was obtained from the interception of the abscissa axis with the straight line of the  $(ahv)^{1/2}$  vs  $hv$  plot. The band gaps obtained from the extrapolating in pure TiO<sub>2</sub>, 0.30, 0.50 and 0.70 wt% Graphene-TiO<sub>2</sub> nanocomposites were about 3.18, 3.24, 3.12 and 3.06 eV respectively. For 0.5 and 0.7 wt% Graphene-TiO<sub>2</sub>, band gap obtained is only slightly reduced compared to

pure TiO<sub>2</sub> because less than 1 wt % of graphene is used. Based on previous report, the amount of graphene used was more than 1 wt % which are 1, 5 and 10 wt % Graphene-TiO<sub>2</sub> and give lower band gap value of 2.94, 2.25 and 2.11 eV respectively [18].

Therefore, by using more amount of graphene will further reduce the band gap. It is clearly that the addition of graphene into TiO<sub>2</sub> has shifted the fundamental absorption edge of Graphene- TiO<sub>2</sub> nanocomposites towards the longer wavelength. Wavelength ranges absorbed are closely related to the band gaps in semiconductor materials, where, when the absorption wavelengths increase, the band gap will decrease. It is also show that the optical band gap is decreasing with increase in graphene concentration [13]. Therefore, the incorporation if graphene into TiO<sub>2</sub> are expected to enhance the DSSC performance by increase the absorption intensity of light. However, the band gap for 0.3 wt % Graphene-TiO<sub>2</sub> showed an increment compare to pure TiO<sub>2</sub> at value of 3.24 eV. This might be because of unsuitable concentration and too low amount of graphene.

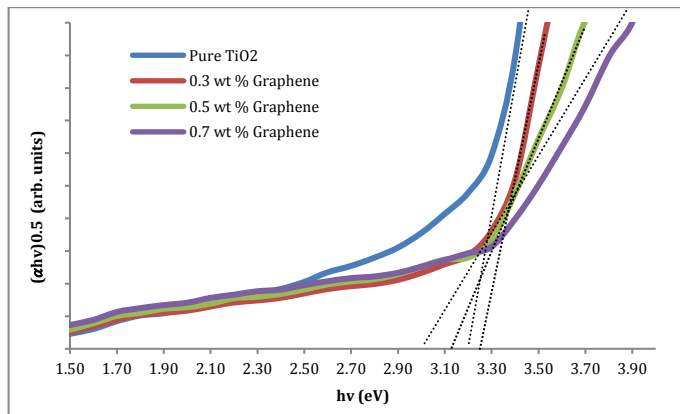


Figure 4: Tauc plots

#### 4. CONCLUSION

In conclusion, Graphene-TiO<sub>2</sub> nanocomposites has been successfully fabricated by using doctor blade method. Compared with pure TiO<sub>2</sub> photoanode layer, the Graphene-TiO<sub>2</sub> nanocomposites films had bigger surface area which favors photon absorption efficiency. UV-Vis spectroscopy showed that incorporation of graphene in TiO<sub>2</sub> has enhanced the optical properties of the photoanode by reduce the optical band gap. This improvement will enhance DSSC performance which associated with the higher light absorption and a wide range of absorption wavelengths.

#### ACKNOWLEDGEMENT

The authors are grateful to the UTM for the interest and encouragement.

#### REFERENCES

- [1] Capellán-Pérez, I. 2014. Fossil fuel depletion and socio-economic scenarios: An integrated approach. *Energy*, 77(Supplement C), 641-666.
- [2] Gong, J. 2017. Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. *Renewable and Sustainable Energy Reviews*, 68 (Part 1), 234-246.
- [3] Modi, A. 2017. A review of solar energy-based heat and power generation systems. *Renewable and Sustainable Energy Reviews*, 67 (Supplement C), 1047-1064.
- [4] Richhariya, G. 2017. Natural dyes for dye sensitized solar cell: A review. *Renewable and Sustainable Energy Reviews*, 69 (Supplement C), 705-718.
- [5] Chou, C.S. 2015. Preparation of TiO<sub>2</sub>/bamboo-charcoal-powder composite particles and their applications in dye-sensitized solar cells. *Advanced Powder Technology*, 26 (3), 711-717.
- [6] Sengupta, D. 2016. Effects of doping, morphology and film-thickness of photo-anode materials for dye sensitized solar cell application – A review. *Renewable and Sustainable Energy Reviews*, 60 (Supplement C), 356-376.
- [7] Taleb, A. 2016. Optimized TiO<sub>2</sub> nanoparticle packing for DSSC photovoltaic applications. *Solar Energy Materials and Solar Cells*, 148 (Supplement C), 52-59.
- [8] Ellis, H. 2014. Characterization of dye-sensitized solar cells: Components for environmentally friendly photovoltaics. Ångström: Uppsala, 67.
- [9] Chaiamornnugool, P. 2017. Performance and stability of low-cost dye-sensitized solar cell based crude and pre-concentrated anthocyanins: Combined experimental and DFT/TDDFT study. *Journal of Molecular Structure*, 1127 (Supplement C), 145-155.
- [10] Mehmood, U. 2016. Improvement in Photovoltaic Performance of Dye Sensitized Solar Cell Using Activated Carbon-TiO<sub>2</sub> Composites-Based Photoanode.
- [11] Hu, X. 2011. Enhanced performances of dye-sensitized solar cells based on graphite-TiO<sub>2</sub> composites. *Materials Science and Engineering: B*, 176 (5), 431-435.
- [12] Mohamad, A.A. 2016. Absorbency and conductivity of quasi-solid-state polymer electrolytes for dye-sensitized solar cells: A characterization review. *Journal of Power Sources*, 329 (Supplement C), 57-71.
- [13] Kazmi, S.A. 2017. Electrical and optical properties of graphene-TiO<sub>2</sub> nanocomposite and its applications in dye sensitized solar cells (DSSC). *Journal of Alloys and Compounds*, 691 (Supplement C), 659-665.
- [14] Guo, X., Lu, G., Chen, J. 2015. Graphene-Based Materials for Photoanodes in Dye-Sensitized Solar Cells. *Frontiers in Energy Research*, 3 (50).
- [15] Park, J.G. 2012. Application of single walled carbon nanotubes as counter electrode for dye sensitized solar cells. *Electrochimica Acta*, 85 (Supplement C), 600-604.
- [16] Chen, L. 2013. Enhanced photovoltaic performance of a dye-sensitized solar cell using graphene-TiO<sub>2</sub> photoanode prepared by a novel in situ simultaneous reduction-hydrolysis technique, 5.
- [17] Kazmi, S., Hameed, S., Azam, A. 2015. Investigation of electrical and optical properties of TiO<sub>2</sub>-graphene for dye-sensitized solar cells. in 2015 Annual IEEE India Conference (INDICON).
- [18] Kim, A.Y.K., Ji-Eun, Min-Young, K., Seung-Won, H., Ngyen Thi Thuy, T., Mi-Sook, K. 2012. Photovoltaic Efficiencies on Dye-Sensitized Solar Cells Assembled with Graphene-Linked TiO<sub>2</sub> Anode Films. *Bulletin of the Korean Chemical Society*, 33 (10), 3355-3360.