Research Article

Achieving Enhanced Dye-Sensitized Solar Cell Performance by $\text{TiCl}_4/\text{Al}_2\text{O}_3$ Doped TiO_2 Nanotube Array Photoelectrodes

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For various reasons, low cost, easy fabrication, and so forth, dye-sensitized solar cells (DSSCs) have been consistently studied in many laboratories. To improve the DSSCs performance, using an aqueous solution of titanium tetrachloride (TiCl_4) treatment is one of many processes. Before the treatment of TiCl_4 , nanoporous TiO_2 nanotubes (TNTs) are fabricated through a secondary anodization process. TiCl_4 treatment on TNTs film enhanced short-circuit current density (J_{SC}) and aluminum oxide (Al_2O_3) posttreatment enhanced open-circuit voltage (V_{OC}). As a result, Al_2O_3 posttreatment on TNTs film conversion efficiency of 8.65% is realized, which is 7% higher than TiCl_4 treatment on TNTs film. In this work, we investigated that double dip-coating of $\text{TiCl}_4/\text{Al}_2\text{O}_3$ treatment on TiO_2 nanotubes film had an effect on enhancement of J_{SC} and V_{OC} due to improvement of electron transfer, increment of dye adsorption, and reduction of recombination rate of charge. Photoelectrode DSSCs with light-to-electric energy conversion efficiency were achieved under a simulated solar light irradiation of $100 \text{ mW}\cdot\text{cm}^{-2}$ (AM 1.5).

1. Introduction

Since the first report by Grätzel in 1991, dye-sensitized solar cells (DSSCs) have been consistently researched due to their low manufacturing costs, simple structure, and wide range of applications [1–3]. Generally, DSSCs are composed of as parts titanium oxide (TiO_2) which carries an anchored organic dye on working electrode layer, counter electrode layer made of Pt and an electrolyte containing a redox couple (I^-/I_3^-) between them [4–6].

Some researchers have suggested that the nanostructures such as nanowires, nanorods, nanofibers, or nanotubes need to avoid the electron transport in the nanocrystal boundaries of TiO_2 nanoparticles and the electron recombination with the electrolyte during the electron migration process [7–9]. Recently, TiO_2 nanotubes layers (TNTs) have attracted much attention, because of their geometric shape and simple anodic process of fabrication, which improve the electron transport between electrode layers. One-dimensional TiO_2 nanostructures have function of light scattering, fast electron

transport, and slower recombination rates but reduced dye adsorption by their surface areas [10–12].

To improve the DSSCs performance, well-known method is using an aqueous solution of titanium tetrachloride (TiCl_4) treatment [13–15]. The TiCl_4 treatment effect is not quite clear but many studies explain that TiCl_4 treatment on the starting TiO_2 nanoparticle shifts downwards in the TiO_2 conduction band gap and decreases recombination rate in the electron/electrolyte. Although previous studies that treatment on TiO_2 nanoparticle, which are applied to TNTs because it depends on the starting materials of TiO_2 [16]. Also method of improving the DSSCs efficiency is using incorporation of atomic impurities Zn, Wo, Al, and so forth [17–21]. It results in reduction in the charge recombination rate and progressing of electron mobility at the interface between electrode layers.

The $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment on TNT film were studied in terms of dye adsorption, charge transport, and electron lifetime. To enhance the short-circuit current density (J_{SC})

and open-circuit voltage (V_{OC}), we used the $TiCl_4$ and aluminum oxide (Al_2O_3). As a result, effect of double dip-coating with $TiCl_4/Al_2O_3$ posttreatment on TNTs film enhanced the overall energy conversion efficiency of DSSCs. In this work, we investigated the effects of double dip-coating with $TiCl_4$ treatment and after Al_2O_3 posttreatment on TNTs based DSSCs.

2. Experimental

TiO_2 nanotubes were prepared by an optimized three-step anodization process. Ti foil (0.25 mm thickness, 99.7% purity, Sigma-Aldrich, St. Louis, MO, USA) with an area of $2\text{ cm} \times 3\text{ cm}$ was degreased by ultrasonic agitation in acetone, isopropanol, and deionized water for 30 min each and then dried with N_2 gas. The ethylene glycol electrolyte contained 0.25 wt% NH_4F (99%, Sigma-Aldrich) and 2 vol% deionized water. The anodization was performed in a two-electrode system where the Ti foil served as the working electrode and a Pt plate as the counter electrode. Anodization, using an electrolyte at $0-4^\circ\text{C}$, was conducted at room temperature at a constant voltage of 60 V for 30 min. Then, the as-prepared TNT array was removed by sonication for 5 min in DI water. The second-step anodization was carried out under the same conditions for 5 h. The as-prepared amorphous TNT array was crystallized into an anatase phase at 450°C for 2 h in air at a heating rate of $1^\circ\text{C}/\text{min}$. After another anodization under the same conditions for 20 min and then immersion into a H_2O_2 solution (33%) for 10 min, the anatase TNT array was detached from the Ti substrate. After rinsing and drying, the self-standing TNT array was cut into $5 \times 5\text{ mm}^2$ squares for transfer.

A TiO_2 paste was prepared from TiO_2 powder (anatase, 99.9% purity, Sigma-Aldrich) and used as the reference [22]. The TiO_2 paste was coated onto a fluorine-doped tin oxide (FTO) conductive glass substrate using the doctor blade method, and then the TNT array was transferred onto the TiO_2 paste.

TNTs film was dipped for 30, 60, 90, and 120 min in a 90 mM $TiCl_4$ aqueous solution at 70°C which was prepared by adding titanium tetrachloride (Sigma-Aldrich) to precooled distilled water in an ice bath. Following the posttreatment, the TiO_2 film was annealed at 450°C for 15 min. After $TiCl_4$ doped TNTs film was dipped in Al_2O_3 aqueous solution at 90°C which was prepared by adding aluminum oxide (Sigma-Aldrich), made of different amount of aluminum oxide in ethanol, in different moles of 40, 80, 120, and 160 mM to preheated ethanol at 50°C bath. The substrate was sintered at a temperature of 450°C for 15 min.

A Pt catalyst electrode was prepared by mixing H_2PtCl_6 (5 mM, Sigma-Aldrich) in isopropyl alcohol with an ultrasonic treatment. A counter electrode, which facilitates the redox reaction of the electrolyte, was fabricated by spin coating of the H_2PtCl_6 solution at 1000 rpm for 30 s and annealed at 450°C for 30 min. The dye solution to be adsorbed on the electrode films was prepared by mixing 0.5 mM Ru-dye (N719, Solaronix) with ethanol. To facilitate the adsorption of the dye molecules, the prepared TiO_2 electrode films

FIGURE 1: EDX spectra of Al_2O_3 posttreatment on $TiCl_4$ treatment on TNTs film.

were placed in the dye solution in darkness for 24 h. Finally, the DSSCs were fabricated by sandwiching the prepared electrode film and counter electrode at 120°C for 10 min using a hot melt sealant (60°C). The electrolyte (I^-/I_3^-) was injected between the two electrodes with the inlet and then sealed by a cover glass.

The phases of the TNT array prepared by anodization, as well as those of TNPs, were examined by X-ray diffraction (XRD) using a Rigaku D/MAX-2200 X-ray diffractometer with a $Cu-K\alpha$ radiation source. The morphology of the prepared TNT/TNP photoelectrode film was investigated by field emission-scanning electron microscopy (FE-SEM, S-4700, Hitachi). The absorbance of the TNT/TNP photoelectrode film was measured using a UV-VIS spectrometer (Lambda 750, PerkinElmer). The conversion efficiency and electrochemical impedance spectroscopy (EIS) of the fabricated DSSCs were measured using an $I-V$ solar simulator (K3400, K3000, McScience) under a simulated solar light irradiation of $100\text{ mW}\cdot\text{cm}^{-2}$ (AM 1.5). The active area of the cell exposed to light was approximately 0.25 cm^2 ($0.5\text{ cm} \times 0.5\text{ cm}$).

3. Results and Discussion

The Energy Dispersive X-ray Spectroscopy (EDX) analysis of the $TiCl_4$ 90 mM treatment for 90 min and Al_2O_3 120 mM posttreatment for 60 min on TNTs film is shown in Figure 1, which indicated the presence of about 6.18 atomic % of Al and 22.28 atomic % of Ti.

Figure 2(a) shows the field emission-scanning electron microscopy (FE-SEM) image of the surface morphologies of bare TNTs array. TNTs array was processed by a secondary anodization. Then, diameter of uniform surface is about 100 nm and according to anodic oxidation at present conditions TNTs array can come to various lengths. We used $18\text{ }\mu\text{m}$ of TNTs in study; the fast electron transportation in the film is helpful (Figure 2(b)). Figure 2(c) shows surface of $TiCl_4$ treatment on TNTs film and Figure 2(d) shows surface of $TiCl_4/Al_2O_3$ posttreatment on TNTs film. The surface morphologies of $TiCl_4/Al_2O_3$ posttreatment on TNTs film are rougher than $TiCl_4$ treatment or bare TNTs.

FIGURE 2: FE-SEM images of (a) the surface of TiO₂ nanotubes array; (b) the cross section of a TiO₂ nanotube array; (c) the surface of TiCl₄ treatment on TiO₂ nanotubes array; and (d) the surface of TiCl₄/Al₂O₃ posttreatment on TiO₂ nanotubes array.

FIGURE 3: UV-VIS absorbance of TiCl₄ treatment on TiO₂ nanotubes film for different time conditions.

Figure 3 shows UV-VIS absorption spectrum of N-719 dye in the 400–800 nm wavelength in the different TiCl₄ posttreatment for time from 30 to 120 min on TNTs films. It was found that absorbance increased with increasing TiCl₄

dip-coating times, excluding TiCl₄ treatment for 120 min. An appropriate amount of TiCl₄ in the TNTs films can have effect on providing a large surface area for dye adsorption reported [23–25]. The number of dye molecules influences photocurrent of DSSCs indirectly; thus adsorption of dye molecules is connected to increasing of more light harvesting and J_{SC} as expected. TiCl₄ treatment increased the amount of adsorbed dye because TiCl₄ treatment can decrease the TiO₂ particle size on the electrode surface, leading to the increased active surface area [15, 26]. In case of TiCl₄ treatment for 120 min, the absorbance value was lower than TiCl₄ treatment for 90 min. Reduction of the TNTs films porosity by increasing of the nucleation in the nanoparticle caused decrement of dye absorption in TNTs film with many chances over dip-coating time. Therefore, the increase of inefficient charge-transfer routes and recombination rate of electrons can decrease the photocurrent density and conversion efficiency, as discussed [16].

The I - V curves of TiCl₄ treatment on TNTs photoanodes with different dip-coating time conditions are shown in Figure 4, and the photovoltaic parameters including short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and photovoltaic efficiency (η) are listed in Table 1. The light-to-electric energy conversion efficiency was achieved under a simulated solar light irradiation of 100 mW·cm⁻² (AM 1.5). The DSSCs with bare TNTs film exhibited a J_{SC} of 12.53 mA/cm² and yielded η of 4.69%. However, TiCl₄ treatment on TNTs film enhanced energy

FIGURE 4: I - V curve of TiCl_4 treatment on TiO_2 nanotubes film for different time conditions.

TABLE 1: The integral photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and efficiency (η) of dye-sensitized solar cells fabricated using TiCl_4 treatment on TiO_2 nanotubes film.

Sample	V_{OC} (V)	J_{SC} (A/cm ²)	FF (%)	η (%)
Bare TNTs film	0.61	12.53	60.78	4.69
TiCl_4 90 mM (30 min)	0.60	18.94	62.57	7.16
TiCl_4 90 mM (60 min)	0.60	20.09	62.50	7.59
TiCl_4 90 mM (90 min)	0.61	20.72	63.90	8.08
TiCl_4 90 mM (120 min)	0.60	20.26	66.92	7.71

conversion efficiencies in cells due to increment of dye adsorption, improvement of charge transport, and reduction of electron recombination rate. When the TNTs film was electrochemically dip-coated, the values of η increased with TiCl_4 treatment time to reach a maximum of 8.08% at 90 min and thereafter decreased. It is well known that the η of DSSCs performance is significantly affected by the amount of dye loading to photoanodes [26–28].

The Nyquist plots of real axis residence (Z') and imaginary axis residence (Z'') analyzed by the classical equivalent electrical circuit are shown in Figure 5. In the EIS, R_s (ohmic series resistance), R_{CT1} (3 charge-transfer resistance of the counter electrode), C_{PE1} (constant phase element of the counter electrode), R_{CT2} (4 charge-transfer resistance of the working electrode), and C_{PE2} (constant phase element of the photoelectrode) are indicated in Figure 5. The small semicircle is fit to a charge-transfer resistance (R_{CT1}) and constant phase, while the large semicircle is fit to a transfer resistance (R_{CT2}) and constant phase. As R_{CT2} is affected by the use of TiO_2 nanoparticles/TNTs, large one appearing at intermediate frequency (around 10 Hz) represents electron transfer resistance (R_{CT2}) at photoelectrode and electrolyte interface

FIGURE 5: Electrochemical impedance spectroscopy (EIS) Nyquist plots of $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment on TiO_2 nanotubes film with different concentrations.

TABLE 2: The integral photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and efficiency (η) of dye-sensitized solar cells fabricated using $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment on TiO_2 nanotubes film.

Sample	V_{OC} (V)	J_{SC} (A/cm ²)	FF (%)	η (%)
Bare TiCl_4 90 mM	0.61	20.72	63.90	8.08
$\text{TiCl}_4/\text{Al}_2\text{O}_3$ 40 mM	0.65	20.60	60.02	8.11
$\text{TiCl}_4/\text{Al}_2\text{O}_3$ 80 mM	0.66	20.68	60.80	8.40
$\text{TiCl}_4/\text{Al}_2\text{O}_3$ 120 mM	0.67	20.93	61.54	8.65
$\text{TiCl}_4/\text{Al}_2\text{O}_3$ 160 mM	0.67	21.10	55.49	7.93

that is most relevant for TNTs film. In the electrochemical impedance spectroscopy (EIS), all $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment on TNTs film indicated that impedance is smaller than bare condition of TiCl_4 treatment. The smallest semicircle is TiCl_4 treatment and Al_2O_3 120 mM posttreatment on TNTs film. Small R_{CT2} indicates much faster electron transport and it is closely connected to efficiency of DSSCs. Therefore, the $\text{TiCl}_4/\text{Al}_2\text{O}_3$ treatment of a less defective morphology effect significantly improved electron transport.

Figure 6 shows I - V curve of Al_2O_3 posttreatment of TiCl_4 treatment TNTs film with different concentration in 40 to 160 mM and the photovoltaic properties of $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment TNTs film are summarized in Table 2. From Table 2, DSSCs with $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment on TNTs film presented increased V_{OC} from 0.61 to 0.67 V. In reported studies, Al_2O_3 influenced a higher electron lifetime and that contributed to increasing of V_{OC} because Al_2O_3 affects to suppress the charge recombination between the TiO_2 /TNTs/electrolyte interfaces [29]. It was found that Al_2O_3 120 mM posttreatment indicated V_{OC} (0.67 V) and

FIGURE 6: I - V curve of $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment on TiO_2 nanotubes film with different concentrations.

η (8.65%). Therefore, the optimum condition for high conversion efficiency was the treatment of Al_2O_3 120 mM.

4. Conclusions

To improve the efficiency of DSSCs, we took a two-step treatment in the TiO_2 nanotubes film. In the first step, an aqueous solution of titanium tetrachloride (TiCl_4) was treated on TNTs film for different time from 30 to 120 min. The highest efficiency of DSSCs using TiCl_4 90 mM treatment for 90 min reached 8.08% and J_{SC} of that condition was 20.72 mA/cm^2 . In the second step, an aqueous solution of aluminum oxide (Al_2O_3) was treated on TiCl_4 treatment TNTs film with different concentration from 40 to 160 mM. Successfully, performance of DSSCs was improved that V_{OC} was increased to 0.67 V and efficiency was 8.64%. The optimum condition for high conversion efficiency was the treatment of Al_2O_3 120 mM. Al_2O_3 influenced a higher electron lifetime due to the increased interfacial charge-transfer resistance.

In conclusion, using the TNTs and $\text{TiCl}_4/\text{Al}_2\text{O}_3$ posttreatment process was found to be an effective method to improve the efficiency of TiO_2 nanoparticle based DSSCs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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