International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:6, No:5, 2012

Performance Enhancement of Dye-Sensitized Solar Cells by MgO Coating on TiO_2 Electrodes

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

***Abstract*—**TiO_2/MgO composite films were prepared by coating the magnesium acetate solution in the pores of mesoporous TiO_2 films using a dip coating method. Concentrations of magnesium acetate solution were varied in a range of $1x10^{-4}$ – $1x10^{-1}$ M. The TiO_2/MgO composite films were characterized by scanning electron microscopy (SEM), transmission electron microscropy (TEM), electrochemical impedance spectroscopy(EIS) , transient voltage decay and I-V test. The TiO_2 films and TiO_2/MgO composite films were immersed in a 0.3 mM N719 dye solution. The Dye-sensitized solar cells with the TiO_2/MgO/N719 structure showed an optimal concentration of magnesium acetate solution of $1x10^{-3}$ 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, TiO_2/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, TiO_2 photoelectrode, Ru complex photosensitizer such as N719 dye molecules, redox electrolyte such as I^-/I^{3-} (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 TiO_2 electrode and created dye cations. The injected electrons in the conduction band of the TiO_2 transported through the TiO_2 nanoparticles by diffusion towards the back contact (TCO) and consequently to reach the counter electrode through the external load and wiring.

C Photiphitak is with the Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi, 126, Prachautis Road, Trungkru, Bangkok, Thailand

P. Rakkwamsuk is with the Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi, 126, Prachautis Road, Trungkru, Bangkok, Thailand

P. Muthitamongkol is with the National Metal and Material Technology Center, 114, Thailand Science Park, Phaholyothin Road , Klong 1, Klong Luang, ,Pathumthani, Thailand

C. Thanachayanont is with the National Metal and Material Technology Center, 114, Thailand Science Park, Phaholyothin Road , Klong 1, Klong Luang, ,Pathumthani, Thailand

The dye cations accept electrons from I^- and regenerated to the ground state, the I^- was oxidized to the I^{3-} (oxidation process). The I^{3-} diffuses toward the counter electrode and was reduced to I^- (reduction process).

High performance dye-sensitized solar cells require the nanocrystalline TiO_2 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. Recombenation with the dye cations and/or the electrolyte species (I^{3-}) 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 TiO_2 electrode such as MgO, ZnO, Al_2O_3, Nb_2O_5, $CaCO_3$, 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 TiO_2 electrode dip-coating technique. The concentrations of magnesium acetate solution were varied in a range of $1x10^{-4}$ - $1x10^{-1}$ M and performances of the DSSCs were compared. The effect of magnesium oxide thin film on the resistance of the TiO_2/MgO/dye interface and transient voltage was also studied.

II. Experimental Details

TiO_2 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 TiO_2 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 $55\,^{\circ}C$ for 30 min, the electrodes were sintered at 450 $^{\circ}C$ 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 TiO_2 film, a 2×3 cm^2 FTO glass with 0.5x1.2 cm^2 TiO_2 films was immersed in the magnesium acetate solution [$Mg(C_2H_3O_2)_2$] for 10 seconds, then rinsed with ethanol and dried in air at $55^{\circ}C$ for 1 h. The films were then sintered at 450 $^{\circ}C$ 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 $Mg(C_2H_3O_2)2$ solution such as $1x10^{-4}$, $1x10^{-3}$, $1x10^{-2}$ and $1x10^{-1}$ M to study the thickness of the magnesium oxide film. The thickness of MgO film was estimated by calculated as t = (weight of MgO)/Sρ, where S = surface area of TiO_2 films and ρ = 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 TiO_2/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 TiO_2 films were coated with magnesium acetate solution by dip-coating technique described in the experimental section. The Surface morphology of TiO_2/MgO composite films was readily observed by SEM as shown in Fig.1.

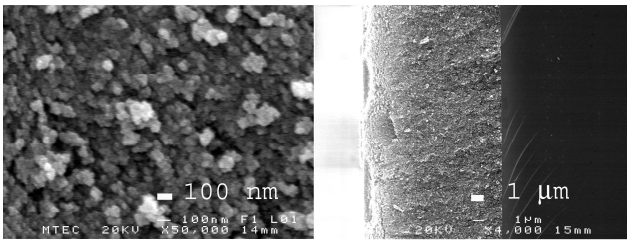


Fig. 1 SEM image of TiO_2/MgO composite films with a) plan-view image and b) cross-sectional image

Fig. 2(a) shows EDX spectra of the TiO_2/MgO composite films at top surface of the TiO_2/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 TiO_2/MgO composite film prepared from $1x10^{-3}$ M of magnesium acetate solution. From a previous study, we found that the TiO_2 particles were nanorods and the length was approximately 25 nm [7]. However, we cannot observe the magnesium oxide thin film on surfaces of the TiO_2 nanoparticles because its ultra thin nature. The hydrolysis of magnesium acetate covers the surface of TiO_2 particles with a layer of MgO (hydrous MgO). Sintering removes moisture and results in the outer shell of MgO attached firmly on the TiO_2 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 $x10^{-4}$, $1x10^{-3}$, $1x10^{-2}$ and $1x10^{-1}$ M were calculated to give the thicknesses of the magnesium oxide film as 0.0780, 0.0963, 0.1605, and 0.4632 nm, respectively.

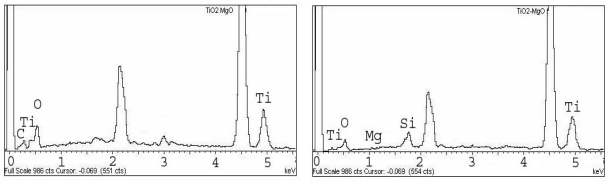


Fig. 2 EDX image of the TiO_2/MgO film prepared from $1x10^{-3}$ M of magnesium acetate solution taken from a) top surface and b) cross-section

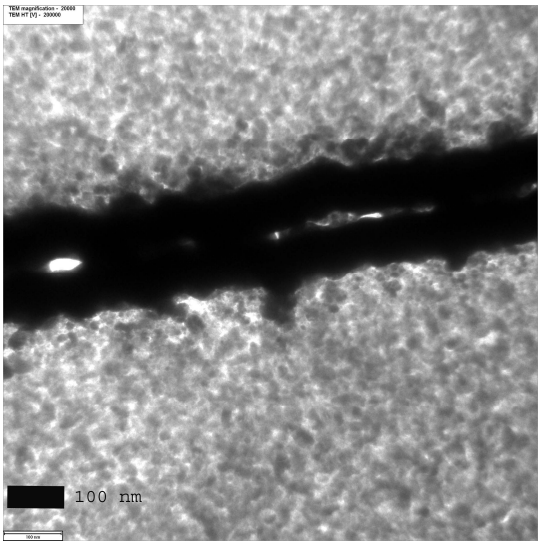
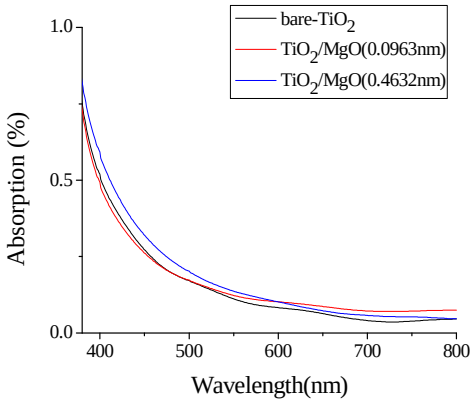
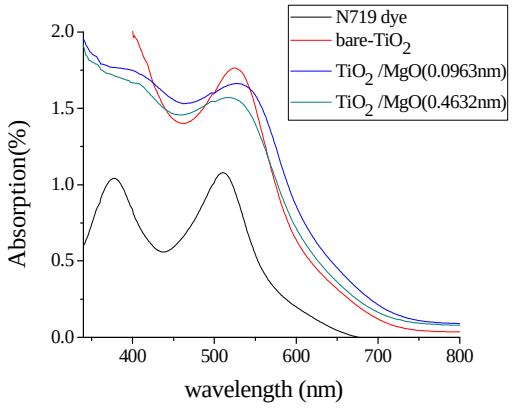


Fig. 3 A crossectional TEM micrograph of the TiO_2/MgO composite films prepared from $1x10^{-3}$ M of magnesium acetate solution

Figs. 4 (a) and (b) show optical absorption spectra of the bare-TiO_2 and TiO_2/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].



a)



b)

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 TiO_2/dye/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].

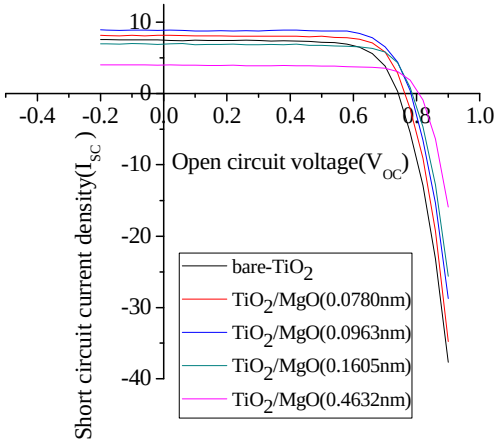


Fig. 5 J-V curves of DSSCs based on TiO_2 and TiO_2/MgO electrodes under AM. 1.5

TABLE I
ESTIMATED THICKNESSES OF THE MGO FILMS, SHORT CIRCUIT CURRENT DENSITIES (JSC), OPEN CIRCUIT VOLTAGES (VOC), FILL FACTORS (FF), EFFICIENCIES, SERIES RESISTANCES (RS) AND SHUNT RESISTANCES (RSH) OF DSCS PREPARED USING THE TIO2/MGO COMPOSITE FILM ELECTRODES COMPARED WITH BARE-TIO2 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 (Ω*cm^2)	R_{SH} (kΩ*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
TiO2/MgO1x10	1x10	~ 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
TiO2/MgO1x10	1x10	~ 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
TiO2/MgO1x10	1x10	~ 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
TiO2/MgO1x10	1x10	~ 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

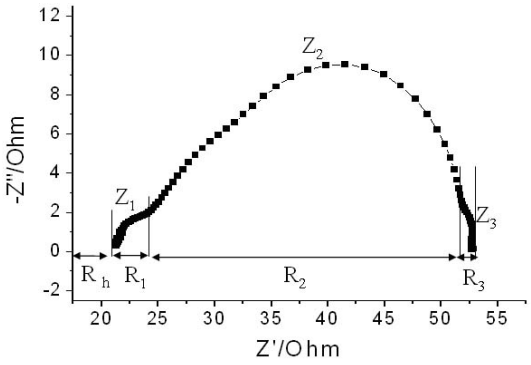


Fig. 6 Model electrochemical impedance spectrum (EIS) of DSC consisting of a TCO/TiO_2-N719 dye/electrolyte with I^-, I^{3-} redox couple /Pt electrode, Z_1, Z_2, and Z_3 describe as impedances. R_1, R_2, R_3 and R_h were internal resistance elements[9,10]

Fig. 7 shows an electrochemical impedance spectrum (EIS) of the DSSCs in this study with the TiO_2 and the TiO_2/MgO electrodes with varied thickness of MgO as shown in Table 1. We found that the EIS of the DSSCs with TiO_2/MgO (0.0963 nm) electrode has a small curve, the low value of R2 and series resistance (R_s) where [$R_s=R_h+R_1+R_3$], 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 TiO_2 electrode to the electrolyte, the high value of R_{sh} indicates a slow back electron transfer rate from the TiO_2 to the electrolytes at the TiO_2/dye/electrolyte interface[10]. However, the R_{sh} cannot be estimated from the EIS because it is included in R_2 , but the shunt resistance (R_{sh}) can be calculated from I-V characteristics.

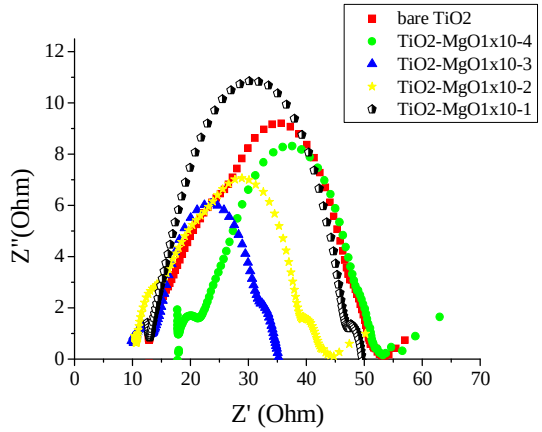


Fig. 7 Electrochemical impedance spectrum (EIS) of DSSCs with the TiO_2 and the TiO_2/MgO electrodes with varied thickness of MgO as shown in Table I

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 TiO_2/MgO(0.0963nm) electrode was the highest when compared with the bare-TiO_2, the TiO_2/MgO (0.078 nm), the TiO_2/MgO (0.1605nm) and the TiO_2MgO (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 TiO_2 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 votage decay is fast because the electron injection from the excited dye molecules to the CB of TiO_2 is hindered by the MgO film as the thickness of MgO increases [12].

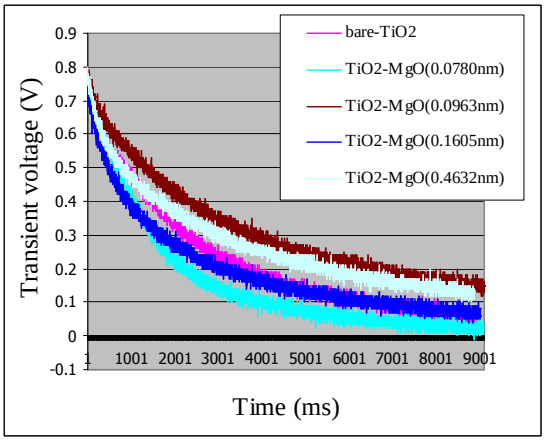


Fig. 8 Transient voltage decay of DSSCs with TiO_2 electrode and TiO_2/MgO electrode with varied thickness of the MgO film in a range 0.0780-0.4632 nm

IV. Conclusion

The DSSCs efficiency was found to enhance by dip-coating MgO thin films on the TiO_2 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 TiO_2/MgO (0.0963nm) electrode had the maximum efficiency when compared with the DSSCs with bare-TiO_2 electrode and other TiO_2/MgO electrodes. The measuring electrochemical impedance spectrum showed that the internal resistance of DSSCs with the TiO_2/MgO (0.0963nm) was lowest at about 12.75 Ω*cm^2. In addition, the transient voltage decay also showed that DSSCs with the TiO_2/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, "Al_2O_3-coated SnO_2/TiO_2 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 TiO_2/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 Jersy : 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 SnO_2 for the degradation of chlorophenol and textile colorant ; the correlation between the photocatalytic activity and the negative shift of flatband potential of SnO_2," 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 TiO_2/MgO composite oxide, "Colloids and Surfaces A: Physicochem. Eng. Aspects, vol. 276, pp. 197 – 202, 2006.