Effect of TiO_2 Compact Layer on DSSC Performance

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DOI: 10.22178/pos.38-10

LCC Subject Category:
TP155-156

Received 22.08.2018
Accepted 25.09.2018

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Abstract. Dye-sensitized solar cells offer an economically reliable and suitable alternative in moderating the challenges presented by the existing convectional photovoltaic cells. Whereas, for convectional solar cells the semiconductor adopts both the duty of light absorption and charge carrier transport, these two functions are separated in dye-sensitized solar cells. However, the efficiency of dye-sensitized solar cells has remained relatively low. For this reason, this research was aimed at how to increase the dye-sensitized solar cells performance. To achieve this, compact cover of TiO_2 was deposited on a conductive glass substrate by using Holmarc's Spray Pyrolysis system, using Ultrasonic Spray Head and spraying in vertical geometry, while TiO_2 nanoparticles and nanotubes were deposited by screen printing technique on top of a transparent conducting FTO glass slide with or without the TiO_2 compact layer. Transmission characteristics showed that introducing TiO_2 compact layer on the conductive film lowers the transmission while reflectance properties were less than 15 % for all the prepared thin films. SEM micrographs showed that TiO_2 nanotubes had a skein-like morphology with abundant number of nanotubes intertwined together to form a large surface area film. Solar cell performance properties revealed that introducing compact layer to dye-sensitized solar cells improved the performance by 145 % (from 1.31 % to 3.21 %) while $TiCl_4$ treatment on compact layered dye-sensitized solar cells increased the efficiency by 28.79 % (from 0.66 % to 0.85 %).

Keywords: Compact layer; Dye sensitized solar cell; solar cell performance; skein-like morphology; screen printing technique; spray pyrolysis.

INTRODUCTION

Dye-sensitized nano-structured solar cells (DSSCs) present themselves as viable alternative to fossil fuels and silicon based solar cell technology in meeting the current state of energy demand [1]. They have a central role to play in providing renewable energy. The development of these solar cells generates not only a source of electricity but thermal energy as well from solar energy [2].

However, since DSSCs fabricated from TiO_2 films were discovered, they have had low efficiencies compared to the other commercial solar cells [3]. Among other causes of low efficiency, the structure of the photo-anode electrode is one of the main sources. The nature of coating on the photo-anode directly contributes on the solar cell performance due to the light harvesting capability, among other factors [4].

Since conversion efficiency of any solar cell is key to commercial competition in the market, there is need to study efficiency improvement strategies possible in these solar cells. Amongst other strategies that can be used is the photo-anode composition. This involves introducing a TiO_2 compact layer in between the photo-anode electrode and the hole-transport material [5]. In this study, the effect of introducing this layer was studied.

The TiO_2 compact layer was deposited onto FTO glass substrates by Holmarc's Spray Pyrolysis system, using Ultrasonic Spray Head, spraying in vertical geometry. The nozzle used ultrasonic atomization and was operated at a frequency of 40 kHz and its scan speed was 25 mm/s. The nozzle to substrate distance was kept constant at 15 cm, substrate temperature was maintained at 450 °C and deposition time was set at 1 minute.

Pressurized air (at 6 bar) was used as shaping gas and the solution was sprayed with a rate of 2 ml/min.

For efficiency comparison, this deposition was not done in some other set of FTO glass substrate. TiO_2 nano-porous layer was coated on the glass with and without the compact film by screen printing method. TiO_2 nanotubes layer was deposited onto glass slides with and without the compact layer using the screen printing technique. The resultant films were dried up in an oven at 80 °C for 10 minutes and then sintered in a furnace at 450 °C for 30 minutes [6]. Two of the glass slides with TiO_2 nanotubes layer were treated with titanium tetrachloride and others used as untreated and the sintering process repeated for the slides with $TiCl_4$ treatment. The films were 0.35 cm by 0.6 cm in dimension. This process produced a set of the following glass slides:

- TiO_2 compact layer/ screen printed nano-porus TiO_2 film against screen printed nano-porus TiO_2 film;
- $TiCl_4$ treated TiO_2 nanotubes against untreated TiO_2 nanotubes;
- TiO_2 compact layer/ $TiCl_4$ treated TiO_2 nanotubes against untreated TiO_2 nanotubes.

Optical analysis was used to determine the optical characteristics of thin films such as band gap energy, absorption co-efficient and film thickness. To measure reflectance and transmittance measurements of TiO_2 films, Shimadzu 3700 DUV UV-VIS-NIR spectrophotometer was used. Transmittance and reflectance data at 200 nm to 1200 nm wavelength was collected.

The samples were then mounted on a holder inserted in the scanning electron microscope (Carl Zeiss Sigma VP FE-SEM). Coating using a slim layer of 20 nm to 30 nm of platinum was done to increase the conductivity and to prevent the build-up of high voltage charges of the thin films in the scanning electron microscope. The voltage was set at 6 kV and the working distance was set at 5.1 mm.

Anodes and cathodes were prepared simultaneously to minimize contamination. The platinum coated slide was placed facing down on top of the dye sensitized TiO_2 photo-electrode. Adhesive polymer gasket of thickness of 25 μm and sourced from Solaronix, was used to join the electrodes together. A 0.5 mm diameter hypodermic needle was then injected in the counter electrode hole to fill the electrolyte in between the electrodes. The solution was drawn into the cell by capillary action and stained the entire oxide layer. The same adhesive polymer gasket was used in the sealing of the electrolyte filling holes. The power conversion efficiency was determined using a solar simulator for two sets of solar cells produced. Comparison of the solar cell efficiencies with respect to the films used in fabrication was made.

RESULTS AND DISCUSSION

Transmission and reflectance characteristics of thin films

Figure 1 shows the transmission characteristics of FTO glass substrate and the prepared TiO_2 films.

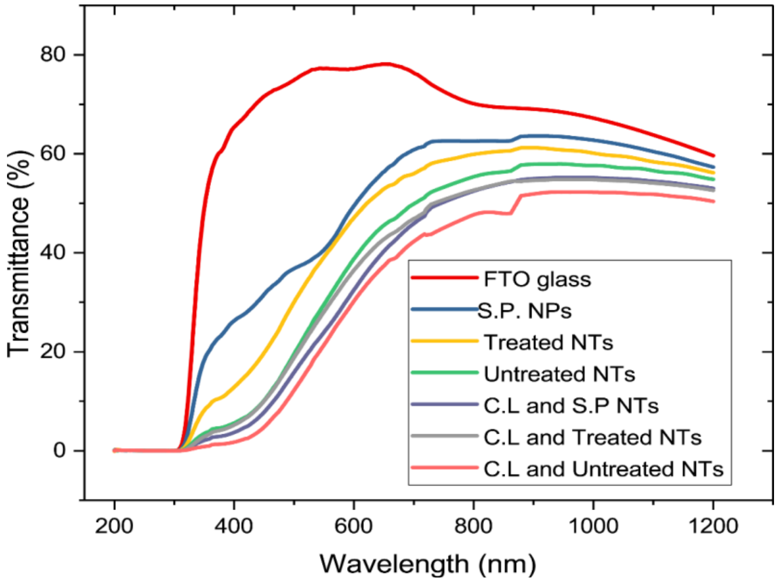

Figure 1 – Transmission characteristics of both FTO glass substrate and TiO_2 films prepared

It was revealed that the introduction of TiO_2 compact layer to both screen printed TiO_2 nanoparticle and nanotube films (whether treated or untreated) tends to reduce the transmittance.

For instance, at 927 nm wavelength, the transmittance of screen printed TiO_2 nanoparticles on a TiO_2 compact layer was found to be 54.77 % which is lower than the transmittance at the same point of screen printed TiO_2 nanoparticle film which was 63.58 %. This was attributed to film thickness, introducing a film on a compact layer meant that there is an increase in the film thickness for which the light was to be transmitted which led to a larger fraction of light not being transmitted [7]. In this figure, the transmittance curves for FTO glass, screen printed nanoparticle film, treated nanotube film and untreated nanotube film were for comparison purposes.

Figure 2 shows the reflectivity characteristics of the prepared TiO_2 thin films where it was observed that all the films have low reflectance (less than 15 % in the visible region on average).

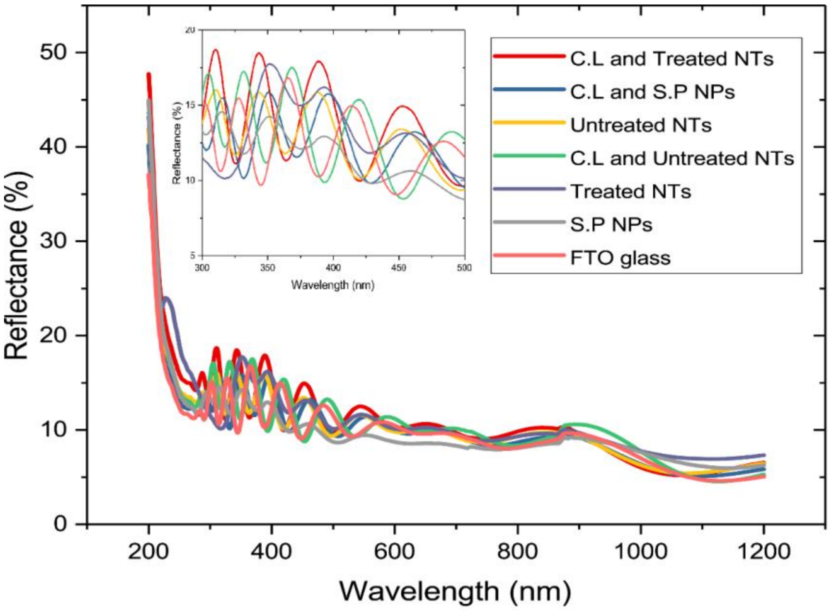

Figure 2 – Spectral plot of reflectance characteristics of FTO and TiO_2 thin films

Moreover, it was observed that there were several peaks in most of the curves which were attributed to the multiple reflection effect the three interfaces of the air/thin film/transparent substrate bi-layer [8].

Multiple reflection happens because the overall reflectance is described by taking into account the product of the reflection co-efficient multiplied by the complex conjugate of the reflection. Another reason as to why there were peaks in the curves is that some reflectivity peaks were due to peaks in the real refractive index and the imaginary refractive index as shown by equation (1).

$$n^* = n + ik, \tag{1}$$

where n^* is the complex refractive index;

n is the real refractive index;

k forms the imaginary part of the refractive index.

Figure 2 also shows that at low wavelengths (not exceeding 250 nm), there was notably high reflectance than at all other wavelength marks which was attributed to high absorption at these wavelengths. This therefore meant that these thin films exhibited high absorption behavior which makes the material a good absorber material for solar cell applications.

SEM analysis

Figure 3 shows the micrograph of TiO_2 compact layer. The film was relatively smooth as compared to the micrograph of TiO_2 nanoparticle (Figure 4) because of the slight movement of the glass substrate during the spray pyrolysis deposition process, which was caused by the pressure of the spray.

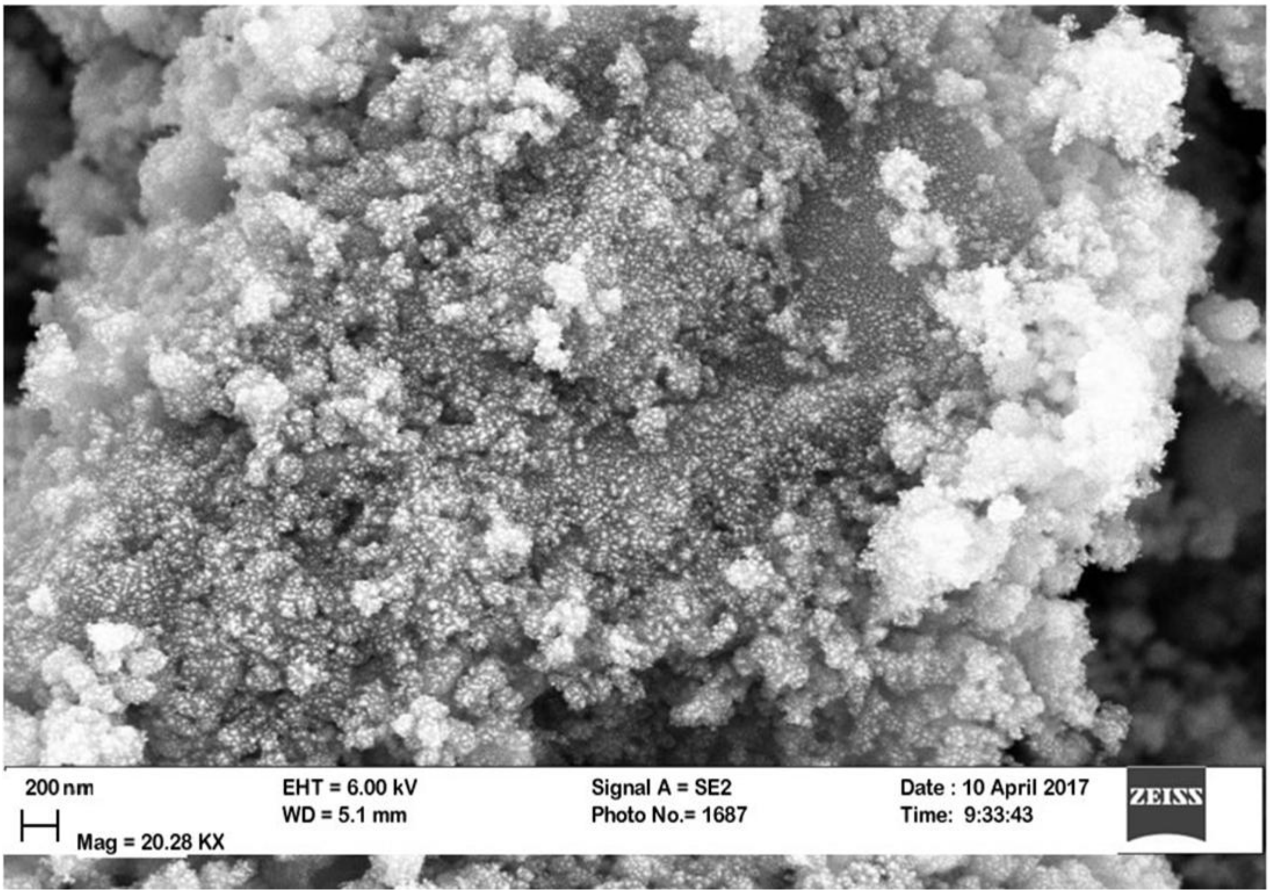

Figure 3 – SEM micrograph of titanium dioxide compact layer

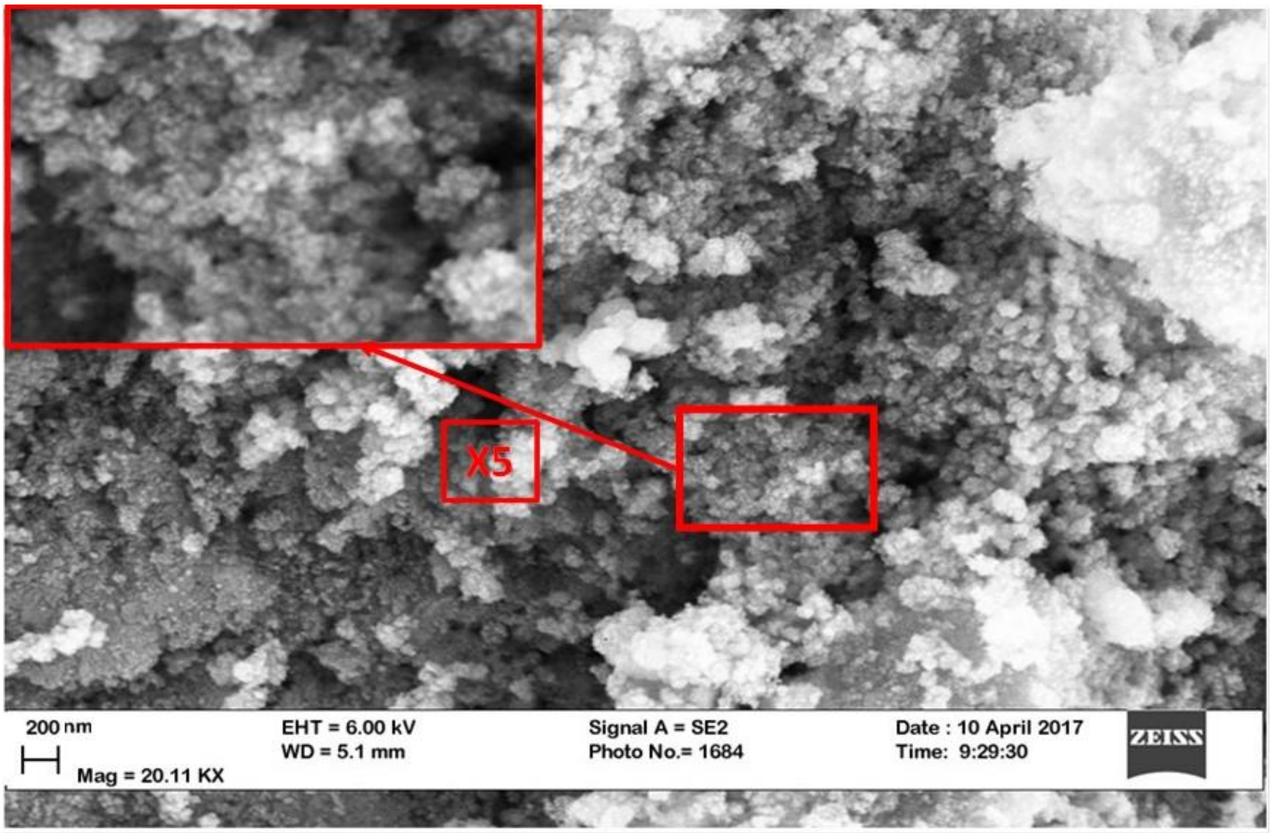

Figure 4 – SEM micrograph of TiO_2 nanoparticle film

It was also noted that the TiO_2 compact layer coated fully the FTO glass which was desirable in the fabrication of high efficient dye-sensitized solar cell.

Figure 4 shows the micrograph of TiO_2 nanoparticle film. From figure 4, the nanoparticles were spongy and had unevenly sphere-shaped profile, which is an important factor to high performing DSSC fabricated out of these films. The spongy trait is important since it ensures that a lot of dye is absorbed into the TiO_2 matrix, a factor that leads to high performing DSSC.

Figure 5 shows the SEM micrograph of TiO_2 nanotube film. SEM analysis revealed that TiO_2 nanotubes had a skein-like morphology with abundant number of nanotubes intertwined together such that their surface area is considerably large [9]. For better I-V performance of the solar cell, the nanotubes' number need to be high so as to have maximum dye adsorption which would translate to efficient light harvesting.

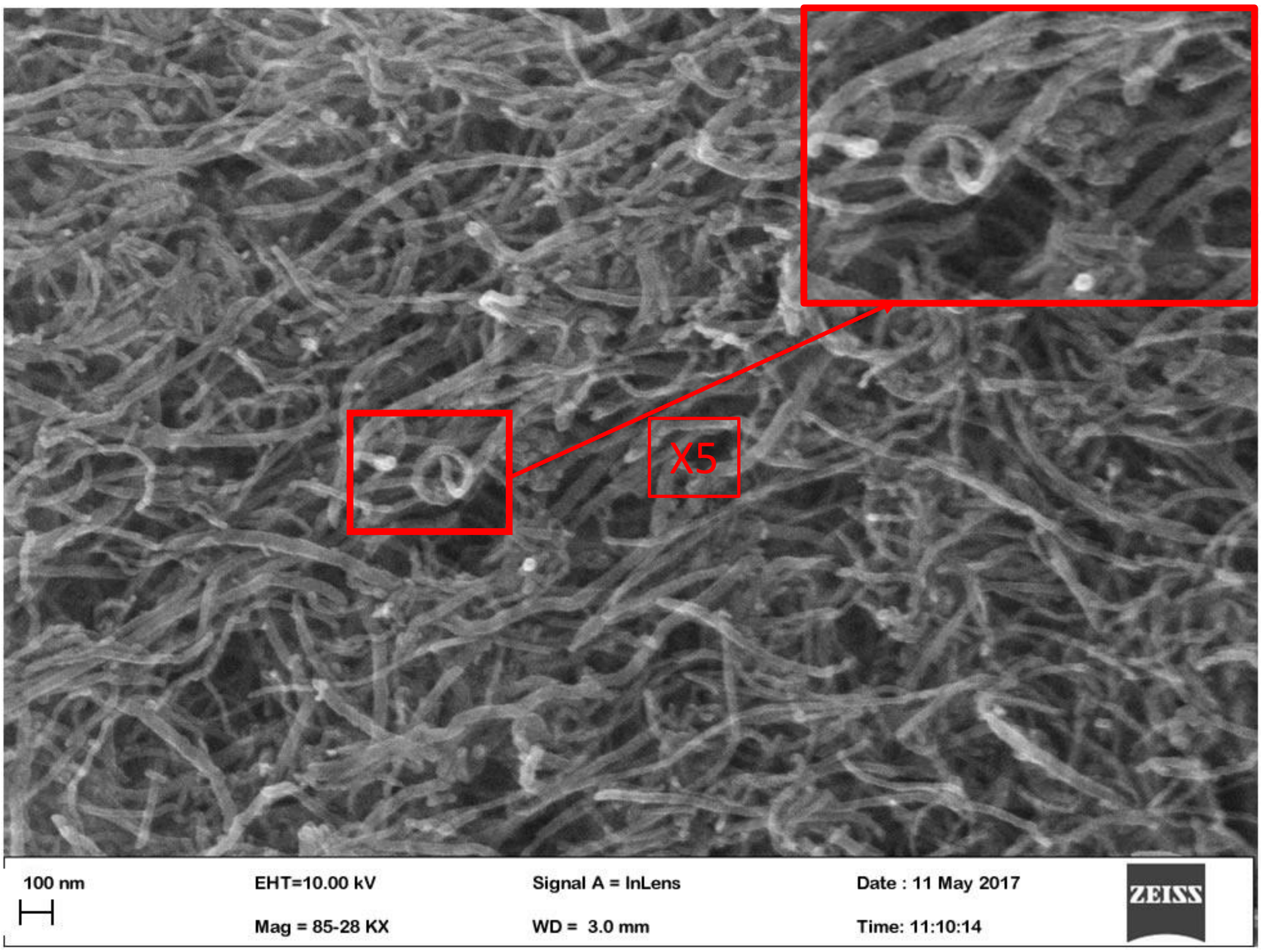

Figure 5 – SEM micrograph of TiO_2 nanotubes

Solar cell performance studies

Effect of TiO_2 compact layer for screen printed nanoporous TiO_2 film. In the study of how TiO_2 compact layer contributed to solar cell efficiency, the performance of two cells (the compact layered and the non-compact layered) were compared. As shown in Figure 6, the compact layered solar cell had increased performance.

For instance, the current density increased from 4.719 mA/cm^2 to 8.329 mA/cm^2 (76.5 % increase) as shown in Table 1. In addition, V_{oc} improved by 6.35 % (from 0.598 V to 0.636 V) while the efficiency increased by 145 % (from 1.31% to 3.21 %) when the compact layer was introduced.

The compact layer blocked the FTO/electrolyte boundary physically thereby reducing recombination greatly. There was an upward electron Fermi level shift due to the reduced recombination reaction and therefore the electron-carrier concentration was increased [10].

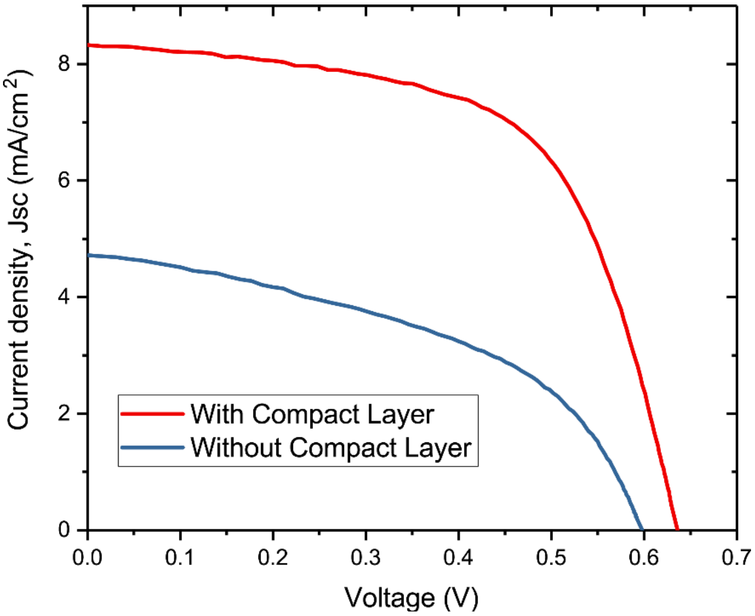

Figure 6 – I–V curves showing the effect of TiO_2 compact layer

For this reason, the I_{sc} values obtained were higher when compared with those from non-compact layered solar cell.

Table 1 – Effect of compact layer on solar cell performance

Solar cell type	Jsc (mA/cm^2)	Voc (V)	F.F (%)	Efficiency (%)
With compact layer	8.329	0.636	60.7	3.21
Without compact layer	4.719	0.598	46.4	1.31

In addition, the TiO_2 compact layer improved the interfacial adhesion between the nanoporous TiO_2 layer and the FTO [11]. This increased the short circuit current and the fill factor [12]. This explains why the fill factor of the compact layered solar cell is greater than that of non-compact layered solar cell.

Effect of TiO_2 compact layer and $TiCl_4$ treated TiO_2 nanotubes against untreated TiO_2 nanotubes. Table 2 shows that the $TiCl_4$ treated solar cell with a compact layer had a better performance than that with compact layer and untreated meaning that $TiCl_4$ treating improved the performance of the solar cell. This was credited to the increase of the surface area of the TiO_2 nanotubes upon treating them with $TiCl_4$ [13].

Table 2 – Effect of compact layer and treating the solar cell performance

Solar cell type	Jsc (mA/cm^2)	Voc (V)	F.F (%)	Efficiency (%)
Compact layer and $TiCl_4$ treated	3.043	0.569	48.9	0.85
Compact layer and untreated	2.405	0.561	48.8	0.66

Increase on the surface area led to more dye absorption which translated to the generation of more photo-current. Table 2 showed that the efficiency improved by 28.79 % (from 0.66 % to 0.85%), V_{oc} by 1.43 % (from 0.561 V to 0.569 V) while the short circuit current improved by 26.52% (from 2.405 mA/cm^2 to 3.043 mA/cm^2).

Figure 7 shows the effect of treating TiO_2 compact layered DSSCs on their performance. It was found out that the performance increased with $TiCl_4$ post-treatment of the TiO_2 nanotubes. Nevertheless, since these cells recorded the highest film thickness in comparison with the other cells, their performance was the lowest. The compact layer increased the cell thickness which in turn increased the electron trap states. Since the thicker cell had more electron trap states, the photo-excited electron pathways were blocked and therefore most electrons were unable to reach the FTO electrode for effective conduction [12]. In addition, the thicker the solar cell, the less the optical transmittance and therefore the less the open circuit voltage and the short circuit current.

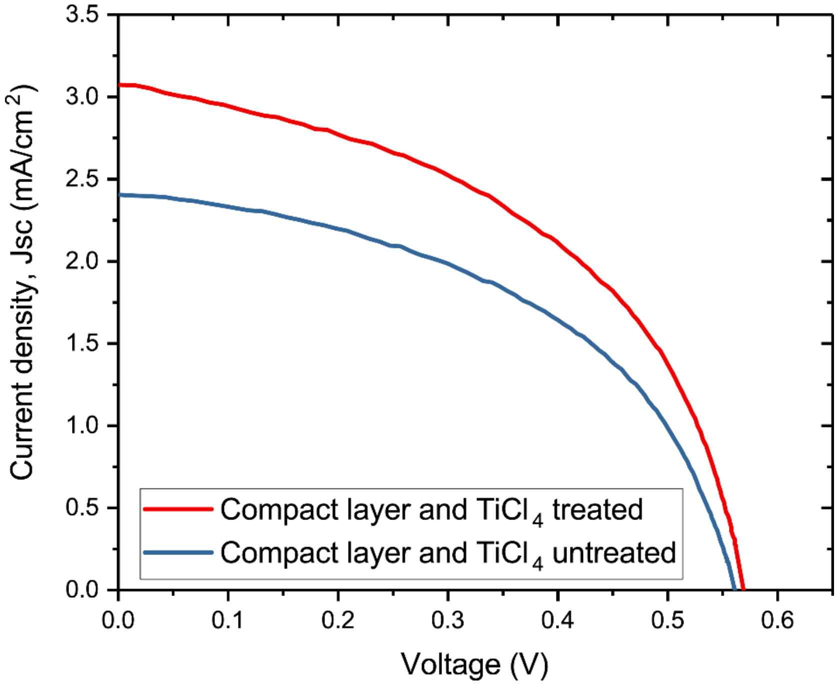

Figure 7 – The effect of TiCl4 treatment on compact layered DSSCs

CONCLUSION

TiO_2 nanoparticle and nanotube films were successfully deposited onto FTO glass slides using both screen printing and spray pyrolysis techniques. Transmission characteristics revealed that TiO_2 compact layer reduces the transmittance of the thin films slightly. Introducing TiO_2 compact layer to screen printed nano-porous TiO_2 solar cell showed 76.5 % increase in the current density while introducing it to $TiCl_4$ treated TiO_2 nanotube solar cell increased the current density by 26.5 %. From these studies, it was concluded that introducing TiO_2 compact layer between the photo-anode electrode and the hole-transport medium increases the overall solar cell performance.

ACKNOWLEDGEMENTS

The authors wish to acknowledge solid state laboratories, University of Nairobi, for the technical support during the optical measurements of the samples and Chemistry department, Kenyatta University for availing chemicals used in this work. In addition, this work was supported by the African Development Bank which provided the corresponding author with a scholarship which enabled these studies to be conducted.

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