PAPER • OPEN ACCESS

Efficiency enhancement in Dye Sensitized Solar Cells by light scattering in photoanode with TiO2 nanotubes

To cite this article: G K R Senadeera et al 2020 J. Phys.: Conf. Ser. 1552 012002

View the article online for updates and enhancements.



IOP ebooks[™]

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection-download the first chapter of every title for free.

This content was downloaded from IP address 112.134.188.197 on 29/05/2020 at 20:26

Efficiency enhancement in Dye Sensitized Solar Cells by light scattering in photoanode with TiO2 nanotubes

G K R Senadeera ^{1,2,*}, C A Thotawatthage ^{1,3} and M A K L Dissanayake ¹

¹ National Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka
² Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka,

*Corresponding author: gksen@ou.ac.lk

Abstract. The effect of incorporating a composite double layered structure of photoanode, based on hydrothermally synthesized TiO₂ nanotubes (TNT) as the light scattering layer, on the efficiency enhancement of dye sensitized solar cells (DSSCs) is reported. Device performances comprising this novel photoanode is compared with the DSSCs fabricated with the conventional type of photoanodes without TNT. Further enhancement in the device performances is obtained with the post treatment of the photoanode with TiCl₄. The DSSC with post treated two layered composite photoanode showed an overall efficiency of 8.31% with a short circuit photocurrent density (J_{sc}) of 16.91 mA cm⁻² and 783.4 mV of an open circuit voltage (V_{oc}) under the irradiance of 1000 W m⁻². In comparison, the reference DSSC with a post treated photoanode having the same thickness showed 7.62% efficiency while delivering a J_{sc} of 15.60 mA cm⁻² with 773.5 mV. The remarkable enhancement in the device performance is achieved due the employment of this double-layered novel photoanode in the DSSCs. However, lower electron life time is observed in the DSSCs with TNT layer suggesting that, rate of electron recombination is higher in the DSSCs with this novel photoanode, although the overall efficiency of the present device and the net result due to the enhanced light harvesting and scattering effect may still be regarded as an favorable alternative for certain applications.

1. Introduction

After the discovery of highly efficient Dye Sensitized Solar Cells (DSSCs) by Gratzel's group in 1991, DSSCs based on nano structured titanium dioxide (TiO₂), have emerged as a low cost alternative to conventional silicon based solar cells [1]. A DSSC typically consists of a nano crystalline mesoporous semiconductor film covered by a monolayer of dye, a redox electrolyte and a platinized counter electrode. Since the dye sensitization occurs at the dye-semiconductor interface, photoanode is one of the crucial elements of a DSSC. Several semiconducting materials such as TiO₂, SnO₂, ZnO etc., have been used as the photoanode in these devices. Among these semiconductors TiO₂ possesses promising applications due to its suitability as well as the low production cost. As it is well known, a large surface area of the nano-particulate semiconductor enables a high dye adsorption [2]. Although the large surface area of the nano-particulate semiconductor enables a high dye adsorption, it also increases the disordered networks of nanoparticles with numerous grain boundaries which negatively effect to the electron transport while increasing the rate of electron recombination of the photo electrons with the oxidized dye molecules and the redox mediator in the electrolyte. Therefore, it leads to enhance the dark current and greatly reduce the overall efficiency of such devices [3,4,5]. However, numerous techniques such

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

12th International Symposium on Modern Opt	ics and Its Applications (IS	SMOA)	IOP Publishing
Journal of Physics: Conference Series	1552 (2020) 012002	doi:10.10	88/1742-6596/1552/1/012002

as usage of, nano particles [1,2], one dimensional nano wires (NW), nano rods (NR) and nano tubes (NT) [4-11], etc., have been tested towards achieving high efficiencies of these devices. Despite the change of the particle size of the semiconductor, another strategy to enhance the light harvesting efficiency is the use of light scattering effects which increases the average path length of light as it travels through the TiO_2 film, improving the probability of light being captured by a dye molecule (particularly in the wavelength range where the dye extinction coefficient is the lowest). This is usually done by increasing the light scattering inside the photoanode by applying a larger particle semiconducting layer on top of the smaller nanoparticle semiconductor. Ferber et, al have reported addition of particles of 125-150 nm radius to the smaller TiO₂ particles of the photoelectrode for efficient light collect in the device [12]. Rothenberger et al [13] have shown that the photoactive layers of TiO₂ in DSSC containing 65% and 35% by weight of transparent and scattering colloids, respectively, can effectively utilize the higher wavelengths of the solar spectrum for photon conversion. However, in most of the work, double layered structures with larger particle layers have been employed to enhance the light scattering effect within the DSSCs [17]. In this context, recently we have reported [11] a novel, three layered, nano structured TiO₂ photoanode by sandwiching a randomly distributed nanofibre (NF) structure made with interconnected elongated beads of TiO₂, fabricated by electro-spinning method together with two conventional nanoparticle (NP) layers. DSSCs fabricated with this TiO₂ NP/electrospun NF/NP composite photo-anode showed remarkably enhanced overall efficiency over the conventional type of photoanode prepared with no NF layer [11]. In this work we report, fabrication of a novel, TiCl₄ post treated, double layered composite photoanode by incorporating a layer of TiO₂ nano tubes prepared by hydrothermal method as a replacement of nano beads in the three layered photoanode, which can be used to further enhance the overall efficiency of DSSCs.

2. Experimental:

2.1. Materials and methods

Starting materials, TiO₂ P25 from Diggusa, TiO₂ P90 from Evonik industries and Ru dye (N719) from Solaronix -SA were purchased and used as it is. Titanium tetra-chloride (TiCl₄), ethylene carbonates (EC), tetrapropyl ammonium iodide (Pr₄NI), acetonitrile (ACN) and iodine chips (I₂) with purity greater than 98 % were purchased from Sigma Aldrich. Pr₄NI and TiO₂ were vacuum dried at 60 °C for 24 hours in a vacuum oven (Eyela VOS – 450D) prior to use.

2.2. Fabrication of P90 compact TiO₂ layer

In order to reduce the recombination and short-circuiting of the device, a compact layer of TiO₂ was first fabricated by using a paste from TiO₂ P90 powder. This layer was prepared by grinding 0.25 g of TiO₂ (Aroxide-P90) with 1 ml of 0.1 M HNO₃ acid (pH 1.0) until a creamy paste is obtained. It was then spin coated on a pre-cleaned, fluorine-doped conducting tin oxide (FTO) glass (Solaronix glass 7 Ω /sq) at 3000 rpm for 60 seconds. Films were then sintered at 450 °C for 45 min.

2.3. Fabrication of P25 nanoporous nanoparticle TiO₂ layer

This layer was prepared by using a paste obtained by grinding 0.25 g of TiO_2 (Degussa P-25) with 1 ml of 0.1 M HNO₃ acid (pH 1.0), one drop (about 0.02 g) of triton X-100 and 0.05 g of PEG-1000 (Polyethylene glycol). The paste was then "doctor bladed" on the aforementioned compact TiO_2 layer with FTO substrates and re-sintered at 450 °C for 45 min.

We consider a gold NP ($\varepsilon_1(\omega)$) capped with dielectric material (ε_2), whose geometry is depicted in Fig. 1, immersed in a host medium (ε_3). With the dimension of the considered composite far less than visible light wavelength, the analysis can be performed using the quasi-static approach.

2.4. Fabrication of TiO₂ nanotube layer

Titanium nano tubes (TNT) were synthesized via hydrothermal method [7]. First, 2 g of P25 Degussa TiO₂ was dispersed in 10 M NaOH_(aq) solution by stirring for 30 min. Then the solution was transferred into a Teflon lined autoclave and kept at 150 °C for 48 h. The resultant product was washed with 0.1 M

12th International Symposium on Modern Opti	cs and Its Applications (IS	SMOA)	IOP Publishing
Journal of Physics: Conference Series	1552 (2020) 012002	doi:10.1088/174	2-6596/1552/1/012002

HCl and distilled water until the pH becomes 8.5. Then the nanotube paste was ultrasonicated for 10 min to make a TNT suspension. Electrophoretic deposition (EPD) technique was used to deposit TNT by mixing the TNT suspension and methanol in 2:1 (v/v) ratio on either a pre-cleaned, bare conducting FTO glass plate or the aforementioned double layered FTO/P90/P25 structure of TiO₂. Conventional two-electrode system with metallic platinum counter electrode was used for this electrodeposition. Electrodeposition was carried out galvanostatically at a constant current density of 0.5 mA cm⁻² for 15 min. Films were then sintered at 450 °C for 45 min and allowed to cool down to room temperature. For the surface mohopological studies these TNT films were also deposited on FTO glass substrates and sintered under the same conditions as mentioned before. Surface morphologies of these films were examined using Scanning Electron Micrographs (SEM).

2.5. TiCl₄ post treatment

For TiCl₄ treatment, 0.04 M aqueous solution was prepared and aforementioned pre-sintered TiO₂ photoanods were immersed in the TiCl₄ solution for 24 hours at 40 °C in a Buchi glass oven (B-585). Then rinsed them with distilled water and again re-sintered at 450 °C for 45 min.

2.6. Dye adsorption on to TiO_2

Dye adsorption was carried out by immersing the each type of photoanode in ethanolic dye solution containing Ruthenium dye N719 [RuL2(NCS)2:2TBA where, L = 2,2-bipyridyl-4, -dicarboxylic acid; TBA = tetrabutylamonium] for 24 h.

2.7. Electrolyte preparation

Tetrapropyl ammonium iodide, Pr_4NI (0.5 M) and I_2 (0.05 M) were mixed in a solution of acetonitrile and ethylene carbonate (1: 3.6 v/v) under continuous magnetic stirring overnight (12 hours) to obtain a homogeneous liquid electrolyte.

2.8. Solar cell fabrication and I-V characterization

The liquid electrolyte based DSSCs were fabricated as schematically shown in figure 1, by sandwiching the electrolyte between a platinum (Pt) coated FTO glass and the dye adsorbed photoanodes prepared in different ways as mentioned above. The area of the each cell was kept as 0.25 cm². A Xenon 500 lamp was used with AM 1.5 filter to obtain the simulated sunlight with required intensity. The photocurrent-voltage (*J-V*) characteristics of the cells were measured under the illumination of 1000 W m⁻² (AM 1.5) simulated sunlight using a homemade computer controlled setup coupled to a Keithley 2000 multimeter and a potentiostat/galvonostat HA-301. The effect of incorporation of TNT layer in the photoanode on the efficiency of the device, was investigated by fabricating different types of DSSCs with photo anodes labeling from A to G as follows; A (FTO/P25), B(FTO/P90/P25), C(FTO/P90/P25) treated with TiCl₄, D(FTO/P90/P25/P25), E (FTO/P90/P25/P25) treated with TiClO₄, F(FTO/P90/P25/TNT) and G(FTO/P90/P25/TNT) treated with TiClO₄. Dark *I-V* measurements were performed on devices fabricated with different types of TiO₂ photoanodes using Autolab PGSTAT 128 N.



Figure 1. Schematic diagram showing liquid electrolyte based dye-sensitized solar cells (DSSCs) of configuration Glass/FTO/TiO₂/Dye/electrolyte/Pt/FTO/glass

2.9. EIS measurements

In order to see the effects of photoanodes of different nanostructures, on the electron life time (τ_e) and the interfacial charge-transfer resistance across the photoanode/electrolyte interface (R_{CT2}), Electrochemical Impedance Spectroscopy (EIS) measurements were performed on the DSSCs using a Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128 N with a FRA 32 M Frequency Response Analyzer (FRA) covering the 1 MHz–0.01 Hz frequency range. These measurements were carried out under the illumination of 1000 W m⁻² using the same solar simulator that was used for *I-V* measurements.

3. Results and Discussion

3.1. TNT Nanotubes

Figure 2 shows the SEM image of the post-sintered titania nanotube films fabricated by the hydrothermal method and deposited on the FTO substrate by electroporosis deposition method (EPD). In the primary stages of the hydrothermal process, a thin layer of sodium titanate is deposited on the surface of the TiO_2 particles available in the precursor solution. Subsequently this thin layer exfoliate and then due to the curling and scrolling processes, nano tubes are formed [18,19].

The TiO₂ nanotubes thus formed seem to have a randomly distributed 3 D network with an average length of 200-300 nm. According to the literature the estimated size of hydrothermally synthesized titania nanotubes are found to be about 8-10 nm diameter and several hundred nanometers in length [19,20].



Figure 2. SEM image of the post-sintered titania nanotube films produced by the hydrothermal method and subsequently deposited on the FTO substrate by Electrophoretic deposition method

3.2. Photovoltaic characterization and performance

In order to see the effect of integration of compact P90 layer in the conventional photoanode of DSSC, initially the DSSCS with (A) FTO/P25), (B) (FTO/P90/P25), (C) (FTO/P90/P25) treated with TiCl₄, photoanodes were used. Figure 3 shows the photocurrent voltage characteristics (I-V) of the DSSCs with above photoanodes. Photovoltaic parameters such as short circuit photocurrent density (J_{sc}), open circuit voltage (V_{oc}), filing factor (FF) and overall efficiency of the device (η) estimated from figure 3 are tabulated in table 1.



Figure 3. I-V curves of three DSSCs fabricated with photoanodes A, B and C

12th International Symposium on Modern Op	ptics and Its Applications (IS	SMOA)	IOP Publishing
Journal of Physics: Conference Series	1552 (2020) 012002	doi:10.1088/1742	-6596/1552/1/012002

The solar cell parameters extracted from figure 3 are summarized in table 1.

Type of the photoanode in DSSC	J _{sc}	V _{oc}	FF	η
	$(mA cm^{-2})$	(mV)	(%)	(%)
A(FTO/P25)	13.10	726.60	62.47	5.94
B(FTO/P90/ P25)	14.00	725.20	64.30	6.52
C(FTO/P90/ P25) treated with	16.20	722.40	60.30	7.06
TiCl ₄				

1 6

Table 1. Photovoltaic parameters of DSSCs with different types of photoanodes

As it is evident from figure 3 and table 1, integration of compact P90 layer in the conventional photoanode of DSSC, increases the photocurrent generation of the device significantly and thereby enhancement in the overall efficiency. Similar effect has been reported by several other groups [20-22]. According to manufacturer's specifications, the particle size of the P90 is 14 nm. Bandara et al has observed a formation of homogeneous crack free compact layer from this P90, which act as a semiconducting shielding for the back electron transfer through the interface of P90/P25 [22]. Therefore, introduction of this P90 layer minimizes the back electron transfer from the FTO surface to the inner side of the DSSC and there by reduces the electron recombination with dye cations as well as with the redox species available in the electrolyte. As a result of that, J_{sc} is increased and hence the higher efficiency could be obtained in these devices. Moreover, the introduction of P90 layer between FTO and P25 improves the interfacial contacts between P25 layer and FTO surface as reflected by the increase in filling factor [23]. The increase of the J_{sc} after TiCl₄ treatment of TiO₂ photo anode could be very likely due to the formation of titania layers on top of TiO₂ particles which leads to an increase of surface roughness causing to increase in dye loading amounts and crosslinking between TiO₂ particles which yielding faster charge transport as observed by the others [24]. In order to further improve the performance of the device, another layer of TiO_2 was fabricated on the top of the above mentioned P25 mesoporous TiO₂ layer before the TiCl₄ treatment. This layer was applied either by using P25 (Photoanode D) or a Titania Nano Tubes (TNT) (Photoanode E). These two photanodes were then treated with TiCl₄ independently and DSSCs were fabricated with them and tested the device performances. The I-V curves of the above four devices are shown in the Figure 4, while the table 2 summarizes their photovoltaic parameters. As it can be seen from the figure and the table, the incorporation of nano tube layer significantly enhanced the short circuit current density and thereby increases the overall efficiency of the device. As observed by the several researchers the TiCl4 treatment further enhances the overall efficiency of the device. The comparison between cells with photoanodes D and F and also between cells with E and G photoanodes clearly shows that the introduction of the top layer consisting of TNT nanorods can be used to enhanced the short circuit photocurrent density and hence the efficiency significantly.



Figure 4. I-V curves of DSSCs based on four types of TiO₂ photoanodes D, E, F and G

Type of the photo	J _{sc}	V _{oc}	FF	η
anode	$(mA cm^{-2})$	(mV)	(%)	(%)
D	14.36	724.9	65.6	6.83
Ε	15.60	773.5	63.1	7.62
F	15.16	723.3	64.6	7.08
G	16.91	783.4	62.7	8.31

Table 2. Parameters of DSSCs made with different layered structures of TiO₂

The SEM images of the cross sections of the TiCl₄ post treated photoanodes, E (P90+ P25/P25 and G (P90 + P25/TNT) taken with Zeiss Model EVO LS15 SEM are shown in Figure 5.



Figure 5. SEM images of the cross sections of the TiCl₄ post treated photoanodes, E (P90+ P25/P25 and G (P90 + P25/TNT)

According to the SEM images shown in Figure 5, the average total thickness of the TiCl₄ treated P90+P25/P25 photoanode is about 25 μ m and the TiCl₄ treated P90+P25/TNT photoanode is about 17.0 μ m with a thickness of 1.61 μ m of the TNT layer as shown in the Figure 5 (b). It has been reported that various TiO₂ nano structures like elongated bead shape, nano tubes, nano rods, larger nano particles (~ 200 - 400 nm) etc can act as a scattering layer within a photoanode and enhance the light absorption by scattering [11, 25,26]. Similarly, in this work also randomly distributed titania nanotube 3D network with nanotubes of length 200-300 nm can be expected to scatter the incident light in different directions effectively resulting a substantial increase in light absorption. Therefore, observed enhancement in J_{sc} values are most likely to be due to the improved light harvesting by multiple scattering events by the TiO₂ network structure in the composite photoanode.

3.3. EIS analysis

Figure 6 (a) shows the Nyquist plots of the electrochemical impedance spectra of DSSCs with photoanodes D, E, F and G measured in the frequency range from 1×10^{-2} to 1×10^{6} Hz. Each Nyquist plot shows three semicircles. The larger semicircle in the low frequency range is related to the charge transport/accumulation at dye-attached TiO₂/electrolyte interface resistance (R_{ct2}), and the smaller semicircle in the high-frequency region is related to the charge-transfer resistance of the Pt counter electrode/electrolyte interface (R_{ct1}) [18, 19].



Figure 6. (a) Nyquist plots and (b) Bode phase plots, taken for DSSCs with photoanodes D, E, F and G

The impedance parameters were extracted using the equivalent circuit model (inset of Fig. 6 (a)), and the fitted lines are shown as solid lines in the Nyquist plots. The calculated values of the series resistance (R_s), the charge-transfer resistance of the Pt/electrolyte interface (R_{ctl}) and the charge-transfer resistance of the TiO₂/electrolyte interface (R_{ct2}) based on the equivalent circuits for the DSSCs with three types of photoanodes are tabulated in Table 3.

Table 3. Series resistance (R_s), charge-transfer resistance of the Pt/electrolyte (R_{CT1}), charge-transfer resistances of the TiO₂/electrolyte (R_{CT2}) of DSSCs with photoanode D, E, F and G.

Photoanode Type	$R_{ m s}\left(\Omega ight)$	$R_{ ext{ct1}}\left(\Omega ight)$	$R_{ ext{ct2}}\left(\Omega ight)$	$R_{ ext{ct3}}\left(\Omega ight)$	$J_{\rm sc}$ (mA	$V_{\rm oc}({ m mV})$	Eff %
					cm ⁻²)		
D: P90/ P25/P25	13.80	10.10	10.10	4.93	14.36	724.9	6.83
E: P90/ P25/P25	+ 14.20	1.72	12.6	3.53	15.16	723.3	7.62
TiCl ₄							
F: P90/ P25/TNT	17.80	3.91	6.55	17.7	15.60	773.5	7.08
G: P90/P25/TNT	+ 12.90	3.40	7.74	18.4	16.91	783.4	8.31
TiCl ₄							

When comparing the charge transfer resistance values extracted from the equivalent circuit analysis of the Nyquist plots, the solar cells with P90/P25/TNT photoanodes have relatively lower values for R_{ct1} and R_{ct2} compared to the solar cells with P90/P25/P25 photoanodes. Therefore, the titania nanotube (TNT) structure appears to improve the interfacial contacts between the photoanode and the electrolyte thereby increasing the J_{sc} and enhancing the efficiency.

The Bode phase plots derived from EIS spectra are shown in shown in Figure 6 (b). The peak frequencies at the TiO₂ /electrolyte interfaces of DSSCs fabricated with above photoanodes are also shown in the same. The values of the characteristic low-frequency peak f_{max} and the values of the corresponding electron lifetime (τ_e) as determined from the values of f_{max} are tabulated in Table 4 along with V_{oc}, J_{sc}, Eff values of the DSSCs made with above four types of photoanodes, D, E, F and G. The electron lifetime (τ_e) values determined from the bode phase plots are lower for the cells with P90/P25/TNT photoanodes than for cells with P90/P25/P25 photoanodes. Shorter recombination lifetime means faster recombination [23, 27-30]. Therefore, presence of TNT layer as a second layer

instead of P25 layer promotes nonradiative recombination either with dye cation or I_3^- redox species [29].

Photoanode Type	$f_{\rm max}$ (Hz)	$\tau_{\rm e}~({\rm mS})$	$J_{ m sc}$	$V_{ m oc}$	η (%)
			$(mA cm^{-2})$	(mV)	
D: P90/P25/P25	12.97	12.27	14.36	724.9	6.83
E: P90/P25/P25 + TiCl ₄	12.77	12.46	15.16	723.3	7.08
F: P90/P25/TNT	18.05	8.82	15.60	773.5	7.62
G: P90/P25/TNT + TiCl ₄	17.77	8.96	16.91	783.4	8.31

Table 4 . Electron lifetimes (τ_e) extracted from bode phase plots

3.4. Dark I-V analysis

Dark *I-V* charateristics for the DSSCs based on four different types of photoanodes D, E, F and G are shown in Figure 7. The onset reverse breakdown voltages are tabulated in Table 5. When a dye sensitized solar cell is in action by generating electricity from light, it goes through several interfacial electron transfer processes. These are: (a) dye excitation, (b) electron injection from excited dye to TiO_2 semiconductor photoanode and from the redox couple to dye cation, (c) dye regeneration and (d) electron recombination with dye cation and redox electron. The recombination with redox species is referred as the dark current.



Figure 7. Dark I-V charateristics for the DSSCs fabricated with photoanodes D, E, F and G.

Table 5. Onsets of reverse breakdown voltages of DSSCs fabricated with D, E, F and G photoanodes

Photoanode type	Reverse breakdown voltage (mV)	$V_{\rm oc}~({\rm mV})$
D: P90 + P25/P25	-250	724.9
E: P90 + P25/P25 + TiCl ₄	-310	723.3
F: P90 + P25/TNT	-351	773.5
G: P90 + P25/TNT + TiCl ₄	-353	783.4

The recombination that occurs at TiO₂ conduction band to redox electrolyte interface plays a major role in determining the photo voltage [23,27]. Therefore, a higher onset breakdown voltage gives a higher open circuit voltage due to less recombination with I_3^- redox species. Although the recombination is faster with dye cations, more electrons can be generated within the cell and lower interfacial resistance helps to transfer the electrons easily in the forward direction. Therefore, the overall effect gives a much

12th International Symposium on Modern Opt	ics and Its Applications (IS	SMOA)	IOP Publishing
Journal of Physics: Conference Series	1552 (2020) 012002	doi:10.1088/	1742-6596/1552/1/012002

higher photocurrent. Further, the open circuit voltage is higher for the cells with P90/P25/TNT compared to cells with P90/P25/P25 in agreement with results reported by several research groups obtaining higher Voc values for TiO2 nanotube based DSSCs [20,32,33]. Many research investigations are in progress to minimize the charge carrier recombination in DSSCs with TiO₂ naoparticle (TNP) based photoanodes. 1-D structures such as TNT are found to be promising substitute materials for the TNPs in DSSCs as they provide direct electron pathways and fast electron transport reducing charge carrier recombination. In 2014, Akilavasan et al. has reported a DSSC with an efficiency of 1.07% comprising with bare TNT photoanode and increased efficiency of 7.04% by post treatment with high concentrated TiCl₄ [20]. In another context, Xu et al. [34] has explored the possibility of fabricating double layered photoande with nanocrystal/nanotube structure exhibiting higher efficiency then the single layered structured DSSCs. They were able to obtain 6.15% efficiency in DSSCs with above double layered structure. DSSCs with single layered nanoparticle photoanode showed an efficiency of 4.25% while the photoanode fabricated with bare nanotubes showed an efficiency of 0.37%. Hafez et al. [35] also reported a DSSC with double layered photoanode structure consisting with nanoparticles/nanorods and obtained a significantly higher efficiency (7.1 %) in comparable with 4.4% and 5.8 % efficiencies obtained for the DSSCs having either only nanorods or nanoparticles photoanodes respectively. As they have discussed, the 1D TiO₂ electrodes with nanorods or nanotubes or both can enhance the light harvesting and straight pathways for the electron transportation through the photoanode while minimizing the light loss due to back scattering. In 2012 Xin et al. [36] also reported a dye sensitized solar cell based on a nanoparticle/nanotube bilayer structure. Here the electrochemical anodization of Ti was carried out to fabricate oriented TNTs on top of nano particles. They reported DSSCs with maximum power conversion efficiency of 8.02%.

In our study we have employed a low cost technique to fabricate double layered structure with TNT on top of the nanoparticle layer of TiO_2 by electrophoretic deposition method and reports a novel method of achieving an efficiency of 7.62% in DSSCs. Comparison was also done with the DSSCs fabricated in conventional method having a double layer of nanoparticles. Further improvements in the efficiency of DSSCs is achieved by TiCl₄ post treatment on the above double layered TNT based photoanode and obtained an efficiency of 8.31% with short circuit current density of 16.91 mA cm⁻² and open circuit voltage of 783.4 mV.

4. Conclusion

Considerable enhancement in the efficiency of DSSC can be achieved by incorporating hydrothermally synthesized TiO_2 nanotube layer (TNT) in to the conventional photoanode of the device. DSSCs with 8% overall light to electricity conversion efficiency can be fabricated with the proposed FTO/P90/P25/TNT structure of photoanode with $TiCl_4$ post treatment. The effective light harvesting due to the enhanced light scattering in the photoanode is indicated to contribute towards this efficiency enhancement as reflected by the increment in the photocurrent of these DSSCs with nanotubes. Although incorporation of this TNT layer in the photoanode increases the rate of recombination in the device as reflected by the lower electron lifetime. However, the increment in the photocurrent generation due to the enhanced light scattering overwhelmed over negative effect ending up with overall enhancement in the device efficiency.

References

- [1] Regan B O, Gratzel M 1991 Nature 353 737
- [2] Grätzel M 2003 J.Photochem. and Photobiol. C: Photochemistry Reviews 4 145
- [3] Zhu K, Kopidakis N, Neale N R, Lagemaat J V, and Frank A J, 2006 *J. Phys. Chem. B* **110** (50) 25174
- [4] Roy P, Albu S P and Schmuki P 2010 *Electrochemistry Communications* **12** 7 949
- [5] Huang Q, Zhou G, Fang L, Hua L and Wang S H 2011 Energy & Environmental Science **4 6** 2145

Journal of Physics: Conference Series

1552 (2020) 012002 doi:10.1088/1742-6596/1552/1/012002

- [6] Feng X, Zhu K, Frank A J, Grimes C A, Mallouk T E 2012 Angew. Chem. Int. Ed. 124, 11, 2781
- [7] Kim G S, Seo H K, Godble V P, Kim Y S, Shin H S, 2006 Electrochemistry Communications, 8, 6 961
- [8] Maheswari D and Sreenivasan D 2015 Applied Solar Energy **51** 2 112
- [9] Wang J and Lin Z, 2012 Chem. Asian J. 7 2754
- [10] Yang S C, Yang D J, Kim J K, Hong J M, Kim H G, Kim I D, Lee H J 2008 Adv. Mater. 20 1059
- [11] Dissanayake M A K L, Divarathna H K D W M N, Dissanayake C B, Senadeera G K R, Ekanayake P M P C, Thotawattage C A 2016 Journal of Photochemistry and Photobiology A: Chemistry 322 110
- [12] Ferber J and Luther J 1998 Sol. Energy Mater. Sol. Cells, 54, 1–4 265
- [13] Rothenberger G, Comte P, and Grätzel M 1999 Sol. Energy Mater. Sol. Cells 58 3 321
- [14] Wang Z S., Kawauchi H , Kashima T , H. Arakawa H 2004 Coordinat. Chem. Rev. 248 1381
- [15] Vargas W E and Niklasson G R A 2001 Appl. Opt. 40 1 85
- [16] Hore S. Nitz P, Vetter C, Prahl C, Niggemann M, Kern R 2005 Chem. Commun. 15 2011
- [17] Hoda H, Zhang T. Qinghua L, Jihuai W 2010 Nanotechnology, Science and Applications, 3 45
- [18] Nakahira A, Kubo T and Numako, 2010 Inorg. Chem.49 5845
- [19] Liu N, Chen X, Zhang J and Schwank J W 2014 Catalyst today 225 34
- [20] Akilavasan J, Wijeratne K, Gannoruwa A, Alamoud A R M and Bandara J 2014 *Appl. Nanosci.* 4 185
- [21] Choi H, Nahm C, Kim J, Moon J, Nam S, Jung D, Park B 2012 Current Applied Physics 12 737
- [22] Bandara T M W J, Fernando H D N S, Rupasinghe E J, Ratnasekera J L, Chandrasena P H N J, Furlani M, Albinsson I, Dissanayake M A K L, Mellander B.E 2016 Ceylon Journal of Science 45 2 61
- [23] Ariyasinghe Y P Y P,Wijayarathna T R C K, Kumara I G C K, Jayarathna I P L, Thotawatthage C A, Gunathilake W S S, Senadeera G K R, Perera V P S 2010 *Journal of Photo chemistry and Photobiology A: Chemistry* 217 1 249
- [24] Pan M, Huang N, Zhao X, Fu J, and Zhong X 2013 Nanomaterials 760685
- [25] Hoda H, ZhangL, Qinghua L, Jihuai W 2010 Nanotechnology, Science and Applications 3 45
- [26] Tsai C, Tsai Y, Huang T, 2013 Journal of Nanomaterials Article ID 915461
- [27] Dissanayake M A K L, Kumari J M K W, Senadeera G K R, Thotawatthage C A 2016 Journal of Applied Electrochemistry **46** 47
- [28] Hsu C, Lee K, Huang J T, Lin C, Lee C, Wang C, Tsai S, Ho K 2008 Electrochimica Acta 53, 25, 7514
- [29] Dissanayake M A K L, Kumari J M K W, Senadeera G K R and Thotawatthage C A 2016 Journal of Applied Electrochemistry **46**, 47
- [30] Hsu C, Lee K, Huang J T, Lin C, Lee C, Wang C, Tsai S and Ho K 2008 *Electrochimica Acta*, 53 25 7514
- [31] Xin X, Wang J, Han W, Ye M, Lin Z 2012 Nanoscale, 4, 964
- [32] Kim G S, Seo H K, Godble V P, Kim Y S, Yang O B, Shin H S 2006 Electrochem Commun 8 961
- [33] Xin X, Wang J, Han W, Ye M, Lin Z 2012 Nanoscale 4, 964
- [34] Xu, H, Tao X, Wang D T, Zheng Y Z and Chen, J F 2010 *Electrochimica Acta*, **55** 2280
- [35] Hafez H, Lan Z, Li Q and Wu J 2010 Nanotechnology, Science and Applications 3, 45
- [36] Xin X, Wang J, Han W, Ye M and Lin Z 2012 Nanoscale 4 964