Results in Physics 15 (2019) 102725

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.elsevier.com/locate/rinp

The effect of titanium (IV) chloride surface treatment to enhance charge transport and performance of dye-sensitized solar cell

N. Fadzilah M. Sharif[a,b,*], Suhaidi Shafie[a,c], M.Z.A. Ab. Kadir[d,e], W.Z. Wan Hasan[a], Muhammad Norhaffis Mustafa[f], Buda Samaila[c]

[a] *Department of Electrical and Electronics Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[b] *Department of Electrical and Electronics Engineering, Faculty of Engineering, UPNM, Kuala Lumpur 57000, Malaysia*
[c] *Institute of Advanced Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor Darul Ehsan, Malaysia*
[d] *Centre for Electromagnetic & Lightning Protection (CELP), Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[e] *Institute of Power Engineering (IPE), Universiti Tenaga Nasional, Kuala Lumpur 57000, Malaysia*
[f] *Department of Chemistry, Faculty of Science, Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia*

ARTICLE INFO

Keywords:
Charge collection efficiency (CCE)
Charge transport
DSSC surface treatment

ABSTRACT

In this study, the photovoltaic and electrochemical characteristics of the dye-sensitised solar cell (DSSC) after titanium (IV) chloride ($TiCl_4$) treatment on a TiO_2 photoelectrode were investigated. Photoelectrodes of untreated, pre-$TiCl_4$ and post-$TiCl_4$ treatment were prepared to form a complete DSSC. The photoelectrode was sensitised in 40 mM of $TiCl_4$ solution at 80 °C for 30 min, and then it is sintered at 500 °C. The morphology of photoelectrodes has been studied using FESEM, and it was found that, after $TiCl_4$ treatment, the particle necking and particle size of TiO_2 nanoparticles were increased significantly. Therefore, it improved the electron transfer path on the TiO_2 layer. Subsequently, the light absorption intensity after post-$TiCl_4$ treatments was increased due to strong adhesion and homogeneity of the TiO_2 layer on the FTO substrate, which results in higher current density and photon-conversion efficiency by 18.95 $mAcm^{-2}$ and 8.03% when compared to an untreated electrode at 12.1 $mAcm^{-2}$ and 4.08% (increment of 56.7% and 96.9%), respectively. Electrochemical impedance spectroscopy used to study the internal electrochemical characteristics of DSSC after the treatment. Thus, it proves that the treatment suppresses the charge recombination between TiO_2 and the electrolyte interface by increasing charge transfer resistance after post-$TiCl_4$ treatment by 24.06 Ω from 16.11 Ω for untreated photoelectrodes (increment of 49.39%). The electron lifetime also improved from 0.4 to 1.59 ms, which results in the enhancement of charge collection efficiency after post-treatment by 31.09% compared to the untreated electrode. Improvement of charge collection efficiency indicated that the $TiCl_4$ treatment had played an important role in charge separation and charge collection on the TiO_2 and electrolyte interface of DSSC.

Introduction

The dye-sensitised solar cell (DSSC) is a third-generation solar cell that offers several advantages over silicon cells due to economical and environmentally friendly device, which the DSSCs has shown its potential for future renewable solar electricity generation device [1–4]. It was first developed in 1991 by O'Regan and Gratzel. Recently the same group is announced the power conversion efficiency (PCE) is reached 14.1% [5]. However, despite the DSSC advantages, the PCE is still less than half compared to a crystal silicon solar cell. If the PCE of DSSCs can be enhanced, these cells could significantly reduce the fabrication cost compared to first and second-generation photovoltaic devices. To tackle this issue, designing a novel DSSC elements are crucial to generate better PCE.

DSSC consists of Fluorine-tin oxide (FTO) transparent electrode, electrolyte, counter, and photoelectrode elements. Photoelectrode contains dye sensitiser and the TiO_2 semiconductor layer. The TiO_2 layer is an essential part of DSSC since it will hold and transport excited electrons from the sensitiser to the external load [6,7]. TiO_2 semiconductor material is widely used in DSSC because it is abundant, low cost, and offers high photostability [8]. However, the use of TiO_2 in DSSC exposes random electron transport and high electron recombination between the TiO_2/dye/electrolyte interface, which slow electron diffusion and reduce the current density amount. To overcome this issue, chemical treatment using different precursor such as titanium (IV), indium (III) and zirconium (IV) oxide [9], titanium (III) chloride

---

* Corresponding author at: Department of Electrical and Electronics Engineering, Faculty of Engineering, UPNM, Kuala Lumpur 57000, Malaysia.
E-mail address: noorfadzilah@upnm.edu.my (N.F. M. Sharif).

https://doi.org/10.1016/j.rinp.2019.102725
Received 9 July 2019; Received in revised form 23 September 2019; Accepted 1 October 2019
Available online 04 October 2019

($TiCl_3$) [10], and titanium tetrachloride ($TiCl_4$) [11–15] on photoelectrode elements have been done by many researchers. However, $TiCl_4$ treatment is widely chosen to enhance the performance of DSSC due to its availability and low cost among precursors. From past research, the post-$TiCl_4$ treatment is proven to improve the morphology of TiO_2 structure and suppress the recombination rate of electrons between the TiO_2/dye/electrolyte interface. Many works prove the advantages of $TiCl_4$ treatments on the morphology and performance on DSSC, which enhanced charge transport [15], surface area [16], dye adsorption [17], and TiO_2 film purity [18]. Moreover, the treatments also improve the adhesion of the TiO_2 growth onto FTO glass, which enhances the conductivity of the TiO_2 semiconductor layer.

Although research on the $TiCl_4$ treatment was reported more than a decade ago, which generated better DSSC performance, little attention has been paid to the advantage of $TiCl_4$ treatments on prior and after TiO_2 paste deposition on photoelectrodes known as post-$TiCl_4$ at a concentration of 40 mM. Hence, this study investigates the enhancement of PCE and charge transport at concentration of 40 mM $TiCl_4$ where previous research used different parameters such as concentration and $TiCl_4$ immersing temperature during the treatment [15,20]. A concentration of the 40 mM of $TiCl_4$ solution chosen based on compatibility of materials used in previous work by Eunwoo et al. [20] where similar material namely graphene quantum dots will be incorporated in photoelectrodes for light harvesting enhancement [21].

A TiO_2 paste deposition method on photoelectrodes by screen printing is chosen in this work because it is a well-applied method for producing homogenous, thickness controllable, excellent printing characteristics, and porous film [22]. Furthermore, an enhancement of solar cell performance of PCE after post-$TiCl_4$ treatment have been studied by factors of TiO_2 nanoparticle necking, absorption intensity after sensitising dye, and TiO_2 growth on FTO surface in order to achieve better performance of DSSC.

Experimental method

Material

Titania powder (anatase) and titanium tetrachloride ($TiCl_4$) solution were purchased from Sigma Aldrich. Afterwards FTO glass with sheet resistance $< 15\,\Omega$/sq and T ~90% were purchased from Kaivo optoelectronic Technology. Also, the N-719 Dye, electrolyte, and polymer spacer of 25 µm were obtained from Solaronix Switzerland. Lastly, the platinum solution was added to the counter electrode. The platinum solution consists of isopropyl alcohol (IPA), and hexachloroplanitic acid hexahydrate was prepared in our lab. Ethanol, acetone, and IPA were obtained from Merck and used without purification. In this study, the morphology and thickness of untreated and treated photoelectrodes were studied using FESEM (FEI, NovaNanoSem230, Holland). The absorption intensity was measured by Ultraviolet spectroscopy of (Lambda 25, PerkinElmer, USA) to study the impact of the treatment on dye adsorption before and after the treatment. Electrochemical impedance spectroscopy (EIS) study was obtained by using Autolab PGSTAT204, Current-voltage performance of complete DSSC was obtained using (Keithley 2601, USA) solar simulator under the illumination of AM 1.5 simulated light with an intensity of $100\ \mathrm{mW\ cm^{-2}}$.

Synthesis of TiO_2 paste

Initially, solution A consisting of 6 g of TiO_2 powder with 0.5 ml acetic acid and DI water was ground for 5 min. Then 21 ml of ethanol was added and continued the grinding for 20 min. Next, 100 ml of ethanol was added to the mixture. The mixture was sonicated for 1 h to disperse the nanoparticles. Another mixture called solution B, which consisted of 38 ml ethanol and 3 g of ethyl cellulose, was stirred for 2 h to form a binder solution. Then both solutions A and B were stirred for 12 h, and both mixtures evaporated to reach about 1/10th the size from the initial volume.

$TiCl_4$ treatment

The $TiCl_4$ treatment applied in this study was modified from Ref. [19]. At first, the FTO glass of 2 cm × 2 cm were washed properly using acetone and IPA for 15 min to get rid of dust and other contamination, which resulted in better PV performance of DSSC. Then the FTO glass was dried and placed in the closed container to avoid contamination. The conductive side of the FTO glass was placed on top of the petri dish and immersed in a 40 mM $TiCl_4$ solution at 80 °C for 30 min. The concentration of $TiCl_4$ chosen in this work was based on Ref. [20] where similar material will be added in the future for light-harvesting enhancement. During the immersing process, $TiCl_4$ solution covered the whole FTO glass to make sure the coating process was homogeneous. Then the FTO glass was sintered at 500 °C for 30 min and cooled at room temperature. It was coated with $\sim 10 \pm 2\,\mu m$ TiO_2 paste by screen-printing technique with an active area of 1 cm^2. The TiO_2 coated glass was kept for 5–10 min to make sure the TiO_2 layer was homogenous. Then the FTO glass was sintered at 500 °C for 30 min. After cooling, the post-$TiCl_4$ treatment was done by immersing the FTO glass in 40 mM $TiCl_4$ solution. Finally, the FTO glass was sintered at 500 °C for 30 min and then cooled to 80 °C. The photoelectrode sintering temperature is chosen at 500 °C to evaporate the organic binder in TiO_2 paste to improve electrical conductivity between TiO_2 particles [23]. Thus, increase electron diffusion through the photoelectrode.

Preparation of DSSC photoelectrode and device assembly

After TiO_2 coating and post $TiCl_4$ treatment, the photoelectrode was subjected to dye adsorption using N-719 dye for 24 h. Ethanol was used to clean the TiO_2 film and remove any loose dye particle. To make a counter electrode, a 2 mM hexachloroplanitic acid hexahydrate and isopropyl alcohol (IPA) was mixed. Then the mixture was deposited on the FTO substrate. The substrate was sintered at 500 °C for 30 min to evaporate the solvent and lastly formed the platinum layer on the counter electrode by decomposing the acid at a high temperature. To make a complete cell of DSSC, an electrolyte was dropped between the FTO glass of the photoelectrode and the counter electrode, which were attached by a 25 µm polymer spacer to form a sandwich structure of the solar cell. The complete $TiCl_4$ treatment and DSSC fabrication process are depicted in Fig. 1.

Results

Field emission scanning electron microscopy (FESEM)

The morphology of untreated and $TiCl_4$ treated photoelectrodes was studied using FESEM. Fig. 2 (a,b,c) shows the cross-sectional SEM images of the incremental thickness of 8.98 µm, 9.05 µm, and 10.73 µm of untreated TiO_2 film, which includes pre-$TiCl_4$ and Post-$TiCl_4$ treatment on photoelectrodes respectively. A multilayer $TiCl_4$ treatment caused thickness increased from 8.98 µm to 10.73 µm (19.5% increment) due to the formation of another TiO_2 layer during hydrolysis of $TiCl_4$ treatment [14]. The method chosen to deposit the TiO_2 layer for photoelectrodes is vital in order to provide a porous structure. In this study, the screen-printing technique was applied to prepare a porous structure of TiO_2 thin film. Fig. 3(a)–(f) shows the photoelectrode morphology using FESEM and particle size distribution of TiO_2 films with the Gaussian fitting curve. Fig. 3(a) shows the nonhomogeneous and weak attachment of TiO_2 particles for untreated photoelectrode, which may reduce electrical conductivity and resulting low electron transfer within TiO_2 particles to external circuits. In this work, $TiCl_4$ is proven to enhance the morphology of the TiO_2 layer because another layer of TiO_2 nanocrystal was grown before and after TiO_2 paste deposition. Thus, after $TiCl_4$ treatment, the growth of the TiO_2 film on the

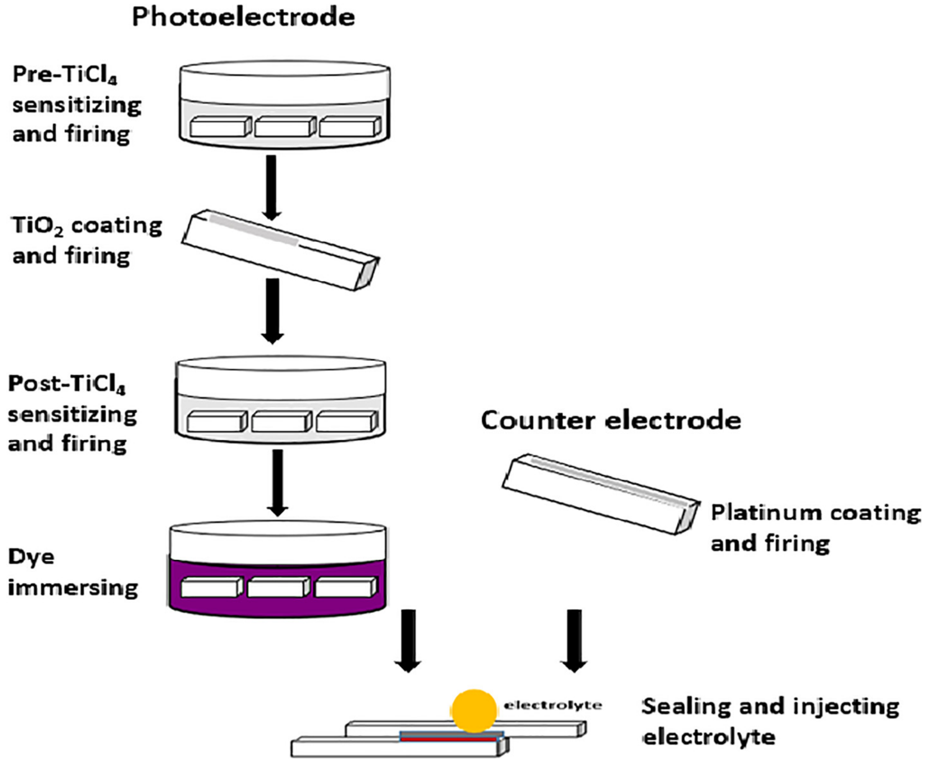

Fig. 1. $TiCl_4$ treatment and DSSC fabrication process.

FTO substrate is improved and the films show surface homogeneity as shown in Fig. 3(c) and (e). The impact of the treatment was shown clearly in both treated films due to the improvement of particle necking of the TiO_2 film and the distribution of TiO_2 nanoparticles size. Fig. 3(f) shows the best improvement after post-$TiCl_4$ treatment because the necking and TiO_2 nanoparticle became larger and reached sizes of 60–70 nm when compared to the untreated film at 20–24 nm and pre-$TiCl_4$ layer at 40–50 nm. The improvement of necking and larger particle sizes between one to another will help accelerate the diffusion of electrons in TiO_2 film [19]. Therefore, it suppresses the electron recombination from TiO_2 to the HOMO of the dye molecule. The lack of particle necking on untreated TiO_2 film makes the electron diffusion harder, which reduces in short-circuit current density.

Ultraviolet–Visible spectroscopy (UV–Vis)

UV–Vis was used to study the dye adsorption ability of untreated and treated photoelectrodes at a 200 nm to 800 nm wavelength. The dye adsorption study is vital because it is related to thickness and can enhance the generation of photocurrent in DSSC. Since the TiO_2 film was increased after the $TiCl_4$ treatment, the dye loading also increase and result in higher photon absorption at peaks of 3.8 for post-$TiCl_4$ treatment when compared to 2.8 and 1.6 for pre-$TiCl_4$ and untreated electrodes, respectively, at 290 nm in the UV region, which is shown in Fig. 4. However, the absorption spectra only slightly improved after $TiCl_4$ treatment when compared to untreated film in the visible region because TiO_2 is known as a UV-absorber material. Therefore, the absorption spectra improved in UV-region after the treatment may be due to strong adhesion and homogeneity of the TiO_2 layer on the film before TiO_2 coating, which will produce higher short-circuit current density and improve photon-current conversion efficiency in DSSC [24].

Electrochemical impedance spectroscopy (EIS)

EIS has been used extensively in DSSC research to investigate the charge transfer process in DSSC. The Nyquist and Bode plots generated on EIS measurements explained the electrochemical behaviour in DSSC. The Nyquist plot generated the impedance values of DSSCs, which generally consist of two or three semicircles [24–26]. The first semicircle typically represents the sheet resistance (Rs) of the photoelectrode, while a second semicircle is related to the impedance of the dye/TiO_2/electrolyte interface, which is shown in Fig. 5. EIS also generated

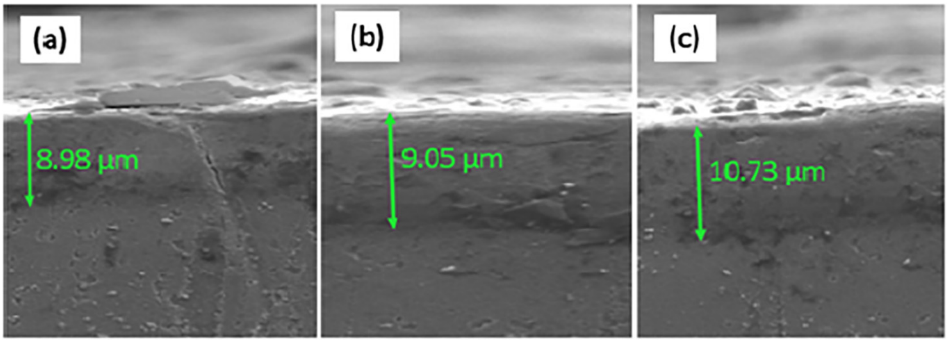

Fig. 2. Cross-sectional SEM images of thickness on (a) untreated (c) pre-$TiCl_4$ treatment and (e) post-$TiCl_4$ treatment on photoelectrodes.

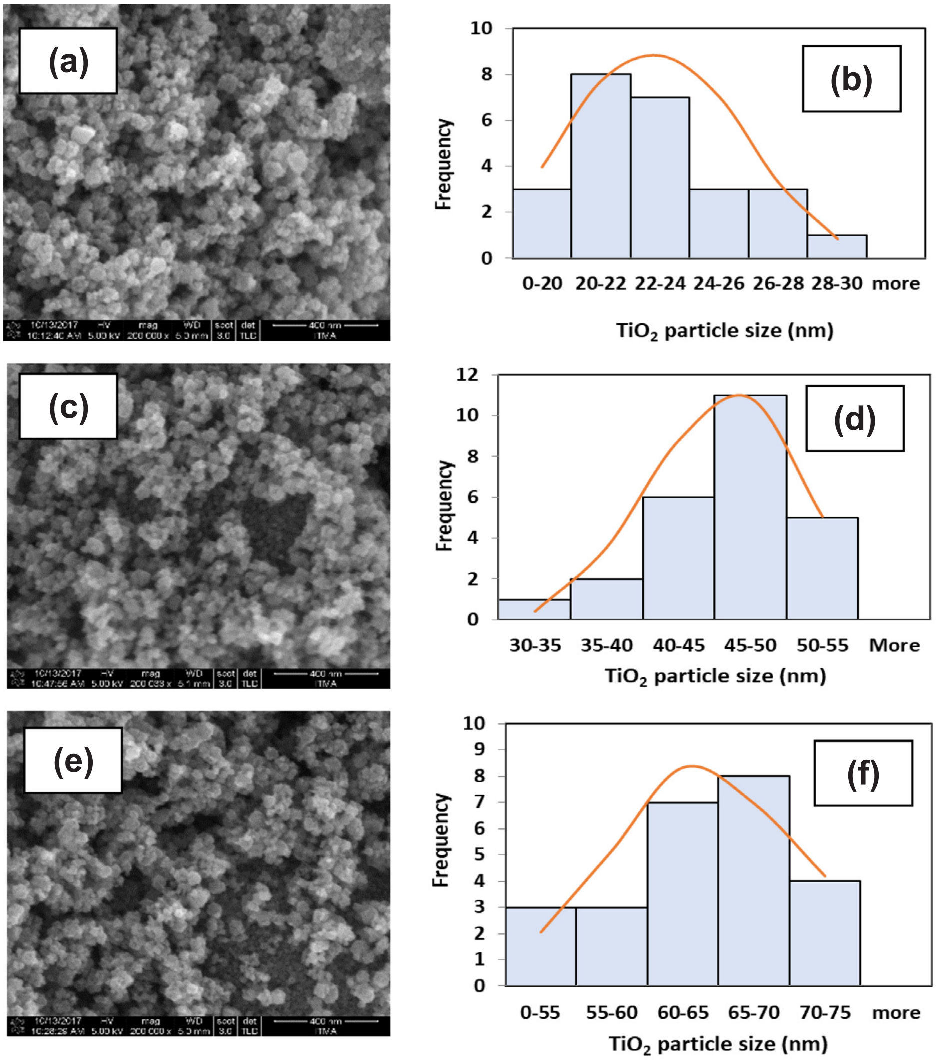

Fig. 3. FESEM morphology of particle necking and distribution of TiO_2 nanoparticle with the Gaussian fitting curve (orange line) of (a)(b): Untreated electrode, (c)(d): pre-$TiCl_4$ treatment, and (e)(f): Post-$TiCl_4$ treatment photoelectrode, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

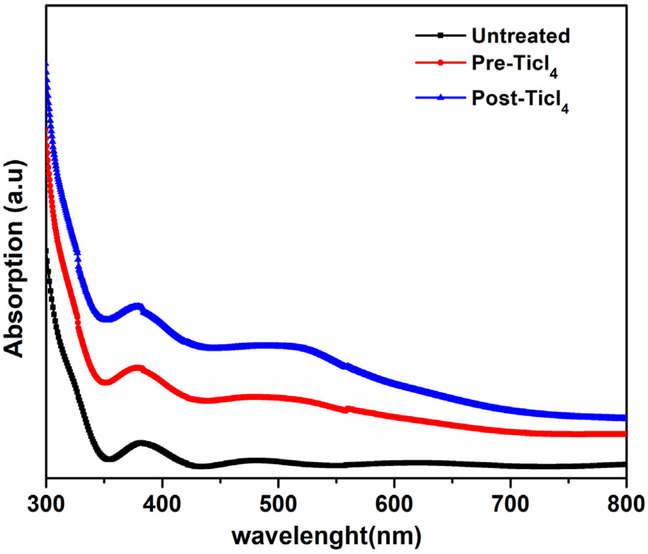

Fig. 4. Absorption spectra of untreated, pre-$TiCl_4$, and post-$TiCl_4$ treatment on TiO_2 film after N-719 dye sensitising.

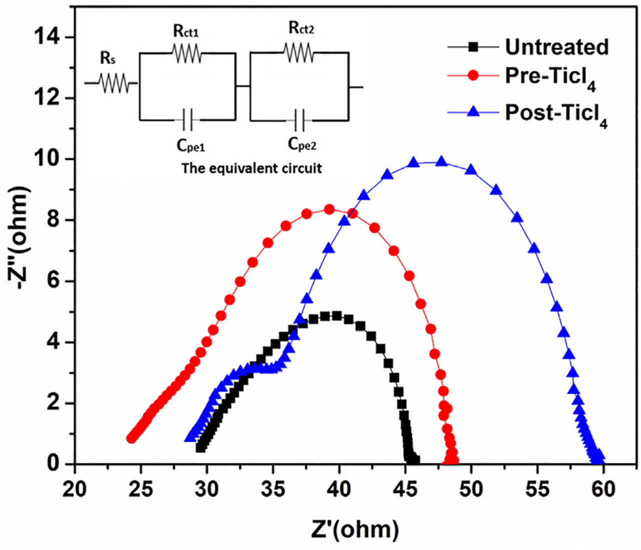

Fig. 5. Nyquist plot of treated, pre-$TiCl_4$, and post $TiCl_4$ treatment with the equivalent circuit (inlet) represent the impedance of the cell; sheet resistance Rs, electrochemical capacitance Cpe and charge transfer resistance R_{ct}.

a bode plot to represent electrochemical behaviour by presenting the relationship of frequency on the x-axis and a phase on the y-axis. The maximum angular frequency (ω_{max}) can be obtained from the Bode plot and the electron lifetime (τ_n) can be calculated from Eq. (1) [26]. For this measurement, EIS was set-up in the frequency range from 0.01 Hz to 100 kHz to study the interfacial charge transfer process of DSSC.

$$\tau_n = 1/2\pi\omega_{max} \tag{1}$$

Using τ_n and R_{ct} value from the Nyquist plot, the chemical capacitance was calculated from Eq. (2).

$$\tau_n = R_{ct}C_u \tag{2}$$

Therefore, electron transport time τ_s is given in Eq. (3).

$$\tau_s = R_sC_u \tag{3}$$

Lastly, the charge collection efficiency η_c is calculated below in Eq. (4).

$$\eta_c = (1 + Rs/Rct)^{-1} \tag{4}$$

The Nyquist plot in Fig. 5 shows that the value of sheet resistance (Rs) on the post-treatment electrode was decreased to 28.38 Ω from 29.91 Ω. In this case, the Rs reduction is possibly due to photoelectrode surface enhancement after $TiCl_4$ treatment. However, the value of charge-transfer resistance (R_{ct}) of dye/TiO_2/electrolyte interface was increased after $TiCl_4$ treatment from 16.18 Ω, 19.81 Ω, and 24.06 Ω for untreated, pre-$TiCl_4$ and post $TiCl_4$, respectively. Thus, after post-$TiCl_4$ treatment, the R_{ct} was increased by 49.39% when compared to the untreated electrode due to suppression of a recombination electron between the TiO_2/electrolyte interface [27]. Table 1 and Fig. 7 summarise the EIS parameter to represent electron lifetime Ʈn, electron transport time Ʈs, and charge collection efficiency Ƞc of the cell. Fig. 6 shows the bode plot of untreated and treated electrodes where the maximum frequency was shifted from 398.11 Hz to 100 Hz after the $TiCl_4$ treatment. The reduction of frequency in the EIS measurement generated a higher electron lifetime, which is explained in Eq. (1) [28]. In this scenario, the relationship is inversely proportional to the maximum frequency. After the treatment, the electron lifetime was increased due to suppression of electron recombination at the TiO_2/electrolyte interface, which resulted in the enhancement of charge collection efficiency after post-treatment by 31.09% when compared to the untreated electrode, which is shown in Table 1. An improvement charge collection efficiency indicated that the chemical treatment played an important role in charge separation and charge collection on the TiO_2 and electrolyte interface of DSSC. An equivalent circuit is shown in the inset of Fig. 5 to represent electrochemical impedance, which consists of electrical components of sheet resistance Rs, charge transfer resistance R_{ct1} and R_{ct2}, and electrochemical capacitance Cpe for first and second semicircle of the Nyquist plot. It can be seen clearly in Fig. 7, the EIS parameters were enhanced after the $TiCl_4$ treatment which shown an improvement of electron lifetime Ʈn, electron transport time Ʈs, and charge collection efficiency Ƞc for untreated, pre-$TiCl_4$, and post-$TiCl_4$ photoelectrode of DSSC.

Table 1
Comparison of EIS parameters on untreated and $TiCl_4$-treated DSSC.

Working electrode	R_s (Ω)	R_{ct2} (Ω)	ω_{max} (Hz)	Ʈ$_n$ (ms)	C_u (μF)	Ʈ$_s$ (ms)	Ƞ$_c$ (%)
Untreated	29.91	16.11	398.11	0.40	25	0.74	35.00
Pre-$TiCl_4$	24.00	19.81	158.49	1.00	51	1.22	45.22
Post-$TiCl_4$	28.38	24.06	100.00	1.59	66	1.88	45.88

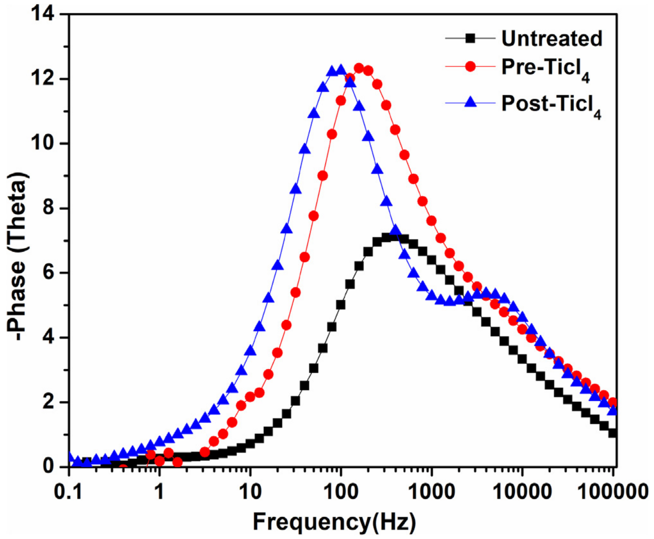

Fig. 6. Bode plot of treated, pre-$TiCl_4$ and post-$TiCl_4$.

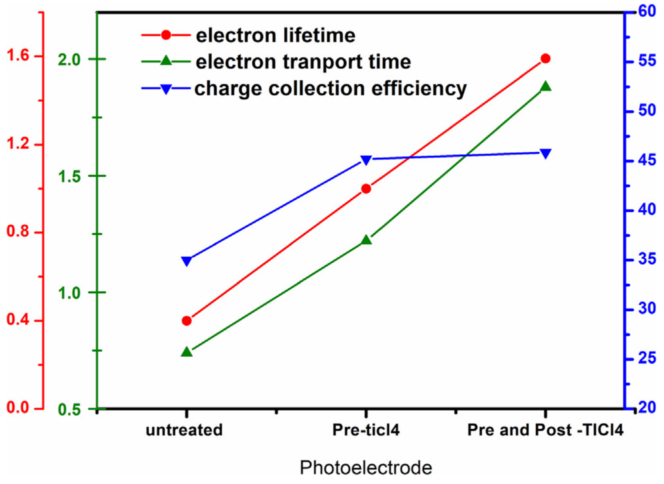

Fig. 7. Comparison of electron lifetime Ʈn, electron transport time Ʈs, and charge collection efficiency Ƞc for untreated, pre-$TiCl_4$, and post-$TiCl_4$ photoelectrode of DSSC.

Table 2
J–V characteristic on untreated and $TiCl_4$-treated DSSC.

Working electrode	Jsc (mA)	Voc (V)	Fill Factor	Ƞ (%)
Untreated	12.10 ± 0.02	0.60 ± 0.01	0.56 ± 0.01	4.08
Pre-TiCl4	17.06 ± 0.02	0.70 ± 0.01	0.54 ± 0.01	6.50
Post-TiCl4	18.95 ± 0.02	0.75 ± 0.01	0.56 ± 0.01	8.03

Current density-voltage measurement (Jsc-Voc) characteristic

The J–V measurement of DSSC was measured under simulated solar illumination of 1.5 AM (Keithley model 2601) with a power density of 100 mW/cm^{-2}. The parameters of the J–V measurement of untreated and $TiCl_4$ treated DSSC are shown in Table 2 and the relationship of short-circuit current density against open-circuit voltage of untreated and post-$TiCl_4$ of complete DSSC was depicted in Fig. 8. Table 2 indicated the improvement in short-circuit current density, Jsc of pre-$TiCl_4$ treatment, and post $TiCl_4$ treatment when compared to an untreated TiO_2 working electrode were 17.06 mA/cm^2 and 18.95 mA/cm^2, respectively, from 12.10 mA/cm^2. Jsc was increased after pre-treatment because the adhesion of TiO_2 onto FTO was improved, which caused the TiO_2 surface homogeneity and resulted in an enhancement of TiO_2 interconnection [19]. Therefore, the diffusion of electrons occurred efficiently, and the recombination of the electron was significantly suppressed. Post-treatment also increased Jsc, possibly due to

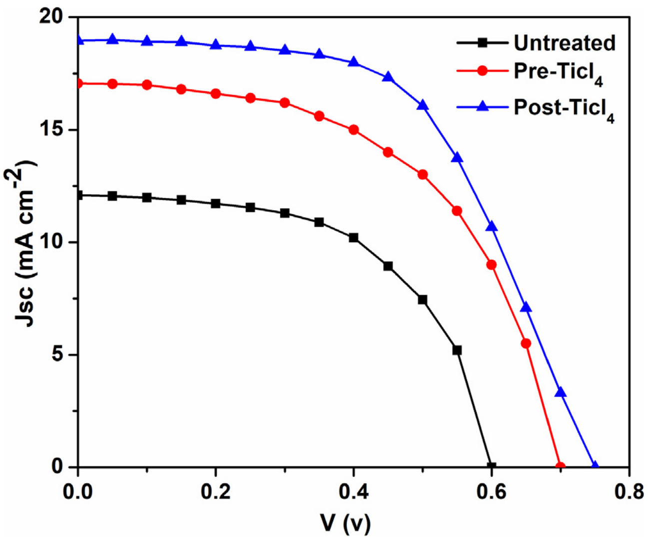

Fig. 8. J–V curve for DSSC of untreated, Pre-TiCl$_4$, and Post-TiCl$_4$.

the enhancement of TiO$_2$ nanoparticles necking on the working electrode, which is shown in Fig. 3c. Both pre-TiCl$_4$ and post-TiCl$_4$ treatments are resulting in easy electron diffusion and higher electron lifetime based on the enhancement of Jsc and PCE in DSSC. Also, post-treatment improved the photon absorption intensity, which resulted in the increasing of open-circuit voltage, Voc. The Voc was increased by 25% after treatment from 0.6 V to 0.75 V. Therefore, with the enhancement of Jsc and Voc, the photon to current conversion efficiency was improved by 96.9% after post-treatment compared to an untreated electrode of DSSC.

Conclusions

We have studied the impact of TiCl$_4$ treatment on DSSC performance by using a 40 mM titanium tetrachloride (TiCl$_4$) solution. The pre-treatment and post-treatment improved adhesion of TiO$_2$ onto FTO glass and also increased particle necking, which resulted in faster electron diffusion and a higher electron lifetime. Photoelectrode of post-treated TiCl$_4$ shown enhancement of photon absorption intensity, which increased the current density. Moreover, the EIS study indicated device resistance Rs, which were reduced due to the surface enhancement and R$_{ct}$ was increased due to the suppression of electron recombination between the dye/TiO$_2$/electrolyte interface. This resulted in the enhancement of charge collection efficiency of treated working electrodes by 31.09% when compared to the untreated electrode. An improvement in the electrochemical characteristics was reflected in the photovoltaic property since power conversion efficiency (PCE) was improved by 96.9% compared to the untreated electrode DSSC. In summary, this study proved that TiCl$_4$ treatments help to enhance power conversion efficiency and charge transport for DSSC.

CRediT authorship contribution statement

N. Fadzilah M. Sharif: Conceptualization, Funding acquisition, Formal analysis, Writing - original draft. **Suhaidi Shafie:** Conceptualization, Formal analysis, Validation. **M.Z.A. Ab. Kadir:** Formal analysis, Supervision, Resources. **W.Z. Wan Hassan:** Supervision. **Muhammad Norhaffis Mustafa:** Software, Methodology. **Buda Samaila:** Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research work was supported by the University Putra Malaysia grant (PUTRA IPB/2016/9515402) and FRGS/1/2015/SG06/UPNM/03/3 by Department of Electrical and Electronics Engineering, Faculty of Engineering, UPNM, Kuala Lumpur, 57000, Malaysia for financial support for researcher and data analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rinp.2019.102725.

References

[1] Fan J, Liu S, Yu J. Enhanced photovoltaic performance of dye-sensitised solar cells based on TiO2 nanosheets/graphene composite films. J Mater Chem 2012;22(33):17027–36.

[2] Gong J, Liang J, Sumathy K. Review on dye-sensitized solar cells (DSSCs): fundamental concepts and novel materials. Renew Sustain Energy Rev 2012;16(8):5848–60.

[3] Taleb A, Mesguish F, Yanpeng X. Effect of cracking and aggregation on the efficiency of DSSC. In: 2014 international renewable and sustainable energy conference (IRSEC), Ouarzazate, Morocco; 2014, pp. 46–51.

[4] Gonçalves LM, de Zea Bermudez V, Ribeiro HA, Mendes AM. Dye-sensitized solar cells: a safe bet for the future. Energy Environ Sci 2008;1(6):655–67.

[5] G24 Power, Efficiency of DSSC, G24 Power Limited, South Lake Drive, Imperial Park, Newport, United Kingdom [Online]. Available: http://gcell.com/dye-sensitized-solar-cells/advantages-of-dscc/efficiency; 2013.

[6] Ito S, Chen P, Comte P, Mohammad KN, Liska P, Michael Gratzel. Fabrication of screen-printing pastes from TiO2 powders for dye-sensitised solar cells. Prog Photovoltaics Res Appl 2007:603–12.

[7] Seo YG, Woo K, Kim J, Lee H, Lee W. Rapid fabrication of an inverse opal TiO2 photoelectrode for DSSC using a binary mixture of TiO2 nanoparticles and polymer microspheres. Adv Funct Mater 2011;21(16):3094–103.

[8] Ye M, Wen X, Wang M, Iocozzia J, Zhang N, Lin C, et al. Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes. Mater Today 2015;18(3):155–62.

[9] Menzies DB, Dai Q, Bourgeois L, Caruso RA, Cheng Y-B, Simon GP, et al. Modification of mesoporous TiO2 electrodes by surface treatment with titanium (IV), indium(III) and zirconium(IV) oxide precursors: preparation, characterization and photovoltaic performance in dye-sensitized nanocrystalline solar cells. Nanotechnology 2007;18(12):125608.

[10] Kavan L, O'Regan B, Kay A, Grätzel M. Preparation of TiO2 (anatase) films on electrodes by anodic oxidative hydrolysis of TiCl3. J Electroanal Chem 1993;346(1–2):291–307.

[11] Jiajie F, Shengwei L, Jiaguo Y. Enhanced photovoltaic performance of dye-sensitized solar cells based on TiO2 nanosheets/graphene composite film. J Mater Chem View 2012;22:17027–36.

[12] Sangiorgi A, Bendoni R, Sangiorgi N, Sanson A, Ballarin B. Optimized TiO2 blocking layer for dye-sensitized solar cells. Ceram Int 2014;40(7 Part B):10727–35.

[13] Lee JS, Kim KH, Kim CS, Choi HW. Synergistic effect of TiCl 4 – ZnO treated TiO2 nanotubes in dye-sensitized solar cell. Jpn J Appl Phys 2015;54(06FK02).

[14] Lee S-W, Ahn K-S, Zhu K, Neale NR, Frank AJ. Effects of TiCl4 treatment of nanoporous TiO2 films on morphology, light harvesting, and charge-carrier dynamics in dye-sensitized solar cells. J Phys Chem C 2012;116(40):21285–90.

[15] Schlichthörl G, Park NG, Frank AJ. Evaluation of the charge-collection efficiency of dye-sensitized nanocrystalline TiO2 solar cells. J Phys Chem B 1999;103(5):782–91.

[16] Barbe CJC, Arendse F, Comte P, Jirousek M, Lenzmann F, Shklover V, et al. Nanocrystalline titanium oxide electrodes for photovoltaic applications. J Am Ceram Soc 1997;80(12):3157–71.

[17] Long-Yue Z, Dai S, Kong-Jia W, Pan X, Cheng-Wu S, Li G. Mechanism of enhanced performance of dye-sensitized solar cell based TiO2 films treated by titanium tetrachloride. Chinese Phys Lett 2004;21(9):1835.

[18] Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Mueller E, Liska P, et al. Conversion of light to electricity by cis-X2bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes. J Am Chem Soc 1993;115(14):6382–90.

[19] Sedghi A, Miankushki HN. Influence of TiCl4 treatment on structure and performance of dye-sensitized solar cells. Jpn J Appl Phys 2013;52. pp. 075002-1-075002-5.

[20] Lee E, Ryu J, Jang J. Fabrication of graphene quantum dots via size-selective precipitation and their application in upconversion-based DSSCs 1. Experimental section. Chem Commun 2013;49:9995.

[21] Fadzilah N, Kadir M, Shafie S, Rashid SA, Hasan WZW, Shaban S. Charge transport and electron recombination suppression in dye-sensitized solar cells using graphene quantum dots. Results Phys 2019:102171.

[22] Huang AN, Pien WC, Kuo HP. Preparation of the working electrode of dye-

sensitized solar cells using screen printing with alkyd resins. Energy Procedia 2014;61:1528–31.

[23] Holliman Peter J, Muslem Dhiyaa K, Jones Eurig W, Connell Arthur, Davies Matthew L, Charbonneau Cecile, Carnie Matthew J, Worsley David A. Low-temperature sintering of binder-containing TiO2/metal peroxide pastes for dye-sensitized solar cells. Mater Chem A 2014;2:11134–43.

[24] Yang J, Bark C, Kim K, Choi H. Characteristics of the dye-sensitized solar cells using TiO2 nanotubes treated with TiCl4. Materials (Basel) 2014;7(5):3522–32.

[25] Lee C, Lin C, Wei T, Tsai M. Economical low-light photovoltaics by using the Pt-free dye-sensitized solar cell with graphene dot/PEDOT: PSS counter electrodes. Nano Energy 2015;18:109–17.

[26] Samaila B, Shafie S, Rashid SA, Jaafar H, Khalifa A. Response surface modeling of photogenerated charge collection of silver-based plasmonic dye-sensitized solar cell using central composite design experiments. Results Phys 2017(January):1–5.

[27] Buda S, Shafie S, Rashid SA, Jaafar H, Sharif NFM. Enhanced visible light absorption and reduced charge recombination in AgNP plasmonic photoelectrochemical cell. Results Phys 2017;7:2311–6.

[28] Fuke N, Katoh R, Islam A, Kasuya M, Furube A, Fukui A, et al. Influence of TiCl4 treatment on back contact dye-sensitized solar cells sensitized with black dye. Energy Environ Sci 2009;2(11):1205.