

## Research Article

# A Combined Effect of Plasmon Energy Transfer and Recombination Barrier in a Novel TiO<sub>2</sub>/MgO/Ag Working Electrode for Dye-Sensitized Solar Cells

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Received 15 June 2015; Revised 9 August 2015; Accepted 13 August 2015

Academic Editor: Leonardo Palmisano

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Novel TiO<sub>2</sub>/MgO/Ag composite electrodes were applied as working electrodes of dye-sensitized solar cells (DSSCs). The TiO<sub>2</sub>/MgO/Ag composite films were prepared by dip coating method for MgO thin films and photoreduction method for Ag nanoparticles. The MgO film thicknesses and the Ag nanoparticle sizes were in ranges of 0.08–0.46 nm and 4.4–38.6 nm, respectively. The TiO<sub>2</sub>/MgO/Ag composite films were characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The TiO<sub>2</sub>/MgO/Ag composite electrodes were sensitized by immersing in a 0.3 mM of N719 dye solution and fabricated for conventional DSSCs. *J-V* characteristics of the TiO<sub>2</sub>/MgO/Ag DSSCs showed that the MgO film thickness of 0.1 nm and the Ag nanoparticle size of 4.4 nm resulted in maximum short circuit current density and efficiency of 8.6 mA/cm<sup>2</sup> and 5.2%, respectively. Electrochemical Impedance Spectroscopy showed that such values of short circuit current density and efficiency were optimal values obtained from plasmon energy transfer by 4.4 nm Ag nanoparticles and recombination barrier by the ultrathin MgO film.

## 1. Introduction

For more than 20 years, the first dye-sensitized solar cell (DSSC) has been published by O'Regan and Grätzel [1]. The DSSCs have been extensively studied because of their high performance, simple fabrication processes, low-cost materials, and manufacturing processes. The DSSCs consist of transparent conducting oxide (TCO) coated glass, TiO<sub>2</sub> photoelectrode, Ru complex photosensitizer such as N719 dye molecules, redox electrolyte such as I<sup>-</sup>/I<sup>3-</sup> (iodide/triiodide), and Pt counter electrode [2]. High performance dye-sensitized solar cells require the nanocrystalline TiO<sub>2</sub> electrode to have a large surface area, high crystallinity without cracks, and good electrical contact with the conducting

glass substrate so that a high amount of dye molecules can be adsorbed and the electrons can be quickly transferred [3]. However, a problem of the DSSC is the low energy conversion efficiency when compared with silicon solar cells. Main reasons are charge recombination loss arising at the semiconductor/dye/electrolyte interface and low dye absorption towards the infrared region.

Recombination with the dye cations and the electrolyte species (I<sup>3-</sup>) 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<sub>2</sub> electrode such as MgO, ZnO, Al<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, CaCO<sub>3</sub>, and SrTiO<sub>3</sub> [3, 7, 8]. 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 addition, the surface plasmon resonance induced by silver (Ag) nanoparticles leads to an increase in absorption coefficient of dye in dye-sensitized solar cells (DSCs) [9–14]. The effect has been theoretically described as an increase of local electromagnetic field nearby metal surfaces which is found when wavelengths of irradiation sources are correlated with the optical absorption of the surface plasmon resonance [15–19]. The modification of the surfaces for an enhancement of optical absorption, hence, provides a good method to improve efficiency of an optoelectronic device involving photon absorption [20].

This research will improve the working electrode of the DSSCs by using both concepts of decreasing of recombination process between the electron on conduction band of  $\text{TiO}_2$  and triiodide ion in electrolyte ( $\text{I}_3^-$ ) by MgO thin film [6] and increasing of light absorption coefficient of dye molecules by silver nanoparticles [4, 5]. These are known as effects of recombination barrier and plasmon energy transfer, respectively. Therefore, the  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite film was demonstrated to be an efficient working electrode for DSSCs.

## 2. Materials and Methods

**2.1. The Preparation of Mesoporous  $\text{TiO}_2$  Electrodes.** The  $\text{TiO}_2$  electrodes were screen-printed from a  $\text{TiO}_2$  paste (Dyesol) 3 times on a fluorine-doped-tin-oxide (FTO) glass substrate ( $2 \times 3 \text{ cm}^2$  in size). A 200-mesh was used to obtain a  $\text{TiO}_2$  layer with area of  $0.5 \times 1.2 \text{ cm}^2$  and a thickness of approximately  $13.8 \mu\text{m}$ . In order to avoid contamination on the fresh film, screen printing was performed in a clean-room environment. After drying at  $55^\circ\text{C}$  for 30 minutes, the electrodes were sintered at  $450^\circ\text{C}$  for 30 minutes and then cooled down to room temperature. The electrodes were immersed in a  $3 \times 10^{-4} \text{ M}$  of N719 dye solution, namely, *cis*-diisothiocyanato-bis(2,2-bipyridyl-4,4-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) in absolute ethanol for 24 hours. The excess dye was removed from the electrode by rinsing in ethanol.

**2.2. The Preparation of Mesoporous  $\text{TiO}_2/\text{MgO}/\text{Ag}$  Composite Films.** The  $\text{TiO}_2$  film was prepared by screen printing with 3 layers and calcined at  $450^\circ\text{C}$  for 30 minutes. Then the  $\text{TiO}_2$  film was dipped in a magnesium acetate solution with concentrations of  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , and  $1 \times 10^{-1} \text{ M}$ , respectively, at  $40^\circ\text{C}$  for 30 seconds. An excess solution in the  $\text{TiO}_2/\text{MgO}$  films was washed with ethanol and calcined at  $450^\circ\text{C}$  for 30 minutes. Then, the  $\text{TiO}_2/\text{MgO}$  composite films were immersed in the  $0.1 \text{ M}$   $\text{AgNO}_3$  solution for 5 seconds, then rinsed with DI water, and dried in a  $\text{N}_2$  stream. The films were then exposed to UV irradiation at  $\lambda = 254 \text{ nm}$  using a Spectroline CM-10 Fluorescence Analysis Cabinet at an intensity of  $\sim 0.31 \text{ mW}/\text{cm}^2$ . We designed the experiment to vary exposure times for 5, 120, and 240 minutes for the photocatalytic reduction of  $\text{Ag}^+$  to the metallic Ag

nanoparticles [4], to form the Ag nanoparticles size of approximately 4.4, 19.2, and 38.6 nm, respectively. Finally, the  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite electrodes were immersed in dye solution for 48 hours at room temperature and prepared as working electrodes of the DSSCs.

**2.3. The Preparation of Pt Counter Electrodes.** The counter electrodes were prepared by screen printing a thin layer of platinum (Pt) with a size of  $0.5 \times 1.2 \text{ cm}^2$  using a platinum paste (Dyesol), on a FTO glass substrate ( $2 \times 3 \text{ cm}^2$ ), and then sintered at  $450^\circ\text{C}$  for 30 minutes.

**2.4. DSC Fabrication.** A sandwich-type cell [21] was fabricated by assembling a sensitized  $\text{TiO}_2$  electrode using Surlyn-based polymer sheet ( $80 \mu\text{m}$  thick) and sealed by a hot gun for a few seconds. The liquid electrolyte contained  $0.5 \text{ M}$  LiI,  $0.05 \text{ M}$   $\text{I}_2$ , and  $0.5 \text{ M}$  4-*tert*-butylpyridine in 90 : 10 v/v of acetonitrile : 3-methyl-2-oxazolidinone. Electrolyte injecting holes, made on the counter-electrode side, were sealed with Surlyn and glass cover.

**2.5. Measurements.** Optical absorption spectra of the film electrode samples were measured using a UV-Visible Spectrophotometer (Jasco model: V-530). In order to observe the microstructure and elemental analysis of the obtained Ag nanoparticles, the Ag nanoparticles were prepared on carbon-coated copper grids for observations by transmission electron microscopy (TEM JEOL model: JSM-2010). The X-ray diffraction (XRD JEOL-300) patterns were obtained by analyzing the  $\text{Ag}/\text{TiO}_2$  films on the glass substrates. Scanning electron microscope (SEM JEOL model: JSM-6301F with attached energy dispersive X-Ray Spectrometer (EDX)) was employed to record cross-sectional micrographs of the  $\text{Ag}/\text{TiO}_2$  films. *J-V* measurements were performed under a 450 W xenon light source which is able to provide  $1000 \text{ W}\cdot\text{m}^{-2}$  sunlight equivalent irradiation (AM 1.5), using Keithley digital source meter (model 2400) under the illuminated condition.

## 3. Results and Discussion

**3.1. The Morphology of the  $\text{TiO}_2/\text{MgO}/\text{Ag}$  Composite Films.** Figures 1–3 show appearances of the  $\text{TiO}_2/\text{Ag}$ ,  $\text{TiO}_2/\text{MgO}$ , and  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films, respectively.

Results show that the  $\text{TiO}_2/\text{Ag}$  composite films are brown and become darker with the longer UV exposure time due to a prolonged photocatalytic reduction of  $\text{Ag}^+$  to Ag [22], while the  $\text{TiO}_2/\text{MgO}$  composite films are white and translucent. Therefore, the colors of the  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films come from the Ag nanoparticles.

Figures 4(a), 4(b), and 4(c) show surface images of bare- $\text{TiO}_2$ ,  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.4 nm), and  $\text{TiO}_2/\text{MgO}$  (0.46 nm)/Ag (4.4 nm) composited films by SEM, respectively. The MgO thin film and Ag nanoparticles cannot be observed because of their ultrathin and ultrasmall nature [6, 23]. Figure 4(d) shows cross section image of the  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.4 nm) composite film showing the film thickness of approximately  $11.15 \mu\text{m}$ .

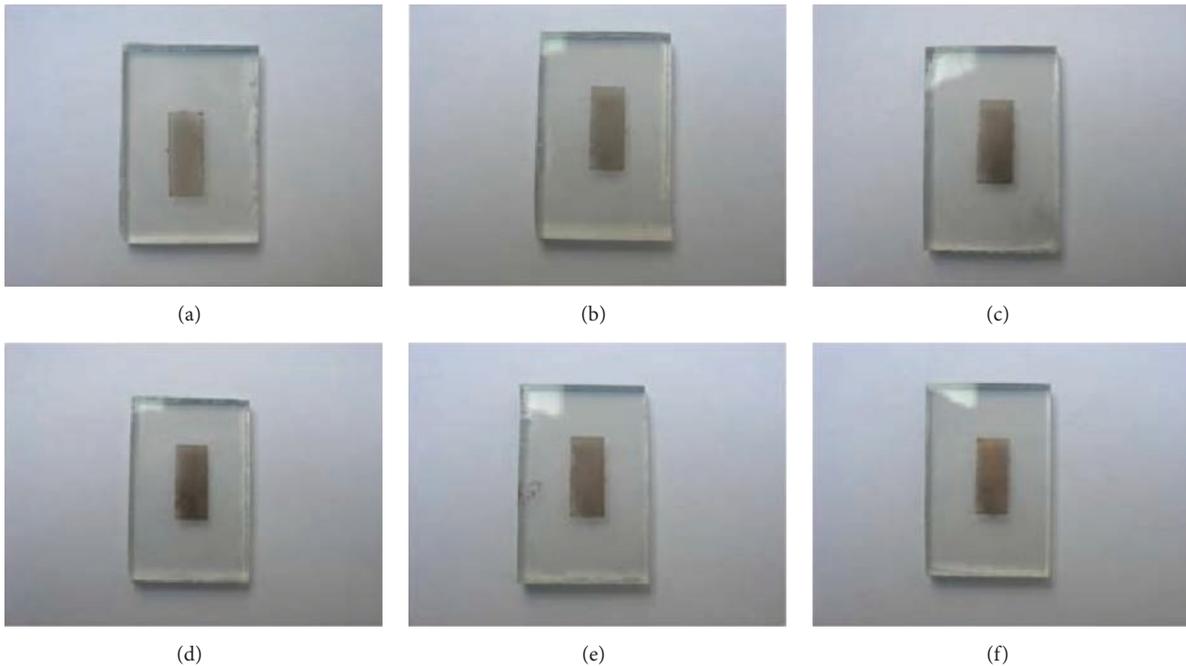


FIGURE 1: The  $\text{TiO}_2/\text{Ag}$  composite films with varied UV exposure time as 5, 30, 60, 120, 180, and 240 min, corresponding to the silver nanoparticle sizes of (a) 4.4 nm, (b) 7.2 nm, (c) 11 nm, (d) 19.2 nm, (e) 27.5 nm, and (f) 38.6 nm, respectively [4, 5].

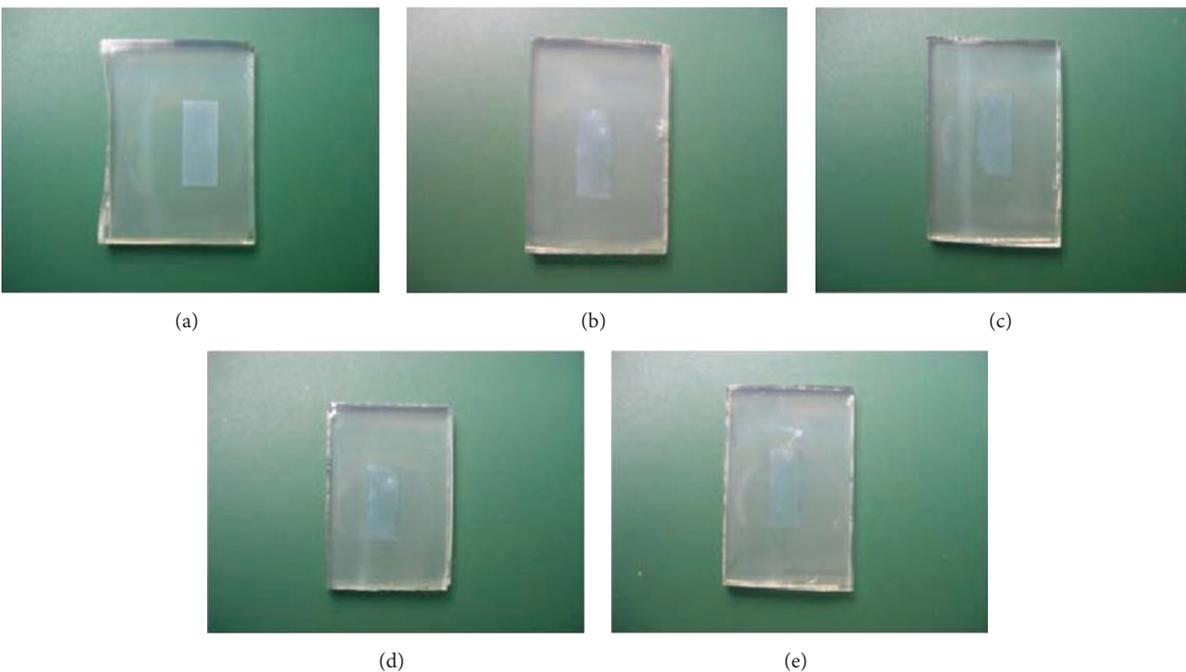


FIGURE 2: The  $\text{TiO}_2/\text{MgO}$  composite films with varied magnesium acetate solution concentrations of  $1 \times 10^{-4}$  M,  $1 \times 10^{-3}$  M,  $1 \times 10^{-2}$  M, and  $1 \times 10^{-1}$  M. These correspond to the MgO film thicknesses of (a) bare- $\text{TiO}_2$ , (b) 0.08 nm, (c) 0.10 nm, (d) 0.16 nm, and (e) 0.46 nm, respectively [6].

The EDX technique of SEM was used to analyze the elements of Ti, Mg, and Ag, resulting in the peaks of Ti and Ag that were found on the surface image of the  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.4 nm) composite film but the Mg peak was not found suggesting that it was rinsed

off from the film surface as shown in Figure 5(a). However, Mg peak was present in the cross section of the  $\text{TiO}_2/\text{MgO}$  (0.10 nm) Ag (4.4 nm) composite film (see Figure 4(d)) indicating the presence of Mg element as shown in Figure 5(b).

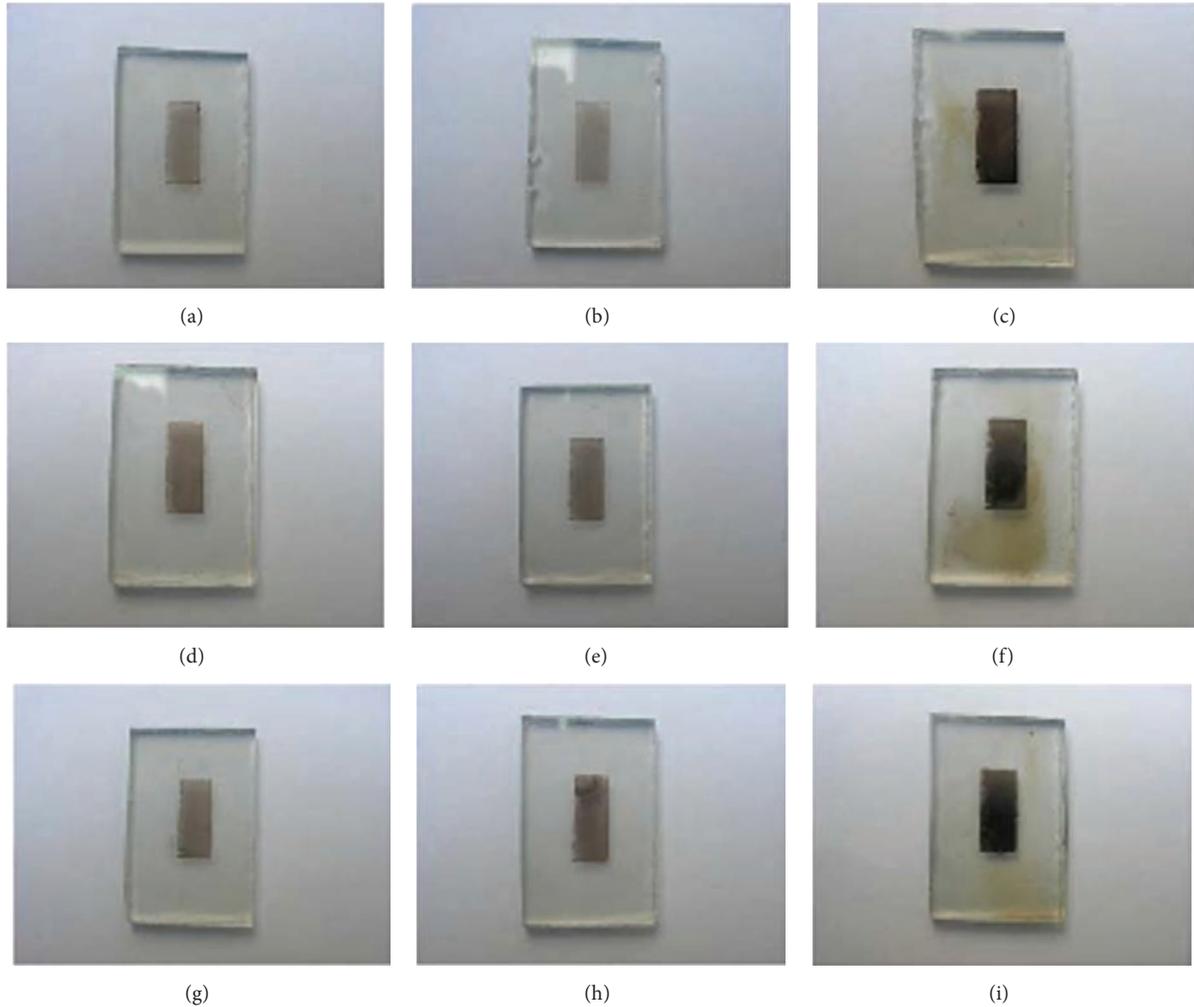


FIGURE 3: The  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films with varied magnesium acetate solution concentrations and silver nanoparticles sizes: (a)  $\text{TiO}_2/\text{MgO}$  (0.08 nm)/Ag (4.4 nm), (b)  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.4 nm), (c)  $\text{TiO}_2/\text{MgO}$  (0.46 nm)/Ag (4.4 nm), (d)  $\text{TiO}_2/\text{MgO}$  (0.08 nm)/Ag (19.2 nm), (e)  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (19.2 nm), (f)  $\text{TiO}_2/\text{MgO}$  (0.46 nm)/Ag (19.2 nm), (g)  $\text{TiO}_2/\text{MgO}$  (0.08 nm)/Ag (38.6 nm), (h)  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (38.6 nm), and (i)  $\text{TiO}_2/\text{MgO}$  (0.46 nm)/Ag (38.6 nm).

Figure 6 shows a TEM image of the  $\text{TiO}_2/\text{MgO}$  (0.10 nm) composite film. However, we can not observe the magnesium oxide thin film on surfaces of the  $\text{TiO}_2$  nanoparticles because of its ultrathin nature. The MgO content of the film was estimated by the extraction of MgO with HCl and atomic adsorption spectrophotometric estimation. The thickness  $t$  of the MgO film was calculated as  $t = (\text{weight of MgO})/S\rho$ , where  $S$  = surface area of  $\text{TiO}_2$  ( $S$  determined by the desorption of the dye into an alcoholic alkaline solution and spectrophotometric estimation = 560 times geometrical cross section of the film =  $1 \text{ cm}^2$ ) and  $\rho$  = density of MgO [23]. The concentrations of magnesium acetate solution of  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , and  $1 \times 10^{-1} \text{ M}$  were calculated to give the thicknesses of the magnesium oxide film as 0.08, 0.10, and 0.46 nm, respectively.

**3.2. The Effect of the MgO Thin Film and Ag Nanoparticle Size on Optical Absorption Spectra.** Figure 7 shows a comparison

of the optical absorption spectra in the range of 370–800 nm between the bare- $\text{TiO}_2$ ,  $\text{TiO}_2/\text{Ag}$ ,  $\text{TiO}_2/\text{MgO}$ , and  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films. The optical absorption spectra of the bare- $\text{TiO}_2$  film and  $\text{TiO}_2/\text{MgO}$  composite film were found to be similar and lower than those of the  $\text{TiO}_2/\text{Ag}$  (19.20 nm) and  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.40 nm) composite films. This agrees with research results of Bandara et al., reporting that a coating of MgO on  $\text{TiO}_2$  does not change the absorption property of  $\text{TiO}_2$  as MgO electron excitation energy falls above the excitation energy of  $\text{TiO}_2$  [21].

However, for the cases of  $\text{TiO}_2/\text{Ag}$  (19.20 nm) and  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.40 nm) composite films, the optical absorption spectra have much higher absorption than the previous two cases at a wavelength range of around 400–600 nm. The optical absorption of the  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.40 nm) composite film is slightly higher than the  $\text{TiO}_2/\text{Ag}$  (19.20 nm) film in the wavelength range

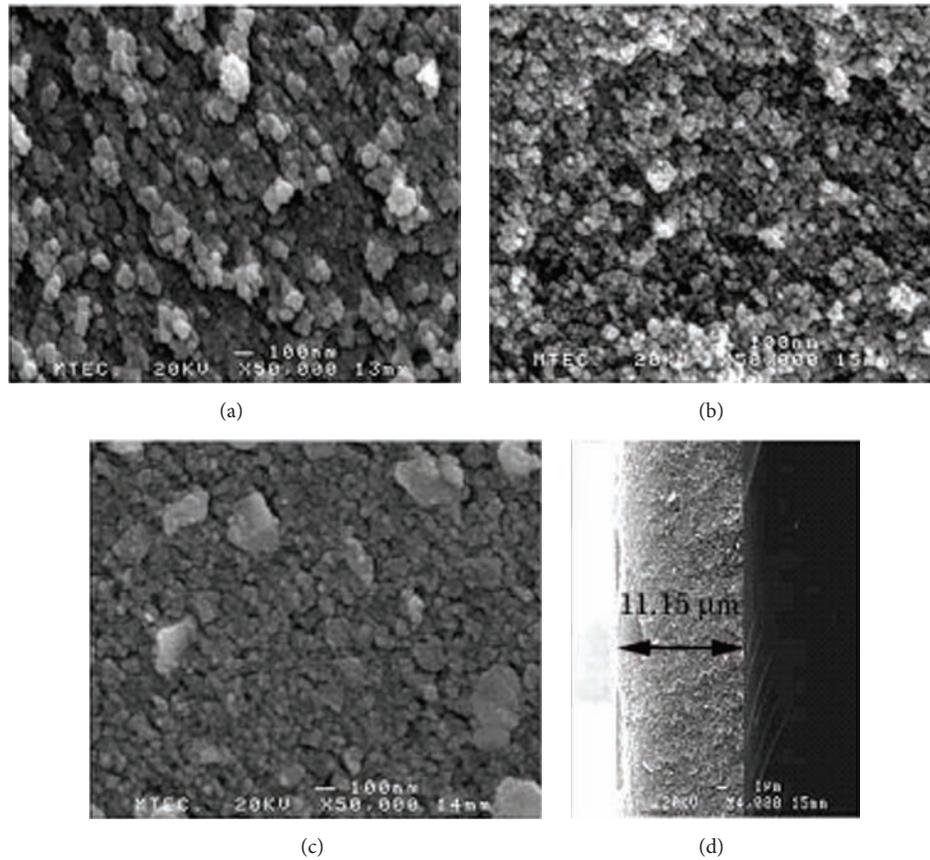


FIGURE 4: SEM images of  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films: (a) bare- $\text{TiO}_2$ , (b)  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.4 nm), (c)  $\text{TiO}_2/\text{MgO}$  (0.46 nm)/Ag (4.4 nm), and (d) cross section of  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.4 nm).

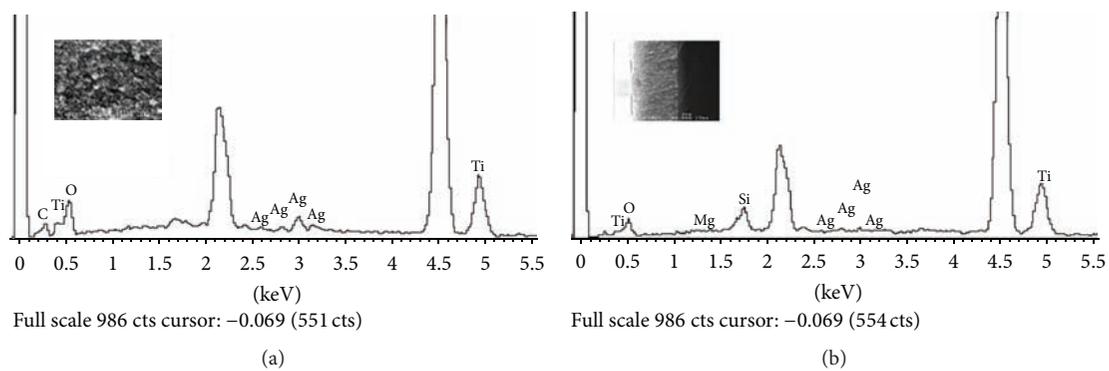


FIGURE 5: EDX spectra taken from (a) surface and (b) cross section of  $\text{TiO}_2/\text{MgO}/\text{Ag}$  (4.4 nm) composite film.

of 400–600 nm, whereas in the wavelength range of 600–800 nm we found that the optical absorption spectrum of the  $\text{TiO}_2/\text{Ag}$  (19.2 nm) composite film is higher than that of the  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (4.40 nm) composite film. Therefore, the Ag nanoparticles have been shown clearly to improve optical adsorption due to plasmon energy transfer effect [4, 9, 12, 13]. In addition, the light scattering effect of Ag nanoparticles enhances the absorption of photoanode [24].

When we consider the optical absorption spectrum of

$\text{TiO}_2/\text{MgO}/\text{Ag}$  with the fixed MgO film thickness of 0.10 nm and varied Ag nanoparticles size in a range of 4.40–38.60 nm, the optical absorption of the bare- $\text{TiO}_2$  has the lowest value, while the optical absorption of  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag (38.60 nm) has the highest value as shown in Figure 8. The red shifted nature of the spectrum indicates surface plasmon effect [4, 25].

Although, for the 0.1 nm thick MgO thin films, the Ag nanoparticles are more influential than the MgO thin film

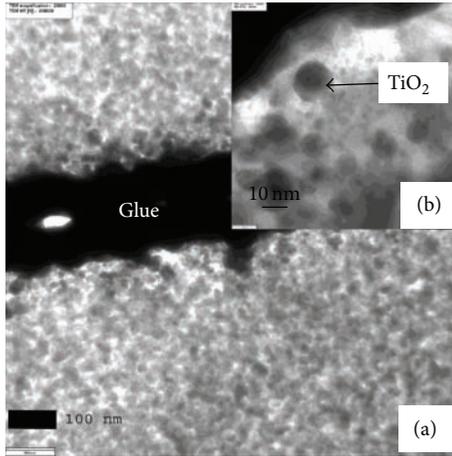


FIGURE 6: A cross-sectional TEM micrograph of the  $\text{TiO}_2/\text{MgO}$  (0.10 nm) composite films prepared from  $1 \times 10^{-3}$  M of magnesium acetate solution (a)  $\times 20,000$ , (b)  $\times 200,000$ .

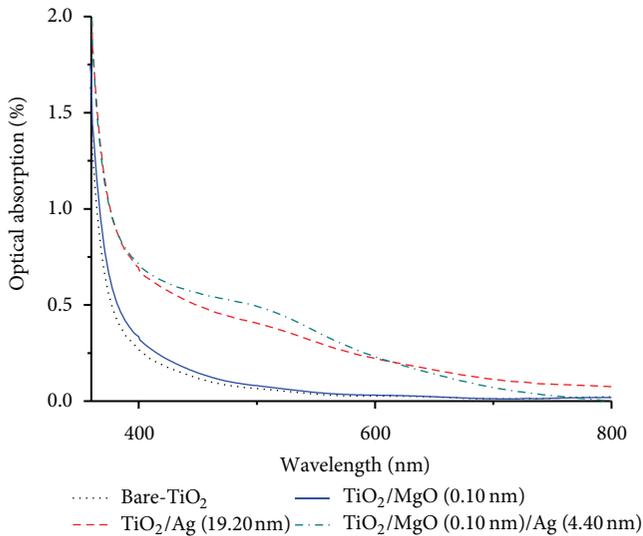


FIGURE 7: Optical absorption spectra of the bare- $\text{TiO}_2$  film compared with the  $\text{TiO}_2/\text{Ag}$  (19.2 nm),  $\text{TiO}_2/\text{MgO}$  (0.10 nm), and  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films.

on the  $\text{TiO}_2$  film for optical absorption (Figure 7), the optical absorption can be increased with increasing thickness of the  $\text{MgO}$  thin film as shown in Figure 9.

**3.3. The Effect of the  $\text{MgO}$  Ultrathin Film and  $\text{Ag}$  Nanoparticles on Efficiency of the DSSCs.** The efficiency of DSSCs with  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/ $\text{Ag}$  (4.40 nm) composite electrode has the highest efficiency among all conditions prepared including the bare- $\text{TiO}_2$  electrode as shown in Table I.

The results showed that the maximum efficiency of the DSSCs was obtained with  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/ $\text{Ag}$  (4.4 nm) composite electrode (Figure 10). The DSSCs with  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/ $\text{Ag}$  (4.4 nm) have the maximum efficiency, although this condition did not give the highest optical absorption (see Figure 9). The maximum efficiency

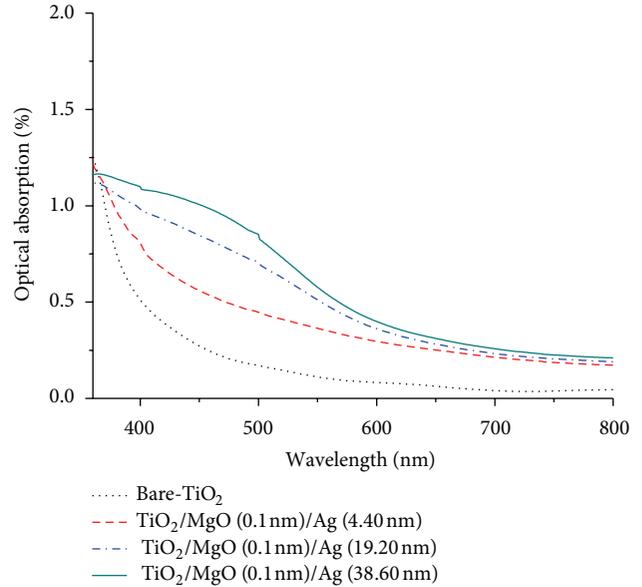


FIGURE 8: Optical absorption spectra of the bare- $\text{TiO}_2$  compared with the  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films with varied  $\text{Ag}$  nanoparticle size in range of 4.40–38.60 nm.

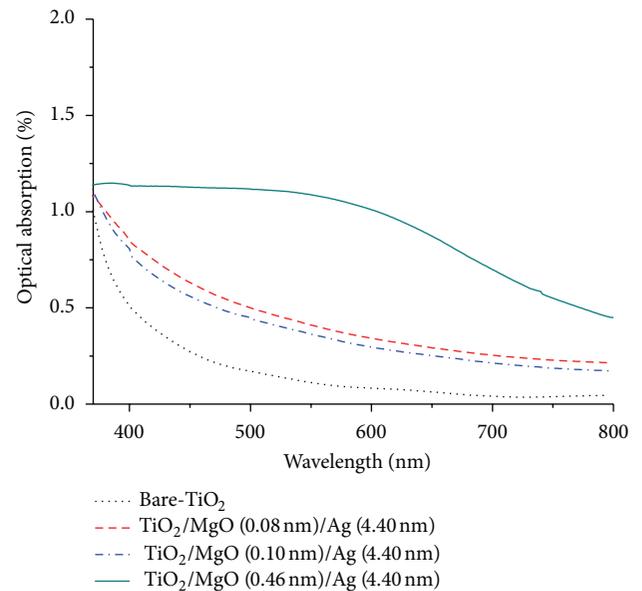


FIGURE 9: Optical absorption spectra of the  $\text{TiO}_2/\text{MgO}/\text{Ag}$  composite films with varied film thicknesses of magnesium oxide in range of 0.08–0.46 nm.

obtained suggests that the  $\text{MgO}$  layer coated on the  $\text{TiO}_2$  film acts as a recombination barrier at the  $\text{TiO}_2/\text{MgO}/\text{Ag}$  contacts and becomes a dominant effect [9, 11, 26, 27].

In addition, the efficiency of the DSSCs depends on the  $\text{MgO}$  film thickness, the maximum efficiency of DSSCs with  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/ $\text{Ag}$  (4.4 nm) working electrode. When the  $\text{MgO}$  film thickness increased, the efficiency of DSSCs is decreased, as shown in Figure 11.

TABLE 1: Optimization of the TiO<sub>2</sub>/MgO/Ag composite films by varying the MgO thin film thickness and the Ag nanoparticles size for enhanced efficiency of the DSSCs.

Silver nanoparticles size (nm)	Efficiency of DSSCs (%)			Efficiency of bare-TiO <sub>2</sub> DSSCs (%)
	Magnesium oxide film thickness (nm)			
	0.08	0.10	0.46	
4.40	5.1 ± 0.1	5.2 ± 0.1	2.6 ± 0.2	3.8 ± 0.1
19.20	4.1 ± 0.2	4.1 ± 0.1	2.0 ± 0.3	
38.60	3.7 ± 0.1	3.8 ± 0.2	1.1 ± 0.6	

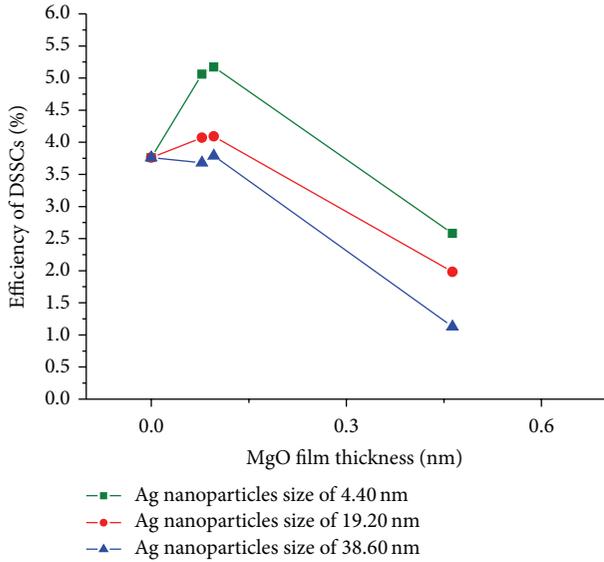


FIGURE 10: The efficiency of DSSCs with the bare-TiO<sub>2</sub> film and the TiO<sub>2</sub>/MgO (0.10 nm)/Ag composite films with various Ag nanoparticles sizes in range of 4.40–38.60 nm.

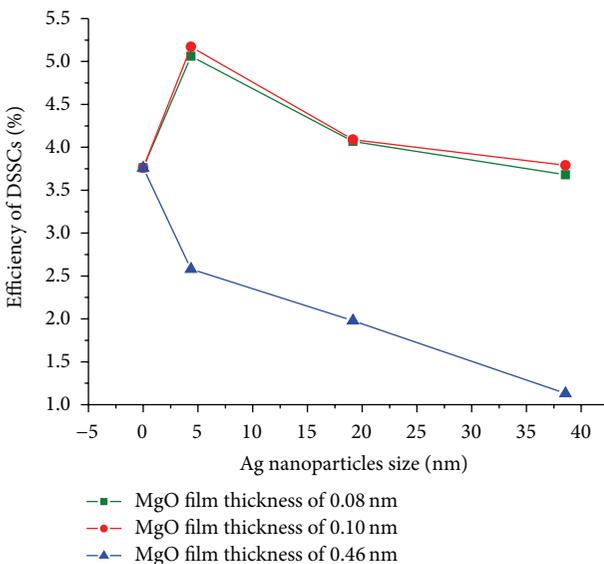


FIGURE 11: The efficiency of DSSCs with the bare-TiO<sub>2</sub> film and the TiO<sub>2</sub>/MgO/Ag composite films with various MgO film thicknesses in range of 0.08–0.46 nm.

Using the same materials and structure and improving the TiO<sub>2</sub> working electrode by coating the Ag nanoparticles alone on the TiO<sub>2</sub> film for increase in light absorption coefficient of the dye molecule, the efficiency up to 4.8% was obtained [4]. The coating of the MgO thin films on the TiO<sub>2</sub> films to reduce the recombination process between the electron on conduction band of TiO<sub>2</sub> and triiodide in the electrolyte was reported to increase the efficiency up to 5.0% [6]. While the conventional DSSCs fabricated have efficiency about 3.8%, both methods can improve the efficiency of DSSCs and lead to the coating TiO<sub>2</sub> working electrode by MgO thin film and Ag nanoparticles for a novel TiO<sub>2</sub>/MgO/Ag working electrode in this study. The DSSCs using the TiO<sub>2</sub>/MgO (0.10 nm)/Ag (4.40 nm) composite film as working electrode have the maximum efficiency of approximately 5.2%, when compared with the DSSCs using other working electrodes such as the bare-TiO<sub>2</sub>, TiO<sub>2</sub>/Ag (19.20 nm) [4], and TiO<sub>2</sub>/MgO (0.10 nm) [6] as shown in Figure 12. When the Ag nanoparticles bigger than 4.4 nm were coated on TiO<sub>2</sub>/MgO (0.10 nm) composite film, the efficiency decreases, supposedly because the Schottky barriers were formed at the TiO<sub>2</sub>/MgO/Ag contacts, became dominant, and retarded electron transport in the conduction bands [9, 11].

Electrochemical impedance spectra (EIS) of the DSSCs can describe the internal resistances of the DSSCs.  $R_1$  is related to the carrier transport resistance at the surface of Pt counter electrode,  $R_2$  is related to carrier transport resistance at the TiO<sub>2</sub>/dye/electrolyte interface, and  $R_3$  is related to the diffusion of iodide and triiodide within the electrolyte.

Figure 13 shows EIS results of the DSSCs with the bare-TiO<sub>2</sub> and the TiO<sub>2</sub>/MgO/Ag (4.4 nm) electrodes with varied MgO film thicknesses. We found that the EIS of the DSSCs with the TiO<sub>2</sub>/MgO (0.10 nm)/Ag (4.4 nm) composite electrode have the smallest curve of  $R_2$ . Thus the carrier transport resistance in TiO<sub>2</sub>/dye/electrolyte interface is the lowest at the MgO film thickness of 0.10 nm, which is consistent with the shunt resistance ( $R_{SH}$ ) of the DSSCs with the TiO<sub>2</sub>/MgO (0.10 nm)/Ag (4.40 nm) composite electrode with lowest value of 2.70 kΩ \* cm<sup>2</sup> (see Table 2). This is due to the high value of  $R_{SH}$  indicating a slow back electron transfer rate from the TiO<sub>2</sub> to the electrolytes at the TiO<sub>2</sub>/dye/electrolyte interface [28]. Increasing the MgO film thickness to exceed 0.10 nm,  $I_{SC}$  decreases because electron injection from the excited dye molecules to the CB of TiO<sub>2</sub> is hindered by the MgO film. An optimum of the MgO film thickness acts as the energy barrier to hinder the recombination process [6, 8]. However, as the MgO film thickness increases,  $V_{OC}$

TABLE 2: The short circuit current densities ( $I_{SC}$ ), open circuit voltages ( $V_{OC}$ ), fill factors (FF), efficiencies, series resistances ( $R_S$ ), and shunt resistances ( $R_{SH}$ ) of DSSCs prepared using the  $TiO_2/MgO/Ag$  composite film electrodes compared with bare- $TiO_2$  electrode (reference) under AM1.5.

Condition of working electrodes	$I_{SC}$ (mA)	$V_{OC}$ (V)	FF	Efficiency (%)	$R_S$ ( $\Omega \cdot cm^2$ )	$R_{SH}$ ( $k\Omega \cdot cm^2$ )
Bare- $TiO_2$	6.60	0.71	0.81	3.80	10.02	2.87
$TiO_2/MgO$ (0.08 nm)/Ag (4.4 nm)	8.37	0.78	0.74	5.10	10.39	2.69
$TiO_2/MgO$ (0.10 nm)/Ag (4.4 nm)	8.63	0.79	0.76	5.20	15.14	2.70
$TiO_2/MgO$ (0.46 nm)/Ag (4.4 nm)	4.42	0.80	0.72	2.60	36.38	4.97
$TiO_2/MgO$ (0.08 nm)/Ag (19.2 nm)	6.70	0.77	0.79	4.10	15.39	3.70
$TiO_2/MgO$ (0.10 nm)/Ag (19.2 nm)	6.94	0.78	0.75	4.10	18.67	4.35
$TiO_2/MgO$ (0.46 nm)/Ag (19.2 nm)	3.46	0.79	0.72	2.0	41.63	4.62
$TiO_2/MgO$ (0.08 nm)/Ag (38.6 nm)	6.25	0.76	0.78	3.70	15.75	4.35
$TiO_2/MgO$ (0.10 nm)/Ag (38.6 nm)	6.29	0.77	0.78	3.80	20.40	3.92
$TiO_2/MgO$ (0.46 nm)/Ag (38.6 nm)	2.00	0.79	0.68	1.10	61.87	6.22

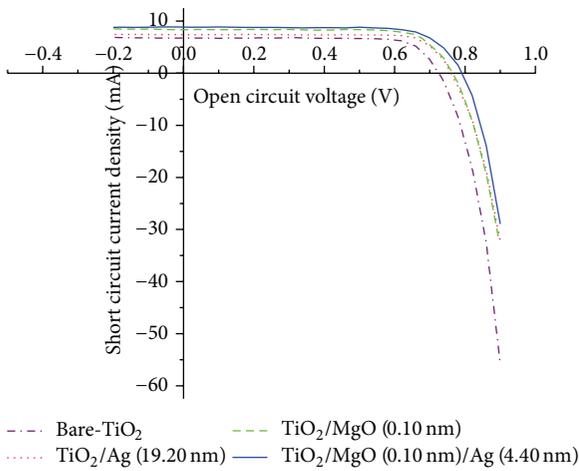


FIGURE 12: Comparison of the efficiencies of DSSCs with different types of electrodes, that is, the bare- $TiO_2$ ,  $TiO_2/Ag$  (19.2 nm),  $TiO_2/MgO$  (0.10 nm), and  $TiO_2/MgO$  (0.10 nm)/Ag (4.4 nm) electrodes.

will increase accordingly (Table 2) due to a negative shift of flat band potential after coating the thin MgO layer on the semiconductor particles.  $V_{OC}$  is determined by the difference between the quasi-Fermi level of electron in the oxide film and the energy of the redox couple in the electrolyte [29].

Electrochemical impedance spectra (EIS) of the DSSCs with varying Ag nanoparticle size ranging from 4.40 to 38.6 nm in the  $TiO_2/MgO$  (0.10 nm)/Ag composite electrodes are shown in Figure 14. The EIS of DSSCs with the  $TiO_2/MgO$  (0.10 nm)/Ag (4.40 nm) composite electrode were found to have the smallest curve, indicating that the carrier transport resistance at the  $TiO_2/dye/electrolyte$  interface is the lowest. When the Ag nanoparticle size increases more than 4.4 nm, the carrier transport resistance in  $TiO_2/dye/electrolyte$  interface was found to increase because of the Schottky barriers formed at the  $TiO_2/MgO/Ag$  contacts [9, 11].

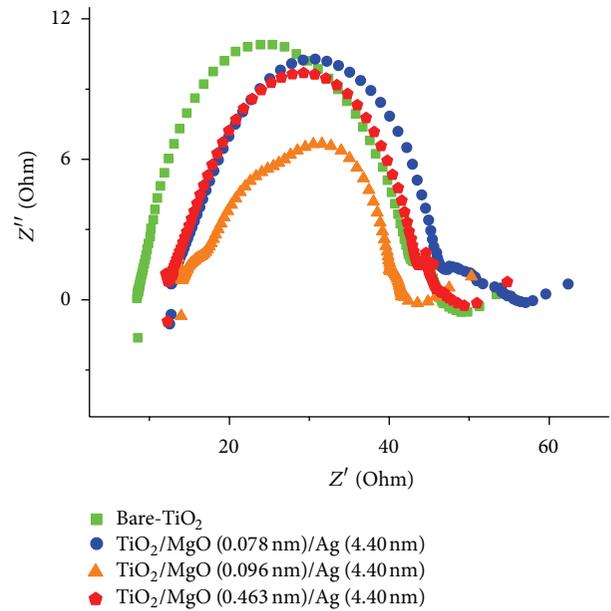


FIGURE 13: Electrochemical impedance spectra (EIS) of DSSCs with the  $TiO_2/MgO/Ag$  (4.4 nm) electrodes with varied thickness of MgO.

## 4. Conclusion

The  $TiO_2/MgO/Ag$  composite electrode was prepared with the MgO thin film and the Ag nanoparticles by dipping and photoreduction method, respectively. The efficiency enhancement of the DSSCs is based on the principle of ultra-thin outer shell of insulator and surface plasmon resonance. The optimum condition obtained was  $TiO_2/MgO/Ag$  composite film consisting of the MgO film thickness of 0.10 nm and Ag nanoparticles size of 4.40 nm to give a maximum efficiency of 5.2%. The EIS of the DSSCs with the  $TiO_2/MgO$  (0.10 nm)/Ag (4.4 nm) composite electrode showed the lowest carrier transport resistance at the  $TiO_2/dye/electrolyte$  interface. The Ag nanoparticles influenced the optical absorption of the  $TiO_2$  film because of the surface plasmon resonance induced by the silver nanoparticles enhancing Raman

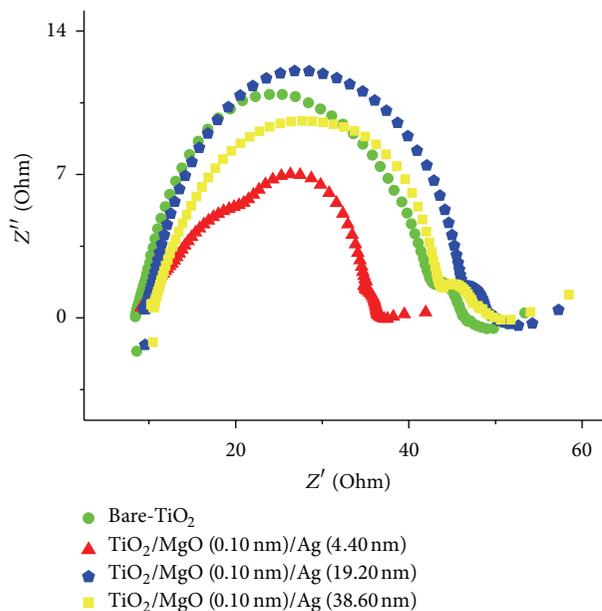


FIGURE 14: Electrochemical impedance spectra (EIS) of DSSCs with the  $\text{TiO}_2/\text{MgO}$  (0.10 nm)/Ag electrodes with varied Ag nanoparticle size.

scattering and optical absorption of the dye. A coating of MgO on the  $\text{TiO}_2$  acted as the energy barrier to hinder the recombination process and was found to significantly improve cell efficiency.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

### Acknowledgments

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

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