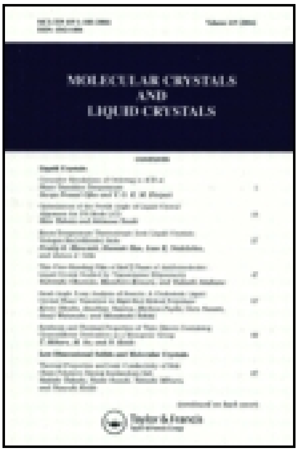

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# The Effect of $TiO_x$ Blocking Layer on the Performance of Dye-Sensitized Titanium Dioxide Solar Cells

Sang-Wha Lee [a]

[a] Department of Chemical and Bio Engineering, Kyungwon University, Seongnam, 461-701, Korea

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# The Effect of $TiO_x$ Blocking Layer on the Performance of Dye-Sensitized Titanium Dioxide Solar Cells

SANG-WHA LEE*

Department of Chemical and Bio Engineering, Kyungwon University,
Seongnam, 461-701, Korea

*Ti oxide blocking layer on the FTO glass was formed by dipping the glass in $TiCl_4$ solution at 70°C with the variation of $TiCl_4$ concentrations, dipping times, alcohol solvents, and dipping sequences. Cyclic voltagram of the $TiCl_4$-pretreated FTO glass indicated that the cathodic peak was very sensitive to the formation of non-electroactive $TiO_x$ layer on the FTO glass. The $TiO_x$ blocking layer was effectively formed on the FTO glass through a double-dipping sequence, i.e., first dipping the FTO glass in aqueous solution (containing 50 mM $TiCl_4$) and subsequently dipping the heat-treated FTO glass in alcohol mixture of 50 vol% (containing 50 mM $TiCl_4$). $TiCl_4$-pretreatment enhanced the photoelectric conversion efficiency (PCE) of dye-sensitized solar cells (DSSCs) by ca. 3.8% and additional $TiCl_4$ post-treatment enhanced the PCE of DSSCs by ca. 13.2% as compared to non-treated DSSC, respectively.*

**Keywords:** Ti oxide layer; $TiCl_4$ pretreatment; Post-treatment; Blocking layer

## Introduction

Charge recombination occurs at the interface of nanocrystalline $TiO_2$ with $I^{3-}$ and/or oxidized dye molecules. Charge recombination between photo-induced electrons in $TiO_2$ and oxidized dyes is negligible because the regeneration of the oxidized dye by $I^-$ is much faster than the charge transfer from $TiO_2$ to the dye sensitizer.[1–3] Thus, it is very important to retard the recombination rate of photo-induced electrons with $I^{3-}$ in the electrolytes. Ti oxide layer formed on fluorine-doped ITO (FTO) glass generally enhances the conversion efficiency of dye-sensitized solar cells (DSSCs) by reducing the charge recombination at the interface of FTO glass with electrolytes.[4–7] Zhu et al. reported that recombination occurs predominantly near the FTO glass.[8] Peter et al. reported that spray-coated $TiO_2$ thick layer prevented the back reaction of photo-induced electrons with $I^{3-}$ in the electrolytes under short-circuit conditions.[4] Ito and coworker confirmed that $TiO_2$ thick layer between the FTO glass and mesoporous $TiO_2$ films was more effective in the prevention of charge recombination than the thin layer formed by normal $TiCl_4$ pretreatment.[3] However, Gratzel and coworker showed that the introduction of compact $TiO_2$ layer has a minimal effect on the photoelectric conversion efficiency (PCE) especially for ruthenium-based sensitizers.[9]

Even though there are still controversies on the location of recombination sites whether mainly on the FTO glass or throughout the bulk $TiO_2$ films, many attempts have been made

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*Corresponding author. E-mail: Lswha@kyungwon.ac.kr to form blocking layer on the FTO glass to minimize the charge recombination at the interface between the FTO glass and $TiO_2$ films—core-shell nanostructured electrodes, surface silanization, and Ti oxide layer on the FTO glass.[10,11] Among them, hydrothermal reaction of $TiCl_4$ precursors induces the formation of titania complex, which is influenced by $TiCl_4$ concentrations, reaction time and dielectric constant of the solvent.[12–14] Hydrolyzed $TiCl_4$ solution contains a large number of octahedral complexes such as $[Ti(OH)_2(OH_2)_4]^{2+}$ and/or $[TiO(OH)_5]^{2+}$ at room temperature.[15,16] When the temperature rises to the reaction temperature, the species in $TiCl_4$ solution are unstable and prone to combine together via oxolation and/or olation process, consequently leading to the growth of Ti complexes.[12]

In the present work, Ti oxide layer on the FTO glass was prepared via the facile $TiCl_4$ dipping method. The formation of Ti oxide layer on the FTO glass was systematically investigated by the variation of $TiCl_4$ concentrations, dipping times, alcohol solvents, and dipping sequences. The $TiCl_4$-treated FTO glass as a working electrode was electrochemically analyzed using the technique of cyclic voltametry, in order to estimate the non-electroactive fraction passivated by $TiO_x$ blocking layer. The effectiveness of blocking layer on the FTO glass was measured based on the performance of DSSCs with $TiCl_4$ pretreatment and $TiCl_4$ post-treatment, respectively.

## Experimental

### *$TiCl_4$ Treatment*

An aliquot of $TiCl_4$ stock solution (2.0 M) was injected into a closed vessel containing aqueous solution with 50 vol% of alcohol solvents (such as methanol, ethanol, and isopropanol). In the $TiCl_4$ pretreatment, the FTO glass ($1.0 \times 1.5$ cm$^2$) was immersed into the aqueous mixture (containing 50 mM $TiCl_4$) in a closed, air-filled chamber for 30 minutes at 70°C. For the $TiCl_4$ post-treatment, the mesoporous $TiO_2$ film deposited on the FTO glass was immersed into the aqueous solution (containing 50 mM $TiCl_4$) and kept in an oven at 70°C for 30 minutes.[8]

### *Fabrication of DSSC*

Mesoporous $TiO_2$ films were deposited on the FTO glass (F-doped $SnO_2$ glass; 8 Ω/sq; Hartford Glass Co.) by the doctor-blade method using a $TiO_2$ paste. The annealed $TiO_2$ films at 450°C for 30 min resulted in 5∼6 $\mu$m thickness with a porosity of ca. 60%. After the annealed film was cooled down to 60°C, it was immediately immersed into an acetonitrile/iso-butanol (50/50 v/v%) solution containing 0.3 mM N719 dye for 24 hr at room temperature. The dye-adsorbed $TiO_2$ electrode was rinsed with the acetonitrile solvent and dried by $N_2$ purging. The counter electrode was prepared by spreading a droplet of 5 mM $H_2PtCl_6$ in 2-propanol onto the FTO glass and heating them at 400°C for 20 min. The assembly of dye-sensitized $TiO_2$ films was filled with an electrolyte of 0.8 M 1-hexyl-2,3-dimethylimidazolium iodide and 50 mM iodine in methoxypropionitrile. The resulting cell had an active area of ca. 0.15 cm.[3,8]

### *Measurements*

The average thickness of $TiO_2$ film was measured by the surface profiler (KLA Tencor Alpha-Step 500). Electrochemical measurements were carried out with a potentiostat

(PAR283) equipped with a frequency response analyzer (Solariton, M1260). The cyclic voltametry (C-V) test was carried out in an acetonitrile solution containing 50 mM ferrocene and 0.1 M $TBAPF_6$ as supporting electrolytes through three-component electrochemical cells composed of Ag/AgCl QRE, platinum wire counter electrode and $TiCl_4$-modified FTO glass as a working electrode.[17] The initial potential was set to 0 V vs. Ag/AgCl QRE, the reversal potential to -0.5 V, the final potential to 1.0 V (or 1.5 V), the scan rate to 0.1 V/sec, and the current sensitivity to $1 \times 10^{-8}$ A.

## Results and Discussion

The aim of the research is to evaluate the relative effectiveness of $TiO_x$ blocking layer on the FTO glass by the variation of alcohol solvents and dipping sequences. In addition, other parameters (such as $TiCl_4$ concentrations and dipping times) were also investigated to get optimized $TiCl_4$ pretreatment on the FTO glass. Cyclic voltammetry (C-V) as an electrochemical analysis was used to estimate the degree of non-electro activeness of $TiCl_4$-treated FTO glass that is inversely proportional to the cathodic peak current.

### *3.1. Effect of $TiCl_4$ Concentrations and Dipping Times*

Figure 1 shows the cyclic voltagram (C-V diagram) for the $TiCl_4$-treated FTO glass as a working electrode using ferrocene in acetonitrile with 0.1 M $TBAPF_6$ as supporting electrolytes. According to a C-V diagram, the cathodic peak current of the $TiCl_4$-treated FTO electrode was fairly reduced as compared to a pristine FTO electrode. However, there was not distinct difference in the cathodic peak currents obtained from all the $TiCl_4$-treated FTO electrodes prepared by different dipping times. The increase of dipping times did not induce the decrease of the cathodic peak currents. The FTO glass pretreated by various $TiCl_4$ concentrations (50∼200 mM) was also analyzed by cyclic voltammetry, as shown in Figure 1b. Overall, the C-V diagram for 50 mM $TiCl_4$-treated FTO glass was very similar to those of other FTO glasses pretreated by higher $TiCl_4$ concentrations.

The $TiCl_4$ pretreatment on the FTO glass in aqueous solution did not exhibit the strong dependence on the TiCl4 concentrations and dipping times. The hydrolysis of aqueous $TiCl_4$ induced the partial passivation of the FTO glass through the formation of Ti oxide layer, consequently leading to the decrease of cathodic peak currents, i.e., non-electroactive Ti oxide layer partially passivated the conductive FTO glass by blocking the electron transfer pathway from the FTO to contacting electrolytes.

### *3.2. Effect of Alcohol Solvent Types*

Mixed solution with lowered dielectric constants induced the fast hydrolysis of $TiCl_4$ with the consequent precipitation of Ti complexes on the FTO glass. The alcohol solvents have the following order of dielectric constants: $H_2O$ (80) > methanol (MeOH) (33) > ethanol (EtOH) (24.3) > isopropanol (IPA) (18.7). In order to induce the rapid hydrolysis of $TiCl_4$, alcohol solvents with low dielectric constants were added as 50 vol% in aqueous $TiCl_4$ solution. When the potential was scanned between −0.5 V and 1.0 V (or 1.5 V), the cathodic peak current on the $TiCl_4$-treated FTO working electrode was observed at ca. −0.2 V vs. Ag/AgCl QRE, which might be attributed to the one electron reduction of ferrocene.[18] As shown in Figure 2, the $TiCl_4$-treated FTO glass in 50 vol% of alcohol mixtures exhibited the decreasing order of cathodic peak currents with the increase of dipping times. That is,

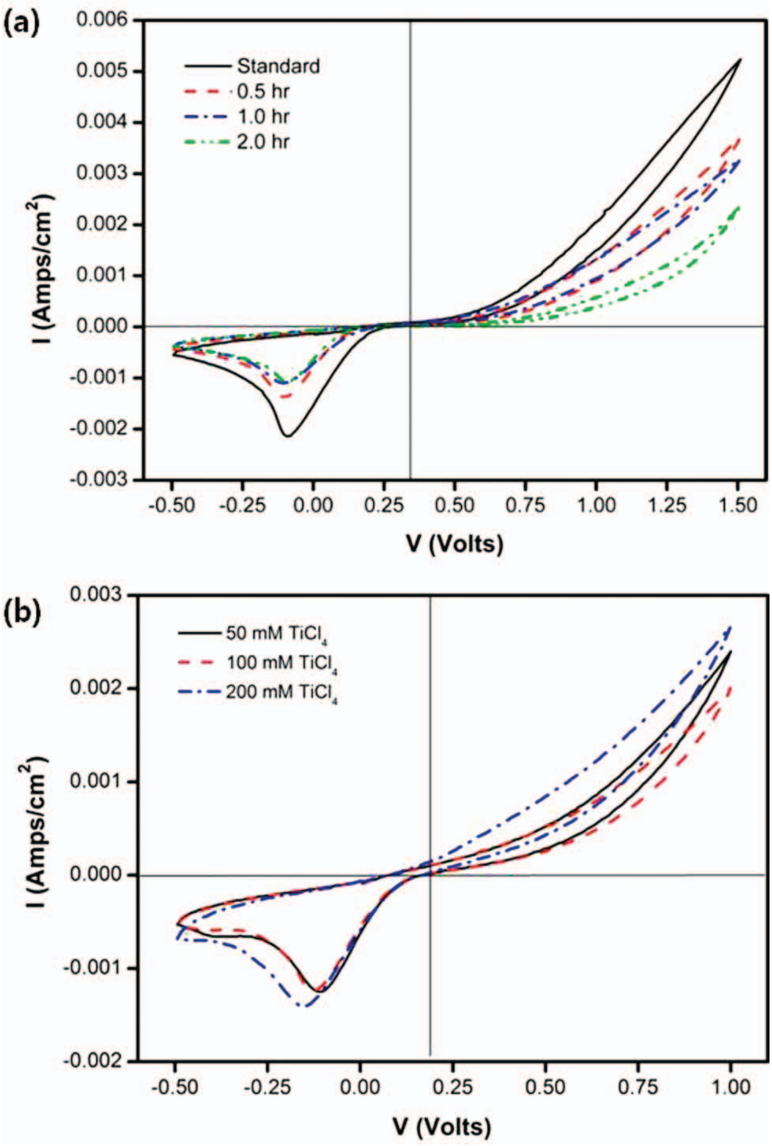

**Figure 1.** Cyclic voltagrams of FTO glass electrode treated by aqueous $TiCl_4$ solution at 70°C: (a) different concentration of $TiCl_4$ for 30 min, (b) different dipping times at 50 mM $TiCl_4$.

the decrease of cathodic peak currents was closely related to the proportional increase of non-electroactive Ti oxide layer deposited on the FTO glass.

The low dielectric constant of the solvent generally promotes the precipitation of the particles in the mixed solution due to the colloidal unstabilization. According to Kim's report, the size of agglomerated particles was decreased as the number of carbons in the alcohol was increased.[14] As expected, the cathodic peak current on the TiCl4-treated FTO glass in 50 vol% alcohols was decreased in the following order: MeOH > EtOH > PrOH. According to the lowest cathodic peak current observed in Figure 2(c), more fine precipitates

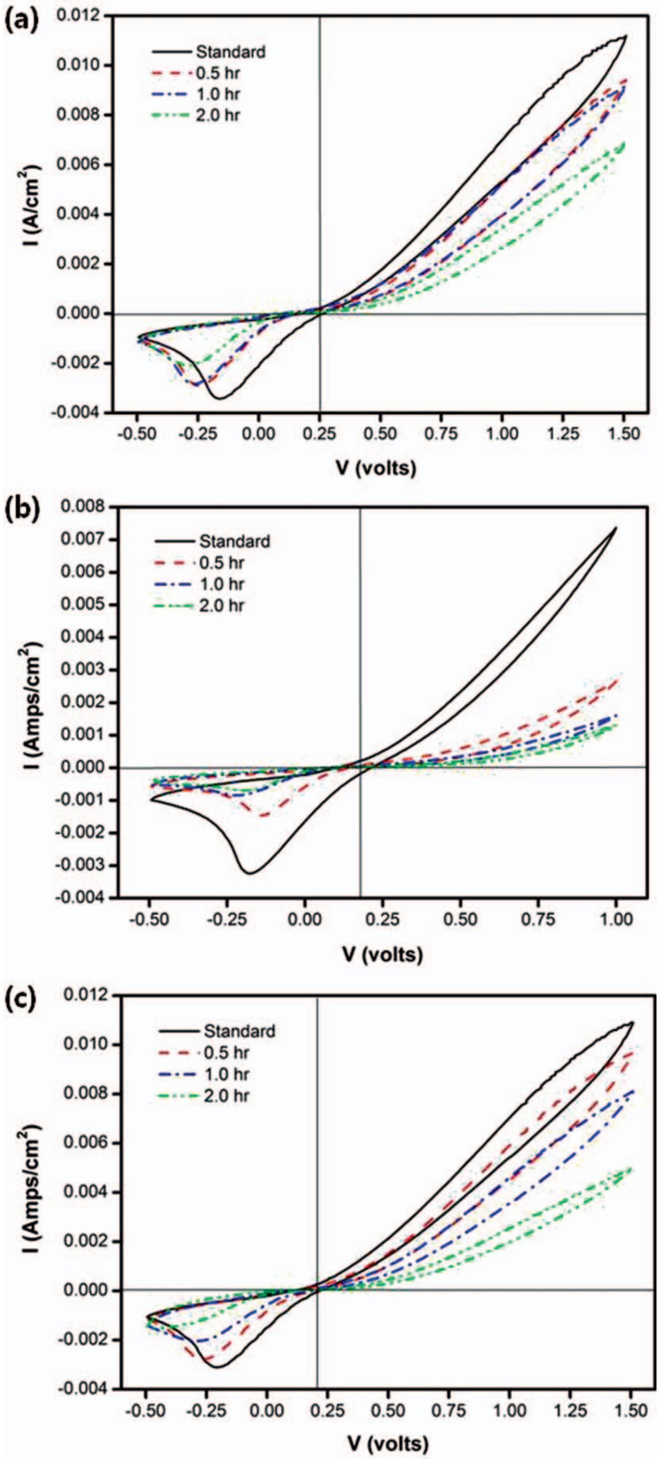

**Figure 2.** Cyclic voltagrams of FTO glass electrode treated by 50 mM $TiCl_4$ in alcohol solvents at different dipping times: a) 50 vol% of methanol (MeOH), b) 50 vol% of ethanol (EtOH), c) 50 vol% of isopropanol (IPA).

were produced in 50 vol% of IPA with the lowest dielectric constant, i.e., consequently leading to the formation of more compact blocking layer on the FTO glass. Other factors such as surface potential, viscosity and volume ratio are assumed to be constant for the $TiCl_4$ hydrolysis in the mixed solution.

### 3.3. *Effect of Dipping Sequence*

The dipping sequence of $TiCl_4$ hydrolysis was investigated to optimize the formation of Ti oxide layer on the FTO glass which can effectively block the electron transfer from the

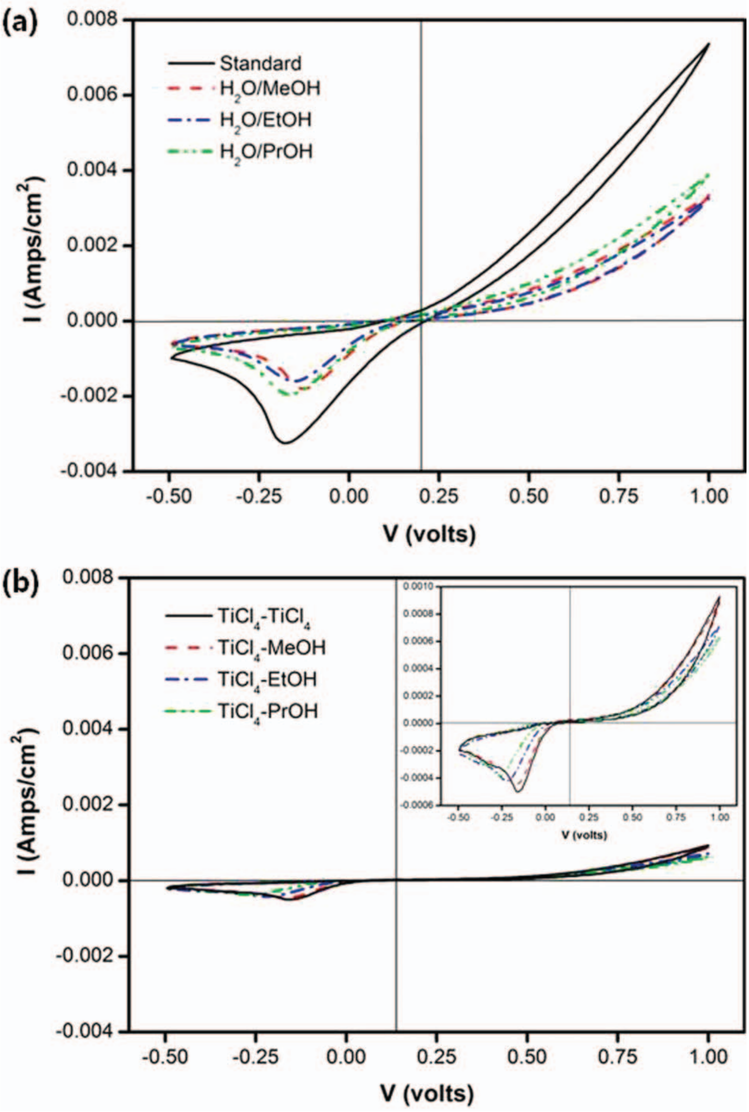

**Figure 3.** Cyclic voltagrams of FTO glass electrode treated by 50 mM $TiCl_4$ in the mixed solution for different dipping sequences: (a) sequential dipping, i.e., FTO glass in aqueous solution followed by alcohol mixtures in one-pot, b) double-dipping, i.e., FTO glass in aqueous solution and the heated FTO glass in alcohol mixture.

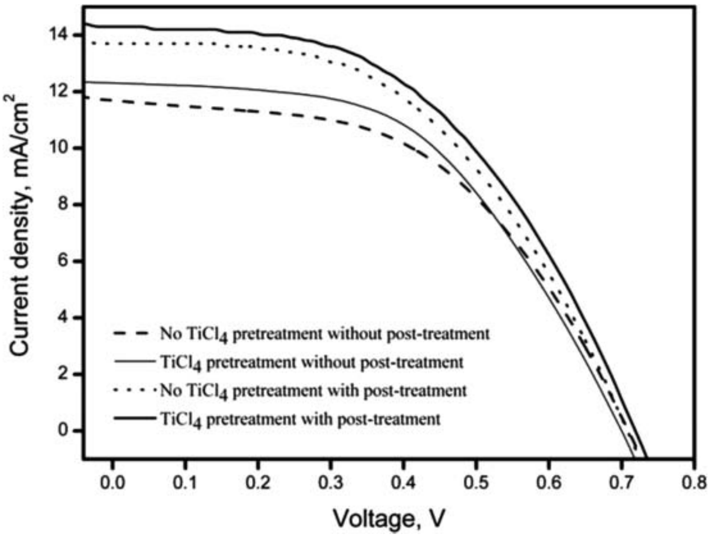

**Figure 4.** Current-Voltage (I-V) characteristics of dye-sensitized solar cells prepared by different $TiCl_4$ treatments under one sun of solar simulator (AM 1.5).

FTO glass to electrolytes. Figure 3(a) shows the C-V diagram of the FTO glass electrode prepared by 50 mM $TiCl_4$ hydrolysis in aqueous solution for 1 hr, followed by the addition of 50 vol% alcohol mixture for another 2 hr. There were not any clear changes in the cathodic peak currents in reference to that of the pristine FTO glass. That is, the addition of alcohol solvents in one-pot after 1 hr did not influence on the formation of non-electroactive $TiO_x$ blocking layers. The initially-deposited Ti oxide layer in aqueous solution determined the I-V characteristics of the modified FTO glass electrode.

The $TiCl_4$-treated FTO glass in aqueous solution was calcined at 400°C for 20 minutes and the heat-treated FTO glass was dipped again into 50 vol% alcohol mixture containing 50 mM $TiCl_4$. The electrochemical characteristics of double-dipped FTO glass were investigated by cyclic voltammetry. As shown in Figure 3b, the cathodic peak current was significantly reduced, in contrast with the minimal changes by the sequential deposition in one-pot (see Figure 3a). The double-dipped FTO glass was almost passivated by Ti oxide layer because the cathodic peak current on the modified FTO glass was negligible in comparison to the pristine FTO glass. The double-dipped FTO glass is expected to give the similar performance to that of spray-coated $TiO_2$ thick layer that usually requires excessive consumption of Ti precursors.[3]

### *3.4. I-V Characteristics of DSSCs*

Four types of DSSCs with different $TiCl_4$ treatments were prepared: i) The first class of DSSCs without $TiCl_4$ pretreatment was prepared as <none-$TiCl_4$/$TiO_2$/post-$TiCl_4$> and <none-$TiCl_4$/$TiO_2$/none-$TiCl_4$>, respectively, with and without $TiCl_4$ post-treatment; ii) the second class of DSSCs with double-dipped $TiCl_4$ pretreatment was prepared as <pre-$TiCl_4$/$TiO_2$/post-$TiCl_4$> and <pre-$TiCl_4$/$TiO_2$/none-$TiCl_4$>, respectively, with and without $TiCl_4$ post-treatment.

Figure 4 shows that the I-V curves of $TiO_2$-based DSSCs prepared by different $TiCl_4$ treatments, and Table 1 summarized the characteristic values of I-V curves obtained from

**Table 1.** The photovoltaic characteristics of dye-sensitized solar cells (DSSCs) prepared by various $TiCl_4$ treatments

| Treatments | No $TiCl_4$ Pretreatment | | Heavy $TiCl_4$ Pretreatment | |
|---|---|---|---|---|
| Parameters | w/out post[a] | with post[b] | w/out post[a] | with post[b] |
| $I_{sc}$ | $11.775 \pm 0.094$ | $13.808 \pm 0.132$ | $12.407 \pm 0.167$ | $14.331 \pm 0.071$ |
| $V_{oc}$ | $0.713 \pm 0.005$ | $0.709 \pm 0.001$ | $0.701 \pm 0.002$ | $0.719 \pm 0.003$ |
| FF | $0.519 \pm 0.008$ | $0.473 \pm 0.025$ | $0.518 \pm 0.007$ | $0.478 \pm 0.020$ |
| Eff% | $4.645 \pm 0.135$ | $5.020 \pm 0.219$ | $4.821 \pm 0.014$ | $5.258 \pm 0.187$ |

[a] $TiO_2$ nanocrystalline films were not treated by 50 mM $TiCl_4$.
[b] $TiO_2$ nanocrystalline films were treated by 50 mM $TiCl_4$.

the different DSSCs. For the case of $TiCl_4$ pretreatment, the $I_{sc}$ of <pre-$TiCl_4$/$TiO_2$/none-$TiCl_4$> was increased from 11.78 to 12.41 mA/cm$^2$ in reference to <none-$TiCl_4$/$TiO_2$/none-$TiCl_4$>. For the case of $TiCl_4$ post-treatment, <pre-$TiCl_4$/$TiO_2$/post-$TiCl_4$> exhibited the increase of $I_{sc}$ from 12.41 to 14.33 mA/cm$^2$ in reference to <pre-$TiCl_4$/$TiO_2$/none-$TiCl_4$>. The $V_{oc}$ obtained from four different DSSCs did not indicate any consistent trends which might be related to the density of electron traps.[2,3]

The enhancement in PCE by $TiCl_4$ pretreatment is usually ascribed to the formation of blocking layer on the FTO glass which can inhibit the recombination of the collected electrons on the FTO glass with electrolytes.[4,8] On the other hand, the increase of PCE by $TiCl_4$ post-treatment is ascribed to the enlarged surface area of $TiO_2$ films along with the consequent increase of dye adsorption (i.e., enhanced harvesting efficiency).[3,19] In summary, <pre-$TiCl_4$/$TiO_2$/post-$TiCl_4$> cell exhibited the highest PCE among four different DSSCs, probably due to the suppression of charge recombination on the FTO glass by the $TiCl_4$ pretreatment and the enhanced harvesting efficiency by the $TiCl_4$ post-treatment.

## Conclusions

In this work, we investigated the $TiCl_4$ treatment on the Fluorine-doped tin oxide (FTO) glass with the variation of $TiCl_4$ concentrations (50∼200 mM), dipping times (0.5∼2.0 hr), alcohol solvent types, and dipping sequences. According to the electrochemical analysis by cyclic voltammetry, the effectiveness of $TiO_x$ blocking layer was strongly influenced by the dielectric constants of dipping solution containing 50 vol% alcohol solvents in the following order: isopropanol > ethanol > methanol. According to the cyclic voltagrams of the modified FTO electrodes, the most effective blocking layer was formed through the double-dipping sequence, i.e., first dipping the FTO glass in aqueous solution of 50 mM $TiCl_4$ and subsequently dipping the heat-treated FTO glass in 50% IPA mixture of 50 mM $TiCl_4$.

The heavily $TiCl_4$-pretreated FTO glass resulted in <pre-$TiCl_4$/$TiO_2$/none-$TiCl_4$> cell with higher PCE by ca. 3.8%, as compared to <none-$TiCl_4$/$TiO_2$/none-$TiCl_4$> cell. The additional $TiCl_4$ post-treatment resulted in <pre-$TiCl_4$/$TiO_2$/post-$TiCl_4$> cell to achieve more enhanced PCE by ca. 13.2%, as compared to <none-$TiCl_4$/$TiO_2$/none-$TiCl_4$> cell. DSSC prepared by both $TiCl_4$ pretreatment and $TiCl_4$ post-treatment exhibited the highest PCE, due to the suppression of charge recombination on the FTO glass by $TiCl_4$ pretreatment and the enlarged surface area of titanium dioxide films by $TiCl_4$ post-treatment.

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