

Performance Enhancement of Dye-Sensitized Solar Cells by MgO Coating on TiO₂ Electrodes

C. Photiphitak, P. Rakkwamsuk, P. Muthitamongkol, C. Thanachayanont

Abstract—TiO₂/MgO composite films were prepared by coating the magnesium acetate solution in the pores of mesoporous TiO₂ films using a dip coating method. Concentrations of magnesium acetate solution were varied in a range of 1×10^{-4} – 1×10^{-1} M. The TiO₂/MgO composite films were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS), transient voltage decay and I-V test. The TiO₂ films and TiO₂/MgO composite films were immersed in a 0.3 mM N719 dye solution. The Dye-sensitized solar cells with the TiO₂/MgO/N719 structure showed an optimal concentration of magnesium acetate solution of 1×10^{-3} M resulting in the MgO film estimated thickness of 0.0963 nm and giving the maximum efficiency of 4.85%. The improved efficiency of dye-sensitized solar cell was due to the magnesium oxide film as the wide band gap coating decays the electron back transfer to the triiodide electrolyte and reduce charge recombination.

Keywords—Magnesium oxide thin film, TiO₂/MgO composite films, Electrochemical Impedance Spectrum, Transient voltage decay

I. INTRODUCTION

FOR more than 20 years, dye-sensitized solar cell has been published by Gratzel and O'Regan. Dye-sensitized solar cells have been extensively studied because of its high performance, simple fabrication processes, low-cost materials and manufacturing processes[1]. The dye-sensitized solar cells consist of transparent conducting oxide (TCO) coated glass, TiO₂ photoelectrode, Ru complex photosensitizer such as N719 dye molecules, redox electrolyte such as I⁻/I³⁻ (iodide/triiodide) and Pt counter electrode[2]. When the dye molecule absorbs light was excited from a ground state to excited state. the excited electrons of the dye molecule were injected into the conduction band of the TiO₂ electrode and created dye cations. The injected electrons in the conduction band of the TiO₂ transported through the TiO₂ nanoparticles by diffusion towards the back contact (TCO) and consequently to reach the counter electrode through the external load and wiring.

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The dye cations accept electrons from I⁻ and regenerated to the ground state, the I⁻ was oxidized to the I³⁻ (oxidation process). The I³⁻ diffuses toward the counter electrode and was reduced to I⁻ (reduction process).

High performance dye-sensitized solar cells require the nanocrystalline TiO₂ electrode with large surface area, high crystallinity without cracks and favorable electrical contact with the conducting glass substrate so that high amounts of dye molecules can be adsorbed and the electrons can be quickly transferred[3].

However, a problem of the DSSC is its low energy conversion efficiency when compared with silicon solar cells. The main reason is that charge recombination loss arises at the semiconductor/dye/electrolyte interface and low dye absorption towards the infarred region. Recombination with the dye cations and/or the electrolyte species (I³⁻) can drastically affect the open circuit voltage (V_{OC}). Improving the efficiency of DSSCs can be achieved by coating a thin film of oxide layers on the TiO₂ electrode such as MgO, ZnO, Al₂O₃, Nb₂O₅, CaCO₃, and SrTiO₃ etc[3-5]. The oxide film has a wide band gap that delays the electrons back transfer to the electrolyte and minimizes charge recombination. In addition, the coating layer can increase the dye adsorption on the porous electrode and, hence, increase the photocurrent[3].

In this report, magnesium oxide coating was applied to the TiO₂ electrode dip-coating technique. The concentrations of magnesium acetate solution were varied in a range of 1×10^{-4} - 1×10^{-1} M and performances of the DSSCs were compared. The effect of magnesium oxide thin film on the resistance of the TiO₂/MgO/dye interface and transient voltage was also studied.

II. EXPERIMENTAL DETAILS

TiO₂ paste (Dyesol) was screen printed 3 times on a fluorine-doped-tin-oxide (FTO) glass substrate (2×3 cm.). A screen with a 200 mesh was used to obtain a TiO₂ layer with a thickness of approximately 14 μm as shown in fig. 1b. In order to avoid contamination on the fresh film, the screen-printing was performed in a clean-room environment. After drying at 55 °C for 30 min, the electrodes were sintered at 450 °C for 30 min, and then cooled down at room-temperature. The electrodes were immersed in a 3×10^{-4} M of N719 dye solution, namely, *cis*-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis (tetrabutyl -ammonium) in absolute ethanol for 24 h. The excess dye was removed from the electrode by rinsing in ethanol.

In order to deposit the MgO thin film on the TiO₂ film, a 2×3 cm² FTO glass with 0.5×1.2 cm² TiO₂ films was immersed in the magnesium acetate solution [Mg(C₂H₃O₂)₂] for 10 seconds, then rinsed with ethanol and dried in air at 55 °C for 1 h. The films were then sintered at 450 °C for 30 min. Magnesium acetate was the magnesium salt of acetic acid, when heated, it decomposes into magnesium oxide. We designed the experiment to vary the concentration of the Mg(C₂H₃O₂)₂ solution such as 1×10⁻⁴, 1×10⁻³, 1×10⁻² and 1×10⁻¹ M to study the thickness of the magnesium oxide film. The thickness of MgO film was estimated by calculated as $t = (\text{weight of MgO})/Sp$, where $S = \text{surface area of TiO}_2 \text{ films}$ and $\rho = \text{density of MgO}$ [6].

In order to investigate the microstructure and elemental analysis of the obtained MgO thin films, the films were characterized by transmission electron microscopy (JEOL model: JSM-2010). Scanning electron microscope (JEOL model: JSM-6301F) and attached energy dispersive X-Ray Spectrometer (EDX) were, respectively, employed to record cross-sectional view of the TiO₂/MgO films and elemental analysis. The transient voltage decay was characterized by digital oscilloscope (Tektronix model: TDS 3034B) and the electrochemical impedance spectrum was characterized by potentiostats/ galvanostats (Autolab model: PGSTAT100). *J-V* measurements were performed under a 450W xenon light source which was able to provide 1000Wm⁻² sunlight equivalent irradiation (AM 1.5), using Keithley digital source meter (Model 2400) under the illuminated condition.

III. RESULTS AND DISCUSSION

The TiO₂ films were coated with magnesium acetate solution by dip-coating technique described in the experimental section. The Surface morphology of TiO₂/MgO composite films was readily observed by SEM as shown in Fig.1.

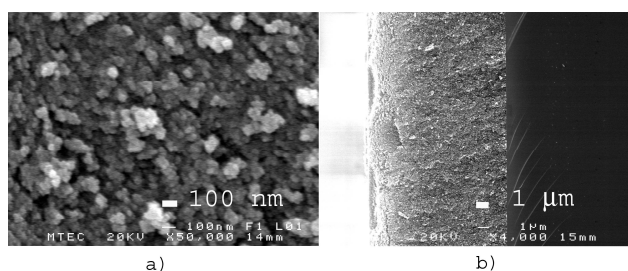


Fig. 1 SEM image of TiO₂/MgO composite films with a) plan-view image and b) cross-sectional image

Fig. 2(a) shows EDX spectra of the TiO₂/MgO composite films at top surface of the TiO₂/MgO electrodes. No MgO is observed. However, cross-sectional sample, Fig. 2(b), indicate the MgO presence.

Fig. 3 shows a TEM image of the TiO₂/MgO composite film prepared from 1×10⁻³ M of magnesium acetate solution. From a previous study, we found that the TiO₂ particles were nanorods and the length was approximately 25 nm [7]. However, we cannot observe the magnesium oxide thin film on

surfaces of the TiO₂ nanoparticles because its ultra thin nature. The hydrolysis of magnesium acetate covers the surface of TiO₂ particles with a layer of MgO (hydrated MgO). Sintering removes moisture and results in the outer shell of MgO attached firmly on the TiO₂ particles. Since the thickness of MgO film cannot be observed and measured from the TEM images, the MgO film thickness was estimated from the weight of the MgO as described in the section of experimental details. The concentrations of magnesium acetate solution of 1×10⁻⁴, 1×10⁻³, 1×10⁻² and 1×10⁻¹ M were calculated to give the thicknesses of the magnesium oxide film as 0.0780, 0.0963, 0.1605, and 0.4632 nm, respectively.

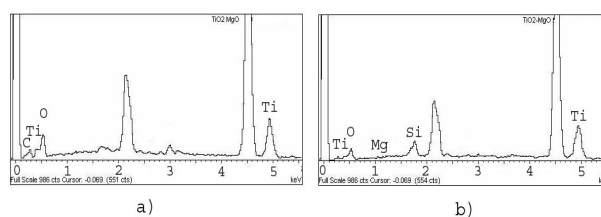


Fig. 2 EDX image of the TiO₂/MgO film prepared from 1×10⁻³ M of magnesium acetate solution taken from a) top surface and b) cross-section

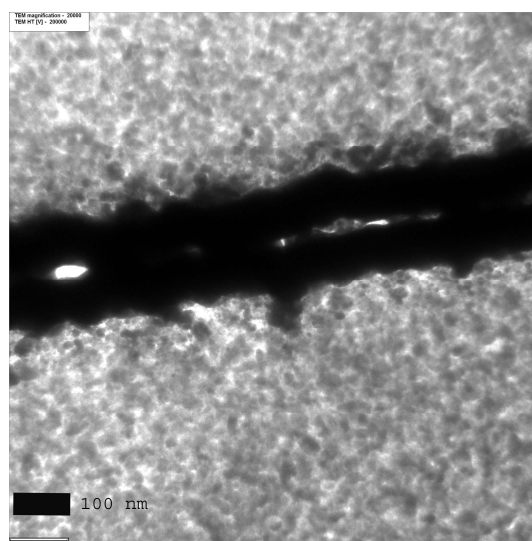


Fig. 3 A cross-sectional TEM micrograph of the TiO₂/MgO composite films prepared from 1×10⁻³ M of magnesium acetate solution

Figs. 4 (a) and (b) show optical absorption spectra of the bare-TiO₂ and TiO₂/MgO films without and with N719 dye, respectively. In Fig. 4b, the absorption spectrum of the N719 dye is also shown. Mechanism of Ru complexes (N719. dye) excitation by light absorption in the visible range is called metal to ligand charge transfer (MLCT), which provides the maximum absorbance at the wavelength of 396 and 534 nm [8].

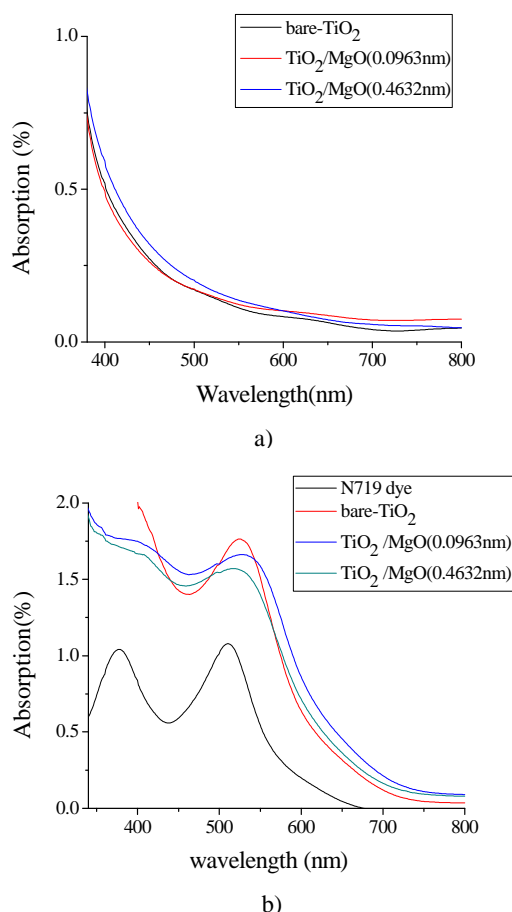


Fig. 4 Optical absorption spectra of the TiO_2/MgO films: a) without N719 dye and b) with N719 dye

Table 1 shows the estimated MgO film thicknesses and performances of the DSSCs with the TiO_2 film and TiO_2/MgO composite films as electrode calculated from I-V characteristics, see Fig. 5. We found that with an increase in thickness of the magnesium oxide thin film from 0.0780 to 0.4632 nm, the V_{oc} was increased from 0.72 ± 0.015 V to 0.81 ± 0.023 V, whereas the FF was decreased from 0.79 ± 0.012 to 0.73 ± 0.012 . The J_{sc} and Efficiency was initially increased and decreased later. The DSSCs with the TiO_2/MgO (0.0963nm) has a maximum short circuit current density (J_{sc}) and efficiency of 8.44 mA/cm^2 and 5.01 %, respectively.

Fig. 6 shows an example of electrochemical impedance spectrum of DSSCs using N719 dye. Three semicircles were observed in the measured frequency range of 0.1 Hz - 1 MHz. We defined these impedances between 1 kHz - 100 kHz as Z_1 , 1 Hz - 1 kHz as Z_2 , and 20 mHz - 1 Hz as Z_3 . The internal resistances of R_1 , R_2 , and R_3 describe the real parts of Z_1 , Z_2 and Z_3 , respectively. Where, the R_1 was related to the carrier transport resistance at the surface of Pt counter electrode (R_1 inversely proportional to the roughness factor of the counter electrode). The R_2 was related to carrier transport resistance in $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface ($1/R_2$ directly proportional to the applied bias voltage or R_2 shows the resistance of the diode element in the DSSCs). The R_3 was related to the diffusion of iodide and triiodide within the electrolyte (R_3 was directly proportional to the distance between TCO and Pt electrode). And R_h was dependence on the sheet resistance of TCO glass substrate [9,10].

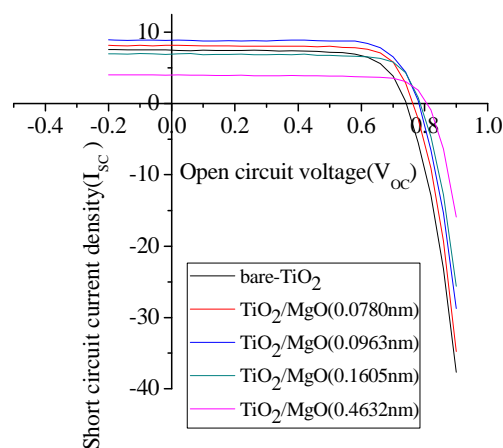


Fig. 5 J-V curves of DSSCs based on TiO_2 and TiO_2/MgO electrodes under AM. 1.5

TABLE I
ESTIMATED THICKNESSES OF THE MGO FILMS, SHORT CIRCUIT CURRENT DENSITIES (J_{sc}), OPEN CIRCUIT VOLTAGES (V_{oc}), FILL FACTORS (FF), EFFICIENCIES, SERIES RESISTANCES (R_s) AND SHUNT RESISTANCES (R_{sh}) OF DSSCs PREPARED USING THE TiO_2/MgO COMPOSITE FILM ELECTRODES COMPARED WITH BARE- TiO_2 ELECTRODE (REFERENCE) UNDER AM1.5

| Condition of electrodes | Concentration of magnesium acetate (M) | Thickness of MgO thin film (nm) | V_{oc} (Volt) | J_{sc} (mA/cm^2) | FF | Eff. (%) | R_s ($\Omega\text{*cm}^2$) | R_{sh} ($\text{k}\Omega\text{*cm}^2$) |
|-------------------------------------|--|---------------------------------|-----------------|-------------------------------|-----------------|-----------------|--------------------------------|---|
| Bare-TiO | 0 | - | 0.72 ± 0.015 | 6.99 ± 0.861 | 0.79 ± 0.012 | 3.99 ± 0.606 | 10.87 ± 1.28 | 1.89 ± 0.07 |
| $\text{TiO}_2/\text{MgO}1\times 10$ | 1×10 | ~ 0.0780 | 0.75 ± 0.008 | 8.15 ± 0.282 | 0.78 ± 0.006 | 4.77 ± 0.133 | 13.42 ± 1.15 | 2.86 ± 1.43 |
| $\text{TiO}_2/\text{MgO}1\times 10$ | 1×10 | ~ 0.0963 | 0.75 ± 0.014 | 8.44 ± 0.396 | 0.79 ± 0.023 | 5.01 ± 0.184 | 12.75 ± 1.20 | 2.96 ± 1.30 |
| $\text{TiO}_2/\text{MgO}1\times 10$ | 1×10 | ~ 0.1605 | 0.79 ± 0.030 | 6.29 ± 1.574 | 0.74 ± 0.022 | 3.68 ± 0.794 | 24.81 ± 11.93 | 3.51 ± 1.86 |
| $\text{TiO}_2/\text{MgO}1\times 10$ | 1×10 | ~ 0.4632 | 0.81 ± 0.023 | 4.45 ± 0.565 | 0.73 ± 0.012 | 2.66 ± 0.321 | 38.40 ± 8.79 | 4.34 ± 1.56 |

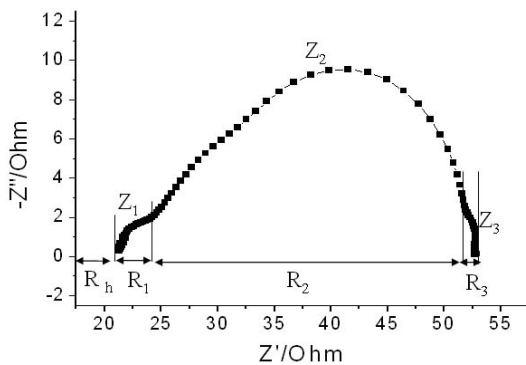


Fig. 6 Model electrochemical impedance spectrum (EIS) of DSC consisting of a TCO/TiO₂-N719 dye/electrolyte with I⁻, I³⁻ redox couple /Pt electrode, Z₁, Z₂, and Z₃ describe as impedances. R₁, R₂, R₃ and R_h were internal resistance elements[9,10]

Fig. 7 shows an electrochemical impedance spectrum (EIS) of the DSSCs in this study with the TiO₂ and the TiO₂/MgO electrodes with varied thickness of MgO as shown in Table 1. We found that the EIS of the DSSCs with TiO₂/MgO (0.0963 nm) electrode has a small curve, the low value of R₂ and series resistance (R_s) where [R_s=R_h+R₁+R₃], this was consistent with results obtained from I-V characteristics as shown in Table 1. The shunt resistance (R_{sh}) describes the recombination of the electron from the TiO₂ electrode to the electrolyte, the high value of R_{sh} indicates a slow back electron transfer rate from the TiO₂ to the electrolytes at the TiO₂/dye/electrolyte interface[10]. However, the R_{sh} cannot be estimated from the EIS because it is included in R₂, but the shunt resistance (R_{sh}) can be calculated from I-V characteristics.

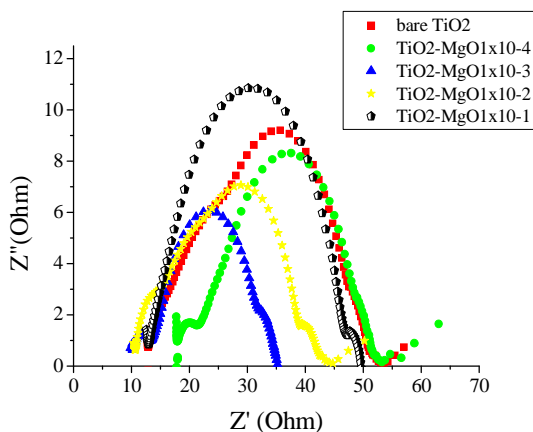


Fig. 7 Electrochemical impedance spectrum (EIS) of DSSCs with the TiO₂ and the TiO₂/MgO electrodes with varied thickness of MgO as shown in Table I

In Fig.8, the voltage value was related to the charge electron transfer yield from excited dye molecules to the oxide film. The voltage of DSSCs with TiO₂/MgO(0.0963nm) electrode was the highest when compared with the bare-TiO₂, the

TiO₂/MgO (0.078 nm), the TiO₂/MgO (0.1605nm) and the TiO₂/MgO (0.4632nm) electrodes, indicating that a very thin MgO film does not hinder the transfer of excited electron from a dye molecule to the CB of oxide. The slower charge recombination in the presence of the MgO layer on TiO₂ is because the MgO layer acts as a barrier for charge recombination of the dye cations [11]. However, when increase the MgO thickness to exceed 0.0963 nm, the voltage decay is fast because the electron injection from the excited dye molecules to the CB of TiO₂ is hindered by the MgO film as the thickness of MgO increases [12].

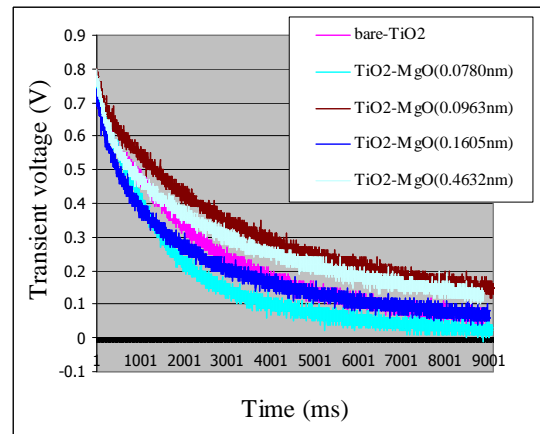


Fig. 8 Transient voltage decay of DSSCs with TiO₂ electrode and TiO₂/MgO electrode with varied thickness of the MgO film in a range 0.0780-0.4632 nm

IV. CONCLUSION

The DSSCs efficiency was found to enhance by dip-coating MgO thin films on the TiO₂ electrodes. The magnesium acetate solutions were prepared at concentrations of 1x10⁻⁴, 1x10⁻³, 1x10⁻² and 1x10⁻¹ M to achieve the MgO thickness of 0.0780, 0.0963, 0.1605 and 0.4632 nm, respectively. The thicknesses of the MgO films could not be measured by TEM imaging because of its ultra thin nature. Thus, the estimation of the MgO thickness was conducted using the known MgO weight. The DSSCs with the TiO₂/MgO (0.0963nm) electrode had the maximum efficiency when compared with the DSSCs with bare-TiO₂ electrode and other TiO₂/MgO electrodes. The measuring electrochemical impedance spectrum showed that the internal resistance of DSSCs with the TiO₂/MgO (0.0963nm) was lowest at about 12.75 Ω*cm². In addition, the transient voltage decay also showed that DSSCs with the TiO₂/MgO (0.0963nm) electrode gave the slowest decay.

ACKNOWLEDGMENT

The authors thank the National Metal and Materials Technology Center (MTEC) and Suan Dusit Rajabhat University (SDU), Thailand for financial support.

REFERENCES

- [1] B. O'Regan, M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films," *Nature*, vol. 353, no. 6346, pp. 737-740, 1991
- [2] D.S. Tsoukleris, I.M. Arabatzis, E. Chatzivasiloglou, A.I. Kontos, V. Belessi, M.C. Bernard, P. Falaras, "2-Ethyl-1-hexanol based screen-printed titania thin films for dye-sensitized solar cells," *Solar Energy*, vol. 79, pp. 422-430, 2005.
- [3] C.O. Avellaneda, A.D. Goncalves, J.E. Benedetti, A.F. Nogueira, "Preparation and characterization of core-shell electrodes for application in gel electrolyte-base dye-sensitized solar cells," *Electrochimica Acta*, vol. 55, pp. 1468 - 1474, 2010.
- [4] Z. Liu, K. Pan, M. Lui, M. Wang, Q. Lu, J. Li, Y. Bai, T. Li, "Al₂O₃-coated SnO₂/TiO₂ composite electrode for the dye-sensitized solar cell," *Electrochimica Acta*, vol. 50, pp. 2583 - 1474, 2589.
- [5] J. Bandara, S.S. Kuruppu, U.W. Pradeep, "The promoting effect of MgO layer in sensitized photodegradation of colorants on TiO₂/MgO composited oxide," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol 276, pp. 197 - 202, 2006.
- [6] G.R.A. Kumara, M. Okuya, K. Murakami, S. Kaneko, V.V. Jayaweera, K. Tennakone, "Dye-sensitized solid-state solar cells made from magnesiumoxide-coated nanocrystalline titanium dioxide films: enhancement of the efficiency," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, pp. 183-185, 2004.
- [7] C. Photiphitak, P. Rakkwamsuk, P. Muthitamongkol, C. Sae-Kung, C. Thanachayanont, "Effect of Silver Nanoparticle Size on Efficiency Enhancement of Dye-Sensitized Solar Cells," *International Journal of Photoenergy*, vol. 2011, Article ID 258635, pp.1-8, 2011.
- [8] K. Che Lee, S. Jein Lin, C. Hong Lin, C. Song Tsai, Y. Jen Lu, "Size effect of Ag nanoparticles on surface plasmon resonance", *Surf Coat Tech*, vol. 202, pp. 5339-5342, Aug 2008.
- [9] B. Evgenij, M.J. Ross, "Impedance spectroscopy theory, experiment, and applications," *New Jersey: Wiley*, 2005.
- [10] L. Han, N. Koide, Y. Chiba, A. Islam, T. Mitate, "Modeling of an equivalent circuit for dye-sensitized solar cells: improvement of efficiency of dye-sensitized solar cells by reducing internal resistance," *C.R. Chimie*, vol.9, pp. 645 - 651, 2006.
- [11] J. Bandara, R.A.S.S. Ranasinghe, "The effect of MgO coating on photocatalytic activity of SnO₂ for the degradation of chlorophenol and textile colorant ; the correlation between the photocatalytic activity and the negative shift of flatband potential of SnO₂," *Applied Catalysis A: General*, vol. 319, pp. 58-63, 2007
- [12] J. Bandara, S.S. Kuruppu, U.W. Pradeep, "The promoting effect of MgO layer in sensitized photodegradation of colorants on TiO₂/MgO composite oxide," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 276, pp. 197 - 202, 2006.