

# Improving Ag-TiO<sub>2</sub> nanocomposites' current density by TiCl<sub>4</sub> pretreated on FTO glass for dye-sensitised solar cells

Muhammad Qisar Lokman<sup>1</sup> | Suraya Shaban<sup>2</sup> | Suhaidi Shafie<sup>2</sup> | Fauzan Ahmad<sup>3</sup> | Hafizal Yahaya<sup>3</sup> | Rizuan Mohd Rosnan<sup>4</sup> | Mohd Adib Ibrahim<sup>1</sup>

<sup>1</sup> Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Bangi, Selangor Darul Ehsan, Malaysia

<sup>2</sup> Institute of Advanced Technology, UPM, Universiti Putra Malaysia, Serdang, Selangor Darul Ehsan, Malaysia

<sup>3</sup> Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Kuala Lumpur, Malaysia

<sup>4</sup> JEOL (Malaysia) Pte. Ltd, Petaling Jaya, Selangor Darul Ehsan, Malaysia

## Correspondence

Muhammad Qisar Lokman, Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Bangi, Selangor Darul Ehsan, 43600, Malaysia.  
Email: [muhammadqisar@gmail.com](mailto:muhammadqisar@gmail.com)

## Abstract

Titanium tetrachloride (TiCl<sub>4</sub>) pretreatment on the fluorine-doped tin oxide (FTO) is one of the alternative techniques to enhance short-circuit current density ( $J_{sc}$ ) and efficiency of dye-sensitised solar cells (DSSC) by improving the inter-particle bonding between FTO grain and nanoporous titanium dioxide (TiO<sub>2</sub>). The present study investigates the effect of TiCl<sub>4</sub> pretreatment on the surface of FTO glass to enhance the  $J_{sc}$  and efficiency of silver-titanium dioxide (Ag-TiO<sub>2</sub>) nanocomposites. The pretreatment process was prepared by immersing FTO glass into TiCl<sub>4</sub> solution at 70°C for 30 min, and then sintered at 500°C for 30 min. Morphological and elemental characteristics were done to observe the structure and composition of pretreatment on the FTO glass. The results showed that the Ag-TiO<sub>2</sub> with TiCl<sub>4</sub> pretreatment achieved high efficiency of 7.27% with  $J_{sc}$  of 18.95 mA/cm<sup>2</sup>. The proposed method shows that the pretreatment can improve the efficiency by improving the inter-particle bonding between nanoporous TiO<sub>2</sub> and FTO grain, which can enhance the electron transfer. Also, the presence of Ag in the nanocomposites as a solar concentrator can increase the light absorption by TiO<sub>2</sub> nanoparticles and also increase the DSSC efficiency.

## 1 | INTRODUCTION

Dye-sensitised solar cells (DSSC) lie in third-generation photovoltaics that has attracted scientific and technological interest due to low-cost production, good performance, and environmentally friendly [1]. The breakthrough discovery of DSSC by Grätzel and O' Regan proposed a novel method using nanoporous metal oxide to replace the smooth surface of metal oxide [2, 3]. This nanoporous material, typically titanium dioxide (TiO<sub>2</sub>) nanoparticles were deposited on the conductive transparent substrates with known thickness and provided nanoscopic pores arising from the voids between the nanoparticles. Then, the dye was filled through the pores and adsorbed onto the TiO<sub>2</sub>. In addition, DSSC typically comprises four components: Semiconductor photoanode, dye-sensitiser, electrolyte, and a counter electrode; and dye-sensitiser was employed as light absorbent material. Unlike the p-n junction, the working principle is confined in the semiconductor material [4]. The DSSC cells are able to achieve an efficiency of 13% using D- $\pi$ -A porphyrin dye-sensitiser and cobalt-based redox media-

tor [5]. However, their efficiency is still lower, compared to other generation of photovoltaics [6]. Thus, DSSC is extensively studied to find alternative methods either by doping, replacing new material, or nanostructuring for high efficiency and stability.

Increasing electron transportation is the key to enhance the short-circuit current density ( $J_{sc}$ ) and efficiency of the DSSC device. Therefore, a semiconductor layer, usually TiO<sub>2</sub>, plays an essential role in DSSC for this improvement. The semiconductor layer not only provides sufficient area for dye loading but also acts as electron transportation to transfer the excited electron from the lowest unoccupied molecular orbital (LUMO) to the conduction band (CB) of the semiconductor [7]. Thus, the energy levels between semiconductors and dye should match the synergetic requirement. The electron pathway should need to be considered when the irradiating light passes through the semiconductor film, which means, the semiconductor structure must be designated to reduce the electron loss and recombination of the illuminating light. Thus, the structural and crystal phase of the semiconductor greatly

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affects the  $J_{sc}$  and efficiency of DSSC [8]. Fan et al. (2017) have provided strategies to improve DSSC efficiency, including nano-architectures, light scattering, composites, titanium tetrachloride ( $TiCl_4$ ) treatment, interfacial engineering, and doping [9]. The improvement of strategies by composites, for example, by doping with plasmonic nanoparticles, can enhance the  $J_{sc}$  and efficiency of DSSC. Plasmonic nanoparticles, especially silver (Ag) and gold (Au), are able to enhance light absorption and broaden the light spectrum of dye by plasmon resonance [10]. These plasmonic nanoparticles can function as light scattering that can increase the number of optical pathways allowing light to stay longer and can cause an increase in light absorption [11, 12]. In addition, plasmonic alloy nanoparticles such as mixed alloy (Au-Ag alloy) or core-shell bimetal (Au@Ag) can be an effective solution to attain a broad range of light absorption with tunable optical properties [13, 14].

The most straightforward method to enhance DSSC efficiency is using  $TiCl_4$  pre- and post-treatment. The efficiency can be enhanced by immersing fluorine-doped tin oxide (FTO) glass or  $TiO_2$  film in the  $TiCl_4$  solution and sintered in air conditioner. The sintering process converts species from the  $TiCl_4$  to  $TiO_2$  crystallite on the surface of the film [8]. For the post-treatment, the  $TiCl_4$  can improve the DSSC performance owing to an increased surface area of the films [9], which offers great dye loading with a corresponding increase of light absorption. Also, for the pretreatment, the  $J_{sc}$  is able to increase obviously, and high efficiency can be potentially obtained. However, many efforts have been done to explain the role of  $TiCl_4$  pretreatment in DSSC performance, but up to now, the exact mechanism is unclear yet.

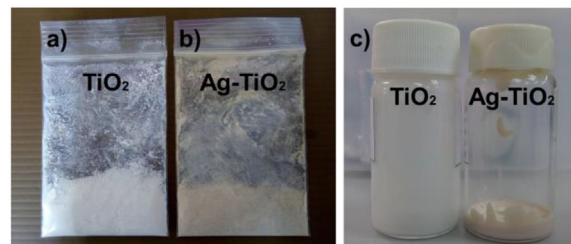
In this letter, we study the effect of  $TiCl_4$  pretreatment on the surface of FTO to improve the  $J_{sc}$  and efficiency of Ag- $TiO_2$  nanocomposites DSSC. However, in our experiment, we used commercially available anatase  $TiO_2$ , and the Ag are not shell-coated on the  $TiO_2$ . In the proposed work, the synthesised Ag was directly mixed with  $TiO_2$  paste; therefore, there is some probability that not all of the Ag was able to couple with the  $TiO_2$ . In this work, the loading Ag is low, and this phenomenon contributes to the slightly lower efficiency than the other reported article [15, 16]. Also, we discuss the mechanism of  $TiCl_4$  pretreatment in enhancing DSSC performance.

## 2 | EXPERIMENT DETAILS

All chemicals were used without any further purification. The FTO glass was purchased from Zhuhai Kaivo. All the chemicals used in this study were purchased from Sigma-Aldrich. An anatase  $TiO_2$  nanoparticles with a diameter of 25 nm were used in the preparation of  $TiO_2$  paste for the photoanode film.

### 2.1 | $TiCl_4$ pretreatment

First, proper substrates cleaning was followed prior to any deposition, mainly to remove any surface contamination by other



**FIGURE 1** The image of (a) titanium dioxide ( $TiO_2$ ), (b) silver- $TiO_2$  ( $Ag-TiO_2$ ) after drying process, and (c)  $TiO_2$  and  $Ag-TiO_2$  paste

cations on the surface of the substrates, which considerably enhances charge recombination in the solar cells. Each of the pieces was cleaned and ultra-sonicated with 1% detergent solution, deionised (DI) water, acetone, and isopropanol at 10 min for each step. Then, the substrates were dried in an oven at  $100^\circ C$  for an hour. Before the treatment, DI water was filtered using a  $0.22 \mu m$  filter and kept in the refrigerator at  $0^\circ C$ . The  $TiCl_4$  is extremely dangerous for inhalation; thus, this preparation needs to be carried out under a fume hood with extra precaution. The 40 mM  $TiCl_4$  was slowly added to the ice-cold DI water with vigorous stirring for 10 min. Fresh  $TiCl_4$  was made before each treatment. For  $TiCl_4$  treatment, the FTO glass was kept immersed in the  $TiCl_4$  solution at  $70^\circ C$  for 30 min in a petri dish. The treated FTO glass was then rinsed with DI water and ethanol. Then, it was heated in an oven at  $100^\circ C$  and sintered at  $500^\circ C$  for 30 min.

### 2.2 | Fabrication of photoanode

The preparation of  $TiO_2$  and  $Ag-TiO_2$  paste was prepared following the procedure from our previous report [15]. The Ag nanoparticles (AgNP) were synthesised through chemical reduction techniques, where tri-sodium citrate was selected as a reducing agent. A 0.05 mmol of silver nitrate was dissolved into 50 ml of DI water and followed by stirring on the hot plate until the solution came to boil. After that, 10 mM of aqueous tri-sodium citrate was added drop by drop with constant stirring at 500 rpm for 15 min until the solution changed from colourless to dark yellow. Next, the hot plate was turned off, and the solution was left to cool until it reached room temperature. The AgNP solution was then centrifuged three times, and each time AgNP was replenished with DI water to ensure the reducing agent was completely removed. For the preparation of  $Ag-TiO_2$ , 5 g of  $TiO_2$  nanopowder was added into 50 ml of AgNP solution, which was then heated at  $100^\circ C$  for 10 min. The resulting powder was filtered using filter paper and dried in an oven at  $80^\circ C$  for 12 h. Figures 1(a) and (b) show the  $TiO_2$  and  $Ag-TiO_2$  after the drying process, and Figure 1(c) shows the product after paste preparation. The mean size of synthesised AgNP is 65.23 nm as optimised in our previous report [15].

The  $TiO_2$  and  $Ag-TiO_2$  paste was deposited on the  $TiCl_4$ -treated FTO glass using the doctor blade method. In this experiment, scotch tape (3 m, Scotch Magic Tape) with a thickness of  $52 \mu m$  was used to control the thickness of the

photoanode. The tape was placed on the edges of the conductive sides of FTO glass to make a  $1\text{ cm}^2$  area for paste deposition. A small amount of paste was then applied to the masked FTO glass and spread across the unmasked area using a squeegee. Then, the tape was removed, leaving an uncoated area of the FTO glass that was used as an electrical contact for current-voltage (I-V) measurement. After that, the photoanode was kept in storage for 3 min to ensure the paste can relax to reduce surface irregularity. Then, it was sintered at  $125^\circ\text{C}$  for 10 min and  $450^\circ\text{C}$  for 30 min to remove the presence of additives and organic binders. The thickness of the photoanode film for this experiment was around  $15\ \mu\text{m}$ .

### 2.3 | Preparation of DSSC device

After the sintering process, the photoanode was immersed for 20 h in 0.2 mM of N719 dye in a mixture of tert-butanol and acetonitrile (1:1). The counter electrode was prepared by spin-coating the  $60\ \mu\text{l}$  of 2 mM hexachloroplatinic acid in isopropanol on the FTO glass and sintered at  $450^\circ\text{C}$  for 30 min. The dye-covered photoanode and Pt counter electrode were assembled into a sandwich structure and sealed with  $60\ \mu\text{m}$  Surlyn polymer spacer. An electrolyte comprising 0.05 M iodine, 0.1 M lithium iodide, 0.5 M 4-tert-butylpyridine, and 0.6 M ethyl-methyl-imidazolium iodide in acetonitrile was mixed and injected into DSSC and immediately tested under a solar simulator.

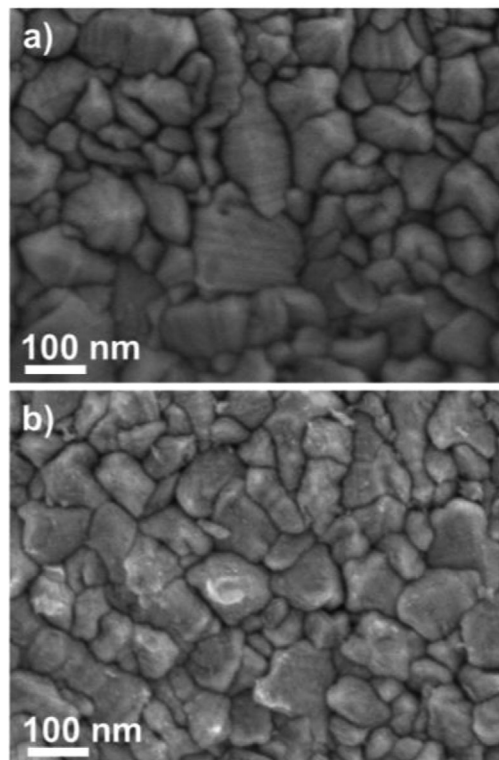
### 2.4 | Characterisation

The surface morphology of  $\text{TiCl}_4$  pretreated on FTO glass was observed using field-emission scanning electron microscopy (FESEM; JSM-7800F, JEOL). The elemental composition was done using FESEM. The I-V characteristic of the DSSC was evaluated using Keithley 2450 SourceMeter, and a solar simulator (Grating Inc.) equipped with Xenon lamp and an air mass 1.5 global filters. The solar simulator was calibrated to an intensity of  $100\ \text{mW}/\text{cm}^2$  (1 Sun) using a solar metre (IM-750, RS Pro).

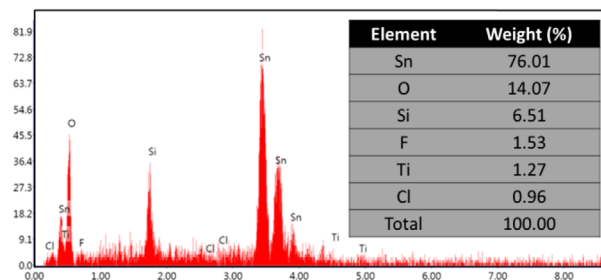
## 3 | RESULTS AND DISCUSSIONS

Figures 2(a) and (b) display the morphological surface images of cleaned FTO glass with and without  $\text{TiCl}_4$  pretreatment at 150 kX magnification captured using FESEM. From Figure 2(a) we can see that bare FTO grains with irregular shapes ranging from 10 up to a few hundred nm in size were observed in the image. However, in Figure 2(b), the image of FTO grains is slightly blurred and a small dot was covered on the grains implying the formation of an extremely thin layer of  $\text{TiO}_2$  on the grains [17].

To confirm the presence of the  $\text{TiO}_2$  thin layer on the FTO grain, energy X-ray dispersive spectroscopy (EDS) was



**FIGURE 2** Field-emission scanning electron microscopy images at high magnification for (a) untreated and (b) treated with  $\text{TiCl}_4$  fluorine-doped tin oxide (FTO) substrates



**FIGURE 3** Elemental composition of FTO treated with  $\text{TiCl}_4$  detected using energy X-ray dispersive spectroscopy

performed using point scanning. Three different points were selected on the FTO grains, and the EDS spectra are shown in Figure 3. The result shows that the presence of tin, oxygen (O), and fluorine elements with a weight percentage of 76.01%, 14.07%, and 1.53%, respectively, on the glass substrates prove that grains deposited on the glass are FTO. The low weight percentage of Ti, 1.27%, proves the presence of the  $\text{TiO}_2$  thin layer on the FTO grains, where the weight of O element is included in the percentage of O in FTO. Besides that, silicon with a 6.51% weight percentage is the elemental composition for glass. Last, the chlorine with a percentage of 0.96% exists because of an excess of  $\text{TiCl}_4$  during the pretreatment process. This excess can be removed by rinsing thoroughly with DI water and ethanol. No other element was detected in the EDS

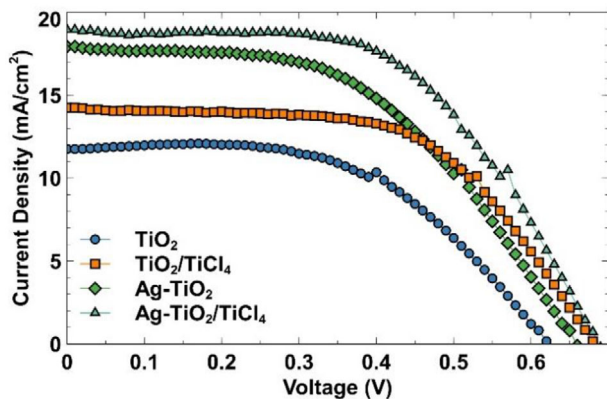


FIGURE 4 Current-voltage characteristic performance for  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{TiCl}_4$ ,  $\text{Ag-TiO}_2$ , and  $\text{Ag-TiO}_2/\text{TiCl}_4$

spectra, which shows that there was no contamination and organic residue on the glass substrates.

### 3.1 | I-V Characteristic

Figure 4 compares the I-V curve characteristic between untreated and treated FTO glass. From the graph in Figure 4, it is apparent that the FTO glass treated with  $\text{TiCl}_4$  achieved a higher I-V curve, compared to the untreated. There is a 36% efficiency increment from untreated to treated  $\text{TiO}_2$  film, and with the addition of AgNP on the film, the efficiency boosts up to 75% if the film was treated with  $\text{TiCl}_4$ .

Figures 5(a) and (b) display the efficiency and  $J_{sc}$  for untreated and treated FTO glass substrates. What stands out in this figure is the increase of  $J_{sc}$  from 11.82 to 18.95  $\text{mA}/\text{cm}^2$  reveals that the presence of the  $\text{TiCl}_4$  layer on the FTO grains can drastically enhance the  $J_{sc}$ . The efficiency for the  $\text{TiCl}_4$  treated FTO also shows a considerably higher, compared to the untreated ones. For untreated FTO with  $\text{TiO}_2$  and  $\text{Ag-TiO}_2$  layer, the efficiencies are 4.14% and 5.93 %, respectively. But with the treatment of  $\text{TiCl}_4$ , the efficiency can rise to 5.64% and 7.27%. Figures 5(c) and (d) show the open-circuit voltage ( $V_{oc}$ ) and fill factor (FF) for treated and untreated FTO glass substrates. The  $V_{oc}$  for both  $\text{TiO}_2/\text{TiCl}_4$  and  $\text{Ag-TiO}_2/\text{TiCl}_4$  shows the same value of 0.69 V. But for the untreated substrates, the  $V_{oc}$  is reduced to 0.63 and 0.66 V for  $\text{TiO}_2$  and  $\text{Ag-TiO}_2$ , respectively. The FF shows a similar value of 0.56 for  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{TiCl}_4$ , and  $\text{Ag-TiO}_2/\text{TiCl}_4$ . However, with the presence of AgNP, the FF drops to 0.51 indicating that the squareness of the I-V curve decreased.

The pretreatment of  $\text{TiCl}_4$  on the FTO glass substrates can influence in two manners; first, through improving the network bonding strength between grain FTO glass substrates and the  $\text{TiO}_2$  nanoporous network [18]. This situation can reduce the electron dead-end problem on the  $\text{TiO}_2$  nanoporous film causing the electron trapped in the  $\text{TiO}_2$  network that can reduce the  $J_{sc}$ . With the  $\text{TiCl}_4$  pretreatment, small particles of  $\text{TiO}_2$  can be connected with the dead-end nanoporous  $\text{TiO}_2$  and enhance electron transport (see Figure 6) [7]. As we can see in Fig-

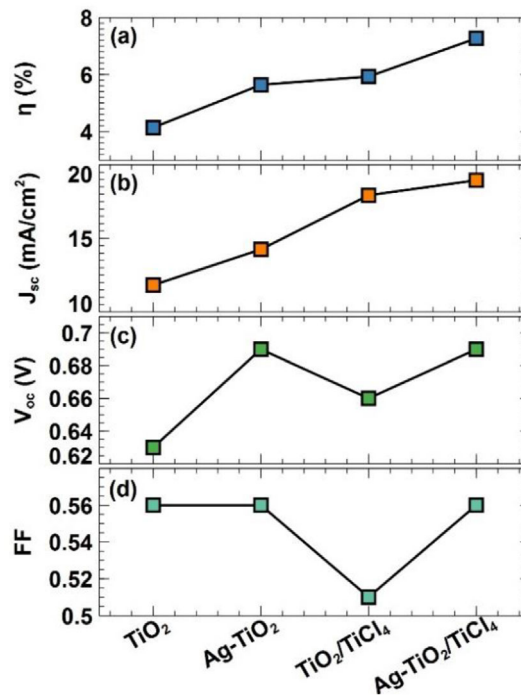


FIGURE 5 (a) Efficiency ( $\eta$ ), short-circuit current density, (c) open-circuit voltage, and (d) fill factor for  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{TiCl}_4$ ,  $\text{Ag-TiO}_2$  and  $\text{Ag-TiO}_2/\text{TiCl}_4$

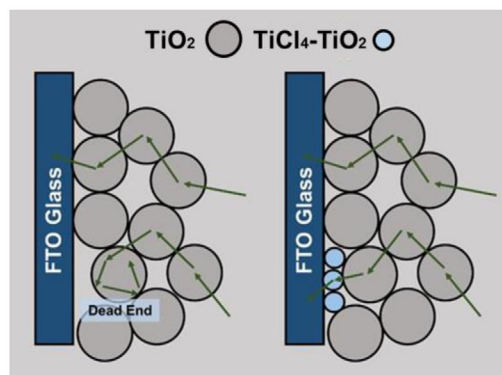


FIGURE 6 Schematic diagram for (a) dead-end electron and (b) effect of  $\text{TiCl}_4$  pretreatment to enhance the electron transportation

ures 5(a) and (b), the efficiency and  $J_{sc}$  increased as the  $\text{TiCl}_4$  pretreatment was applied, and the electron transportation in  $\text{TiO}_2$  nanoporous network is improved leading to an increase in  $J_{sc}$ , and with the help of AgNP, light absorption can be enhanced. Second, to block the electron from recombining with the  $\text{I}_3^-$  in the redox electrolyte [18]. As mentioned before, dead-end of electrons cause the electron trapped in the  $\text{TiO}_2$  nanoporous network; however, this trapped electron also has a probability that some of the electrons will go through a back reaction to the electrolyte that leads to electron recombination. This electron recombination only can lead to reduction of  $J_{sc}$  and efficiency. Besides that,  $V_{oc}$  increased as the  $\text{TiCl}_4$  treatment was applied to the FTO glass. This is because the  $\text{TiO}_2$  thin film shifted the

**TABLE 1** Photovoltaic parameter for titanium dioxide (TiO<sub>2</sub>), TiO<sub>2</sub>/titanium tetrachloride (TiCl<sub>4</sub>), Silver (Ag)-TiO<sub>2</sub>, and Ag-TiO<sub>2</sub>/TiCl<sub>4</sub>

Treatment	Short-circuit current density ( $J_{sc}$ )(mA/cm <sup>2</sup> )	Open-circuit voltage ( $V_{oc}$ )(V)	Fill Factor (FF)	Efficiency ( $\eta$ )(%)		
				Ave.	SD	Max
TiO <sub>2</sub>	11.82	0.63	0.56	3.37	0.56	4.41
TiO <sub>2</sub> /TiCl <sub>4</sub>	14.52	0.69	0.56	5.29	0.22	5.64
Ag-TiO <sub>2</sub>	17.93	0.66	0.51	5.49	0.44	5.93
Ag-TiO <sub>2</sub> /TiCl <sub>4</sub>	18.95	0.69	0.56	6.85	0.29	7.27

Note: Ave. = Average value for five samples, SD = standard deviation and Max = maximum efficiency achieves from five samples.

**TABLE 2** Comparison of this work and previous work report on photovoltaic parameter of dye-sensitised solar cells for Ag-TiO<sub>2</sub> pretreated with TiCl<sub>4</sub>

Synthesis of Ag nanoparticles (AgNP)	AgNP deposition method	Efficiency ( $\eta$ )(%)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	Ref.
Chemical reduction	TiO <sub>2</sub> added into AgNP solution and heated for 10 min	7.27	18.95	0.69	0.56	This work
Polyol	AgNP grinded with TiO <sub>2</sub>	5.61	10.26	0.73	0.74	[21]
Green synthesis ( <i>Carica papaya</i> )	AgNP ball milled with TiO <sub>2</sub>	5.06	10.67	0.75	0.62	[23]

CB edge to the positive direction that resulted in a higher electron density in the FTO glass substrates [18].

With the presence of AgNP in the nanocomposites, light absorption can be improved. Several factors could explain this improvement; first, the AgNP tends to be a near-field coupling agent or, in other words, a nano-sized solar concentrator that focused the incident light on the AgNP surface within a small mode volume. The intensity of these fields are usually orders of magnitude higher than the incident light [19]. Therefore, AgNP can be one of the secondary light sources that can increase the photon and light absorption by the TiO<sub>2</sub> nanoparticles. Also, the dye molecule can directly couple with the strong near field and resulting plasmon-molecule coupling, which can increase the electron-hole pair generation in the dye molecules [20]. Thus, a higher electron density carrier is available to transfer from the LUMO of dye molecules to the CB of TiO<sub>2</sub>, which subsequently improves the photocurrent generation and efficiency of DSSC. Hence, the presence of TiCl<sub>4</sub> pretreatment and AgNP in the DSSC device can boost efficiency and  $J_{sc}$ .

Table 1 listed all the I-V performances for the parameter of  $J_{sc}$ , efficiency,  $V_{oc}$ , and FF. The best performances of Ag-TiO<sub>2</sub>/TiCl<sub>4</sub> with an efficiency of 7.27% clearly shows that the treatment of  $J_{sc}$  and efficiency can be improved by the addition of TiO<sub>2</sub> thin film that can enhance electron transfer. The efficiency of this TiCl<sub>4</sub> treatment is comparable with the report by Kazmi et al. with an efficiency of 7.30% [21]. Note that, Kazmi et al. used two different treatments, which are pre- and post-treatment. The post-treatment was conducted by immersing the Ag-TiO<sub>2</sub> film in the 40 mM aqueous TiCl<sub>4</sub> solution and sintering the film at 450°C for 30 min. However, TiCl<sub>4</sub> is classified as a highly acidic solution, which can damage and detached the AgNP onto the TiO<sub>2</sub> during the treatment [22]. Therefore, in

this experiment, we avoid the post-treatment of Ag-TiO<sub>2</sub> to prevent the detachment of Ag. In addition, Solaiyammal et al. also reported the Ag-TiO<sub>2</sub> nanocomposites using TiCl<sub>4</sub> pretreatment [23]. The AgNP were synthesised using green synthesis, where, *Carica papaya* leaf extract was used as a reducing agent. In the report, they were able to achieve  $J_{sc}$  of 10.67 mA/cm<sup>2</sup> and an efficiency of 5.61%. Looking at the report of Kazmi et al. and Solaiyammal et al. [21, 23], they were able to achieve higher FFs, compared to our report. This is because of the uneven space of electrolyte thickness that can lead to the low FF value. This problem can be encounter by using the heat press process that offers uniform pressure and electrolyte space. Comparing with all results in Table 2, we were able to achieve high  $J_{sc}$ , compared to the other reports, which shows that our proposed method is very promising for high-efficiency DSSC devices.

## 4 | CONCLUSION

In summary, the present study proposed a method to enhance light absorption for the improvement of  $J_{sc}$  and efficiency. The pretreatment using TiCl<sub>4</sub> on the FTO glass can improve the bonding between TiO<sub>2</sub> nanoparticles and FTO glass substrates, which can enhance the electron transfer. The highest efficiency is achieved at 7.27% with  $J_{sc}$  of 18.95 mA/cm<sup>2</sup> using Ag-TiO<sub>2</sub> nanocomposites. The presence of AgNP in the nanocomposites as a solar concentrator can increase the photon and light absorption by TiO<sub>2</sub> nanoparticles.

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