

Research Article

Development of Well-Aligned TiO₂ Nanotube Arrays to Improve Electron Transport in Dye-Sensitized Solar Cells

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We fabricated well-aligned one-dimensional (1-D) titania nanotubes (TNT) on transparent conducting oxide (TCO) by anodization of Ti foil. Different lengths of TNTs were prepared by varying the applied potential (70 V) time, and we investigated the performance of these TNTs in dye-sensitized solar cells (DSSCs), transplanted onto a 6 μm TNP adhesion layer. The fabricated TNTs arrays (length 15 μm) photoelectrode showed 24% increased efficiency compared to the TNP photoelectrode of 17 μm thickness. We further investigated the performances of DSSCs for the TNTs (1 wt%) incorporated TNP photoelectrode and obtained 22% increased efficiency. The increased efficiency of the pure TNTs arrays and TNT-mixed TNP photoelectrodes was attributed to the directional electron movement of TNTs and light scattering effect of the TNT with the decreased rate of back electron transfer. The anodized and fabricated TNTs and DSSCs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), and electrochemical impedance spectroscopy (EIS).

1. Introduction

The mesoporous nanostructured film of titanium dioxide (TiO₂) nanoparticles (TNPs) with anatase crystalline polymorph has been used as unique materials over the last two decades as an efficient photoelectrode material for dye-sensitized solar cells (DSSCs) [1–3]. However, the structural disorder or trap states of TNP led to the elongation of electron collecting path and ultrafast scattering of free electrons, which in turn increases the probability of recombination at the interface between TNP and electrolyte or dye to reduce electron collection efficiency [4].

The pioneering work of Mor et al. [5] has led to the recent application of well-ordered one-dimensional (1-D) titanium nanotube (TNT) arrays for DSSCs. TNTs has attracted enormous interest in DSSCs due to their directional electron movement, photoconversion efficiency of over 16.25% and quantum efficiency of over 80% under 320–400 nm illumination [6], incident photon-to-current

conversion efficiency (IPCE) of the N719 adsorbed TNT photoelectrode was 70–80% at 450–650 nm wavelength, and the suppressed recombination with improved collection efficiency [7]. Based on the fabrication processes, TNT-DSSCs are classified into front-side illuminated DSSCs and back-side illuminated DSSCs. To fabricate the TNT arrays photoelectrodes of front-side illuminated DSSCs, Ti thin film was generally deposited to FTO glass by d.c. sputtering deposition [8] and sol-gel method [9], which only provide a very thin TNT film. However, for the development of efficient DSSCs, conventional thickness of the TNP layer is around 15 μm [4]. On the other hand, photoelectrodes of back-side illuminated DSSCs are fabricated by anodizing Ti foil and longer TNT arrays can be easily grown on Ti foil. Front-side illuminated DSSCs usually show improved light harvesting compared to the back-side illuminated DSSCs with the same thickness of nanotube arrays, because of the light absorption by the iodine electrolyte and light reflection by platinum (Pt) counterelectrode for the latter

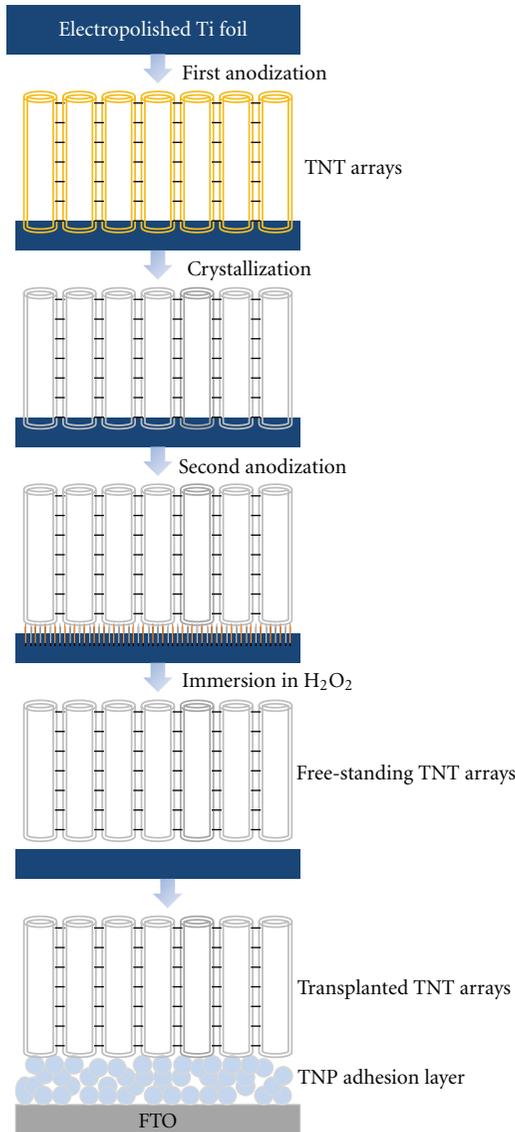


FIGURE 1: Schematic for the preparation of anodized TNT arrays, detachment, and transplantation onto TNP.

[10]. Therefore, for the development of efficient TNT-DSSCs, longer nanotube arrays with front-side illumination are a prerequisite. There are reports on the development of longer transplanted nanotube arrays onto fluorine doped tin oxide (FTO) for high efficient DSSCs [4, 11, 12].

Herein, we have investigated the performance of DSSCs based on the transplanted longer nanotube arrays for front-side illumination. Varying lengths of the nanotube arrays were transplanted onto the FTO by using a TNP adhesion layer and the performance was compared with the TNP-DSSCs. Moreover, performance of the TNT (1 wt%) incorporated into TNP photoelectrode was also investigated and compared. Figure 1 shows the schematic for the preparation of anodized TNT arrays, detachment, and transplantation onto TNP adhesion layer.

2. Experimental

2.1. Preparation of TNT. Titanium (Ti) foil (0.25 mm thickness, 99.7% purity, Aldrich, USA) was cleaned by using de-ionized (DI) water and acetone, and dried with N₂ purging. The cleaned and dried Ti foil was electropolished into the mixture solution of perchloric acid (HClO₄, 60%), butanol, and ethanol (1:6:9 v/v) for 3 min at -10°C with the applied potential of 20 V. Two-step anodic oxidation was carried out to prepare the well-ordered TNT nanotube arrays. Firstly, the electropolished Ti foil was anodized at a constant potential of 70 V in the ethylene glycol (C₂H₆O₂) solution containing ammonium fluoride (NH₄F) (0.38 wt%) and H₂O (1.79 wt%) at 20°C followed by thermal annealing at 500°C for 30 min in an electric muffle furnace (J-FM28, JISICO, Korea) in presence of air. Secondly, the first anodized Ti foil was further anodized in the same solution at a constant potential of 20 V for 3 h at 20°C. The detachment of the anodized TNTs arrays were carried out by immersion in 10% H₂O₂ solution for 24 h.

2.2. Transplanting of TNT Arrays. In order to prevent the recombination between FTO and electrolyte and for the attachment of TNTs arrays on FTO a 6 μm thick adhesion layer of titanium nanoparticles (TNP) (Degussa, P-25, Germany) paste was used. The TNP paste and 1 wt% TNT mixed TNP paste was prepared by the procedure reported elsewhere [2]. Detached TNT arrays were transferred onto the TNP layer on FTO by using tweezers. The transplanted TNTs arrays were then sintered at 500°C for 30 min in the presence of air.

2.3. Preparation of the Photoelectrodes. TNTs arrays photoelectrodes were prepared by transplanting the different lengths of TNT (e.g., 8 μm, 11 μm, and 15 μm) onto the TNP adhesion layer. A 17 μm TNP photoelectrode was also prepared to compare the performance. Front side illumination of the DSSCs having the transplanted TNTs and TNP photoelectrodes were fabricated. For simplicity these cells were denoted as cell type-A. Moreover, the performance of the incorporation of TNTs into TNP photoelectrodes was also investigated, where the thickness of the purely TNP photoelectrodes was 7.5 μm and 13 μm, and 1 wt% TNT (8 μm) containing TNP photoelectrode was 8 μm. These cells were denoted as type-B.

2.4. Device Fabrication. The fabricated and sintered TNTs arrays, TNTs/TNP, and TNP photoelectrodes on FTO were immersed in the 0.4 mM ethanolic solution of *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis-tetrabutylammonium (N719) dye for 24 h. The counter electrodes were prepared by spin coating of 5 mM ethanolic solution of chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) on FTO and sintered in an electric muffle furnace at 400°C for 20 min. The dye-loaded photoelectrodes (active area *ca.* 0.09 cm²) and platinized counterelectrodes were sandwiched with 50 μm thick surlyn film as a spacer and sealing agent. The electrolyte solution having composition of

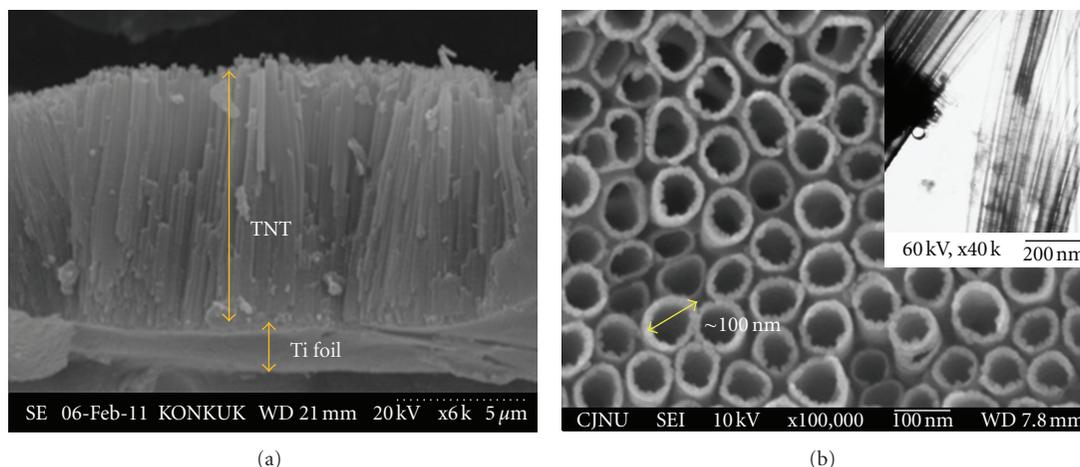


FIGURE 2: SEM images of TNT arrays by anodic oxidation of electropolished Ti foil at a constant voltage of 70 V: (a) cross-sectional image of TNT arrays, (b) top view of the TNT arrays with inset showing the TEM images of TNT.

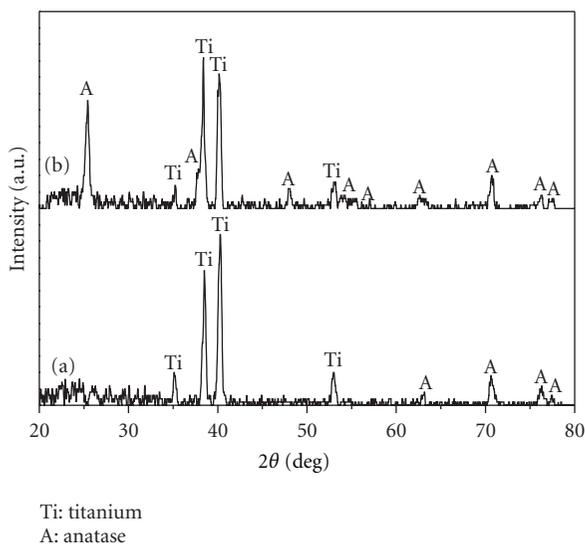


FIGURE 3: XRD pattern of TiO_2 nanotube arrays: (a) as-anodized TiO_2 nanotube arrays, (b) annealed TiO_2 nanotube (TNTs) arrays at 500°C .

0.5 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.1 M I_2 , and 0.5 M 4-*tert*-butylpyridine (*t*BP) in acetonitrile/valeronitrile (85:15 v/v) was injected into the cell through the drilled holes of the counterelectrode and sealed with a transparent scotch tape.

2.5. Instrumentation. Electropolishing and anodization of Ti foil were carried out by using a dc power supply (Sorensen, XHR-150/7, USA). The morphology and structure of the prepared anodized TNTs were characterized by using a scanning electron microscope (SEM, Hitachi S-3000N, Japan), a tunneling electron microscope (TEM, Jeol, JEM-1200 Ex II, Japan), and an X-ray diffractometer (Philips, X'pert, Netherland) using $\text{Cu K}\alpha$ radiation of $\lambda = 0.15406$ nm in the scan range $2\theta = 20\text{--}80^\circ$.

The simulated light AM 1.5 was generated by using a solar simulator (McScience, Polaronix K201, Korea) furnished with a 200 W Xenon lamp. A photovoltaic power meter (McScience, Polaronix K101 LAB20, Republic of Korea) was used to measure the current density-voltage (J - V) curves with the adjusted light intensity to 100 mWcm^{-2} (1 sun) by a standard mono-Si solar cell (PV Measurement Inc, PVM 396, USA), that is certified by the National Renewable Energy Laboratory (NREL, USA). Electrochemical impedance spectra (EIS) were measured by using an impedance analyzer (Zahner-Elektrik GmbH & Co. KG, IM6ex, Germany) under open circuit and dark conditions in the frequency range of 1 MHz–1 mHz with the ac amplitude of 10 mV.

3. Results and Discussion

Figure 2 shows the cross-sectional and top-view SEM images of the TNTs arrays on Ti foil obtained by anodic oxidation. Well-ordered TNT arrays were grown successfully onto Ti foil with an average tube diameter and wall thickness of *ca.* 85 nm and 10 nm, respectively. The top view of the SEM image indicated the formation of closed packed and well-ordered nanotube arrays. Inset of Figure 2(b) shows the HRTEM images of the TNTs with the tube diameter ~ 85 nm that clearly correlated with the SEM data. Figure 3 shows the X-ray diffraction (XRD) pattern of the anodized Ti before and after sintering. This demonstrated that before annealing most of the XRD peaks arose from the Ti due to the amorphous phase of TiO_2 nanotube. After annealing at 500°C for 30 min, the number of peaks and the intensity of anatase polymorph of TiO_2 nanotube increased due to phase transition from amorphous to crystalline.

Figure 4 shows the cross-sectional SEM image of transplanted TNT arrays on FTO and top view of 1 wt% TNT-mixed TNP photoelectrode. The $6\text{ }\mu\text{m}$ thick TNP adhesion layer was used for transplanting TNT arrays. Electrons should pass through the adhesion layer to reach the FTO.

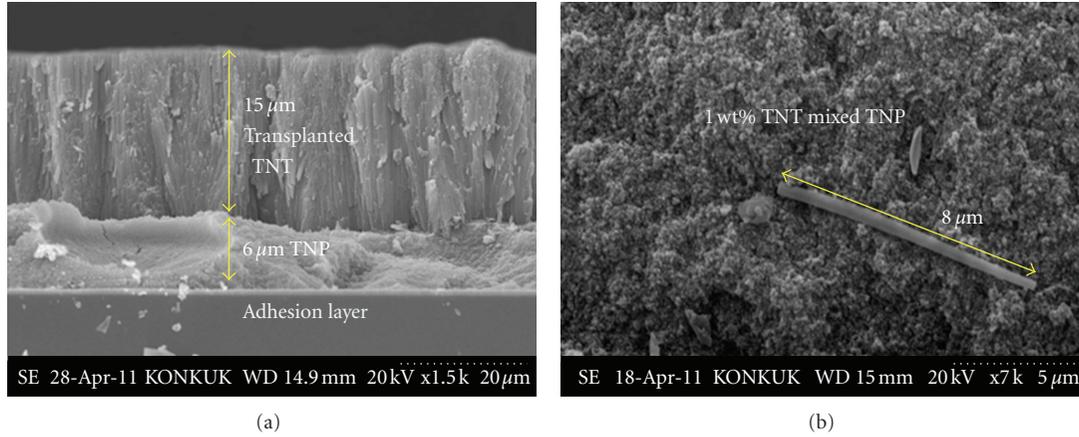


FIGURE 4: Scanning electron microscopic images (SEM): (a) cross-sectional image of transplanted TNT onto TNP, and (b) top view of 1 wt% TNT-mixed TNP photoelectrode.

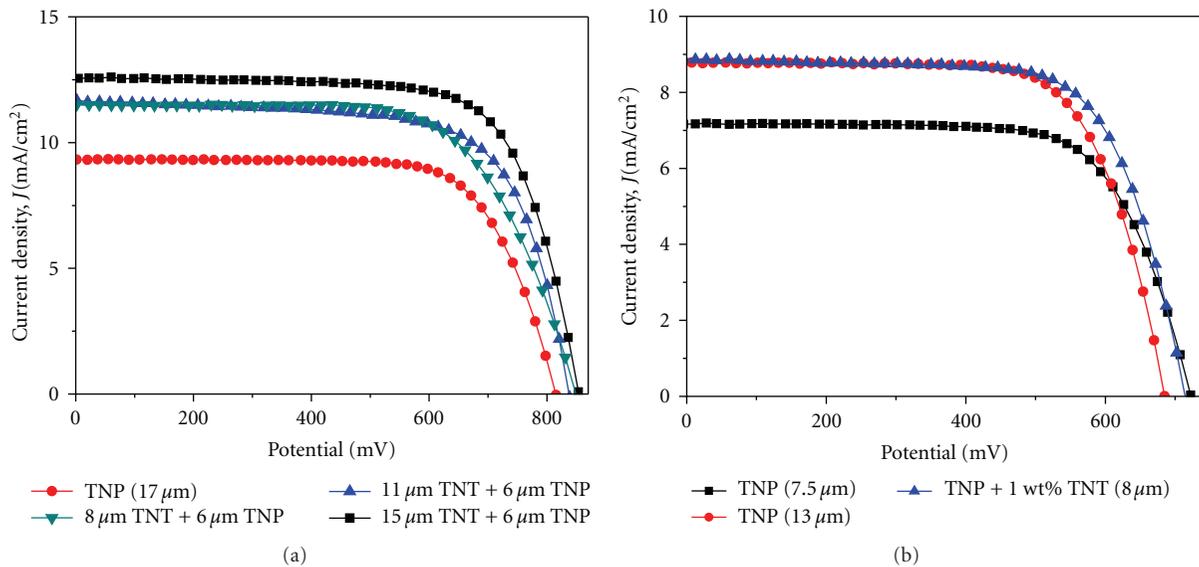


FIGURE 5: Current density-voltage (J - V) characteristics of different DSSCs of cell type-A (a) and cell type-B (b).

Although the thickness of adhesion layer in our experiment is too thick for efficient electron movement, the thickness of the adhesion layer should be very low. Figure 4(b) clearly demonstrated the TNTs (1 wt%) incorporated TNP photoelectrode.

The current density-voltage (J - V) characteristics and parameters based on the different types of photoelectrodes (type-A, and type-B) are summarized in Figure 5 and Table 1. The photovoltaic performance of the transplanted TNT-based DSSCs increased by increasing the lengths of TNT that is mainly responsible for increasing the short circuit current density (J_{sc}). The highest J_{sc} of 12.56 mA/cm² was observed for the 15 μ m transplanted TNT photoelectrode, while the J_{sc} for the 17 μ m TNP film was 9.32 mA/cm². The J_{sc} of the shorter transplanted TNTs (8 μ m and 11 μ m) were also higher than the J_{sc} of 17 μ m TNP film. This improved J_{sc} of the TNT-array-based DSSCs was attributed to ultrafast and directional electron movement, curtail

electron diffusion length, and the light scattering effect [13]. In order to investigate the effect of the anodized TNT on to the TNP photoelectrode, we have further developed DSSCs of type-B. Current density-voltage results demonstrated that the 1 wt% anodized TNT-mixed TNP photoelectrode showed the improved photovoltaic performance compared to the TNP photoelectrode of 7.5 μ m and 13 μ m thickness. The improved performance of the 1 wt% TNT mixed TNP photoelectrode was mainly for the 24% and 1.13% increased of J_{sc} compared to the two different TNP film, respectively that is assumed to be the responsible for the mentioned physical properties of TNTs.

The kinetics of the electron transfer processes at transplanted TNT arrays photoelectrode|electrolyte, TNP photoelectrode|electrolyte, and 1 wt% TNT-mixed TNP photoelectrode|electrolyte interfaces were studied by electrochemical impedance spectroscopy (EIS). The impedance spectra exhibited in the form of Bode phase plot and

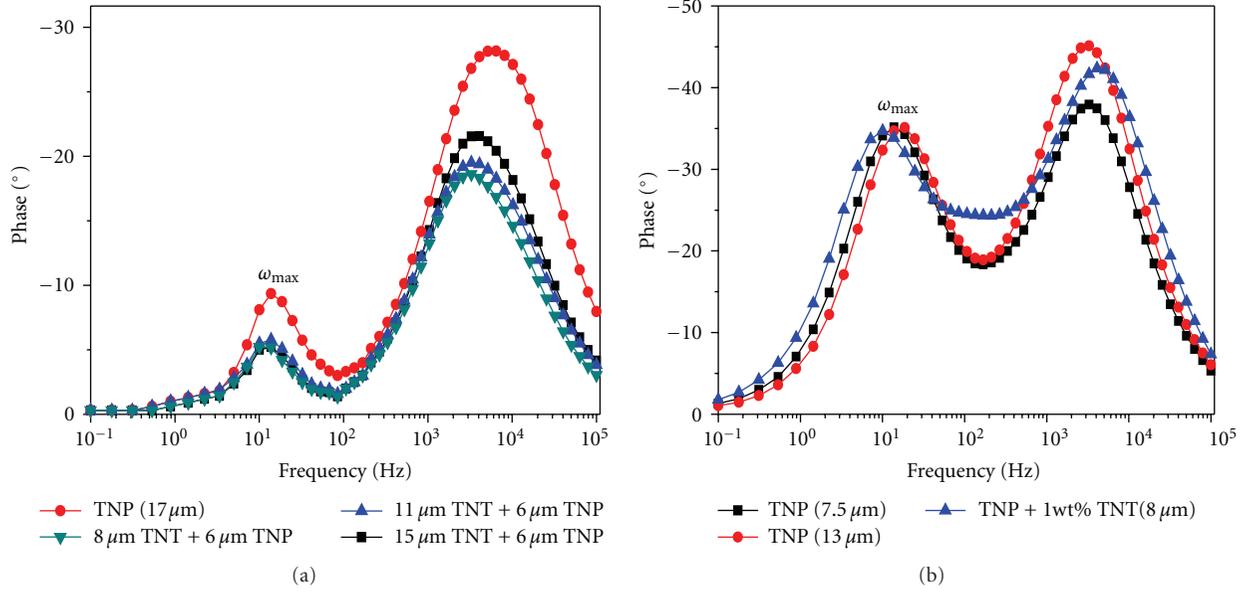


FIGURE 6: Bode plots from electrochemical impedance measurement of DSSCs under dark conditions of (a) cell type-A, and (b) cell type-B.

TABLE 1: Photovoltaic and kinetic parameters of cell type-A, and cell type-B based DSSCs.

DSSCs	Photoelectrode	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)	$k_{T/E}$ (S ⁻¹)
Cell type-A	TNP (17 μ m)	9.32	815	71.75	5.45	13.7
	TNT (8 μ m) + TNP (6 μ m)	11.50	848	66.57	6.50	11.2
	TNT (11 μ m) + TNP (6 μ m)	11.68	837	68.79	6.72	11.2
	TNT (15 μ m) + TNP (6 μ m)	12.56	853	71.76	7.70	11.2
Cell type-B	TNP (7.5 μ m)	7.16	722	70.23	3.63	24.7
	TNP (13 μ m)	8.78	684	70.45	4.23	32.4
	TNP + 1 wt% TNT (8 μ m)	8.88	714	69.92	4.44	18.6

the calculated kinetic information of the cells of type-A and type-B electrodes are summarized in Figure 6 and Table 1. The high frequency peak corresponds to the charge transfer at the Pt-counter electrode, and the uncovered FTO|electrolyte interface; the mid-frequency peak corresponds to the diffusion-recombination at the photoelectrode; the low-frequency peak is related to the ionic diffusion process in the electrolyte, which is often merged with the mid-frequency peak as in our data.

The rates of back electron transfer to I_3^- at the interfaces of different photoelectrodes|electrolyte ($k_{T/E}$) were estimated from the mid-frequency peak according to the following equation [14]:

$$\omega_{max} = k_{T/E}. \quad (1)$$

For the DSSCs of cell type-A, the use of TNT arrays photoelectrode decreased the rate of back electron transfer ($k_{T/E}$) compared to TNP photoelectrode, and our results demonstrated the $k_{T/E}$ values were independent of the nanotube arrays lengths up to 15 μ m. The decrease of the back electron transfer using TNTs arrays photoelectrode increases the open circuit potential (V_{oc}) for every case of TNT arrays

photoelectrodes, and maximum 38 mV increase of V_{oc} was observed for 15 μ m TNT arrays. On the other hand, the $k_{T/E}$ value of the TNT (1 wt%) mixed TNP photoelectrode was decreased from 32.4 S⁻¹ to 18.6 S⁻¹ compared to 13 μ m TNP photoelectrode and thereby increased the V_{oc} of 30 mV.

4. Conclusion

We have applied different lengths of TiO₂ nanotube arrays to front-side illuminated DSSCs with a transplanting process onto a TNP adhesion layer. The performance of the TNT transplanted DSSCs was compared with the TNP-based DSSCs. Front-side illuminated DSSCs based on transplanted TiO₂ nanotube arrays had a better efficiency of 24% than the TNP DSSCs. Further investigation of the 1 wt% TNTs incorporated TNP photoelectrode (8 μ m) showed an increased efficiency of 22% and 5% compared to 7.5 μ m and 13 μ m TNP photoelectrodes, respectively. Therefore, the transplanting process of TNTs along with the incorporation into TNP photoelectrode was an effective method to improve the efficiency of DSSCs and had great potential, which can overcome the limitation of TiO₂ nanoparticle structure.

The DSSCs performance is expected to improve by reducing the thickness of the adhesion layer and making clean surfaces of TNTs arrays. The transplanting TiO₂ nanotube arrays were effective to increase the power conversion efficiency of DSSCs.

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