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Optimization of nanostructured titania photoanodes for dye-sensitized solar cells: Study and experimentation of TiCl_4 treatment

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ABSTRACT

Titanium tetrachloride (TiCl_4) treatment processed by chemical bath deposition is usually adopted as pre- and post-treatment for nanocrystalline titanium dioxide (TiO_2) film deposition in the dye-sensitized solar cell (DSC) technology. Pre-treatment influences positively the bonding strength between the fluorinated tin oxide (FTO) substrate and the porous TiO_2 layer, blocking the charge recombination at the interface between the conduction glass FTO and the I_3^- ions present in the I^-/I_3^- red-ox couple. Additionally, TiCl_4 post-treatment is a widely known method capable of improving the performance of dye-sensitized solar cells, in particular, the photocurrent collected from the device.

In this study, the influence and effect of TiCl_4 pre- and post-treatment on the TiO_2 layer is proposed and compared to the untreated film. The relative DSC devices are characterized in terms of short circuit current density, open circuit voltage, fill factor, conversion efficiency and IPCE.

The dark current characteristics of cells with a treated and untreated TiO_2 layer are also shown in order to evaluate the effect of TiCl_4 pre-treatment as a blocking layer.

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1. Introduction

Since the introduction and development of the dye-sensitized solar cell (DSC) [1] several efforts have been made to optimize the materials involved in the photo-electrochemical process and to improve the light conversion efficiency of the device [2].

Among the different steps in the realization of efficient DSCs, the control of the quality, morphology and design of the mesoporous wide band-gap titanium dioxide (TiO_2) layer is of fundamental importance [3]. In recent designs a highly porous nanocrystalline TiO_2 film (with a large effective surface area), deposited using the techniques of screen-printing or blade coating [4], has been typically optimized by depositing a second light-scattering layer [5]. The first porous layer is responsible for the increase in the amount of the dye adsorbed and makes a simple electrolyte diffusion. The scattering of light, due to the second layer, increases the path length of photons inside the cell and the probability to interact with a dye molecule [6]. The photon-trapping effect can be so induced by the use of a combination of a transparent nanocrystalline TiO_2 film with a

microcrystalline light-scattering layer [7,8], in conjunction with the anti-reflecting film (ARF) [9] and other techniques [10].

A widely known method to improve the DSC performance is treatment of fluorinated tin oxide (FTO) covered glass (pre-treatment) and TiO_2 film (post-treatment) with an aqueous solution of titanium tetrachloride (TiCl_4) [11]. The pre- and post-treatment is the complete treatment.

The pre-treatment influences positively the bonding strength between the FTO substrate and the porous TiO_2 layer and blocks the charge recombination between electrons emanating from the FTO and the I_3^- ions present in the I^-/I_3^- red-ox couple [12]. To reduce the charge recombination at the FTO/electrolyte interface, Ito and his coworkers have demonstrated that a high open circuit photo-voltage is required to prevent the recapture of photo-injected electrons by I_3^- [13].

The TiCl_4 post-treatment results in an improvement of the photocurrent but its real effect is not quite clear. In particular, the hypothesis that can explain the improvement of the injection of an electron is still controversial. O'Regan et al. [14] have shown that the main effects of this treatment are a downward shift in the TiO_2 conduction band edge potential and a decrease in the electron/electrolyte recombination rate constant. Together, these changes increase the quantum efficiency of charge separation at the interface.

Moreover, morphological changes and shifts in the Raman spectra of cells with treated TiO_2 layer have been also remarked [15]. A generation of new rutile layers on the rutile TiO_2 surface has been reported,

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resulting in epitaxial growth of new layers on the electrode surface made entirely of rutile nanoparticles. As has been already shown [16], the TiCl_4 treatment decreases the surface area of the films, as well as the average pore size and the porosity. All these data suggest that the titanium complexes present in the TiCl_4 solution condense at the inter-part of the film. This hypothesis is consistent with the pore-size reduction, the surface-area loss, and the density variation that are observed in the films after TiCl_4 treatment.

In this study, pre- and post- TiCl_4 treatment of a TiO_2 layer was processed and the improvement in the photocurrent for a relative DSC device was evaluated and investigated, analyzing the effect also after two months from the fabrication of cells. In addition, the concentration and volume solution influence on the treatment was highlighted.

2. Experimental section

The DSCs were fabricated by the following procedure [4,17]. The substrates were $8 \Omega/\text{sq}$ FTO-glass ($2 \text{ cm} \times 2 \text{ cm}$, Pilkington) cleaned in an ultrasonic bath for 10 min in acetone and for 5 min in ethanol. $5 \text{ mm} \times 5 \text{ mm}$ TiO_2 films (thickness $\sim 15 \mu\text{m}$) deposited via blade coating using Dyesol DSL 18 NR-T TiO_2 paste, dried for 15 min at 50°C , for 15 min at 70°C and then sintered at 525°C for 30 min. After sintering the transparent substrates were soaked in a 0.5 mM N719 (B2, Dyesol) dye solution in ethanol for 15 h, and then rinsed in ethanol. The counter-electrodes were prepared by screen-printing Dyesol PT1 Platinum paste onto the FTO-coated substrates, dried for 10 min at 80°C and then annealed at 420°C for 15 min. The cells were completed by sealing together the two electrodes via a $60 \mu\text{m}$ thick Surllyn (Solaronix) gasket. One batch of devices with a Dyesol High Stability Electrolyte (HSE) mediator inserted into the cell via vacuum backfilling was fabricated.

The TiCl_4 solution was diluted in aqueous solution with a final concentration of 40 mM. The “pre-treated” photo-electrodes had the TiCl_4 treatment after the cleaning step of the FTO covered glass. The “post-treated” photo-electrodes had the TiCl_4 treatment after the TiO_2 film sintering step. Both treatments were processed by dipping the samples into the TiCl_4 solution at 70°C for 30 min, then rinsing in de-ionized water and ethanol and drying at room temperature in a vertical position. The aqueous TiCl_4 solution for the pre-treatment was not reused for the post-treatment in order to achieve the best result. Following the post-treatment, the TiO_2 film was annealed at 500°C for 30 min.

The experiment was conducted by testing the devices in a solar simulator (Solar constant 1200 KHS) at AM 1.5, $1000 \text{ W}/\text{m}^2$ calibrated with a Skye SKS 1110 sensor and the cells performance was evaluated by the incident photon-to-current conversion efficiency (IPCE) set-up.

3. Results

Fig. 1 compares the scanning electron microscopy (SEM) images of a TiO_2 film untreated and a film treated with the TiCl_4 solution. Fig. 1

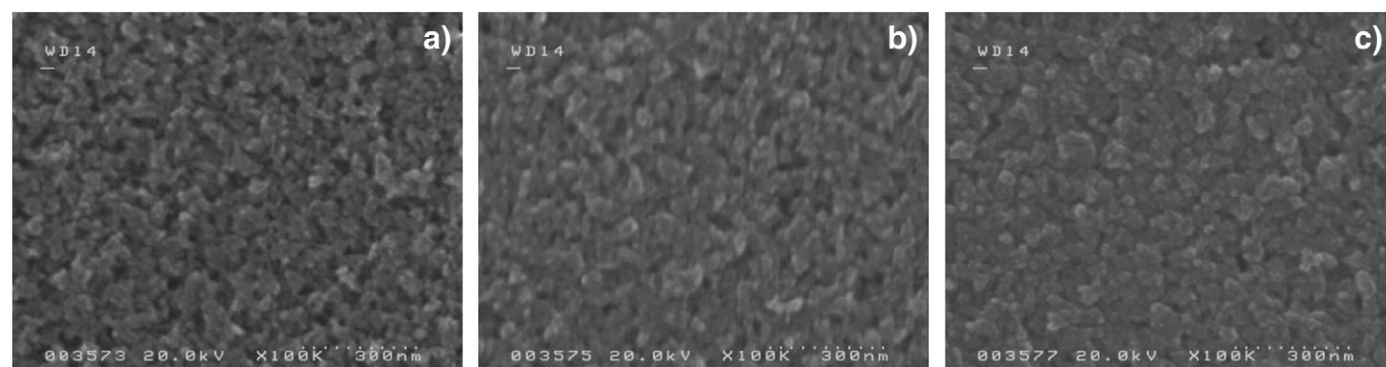


Fig. 1. SEM images of TiO_2 nanoparticles films untreated (a), after TiCl_4 treatment before annealing (b) and after TiCl_4 treatment and annealing (c).

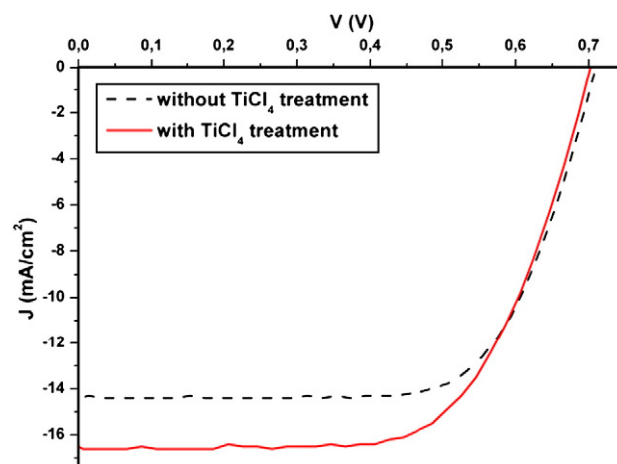


Fig. 2. J–V characteristics curves.

(a) shows the particles and sponge-like morphology of the TiO_2 film before treatment. Fig. 1(b) shows the piled-needle-like shapes after TiCl_4 chemical bath deposition and washing. Fig. 1(c) shows the disappearance of new shapes and improvement of particles necking by re-annealing the photo-electrode [15]. The J/V characteristics of the samples are in Fig. 2 and the cell parameters such as the short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η) are in Table 1. The increase in the current density and cell efficiency upon TiCl_4 treatment is 14.5% and 7% respectively, while V_{oc} does not change considerably. The enhancement in solar cell performance completely produces an improvement in the current density different from efficiency because of the FF decrease. We note that the enhancement of TiCl_4 treatment held out during time, also after two months from the fabrication of the DSCs (Table 1).

IPCE measurements were conducted to analyze enhanced J_{sc} in more detail (Fig. 3). A comparison of the IPCE curves revealed an upward shift of the cell with a treated TiO_2 layer with respect to the cell with the untreated TiO_2 layer in the wavelength range from 400 to 750 nm.

Dark current characteristics of cells with a treated and untreated titania layer are illustrated in Fig. 4 to evaluate the recombination behavior of the devices.

4. Discussion

The TiCl_4 treatment results in an improvement in the photocurrent, normally between 5% and 30%, depending on the quality of TiO_2 used to process the initial film. Typically the largest improvements come when using TiO_2 films of the poorest quality [14]. Considering that TiCl_4 treatment does not significantly raise the amount of the dye present or

Table 1
J–V parameters of cells. Error in efficiency of each cell is less than 4%.

	J_{sc} (mA/cm ²)	J_{sc} after two months (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
Untreated	14.5	12.5	714	68.42	7.06
TiCl ₄ treated	16.6	14.9	706	64.62	7.56

the light scattering, the increased photocurrent must then arise from improvements in either the charge separation or the collection efficiency.

Starting at the assumption that the electron transport in a mesoporous TiO₂ electrode is assumed to proceed by diffusion in absence of a significant electrical potential gradient in the film [18], necking between TiO₂ particles significantly influences the electron transport properties, characterized by the effective diffusion coefficient [19]. As has been already demonstrated, the electron diffusion coefficient of the mesoporous TiO₂ electrode treated with TiCl₄ (post-treatment) increases, with respect to the untreated electrode [15]. The increase in the necking between the particles (Fig. 1) will facilitate percolation of electrons from one particle to another and will reduce the recombination probability between the mediator and the semiconductor layer. Nevertheless, neither the charge collection nor the photocurrent improve as the following formula shows:

$$\Phi_c = \frac{K_T}{K_T + {}^TK_R}, \quad (1)$$

where K_T is the charge transport rate, K_R is the charge recombination rate and Φ_c is the collection efficiency of the injected electrons assumable unitary.

As widely accepted, some of the effects of TiCl₄ post-treatment are a decrease in the BET (Brunauer Emmett Teller) surface area and an increase in the particle diameter and mass of the treated TiO₂ film [20]. We experimentally verified that TiCl₄ treatment produced an increase in the TiO₂ particle diameter (Fig. 1), a significant film mass (35%) and no modification in the layer thickness profile. This is explained by a decrease in the BET surface area; it is possible that the TiCl₄ removes specific surface states that serve to quench the dye excited state, improving the binding of the dye on the TiO₂ film and reducing the fraction of the TiO₂ film inaccessible for the dye [13,20].

The TiCl₄ treatment on TiO₂ film produces a downward shift in the conduction band [20] and consequently results in enhancing the electron injection efficiency. This is the main cause of the upward shift in the photo-injected current (Fig. 2) and the IPCE curve (Fig. 3) of the TiCl₄ treated cells with respect to the untreated cells. A decrease in V_{oc} , caused by the downward shift of the quasi-Fermi level, is compensated

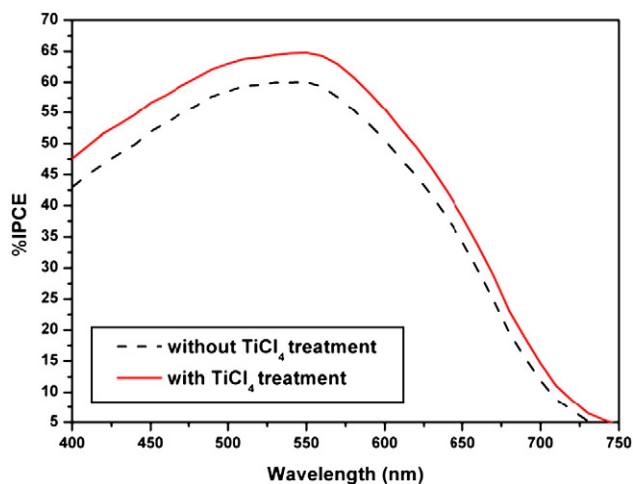


Fig. 3. IPCE of dye-sensitized solar cells without and with TiCl₄ treatment.

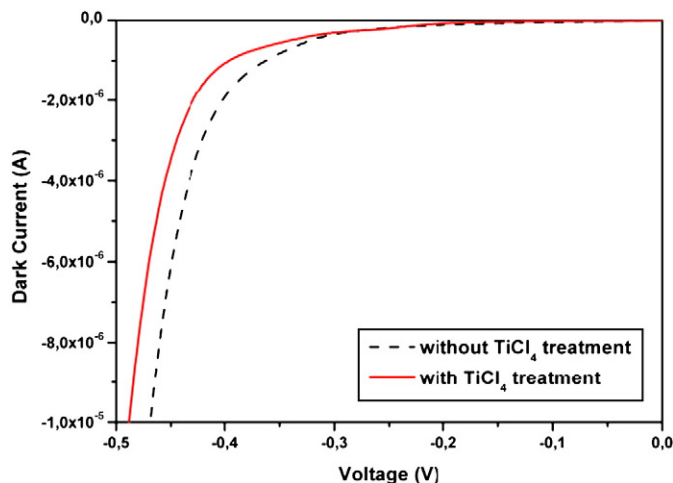


Fig. 4. Dark current–voltage characteristics curves of dye-sensitized solar cells before and after TiCl₄ treatment.

through a significant reduction of the charge recombination rate due to the post- and pre-treatment, letting the V_{oc} value under light practically unchanged (Table 1, Fig. 2).

The effective blocking layer obtained with the TiCl₄ pre-treatment on the glass substrate decreases the transfer resistance (at the expense of FF) of the thin conductive oxide (TCO) and the new nanoparticles enhance the surface area to suppress the charge recombination. The TiCl₄ pre-treatment enlarges the contact interface and increases the contact points between the TiO₂ film and the FTO. We notice, in fact, that the removal of the TiO₂ film from the conductive glass, by using solvents, is harder than in the untreated case. The TiCl₄ pre-treatment also improves the electronic interconnection, so that the photoelectrons can be collected efficiently and the probability of electron recombination can be reduced [21]. Fig. 4 points out the dark current suppression for DSC with the FTO glass treated because of the tri-iodide reduction at the exposed part of TCO.

Finally, experiments with different concentrations from 10 mM to 80 mM and different volumes from 30 to 180 ml of the TiCl₄ solution for six photo-electrodes were also carried out. They demonstrated that 30 to 50 mM could be considered the right concentration of the solution to obtain optimized treatment and any difference could be noticed by varying the TiCl₄ bath volume used for the treatments (not shown).

This can be due to an increase in the electron trap sites on the TiO₂ surface with the surface area decreased by the TiCl₄ treatment [21]. In fact, concentrations higher than 50 mM favor an increase in the nucleation of nanoparticles by reducing the film porosity and introducing a larger dark current, consequently.

5. Conclusions

In summary, although TiCl₄ pre- and post-treatment always produces improvements on the DSC performance, the degree of improvement is variable and strongly depends on the starting TiO₂ material and on precise control of the concentration of the TiCl₄ aqueous solution.

The improvement introduced by pre-treatment is attributed to the enhancement of electrical contiguity at the FTO/TiO₂ interface and to the reduction of the charge recombination due to the exposed part of FTO at the interface between the conducting glass and the electrolyte. In fact, the dark current characteristics demonstrate that the introduction of a blocking layer, between the FTO conducting glass and the TiO₂ film, by the TiCl₄ treatment, suppresses the dark current. At the same time, the increase in the photocurrent is not caused by an increase in light harvesting but by an enhancement in the electron

injection efficiency. Furthermore, the TiCl_4 post-treatment usefully concurs to improve the electrical contiguity of the TiO_2 film by enhancing the neck between the nanoparticles and minimizing the recombination rate between the TiO_2 film and the mediator. As a consequence of complete TiCl_4 treatment, the samples exhibit an improvement of the photocurrent density without any sensible V_{oc} variation.

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