



## Influence of a $\text{TiCl}_4$ Treatment Condition on Dye-Sensitized Solar Cells

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### ABSTRACT

In dye-sensitized solar cells (DSSCs), the back transfer of photo-generated electrons from FTO glass to triiodide ions in an electrolyte is an important loss mechanism, which leads to low cell efficiency. Recently, this back electron transfer was greatly suppressed by the introduction of a compact  $\text{TiO}_2$  blocking layer, which was prepared by the treatment of  $\text{TiCl}_4$  solution. In the present work, more detailed  $\text{TiCl}_4$  treated surface conditions on FTO substrate were investigated and DSSC performances were correlated with the surface morphology as well as dark current behavior.

**Keywords :** Dye-sensitized solar cells, Underlayer, Recombination

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### 1. Introduction

Dye sensitized solar cells (DSSCs) are promising solar cells for commercialization in the near future due to their high-energy conversion efficiency and low production cost, making them considerable alternatives to silicon solar cells.<sup>1-3)</sup> DSSCs composed of a dye-adsorbed 10~15  $\mu\text{m}$ -thick nanoparticulate  $\text{TiO}_2$  film on fluorine-doped tin oxide (FTO) glass as an anode, redox electrolytes as charge carriers and the Pt counter electrode. To obtain high power conversion efficiency, a mesoporous film with large surface area should be used to maximize the amount of photogenerated charge. Photoexcited ruthenium-based dyes inject electrons into the  $\text{TiO}_2$  and the injected electrons diffuse through a disordered  $\text{TiO}_2$  film with a high grain boundary to the FTO substrate. Recently, much attention relating control of dark current with cell performance has been paid to maximize the light-harvesting efficiencies of DSSCs.<sup>4)</sup>

Photogenerated electrons can be recaptured by tri-

oxide in an electrolyte at several interfaces of dye/electrolyte,  $\text{TiO}_2$ /electrolyte and FTO/electrolyte. Recently, many several groups have focused on the interface controlling of  $\text{TiO}_2$ /electrolyte to reduce the loss of the generated electrons especially by introducing  $\text{Al}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{SrTiO}_3$  and  $\text{TiO}_2$  for surface modification of mesoporous electrode.<sup>5-8)</sup> However, only a few researches have investigated the interface controlling of FTO/electrolyte by introducing compact  $\text{TiO}_2$  underlayer to increase cell efficiency.<sup>4,9-14)</sup> Several different effects of underlayer were introduced resulting from the depression of electron recombination on the FTO substrate. From intensity-modulated infrared spectroscopy, Frank *et al.* concluded that electron recombination near the FTO substrate is an important recombination route.<sup>15)</sup> Recently, Yanagida group introduced that the thin  $\text{Nb}_2\text{O}_5$  layer works as a remarkable blocking layer at the FTO/ $\text{TiO}_2$  interface, obtaining an increased cell performance.<sup>13,16)</sup> Our group also investigated the positive effect of the underlayer on the cell performance of metal substrate based DSSC. The J-V curve of flexible DSSC with  $\text{TiO}_2$  underlayer prepared by Ti-isopropoxide gives much enhanced  $J_{\text{sc}}$ .

Up to now, several research papers concerning on

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the effects of the TiO<sub>2</sub> underlayer were investigated and significant progresses have been made in understanding the mechanism of recombination between photogenerated electrons and FTO substrate. Especially, Gratzel group reported on the influence of different FTO surface treatments (TiCl<sub>4</sub> or compact TiO<sub>2</sub> underlayer) on dark and photocurrent behavior in DSSCs. In the case of the surface treatment with TiCl<sub>4</sub>, FTO glass was dipped into 40 mM TiCl<sub>4</sub> aqueous solution at 70°C for 30 min. As far as we know, there is no published paper why this condition should be used for the surface treatment of FTO glass.

In this study, we report on the influence of different TiCl<sub>4</sub> treatment conditions on the dark current and cell performance in DSSCs. The correlations between the surface morphologies of TiCl<sub>4</sub> treated FTO glass and the cell performances were investigated and an optimal condition for maximizing DSSC performance was also obtained.

## 2. Experimental

FTO glass was cleaned by acetone and methanol, successively. Then, the cleaned substrate was treated by a home-made UV-ozone chamber for 20 min. To investigate the effect of under layer, the substrate was immersed in 40 mM TiCl<sub>4</sub> aqueous solution at 70°C for 30 min.

Anatase TiO<sub>2</sub> colloids were made via a sol-gel hydrolysis and autoclaving of titanium isopropoxide at 230°C for 12 hr in an acetic acid aqueous solution, as described elsewhere.<sup>17)</sup> TiO<sub>2</sub> nanoparticles were dispersed in  $\alpha$ -terpinol with ethyl cellulose as a binder. The solution was applied with a doctor blade to produce a TiO<sub>2</sub> film on the supporting substrate. The film (~20  $\mu$ m) was annealed at 600°C for 30 min in air. To coat dye on the TiO<sub>2</sub> film, the samples were immersed in  $3 \times 10^{-4}$  M Ru(II)LL'(NCS)<sub>2</sub> (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, L' = 2,2'-bipyridyl-4,4'-ditetrabutylammonium carboxylate, Solaronix) ethanol solution for 18 hr. Counter electrodes were prepared by applying a drop of H<sub>2</sub>PtCl<sub>6</sub> on fluorine-doped tin oxide (FTO) glass followed by heating at 400°C for 15 min. The electrodes were separated by a 50  $\mu$ m-thick hot melt of a polymer film (Surlyn, Dupont 1702) and sealed by heating. Liquid electrolyte was composed of 0.6 M butylmethylimidazolium iodide, 0.03 M I<sub>2</sub>, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (v/v, 85 : 15).

## 3. Results and Discussion

DSSC is composed of a porous layer of TiO<sub>2</sub> nanoparticles, anchored with a molecular dyes that absorbs sunlight, like the chlorophyll in green leaves. As in a conventional alkaline battery, an anode (TiO<sub>2</sub>) and a cathode (the Pt) are placed on either side of a liquid conductor (the electrolyte). As can be seen in Fig. 1, sunlight passes through the TCO into the dye layer where it can excite electrons that then flow into the TiO<sub>2</sub>. The electrons flow toward the TCO where they are collected for the generation of photocurrent. After flowing through the external circuit, they are re-introduced into the cell on a counter electrode, flowing into the electrolyte. The electrolyte then transports the electrons back to the dye molecules.

Dye-sensitized solar cells separate the exciton generation step and transportation step. In the case of Si based solar cells or organic solar cells, the p-type and n-type materials act as both the source of photoelectrons, as well as providing the electric field to separate the charges and create a current. In the DSSCs, the bulk of the TiO<sub>2</sub> semiconductor is used solely for electron transport. The photoelectrons are provided from a separate photosensitive dye. Diffusion of electrons through the nanocrystalline TiO<sub>2</sub> film to the FTO substrate, and diffusion of the oxidized redox species, R<sup>+</sup>, through the solution or solid electrolyte to the counter electrode, allow both charge carriers to be transferred to the external circuit where useful work is performed. There are several possible electron/R<sup>+</sup> recombination pathways inside the cell. One involve the recombination of electrons in TiO<sub>2</sub> layer with the oxidized dye before the dye can be regenerated. Another possible pathway is the recombination occurred at the interface between a FTO substrate and an electrolyte.

An enhanced photocurrent in DSSC was observed owing to effective blocking layer prepared from TiCl<sub>4</sub> underlayer at interstitial FTO and mesoporous TiO<sub>2</sub>

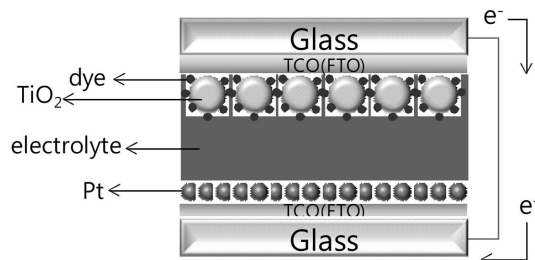
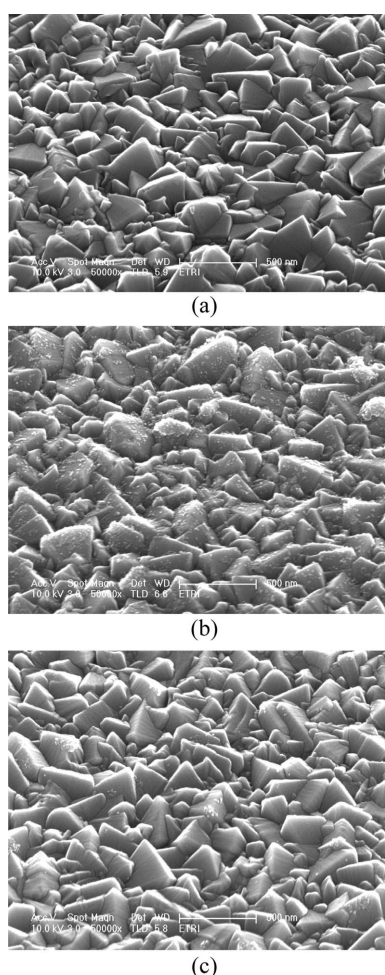


Fig. 1. Working mechanism of DSSC.

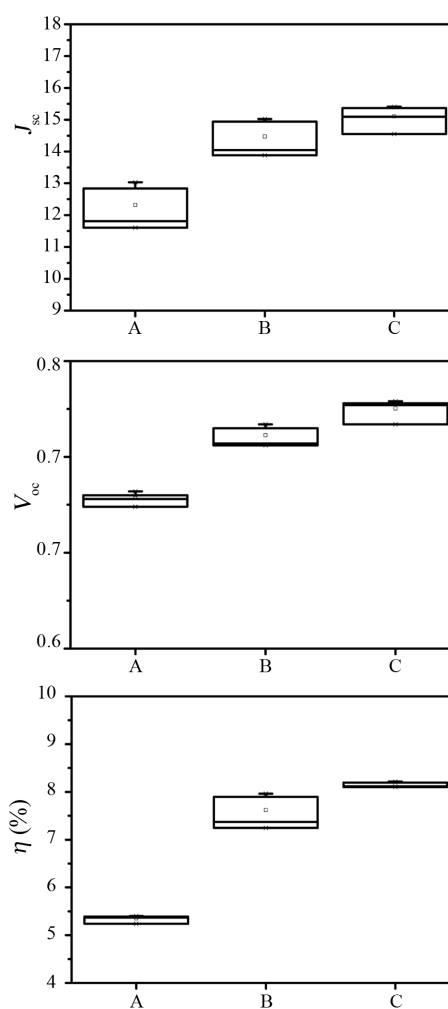
interfaces. Hence, more densely packed underlayer on FTO glass is preferable if the underlayer do not interfere with the transmission of incident light. To prepare densely packed underlayer from  $\text{TiCl}_4$  treatment FTO glass was treated with UV-Ozone before immersing it into  $\text{TiCl}_4$  in water. It is well known that UV-Ozone treated FTO glass have more hydrophilic characteristics compared to neat FTO glass. Fig. 2(a) and (b) present the SEM images of the FTO glass without and with  $\text{TiCl}_4$  treatment. Fig. 2(c) shows the SEM image of the underlayered FTO glass, which was treated by UV-Ozone. In Fig. 2(a), we can find that the FTO layer is composed of crystalline particles which are about 200 nm. As can be seen in Fig. 2(b), small  $\text{TiO}_2$  particles may be covered on the FTO surface. However,



**Fig. 2.** SEM images of neat FTO substrate (a),  $\text{TiCl}_4$  treated FTO substrate without (b) and with (c) UV-Ozone treatment.

it is impossible to differentiate the underlayered FTO glass, which is pre-treated with UV-Ozone for 15 minutes, from the neat FTO glass. This means that the under layer generated from the  $\text{TiCl}_4$  treatment on the UV-Ozone treated substrate has more dense morphology, resulting the decrease of contact between the electrolyte and FTO substrate.

The summarized photocurrent and photovoltage ( $J-V$ ) characteristics of the DSSCs measured with an active area of  $\sim 0.2 \text{ cm}^2$  using simulated solar light at AM 1.5 produced by a 1000 W xenon lamp (Oriel, 91193) were shown in Fig. 3. At 1 sun illumination, the DSSCs without an underlayer exhibited a  $J_{sc}$  of



**Fig. 3.** Summarized cell performances of DSSCs. (A) DSSC without underlayer, (B) DSSC with underlayer (without UV-Ozone treatment), (C) DSSC with underlayer (UV-Ozone treatment).

12.5 mA/cm<sup>2</sup>, a  $V_{oc}$  of 0.726 V, with an overall conversion efficiency of 5.4%. The DSSCs prepared using non-treated FTO glass before TiCl<sub>4</sub> treatment exhibited a  $J_{sc}$  of 14.5 mA/cm<sup>2</sup>, a  $V_{oc}$  of 0.760 V, with an overall conversion efficiency of 7.5%. The DSSCs prepared using UV-Ozone treated FTO glass before TiCl<sub>4</sub> treatment exhibited a  $J_{sc}$  of 15.0 mA/cm<sup>2</sup>, a  $V_{oc}$  of 0.775 V, with an overall conversion efficiency of 8.2%. We believe that this enhancement can be attributed to a reduction of charge recombination between photo injected electrons in the substrate and the oxidized dye.<sup>15)</sup>

#### 4. Conclusions

In summary, we have introduced the effect of UV-Ozone treatment on cell performances of DSSCs. To date, most researchers have used TiCl<sub>4</sub> treatment method for the fabrication of TiO<sub>2</sub> underlayer in DSSCs. From our results, it was confirmed that the use of UV-Ozon treatment can improve a cell efficiency resulting from the formation of dense TiO<sub>2</sub> underlayer. We believe that the ease of FTO glass pre-treatment method can facilitate increasing the power conversion efficiency of DSSCs.

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