Influence of TiO$_2$ Electrode Properties on Performance of Dye-Sensitized Solar Cells

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Dye sensitized solar cells (DSSC) are working based on adsorption of photon by dye and transfer it to TiO$_2$ electrodes. The control of microstructure and defects of TiO$_2$ electrodes are vital for fabrication of high efficiency dye sensitized solar cells. These properties strongly related to TiO$_2$ electrode fabrication method and its parameters. In this research the effect of different solvent, TiCl$_4$ treatment and carbon nanotubes on microstructure and quality of nanocrystalline TiO$_2$ electrodes were investigated. Nanocrystalline TiO$_2$ thin films with different additives have been deposited on FTO coated glass substrates by tape casting method, then these electrodes were dried at 130°C and sintered. After that, these electrodes were immersed into a dye solution. Then cell were assembled by dye-covered TiO$_2$ electrode, platinum coated FTO and Iodine electrolyte. The samples were characterized by FESEM, OM and the cell performance was measured by solar light simulator at an intensity of 1000 W.m$^{-2}$. Best result was achieved by pre and post treatment of TiO$_2$ electrodes by acetyl acetone and using carbon nanotube additive.

Keywords: Carbon nanotube, dye sensitized solar cells, counter electrodes, Efficiency, microcrack

1. INTRODUCTION

The dye sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity and its performance is based on the sensitization of wide band gap semiconductors [1]. The structure of DSSC is made of a counter electrode (conductive glass coated with platinum (Pt)), a photo anode (TiO$_2$ porous film on a conductive glass substrate anchored a monolayer of dye) and an electrolyte of certain organic solvent (containing a redox couple such as iodide/triiodide). When a DSSC is irradiated by sunlight, the electrons of the dye are excited from ground state to excited state by absorbing the photons. The excited electrons are injected into the conduction band of TiO$_2$ porous film and then transferred to the conducting glass through the porous TiO$_2$ film [2].
The quality and anchoring of the dye to the surface of TiO₂ are important parameters determining the efficiency of the cell [3]. Many defects change the quality of TiO₂ films such as microcrack formation on the films, TiO₂ particle agglomeration in the stored paste, weak interfaces between TiO₂ particles in the coating and between conducting glass and TiO₂ film and the reduction of particle bonding in thick films. Microcracks that occur in the TiO₂ films, were originated from the reduction of the nanoparticle bonding strength, can be minimized by adding some materials. These materials have ability to bond to TiO₂ nanoparticle, into the TiO₂ paste. It is well known that the surface of TiO₂ particles comprises hydroxyl groups, and these groups have interaction with the dye carboxylic groups [4]. Thus, similarly, if adding a material into the TiO₂ solution which has enough length and contain carboxylic group, it should bond to TiO₂ particles and consequently diminish the film crack. Carbon nanotube is one of the most suitable candidates because it has a different aspect ratio from TiO₂ particles and has the capability to form carboxylic group on its surface. Carboxylic groups are introduced to the surface of carbon nanotubes by the acid treatment. Furthermore the well known method to improve the interfaces bonding of the TiO₂ film is chemical treatment. By this treatment, extra layer of TiO₂ is grown on the TiO₂ nanoparticles. The chemical treatment was carried out by several TiO₂ precursors e.g. TiCl₃ [5], titanium isopropoxide [6] and titanium tetrachloride (TiCl₄) treatment.[7-10] A better electrical conductivity was formed at the interfaces between particles in TiO₂ coating and between conducting glass and TiO₂ film through TiCl₄ treatment[11].Furthermore some scientists reported that adding of some solvents like acetyl acetone, ethylene glycol reduce the amount of particle agglomeration and improve cell efficiency.[12]

In this research the effect of different solvent, TiCl₄ treatment and addition of carbon nanotubes on microstructure and quality of nanocrystalline TiO₂ electrodes were studied in DSSC’s and structure and electrical properties of fabricated cells were investigated.

2. EXPERIMENTAL

For fabrication of DSSC devices, TiO₂ paste(Dyesol company, DSL 90T), N719 dye (Dyesol company, B2(N719)) , Multi wall carbon nanotubes, acetyl acetone (Merck, 8.00023), Ethylene glycol (Merck ,1.00949), ethanol(1.00983 , Merck), Iodine electrolyte(Dyesol company , EL-HPE), H₂PtCl₆ (Merck,6.1450), TiCl₄ (Merck ,8.12382).FTO(Fluorine doped SnO₂ coated glasses ,15Ω/sq.m,Dyesolcompany, TEC15 ) and deionized water were used as raw materials.

Experimental steps were done in three parts: using of different solvents, TiCl₄ solution and carbon nanotubes.

2.1. Effect of different solvents

For study the effect of solvent, the FTO coated glasses was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. After that, the FTO glass plates were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30min and washed with water
and ethanol. A layer of pastes with different solvent such as acetyl acetone, ethanol and mixture of acetyl acetone and ethylene glycol were applied on the FTO glass plates by tape casting, kept in a clean box for 3 min in order to homogenize the paste and reduce its surface irregularities and then dried at or 130 °C with same heating rate and holding times. After drying, the electrodes were coated with the TiO$_2$ pastes were gradually heated under an airflow at 325 °C, 375 °C, 450 °C and finally at 500 °C for total 40 min. The TiO$_2$ film thus produced is once again treated with 40mM TiCl$_4$ solution, as described previously, then rinsed with water and ethanol and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO$_2$ electrodes were immersed into 0.5 mM N-719 dye solution and kept at room temperature for 20–24 h to assure complete sensitizer uptake.

2.2. Effect of TiCl$_4$ treatment

For research about the effect of TiCl$_4$ treatment, one of the electrodes was fabricated without pre and post treatment and one fabricated with pre and post treatment. Pre treatment were done before applying paste by immersing electrode into a 40 mM aqueous TiCl$_4$ solution at 70 °C for 30 min and washing with water and ethanol. Post treatment was done at the same condition after coated on all of FTO glass plates by tape casting, kept in a clean box for 3 min in order to homogenize the paste and reduce the surface irregularity. After that, all electrodes were dried at 130 °C with same heating rate and holding time. After drying, the electrodes coated with the TiO$_2$ pastes were gradually heated and treated as same as above.

2.3. Effect of carbon nanotube

To prepare the different working electrodes with carbon nanotube additives, first MWCNTs were modified by the mixed acids (H$_2$SO$_4$:HNO$_3$ at volume ratio of 3:1) for 30 min at room temperature prior to use in order to introduce a carboxylic group on their surface. Then, they were washed with deionized water and filtered with filter paper. The modified carbon nanotubes were rinsed with deionized water three times and dried at 60 °C at the ambient conditions. After that various amounts of acid-treated MWCNTs (0.025 and 0.05 wt%) were added to the TiO$_2$ paste and dispersed using an ultrasonic horn for 30 min. After stirring for 2 h, the paste was coated on FTO coated glass by tape casting method. Then the films that had formed were sintered at 250°C for 4 h. After cooling to 80 °C, the TiO$_2$ electrodes were immersed into 0.5 mM N-719 dye solution and kept at room temperature for 20–24 h to assure complete sensitizer uptake.

2.4. Assembling of cells

To prepare the counter electrode, holes were drilled in the FTO glass by Drilling. The perforated sheet was washed with H$_2$O and 0.1 M HCl–ethanol solution and cleaned by ultrasound in an acetone bath for 10 min. After removing residual organic contaminants by heating in air for 15 min at 400 °C, the Pt catalyst were deposited on the FTO glasses by dipping in the 0.2 wt.% H$_2$PtCl$_6$
solution and heat treated at 400 °C for 15 min. The dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell, filled by electrolyte and sealed.

The microstructure and the thickness of the TiO₂ film was measured by Field emission scanning electron microscopy (FESEM) (cam scan MV2300) and optical microscopy (DMI Victory).

The performance of the dye-sensitized solar cell was examined using a solar simulator at an intensity of 1000 w.cm⁻². The conversion efficiency and fill factor of the cells was characterized by determination of maximum, open and short-circuit voltages and current densities and calculated by the following equations:[11]

\[
\eta = \frac{J_m V_m}{P_m} = \frac{FF (V_{oc} J_{sc})}{P_m} \quad (1)
\]

\[
FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (2)
\]

Which in Eq. (1), \(\eta\) is the conversion efficiency of the cell, \(J_m\) is the maximum current density, \(V_m\) is the maximum voltage, \(P_m\) the intensity of the incident light, \(FF\) is the fill factor, \(V_{oc}\) is the open-circuit voltage and \(J_{sc}\) is the short-circuit photocurrent density.

3. RESULTS AND DISCUSSION

The OM images of different TiO₂ electrodes which were prepared by different solvents is shown in Fig.1. Based on this figure the electrode which was fabricated by acetyl acetone has less cracks and the film is more uniform and smoother than the other ones.

![Figure 1. The OM images of TiO₂ film (a) without solvent (b) with acetyl acetone, (c) with ethanol, (d) with acetyl acetone and ethylene glycol (500x)](image_url)
Fig. 2. shows the photocurrent–photovoltage characteristics of the DSSCs with different TiO$_2$ electrodes. Table 1 summarizes the performance of data of all devices under the illumination intensity of 100mw/cm$^2$, it is seen from the table that the photovoltaic characteristics, including the short circuit current density ($J_{sc}$), the open circuit voltage ($V_{oc}$), the fill factor (FF) and power conversion efficiency ($\eta$) were improved, when electrode was fabricated by TiO$_2$ and acetyl acetone paste. The agglomeration of TiO$_2$ nano particles may be lead to reduction of the active surface area for dye adsorption and as a consequence, it will reduce photocurrent. Moreover, this agglomeration, decrease electrical contact, because it reduce the area of interconnection between nanoparticles and have been mentioned well before[13-15].Therefore, the resistance for charge transfer is increased and charge transporting become lower.[16] In addition, since the interconnection area becomes smaller when the paste is agglomerated, necking of nanoparticles is reduced. As a consequence, electron recombination, which occurs mainly at grain boundaries, is enhanced, and this behavior reduces the electron flow. Finally, it is well known that film characteristics affect the efficiency of the cells, because electron transport is mainly due to diffusion and the diffusion coefficient strongly depends on film properties [16-20]. When acetyl acetone was used as a dispersive agent, the amount of paste agglomeration is decreased, so interconnection and bonding between nanoparticles is increased and the amount of cracks in the structure will be reduced.

![Figure 2](image_url)

**Figure 2.** I–V curves for DSSC with different TiO$_2$ film (a) with acetyl acetone (b) without solvent,(c) with ethanol(d) with acetyl acetone and ethylene
Table 1. J–V parameters of cells with different solvents

<table>
<thead>
<tr>
<th>Type of solvent</th>
<th>Short circuit Current (Jsc) (mA/cm²)</th>
<th>Open circuit voltage (Voc) (V)</th>
<th>Fill factor (%)</th>
<th>conversion efficiency (Ƞ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without solvent</td>
<td>6.5</td>
<td>0.520</td>
<td>0.74</td>
<td>2.5</td>
</tr>
<tr>
<td>With Acetyl acetone</td>
<td>7.5</td>
<td>0.570</td>
<td>0.70</td>
<td>3.8</td>
</tr>
<tr>
<td>With ethanol</td>
<td>5.8</td>
<td>0.500</td>
<td>0.78</td>
<td>2.2</td>
</tr>
<tr>
<td>With Acetyl acetone and glycol</td>
<td>5.3</td>
<td>0.470</td>
<td>0.70</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Fig. 3 compares the field emission scanning electron microscopy (FESEM) images of untreated and pre - post treated TiO₂ films. Fig. 3-a shows the particles morphology of the TiO₂ film before treatment. In this electrode, there are not enough particle necking so electrons diffusion is difficult, furthermore in this electrode the surface of TiO₂ film is smaller than other electrode because these particles are smaller than the other one. Fig. 3-b shows the effect of pre and post treatment on morphology of films. This figure shows the sponge-like morphology of the TiO₂ film. Based on this figure, necks between particles and particles size were increased after TiCl₄ chemical treatment, so in these electrode, electrons transporting is easier than before, furthermore these new nanoparticles enhance the surface area of TiO₂ film.

Figure 3. The FESEM image of TiO₂ films: (a)untreated and (b) pre and post treated (80. 00KX)

Fig.4 and Table 2 shows the J–V curves for fabricated dye sensitized solar cells with different type of TiO₂ electrodes. From these results its reveals that the Jsc and Voc of DSSC were increased by TiCl₄ treatment of the TiO₂ films. These results shows that DSSC which is fabricated by pre -post
treated TiO$_2$ electrode had highest efficiency, TiCl$_4$ pre-treatment on the glass substrate decreases the transfer resistance of the thin conductive oxide (TCO), then the new nanoparticles enhance the surface area and suppress the charge recombination.[21] The TiCl$_4$ pre-treatment also increases the contact points between the TiO$_2$ film and the FTO and improves the electronic interconnection, so that the photogenerated charge can be collected efficiently and the probability of electron recombination will be reduced. Post treatment increases TiO$_2$ particles-necking and Electron transporting ways.[22-23]. Necks between TiO$_2$ particles, significantly influence the electron transport properties which could be characterized by effective diffusion coefficient ($D_e$).[24] It must be considered that after TiCl$_4$ treatment, electrical conductivity at the interfaces between TiO$_2$ particles in the coating and between glass substrate and the coating through TiO$_2$ particles-necking will improve and this will increase short circuit current density up to 40 mv after the TiO$_2$ coating was treated by TiCl$_4$. open circuit voltage can be calculated from the diode equation:[25],

\[
V_{oc} = \left( \frac{nRT}{F} \right) \ln \left[ \frac{i_{sc}}{i_0} \right] - 1 \tag{3}
\]

Where in this equation, $n$ is the ideality factor, whose value is between 1 and 2, $i_{sc}$ is short circuit current, $i_0$ is the reverse saturation dark current and $R$ and $F$ are the ideal gas constant and Faraday's constant, respectively. According to equation (3), increasing $i_{sc}$ and decreasing $i_0$ will be lead to voltage increase up to 40 mv.

![Figure 4. I–V curve for DSSC with different TiO$_2$ film (A:pre and post treated),(B:untreated )](image-url)


**Table 2.** J–V parameters of cells with different type of treatment

<table>
<thead>
<tr>
<th>Type</th>
<th>Short circuit Current ($J_{sc}$) (mA/cm²)</th>
<th>Open circuit voltage ($V_{oc}$) (V)</th>
<th>Fill factor</th>
<th>conversion efficiency (Ƞ%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>7.70</td>
<td>0.600</td>
<td>0.77</td>
<td>3.9</td>
</tr>
<tr>
<td>Pre and post treated by TiCl₄</td>
<td>9.78</td>
<td>0.655</td>
<td>0.79</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The dark current reduction after TiCl₄ treatment have been reported by Ito et al. also [26]. The dark current is partially related to direct exposure of FTO glass to electrolyte and due to incomplete covering of FTO substrate by of TiO₂ nanoparticles. The electrode catalyzing charge recombination reaction of electron and I₃⁻. If FTO surface was not covered well by TiO₂ nanoparticles, the direct connection of the FTO to electrolyte may be change electrode catalyzing behaviour. Zhu et al.[27] pointed out that recombination occurs predominantly near the FTO substrate. After TiCl₄ treatment, a TiO₂ thin layer were deposited on exposed part of FTO and the recombination charge will be limited, this behavior contributes to open circuit voltage increase.

![Figure 5](image1.png)

**Figure 5.** The OM images of TiO₂ film (a) with acetyl acetone,(b) with carbon nanotube(0.025%) and acetyl acetone(c) with acetyl acetone and carbon nanotube(0.05%)(500x)
In this study, acid-treated MWCNT and TiO$_2$ paste nanoparticles were used to fabricate the TiO$_2$ photo electrodes. Due to the favorable electrical conductivity of the CNTs on metal oxide nanocomposites we expected that the presence of the CNTs should enhance the electron transport rate and extend the electron life time in the TiO$_2$ electrodes and this will improve the solar energy conversion efficiency. In addition, from the literature [28], it was noted that the oxidation of CNTs in a concentrated acid treatment could produce CNTs with terminal _COOH groups, which have better contact around TiO$_2$ nanoparticle, improves the electrons collection and bonding of TiO$_2$ nanoparticles.

Fig. 5 reveals that the surface of the pure TiO$_2$ and composite films. Based on this figure, The amount of cracks in composite films are shorter than pure TiO$_2$ films. These results suggest that adding of MWCNT minimized microcrack formation. MWCNTs probably prevents microcrack formation by bonding to TiO$_2$ nanoparticles (via the interaction of carboxylic group with hydroxyl group of TiO$_2$). Schematic view of this type of bonding is illustrated in Fig. 6. Because carbon nanotubes are distributed well in the structure and are adhered tightly to a large number of TiO$_2$ nanoparticles, the bonding strength among TiO$_2$ particles increases. As a result, microcrack formation is reduced. The J–V characteristics of the DSSCs are reported in Table 3. By incorporation of 0.025%Wt.MWCNTs in the TiO$_2$ films, the open-circuit voltage (Voc) and conversion efficiency increases more than the other ones. This result suggests that MWCNTs should play an important role in enhancing the conductivity of the TiO$_2$ films. However, at higher MWCNT contents, the solar conversion efficiencies decrease, which should be explained by the solar energy loss from the optical absorption of the carbon material. Furthermore it’s obvious from OM images that by increasing the amount of carbon nanotubes the amount of micro cracks increased. The formation of cracks on the film’s surface can reduce the electrical contact between TiO$_2$ nanoparticles. If the cracks which are formed on the film’s surface...
reach the conducting substrate, electron recombination will be increased due to contact of the electrolyte with the conducting substrate. On the other hand, access of dye molecules is easier during sensitization when cracks are present on the film’s surface. As a result, the presence of cracks on the film’s surface results to only a slight decrease in the efficiency of the cell.

![Figure 7. I–V curve for DSSC with different TiO₂ film](image)

**Figure 7.** I–V curve for DSSC with different TiO₂ film (a) with 0.025%Wt.carbon nanotube and acetyl acetone, (b) with acetyl acetone, (c) with acetyl acetone and 0.05%Wt.carbon nanotube

**Table 3.** J–V parameters of cells with different type of TiO₂ electrode

<table>
<thead>
<tr>
<th>Type</th>
<th>Short circuit Current (Jsc) (mA/cm²)</th>
<th>Open circuit voltage (Voc) (V)</th>
<th>Fill factor (%)</th>
<th>conversion efficiency (Ƞ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl acetone</td>
<td>7.5</td>
<td>0.570</td>
<td>0.70</td>
<td>3.8</td>
</tr>
<tr>
<td>with 0.025%Wt.carbon nanotube and acetyl acetone</td>
<td>8.3</td>
<td>0.600</td>
<td>0.75</td>
<td>4.1</td>
</tr>
<tr>
<td>with acetyl acetone and 0.05%Wt.carbon nanotube</td>
<td>5.8</td>
<td>0.500</td>
<td>0.73</td>
<td>2.6</td>
</tr>
</tbody>
</table>

**4. CONCLUSIONS**

1. Study the effect of different solvents addition to TiO₂ paste on the performance of DSSC showed that the DSSC’s have been fabricated with acetyl acetone showed highest photovoltaic performances. This behavior may be attributed to paste agglomeration decrease and interconnection and bonding improvement between nanoparticles.
2. The effect of TiCl$_4$ treatment of TiO$_2$ layer on the performance of DSSC showed that the DSSC have been fabricated with pre and post treated TiO$_2$ electrode showed highest photovoltaic performances. This behavior is related to increasing the contact points between the TiO$_2$ film and the FTO, improvement of TiO$_2$ film electrical conductivity by enhancing the neck points between the nanoparticles, increasing dye loading and minimizing the recombination rate between the TiO$_2$ film and the mediator.

3. The effect of carbon nanotubes on quality of TiO$_2$ electrode was investigated, results showed that the incorporation of 0.025%Wt.MWCNT in to the TiO$_2$ films increases the conversion efficiency compared to the other ones. This result suggests that MWCNTs should play an important role in enhancing the conductivity of the TiO$_2$ films. Furthermore adding optimum amount of carbon nanotubes will decrease the amount of microcracks in the electrode microstructure.

References


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