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RESEARCH ARTICLE

The effect of TiO_2 photoanode film thickness on photovoltaic properties of dye-sensitized solar cells

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Abstract: Nanocrystalline titanium dioxide (TiO_2) photoanodes with four different film thicknesses from 5.57µm to 20.65µm were prepared by doctor-blade technique. Performance of dye sensitized solar cells (DSSCs) fabricated with these photoanodes were studied using current-voltage characteristics and incident photon-to-current conversion efficiency (IPCE) measurements. Electrochemical impedance spectroscopy (EIS) was used to analyze the effect of TiO_2 film thickness on the charge transfer resistance and electron life time in the solar cells. Voltage decay measurements were used to study the recombination process of photo generated charge carriers. These studies revealed that the photovoltaic properties of DSSCs largely depend on the film thickness of TiO_2 photoanode. Further, the DSSCs fabricated using a TiO_2 film of 12.73 µm thickness exhibited the best photovoltaic performance with highest incident photon-to-current conversion efficiency, highest short-circuit photocurrent, lowest charge transfer resistance, highest electron life time and lowest recombination life time.

Keywords: Dye sensitized solar cells, TiO_2 photoanode thickness, efficiency, life time.

INTRODUCTION

Nanocrystalline titanium dioxide (TiO_2), well known as a metal oxide semiconductor, has been extensively studied for many applications due to their unique physiochemical properties such as surface area, crystalline structure, grain size, grain boundary density and energy band gap. These properties will significantly affect the performance of energy conversion devices fabricated with TiO_2 such as dye sensitized solar cells (DSSCs) (Choi *et al*., 2010; Xin *et al*., 2012). A typical DSSC consists of a nanoporous metal oxide film such as TiO_2, sensitizing dye, redox electrolyte and a counter electrode (O'Regan *et al*., 1991). The metal oxide film plays a major role in the enhancement of power conversion efficiency of DSSCs and many studies have been focused on the dependence of cell efficiency on film structure and thickness (Kang *et al*., 2004, Mathew *et al*., 2011, Kao *et al*., 2009). A significantly higher power conversion efficiency and incident photon to current conversion efficiency (IPCE) can be expected using TiO_2 photoanode with optimized film thickness, better crystallization and optimized microstructure. Therefore, the thickness optimization of the TiO_2 film is a key factor for efficiency enhancement in DSSCs.

In this research article, the dependence of film thickness as well as nano-crystalline structure of TiO_2 on photocurrent-voltage characteristics and IPCE of DSSC is reported. Films of thicknesses ranging from 5.57µm to 20.65 µm were fabricated using doctor-blade technique. DSSCs fabricated with these TiO_2 films as photo anodes were characterized by current-voltage measurements, electrochemical impedance spectroscopy and voltage decay measurements.

EXPERIMENTAL

TiO_2 electrode preparation

Photo-electrodes were prepared with TiO_2 P25 (Degussa) powder by doctor-blade technique. Nitric acid method was used to prepare the required paste. The weighted amount of 0.25 g of

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TiO_2 P25 powder sample mixed with 0.1 M HNO_3 1.0 ml solution was ground using a mortar and a pestle. 0.02 g of Triton X-100 and 0.05 g of PEG 1000 were added as binder and subsequently well ground until the mixture become a creamy paste. The paste was doctor-bladed on a pre-cleaned Fluorine doped conducting Tin Oxide (FTO) glass plate (Solaronix sheet glass 8 Ω/sq) keeping an active cell area of 0.25 cm^2. The starting thickness of the TiO_2 film was controlled by the number of tapes used for the doctor-blade method. The FTO/TiO_2 plates were sintered at 450 ^oC for 45 minutes and slowly cooled down to room temperature. Subsequently these films were dipped in a dye solution of 3 x 10^{-4} M Ruthenium dye N719 [RuL2 (NCS)2: 2 TBA where, L= 2,2'-bipyridyl-4', dicarboxylic acid; TBA = tetrabutyl ammonium] dissolved in ethanol at 45^{o}C temperature for 15 hours. The thicknesses of the TiO_2 films were determined using SEM images of the cross section of the TiO_2 films taken with Zeiss EVO LS15 Scanning Electron Microscope with 2000 magnification.

Fabrication of DSSCs

The electrolyte solution for the DSSCs containing the I^-/I_3^- redox couple was prepared by adding 0.738 g of tetrapropyl ammonium iodide (Pr_4NI) and 0.060 g of I_2 to a pre-cleaned 10 ml volumetric flask containing 3.6 ml of molten (MP 40 ^oC) ethylene carbonate (EC) and 1.0 ml of acetonitrile. This solution mixture was stirred overnight and subsequently used to fabricate DSSCs by sandwiching the electrolyte solution between the dye coated TiO_2 photo electrode and a platinized counter electrode. DSSCs were made with TiO_2 anodes of different thicknesses ranging from 5.57 to 20.65 µm.

Characterization of DSSCs

The photocurrent-voltage (*I-V*) characteristics of the solar cells were measured under the illumination of 100 $mWcm^{-2}$ (AM 1.5) simulated sunlight using a computer controlled setup coupled to a Keithley 2000 multimeter and a Potentiostat/galvanostat HA-301. A 500 W Xenon lamp was used with an AM 1.5 filter to obtain the simulated sunlight with above intensity. IPCE measurements were taken for the DSSCs made with TiO_2 films of different thicknesses. Experimental setup for the IPCE measurements consisted of monochromatic light illuminated from a Bentham PVE 300 unit with a TMC 300 monochromator based IPCE system with a 150 W Xenon arc lamp covering the 300 nm to 800 nm wavelength range. A calibrated Si photo detector (type DH) was used as the reference.

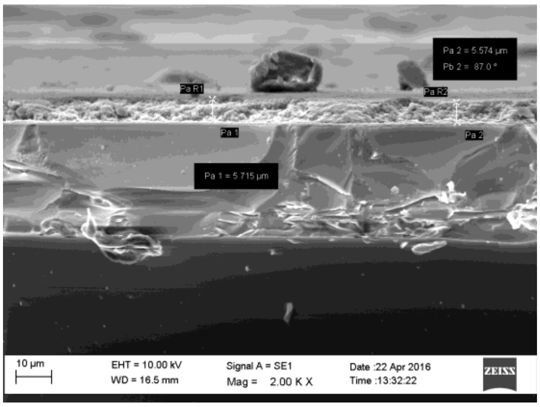
Electrochemical Impedance Spectroscopy (EIS) measurements were performed on the DSSCs using a Metrohm Auto lab Potentiostat/galvanostat PGSTAT 128N with a FRA 32M Frequency Response Analyzer covering the 0.01 Hz - 1x10^6 Hz frequency range. These measurements were carried out under the illumination of 100 mW cm^{-2} using the same solar simulator that was used for I-V measurements. Voltage decay measurements were taken for DSSCs to determine the recombination life time.

RESULTS AND DISCUSSION

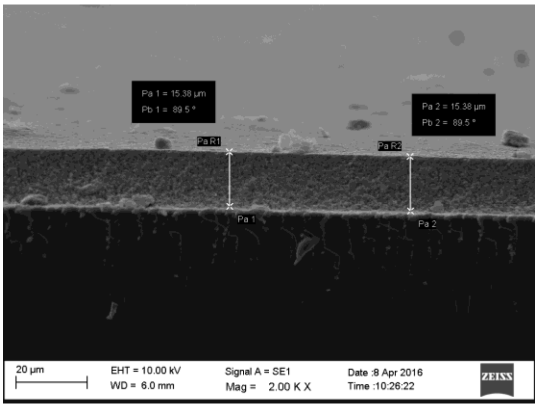
SEM images of the TiO_2 films of five different thicknesses deposited on FTO substrate are shown in Figure 1. According to these cross section images, all the TiO_2 films show uniform thicknesses and also uniform in materials distribution. The photocurrent density-voltage (*J-V*) characteristics for DSSCs made with different TiO_2 film thicknesses are shown in Figure 2. The variation of DSSC efficiency and short circuit current density on TiO_2 film thickness are shown in Figure 3.

Photovoltaic parameters of DSSCs with different TiO_2 film thicknesses are shown in Table 1. As seen from Figure 3 and Table 1, the short circuit photo current density J_{sc} increases from 10.29 to 12.98 mA cm^{-2} when theTiO_2 film thickness increases from 5.57 to 12.73 µm and then starts to decrease when the film thickness increases above 12.73 up to 20.65 µm.

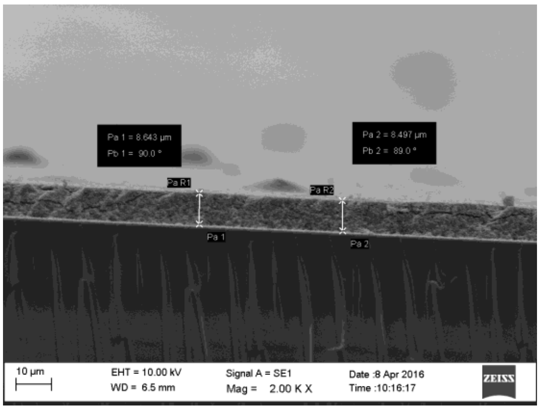
The DSSC efficiency essentially follows the same trend with TiO_2 film thickness, exhibiting the maximum efficiency value of 6.07 % for the 12.73 µm thickness of TiO_2 film. These results suggest that the efficiency in these DSSCs is essentially determined by the short circuit photocurrent density. The enhancement of efficiency when the TiO_2 film thickness increased from 5.57 to 12.73 µm is further confirmed by IPCE measurements shown in Figure 4 and Table 2. The variation of IPCE values with TiO_2 film thickness also follows the same trend as the efficiency variation.



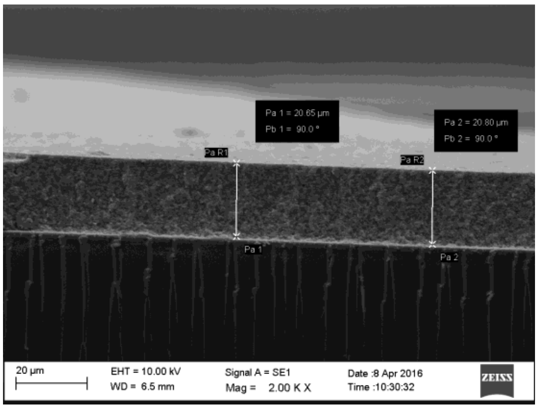
TiO_2 film thickness of 5.57μm



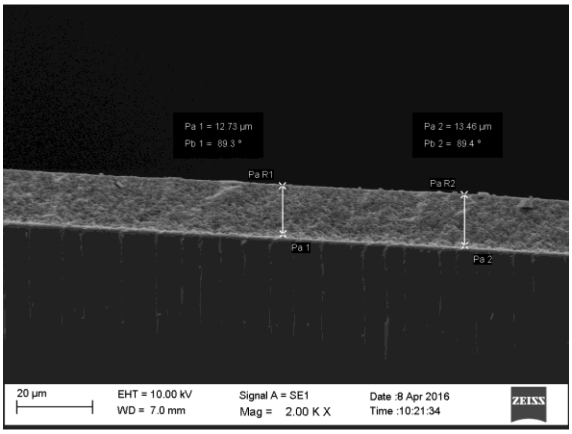
TiO_2 film thickness of 15.35 μm



TiO_2 film thickness of 8.64 μm



TiO_2 film thickness of 20.65 μm



TiO_2 film thickness of 12.73μm

Figure 1: SEM images showing the thicknesses of five TiO_2 photoanode films deposited on FTO glass substrates.

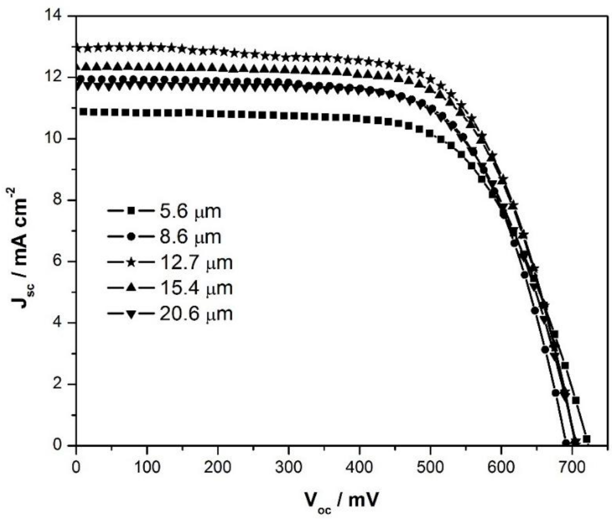


Figure 2: *J-V* characteristics of the DSSCs made with TiO_2 photoanodes of different thicknesses, from 5.6 μm to 20.6 μm.

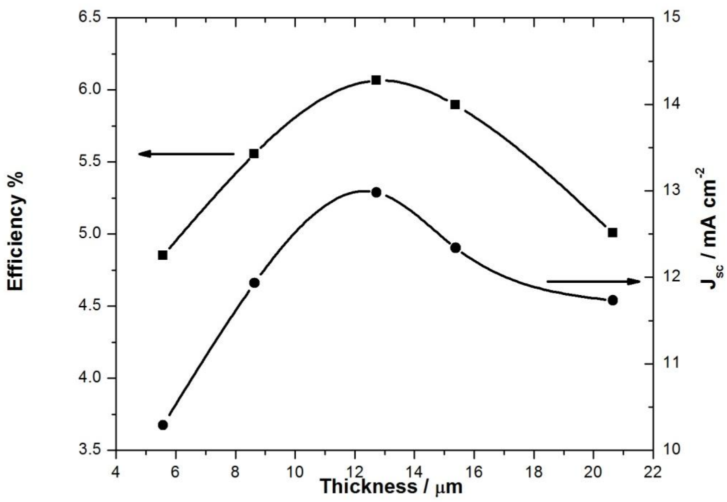


Figure 3: The variation of DSSC efficiency and short circuit current density with TiO_2 film thickness.

Table 1: Photovoltaic parameters of DSSCs with different TiO_2 film thicknesses. Values for the cell with highest efficiency are highlighted in bold.

Thickness (From SEM) (μm)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF %	η %
5.57	10.29	729.5	64.59	4.85 ± 0.06
8.64	11.93	713.6	65.48	5.56 ± 0.05
12.73	**12.98**	**706.9**	**65.10**	**6.07 ± 0.12**
15.38	12.34	706.3	65.15	5.89 ± 0.39
20.65	11.73	707.7	66.64	5.52 ± 0.20

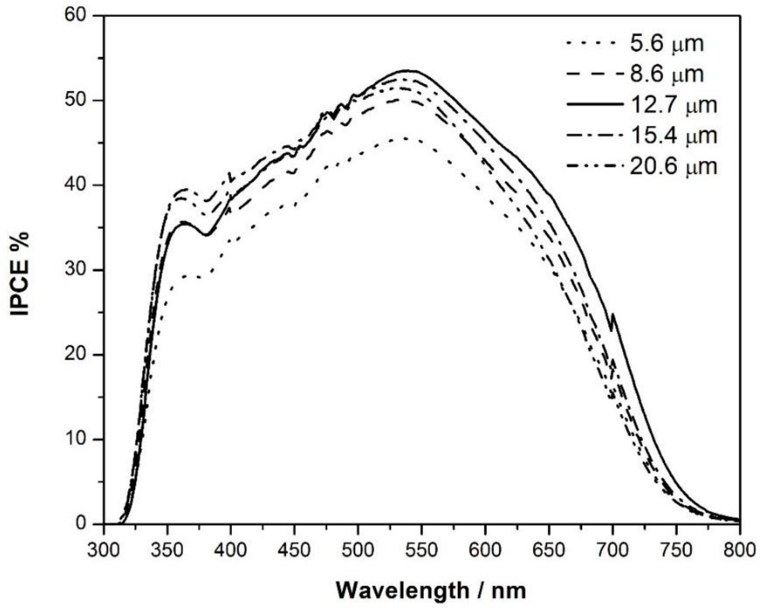


Figure 4: The IPCE spectra of DSSCs made with TiO_2 films of different thicknesses.

Table 2: IPCE wavelength maxima and peak percentages of the DSSCs with different TiO_2 film thicknesses.

TiO_2Thickness (µm)	IPCE peak wavelength (nm)	Peak percentage %
5.57	538.00	45.24
8.64	538.17	49.98
12.73	**542.64**	**53.69**
15.35	542.31	53.40
20.65	533.70	51.32

All the maximum IPCE peak values are in the wavelength range from around 530 to 545 nm. The maximum IPCE peak value of 53.69 % corresponds to the DSSC with the TiO_2 film of thickness of 12.73 µm. The increase in J_{sc} up to this particular thickness is evidently related to the increase in injection current from excited dyes to the conduction band of TiO_2. As the highest J_{sc} corresponds to the 12.73 µm thickness, the maximum rate of photon absorption by the dye and the maximum rate of electron injection from the dye to the conduction band of TiO_2 evidently occur at this optimum thickness.

Although the nanocrystalline TiO_2 films which is thicker than the above optimized thickness have a larger total surface area within the nanoporous structure, it very likely gives rise to a higher electron transport series resistance and thereby enhancing the electron recombination with I_3^- ions at the TiO_2 surface, resulting a lower J_{sc} value and a lower efficiency. In this thickness range, from 12.73 to 20.65 µm, the loss of the conduction band electrons in TiO_2 through their back electron transfer to I_3^- ions (I_3^- + 2e = 3 I^-) is evidently more than what is necessary to offset the J_{sc} increase due to larger surface area.

The variation of open circuit voltage (V_{oc}) with thickness of the TiO_2 photo anode in relation to the variation of the J_{sc} is shown in Figure 5. Increasing the surface area of the nanostructured TiO_2 electrode by increasing the film thickness undoubtedly leads to an increase in the number of trapping surface states, through which the back electron transfer would be increased, resulting in the lowering of the V_{oc} (Kambe *et al*., 2002). Also, the J_{sc} increase up to 12.73 µm can be related to the decrease in V_{oc}. The V_{oc} decrease implies that the conduction band edge (Fermi level) of TiO_2 shifts positively. However, both energy levels of the dye and the redox potential of I^-/I_3^- do not vary with the TiO_2 film thickness. Therefore, the positive shift with respect to dye energy levels narrows the energy difference between TiO_2 and dye. This lower energy gap helps the dye to inject electrons, resulting in enhanced photocurrent in this thickness range, up to 12.73 µm (Jung *et al*., 2003). Electrochemical impedance spectroscopy (EIS) measurements on DSSCs were performed in order to analyze the variations in photovoltaic parameters with TiO_2 film thickness. Figures 6(a) and 6(b) show the Nyquist plots and Bode plots for DSSCs made with different TiO_2 film thicknesses.

As shown in Figure 6(a), the Nyquist plot contains two semicircles: the larger semicircle in the low frequency range is related to the charge transport at dye attached TiO_2/electrolyte interface resistance ($R2_{CT}$), and the smaller semicircle in high frequency region is attributed to the charge transfer resistance of the Pt counter electrode/electrolyte interface ($R1_{CT}$) (Dissanayake *et al*., 2016). The impedance parameters were analyzed using an equivalent circuit as shown in Figure 6(a) inset. The resulting impedance parameters $R2_{CT}$ and f_{max}, along with photovoltaic properties, electron lifetimes (τ_e) and recombination lifetimes (τ_r) extracted from EIS measurements and voltage decay curves are tabulated in Table 3.

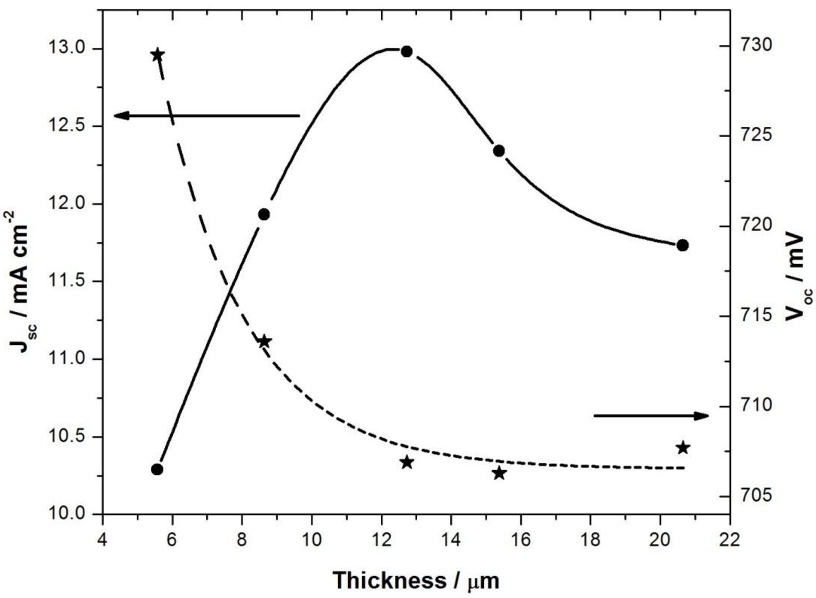


Figure 5: The variation of V_{oc} with thickness of the TiO_2photoanode in relation to the variation of the J_{sc}.

Table 3: DSSC parameters $R2_{CT}$, f_{max}, electron lifetimes (τ_e) and recombination lifetimes (τ_r) extracted from EIS measurements and voltage decay curves.

Thickness (µm)	$R2_{CT}$ (Ω)	f_{max} (Hz)	τ_e(ms)	τ_r (s)
5.57	23.2	18.09	8.79	1.33
8.64	8.38	17.05	9.33	1.20
12.73	**6.02**	**16.75**	**9.50**	**0.91**
15.35	6.45	17.00	9.36	0.95
20.65	7.69	17.62	9.03	1.19

From Table 3, it is clear that the values of the charge transfer resistance $R2_{CT}$ decrease with increasing TiO_2 film thickness from 5.57 to 12.73 µm but shows an increase with further increase in thickness. The results of *J-V* characteristics further show that the J_{sc} and the efficiency of the DSSCs follow a reverse trend as the $R2_{CT}$ as expected. The lowest charge transfer resistance values and highest J_{sc} and efficiency values correspond to DSSCs with optimum TiO_2 film thickness of 12.73 µm. This clearly implies that at the optimum thickness of the TiO_2 film (12.73 µm), the electron transfer mechanism at the TiO_2/electrolyte interface has been the most efficient, quite likely due to the better inter-grain connectivity and more conducting pathways created by optimum surface area and porosity.

On further increasing the TiO_2 film thickness from the optimum value of 12.73 µm, $R2_{CT}$ value have increased with the film thickness. An increasing thickness would lead to an increase in the loss of injected electrons due to recombination in the electron transfer process in TiO_2 nanoparticles and increasing $R2_{CT}$ of the DSSC, resulting in a decrease in efficiency (Hara *et al*., 2000). Also the reaction rate on the TiO_2 photoanode is strictly related to the number of oxidized dye species that are reduced by I^- ions at the interface. This trend may also indicate the dye absorption characteristics. On the other hand, the thicker the TiO_2 film, it is more difficult for the light to reach the TiO_2/dye/electrolyte interface effectively. Therefore, efficiency and J_{sc} values decrease for thicker TiO_2 electrodes (Baglio *et al*., 2011).

Electron life times also contribute to an understanding of the electron transfer process in the TiO_2 photoanode**.** From the Bode phase plot (Figure 6(b)), it is observed that the characteristic frequency peak shifts to lower frequency when the TiO_2 film thickness is increased from 5.57 up to 12.73 µm and then shifts to higher frequency values as the film thickness is increased further. The characteristic frequency at the maximum is related to the inverse of the electron lifetime (τ_e). From Table 3, it can be seen that the electron life time is the highest for the DSSC with film thickness 12.73 µm. Electron life time increases when the thickness of TiO_2 film increases from 5.57 to 12.73 µm and then decreases when the film thickness is increased beyond 12.73 µm. The increase of the electron life time makes the electron diffuse and transfer more easily due to the increase of the diffusion length. The current density and the efficiency are also increased as the TiO_2 film thickness increases up to 12.73 µm because the internal resistance related to the electron transport in the TiO_2/dye/electrolyte interface ($R2_{CT}$) is decreased. The performance of the DSSC with the higher TiO_2 film thickness, however, is reduced because the recombination of the electrons is enhanced.

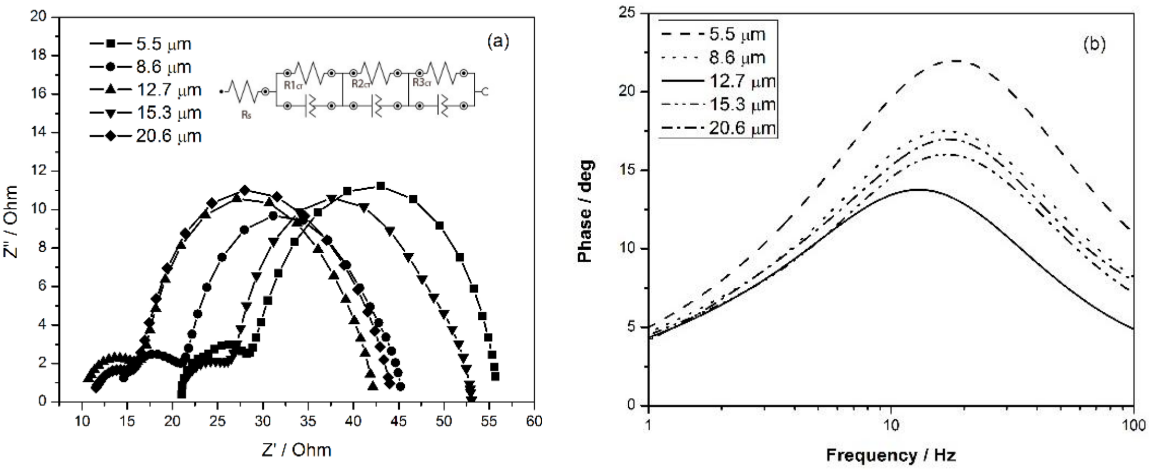


Figure 6: EIS spectra of DSSC based on different thicknesses of TiO_2 films, (a) Nyquist plots (left) and (b) Bode phase plot (right).

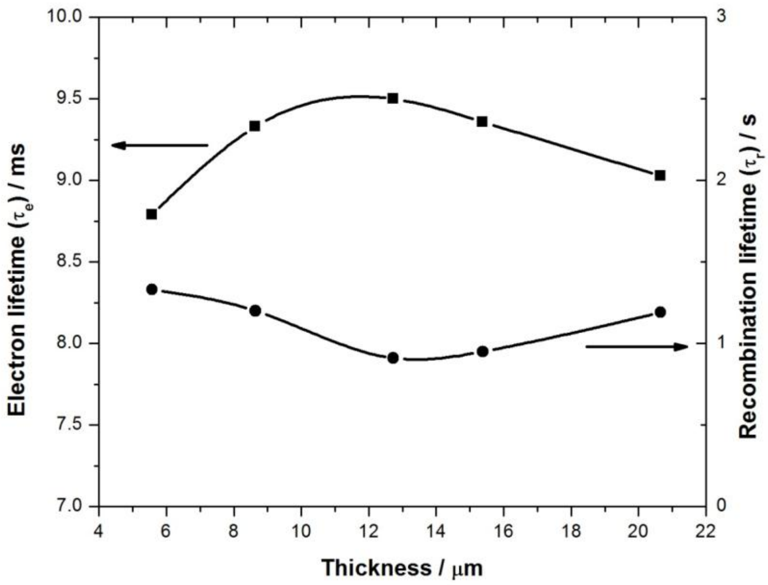


Figure 7: Electron lifetime and recombination lifetime variations with TiO_2 film thickness.

To confirm the trend in electron recombination life time variation, photovoltage decay measurements were taken for the DSSCs (PV decay curves not shown). The recombination life times (τ_r) obtained by curve fitting to photovoltage decay curves is tabulated in Table 3. Recombination life time variation with TiO_2 film thickness follows a trend opposite to the electron life time variation as shown in Figure 7. This implies that in TiO_2 electrodes thicker than the optimum value, electrons travel a longer distance and spends a longer time before encountering I_3^- ions and recombine. Under these circumstances, it increases the electron transfer resistance and decreases the electron recombination life time. The improvement in the electron life time can be attributed to a reduced recombination of photo generated electrons between the TiO_2 electrode and the electrolyte.

Recombination life time decreases when the thickness of TiO_2 film is increased from 5.57 to 12.73 µm, and increases when the film thickness is increased beyond 12.73 µm. This also confirms the increased recombination with increasing the TiO_2 film thickness beyond optimum level.

CONCLUSION

The dependence of TiO_2 photoanode film thickness on the performance of DSSC was studied. The TiO_2 films were formed by the doctor-blade technique. With increasing film thickness from 5.57 to 12.73 µm, the J_{sc} and the efficiency were increased while the V_{oc} decreased. When the TiO_2 film thickness was increased beyond 12.73 µm, the J_{sc} and the efficiency decreased. This has been supported by the IPCE measurements. The V_{oc} decrease is related to the increase of back electron transfer between I_3^- ions and conduction band electrons in the TiO_2 electrode. EIS analysis was used to quantify the charge transport resistance at the TiO_2/dye/electrolyte interface and electron lifetime τ_e. The lowest charge transfer resistance and the highest τ_e value were obtained for the TiO_2 films with optimum thickness of 12. 73 µm. Recombination lifetimes τ_r were determined from photovoltage decay measurements and the highest efficiency cells showed the lowest τ_r due to lowest recombination.

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