APPLICATION OF TiO₂ NANOTUBES FOR DYE SENSITIZED SOLAR CELLS
OVERVIEW

This chapter deals with the fabrication and analysis of Dye Sensitized Solar Cells (DSSCs) fabricated using as fabricated, pulsed crystallized and doped TiO$_2$ nanotubes

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7.1 DYE SENSITIZED SOLAR CELLS (DSSC)

Dye Sensitized Solar Cells is one of the important applications of TiO₂ nanotubes which is a cost effective alternative for the conventional thin film solar cells. In DSSC, the light absorption and carrier transport are done by different materials, in contrast to the conventional p-n junction solar cells. The light absorption in a DSSC is done by a sensitizer and charge transport by the conduction band of a wide band gap oxide material.

Nanotubular TiO₂ layer which acts as the carrier transport layer is an important element of the DSSC. This layer is sensitized with a thin layer of dye molecules. Light absorbed by the dye molecules results in the photo excitation and injection of the carriers in to the conduction band of TiO₂ nanotubes. The dye molecules are regenerated by a redox electrolyte. The maximum generated voltage in a DSSC is equivalent to the difference between fermi level of the TiO₂ layer and the redox potential of the electrolyte.[142]

7.2 FABRICATION AND ANALYSIS OF THE DYE SENSITIZED SOLAR CELLS

In the present work, TiO₂ nanotubes, fabricated by electrochemical anodization, is used for the fabrication of Dye sensitized solar cells. Here, DSSCs are fabricated using [1] as-prepared, [2] Pulsed crystallized as well as [3] doped TONTs. The dye sensitization is done by dipping them in the N 719 dye solution for 24 hours. The redox electrolyte is incorporated on the top of the electrolyte for dye regeneration by vacuum sucking method. Counterelectrode, dye sensitized TONTs, Platinum coated FTO and redox electrolyte together form the DSSC device. For this, the electrolyte is injected through a hole made on the counter electrode platinum coated FTO through a thermoplastic film sandwiched between the counter electrode and sensitized TONTs. The DSSC performance using as prepared, pulsed crystallized and doped TONTs is analysed by taking the current voltage measurements. A Keithley Source measure unit coupled with a solar simulator has been used for the analysis. The solar cell parameters like open circuit voltage (Voc) and short circuit current (Isc) are measured under the standard conditions of illumination (AM 1.5 G and illumination intensity 100 mW/cm²). From I-V graphs, the fill factor of each DSSC is assessed. Then
the efficiency is calculated using the equation.

\[
\text{Efficiency (\%)} = \frac{V_{oc} I_{sc} \text{FF}}{P_{in} A} \times 100
\]

(Eq. 7.1.1)

where, \(V_{oc}\) is the open circuit voltage, \(I_{sc}\) is the short circuit current, FF is the fill factor, \(P_{in}\) is the input power and \(A\) is the area of the solar cell.

### 7.2.1 DSSCs using annealed and unannealed TONTs

**Figure 7.1** shows the I-V characteristics of the DSSCs fabricated with annealed and unannealed TiO\(_2\) nanobuses as working electrode. To obtain annealed TONTs, thermal annealing has been done for 2 hours at 500°C. In the present case with as prepared TONTs of length of 7 \(\mu\)m and diameter of 60 nm, the \(V_{oc}\) and \(I_{sc}\) parameters are 0.3 V and 0.11 mA where as DSSCs with annealed TONTs with same length and diameter shows improved values of \(V_{oc}\) and \(I_{sc}\). The **Table 7.1** depicts the cell performance parameters of both. The amorphous nanotubes show a solar cell conversion efficiency of 0.17 % while annealed nanotubes show slightly increased efficiency (0.19 %).

![Graph A and B](image)

**Figure 7.1**
I-V characteristics of dye sensitized solar cell fabricated using annealed TONTs
<table>
<thead>
<tr>
<th>Sample description</th>
<th>Isc (mA)</th>
<th>Voc (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>0.11</td>
<td>0.3</td>
<td>0.53</td>
<td>0.17</td>
</tr>
<tr>
<td>Annealed</td>
<td>0.61</td>
<td>0.66</td>
<td>0.48</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 7.1
Solar cell characteristics of dye sensitized solar cell fabricated using annealed and unannealed TONTs

7.2.2
DSSC using pulsed crystallized TONTs

The suitability of pulsed crystallized TONTs (P-TONTs) for solar energy conversion applications has been studied by constructing a back illuminated dye sensitized solar cell (DSSC) with P-TONT as electron transport layer. As we go through literature reports on DSSCs using room temperature crystallized TONTs, it is seen that different researchers have obtained their photovoltaic performance as much

Figure 7.2
I-V characteristics of dye sensitized solar cell fabricated using as prepared and pulsed crystallized TONTs
inferior to post annealed TON Ts. This effect has been attributed to the high number of the recombination sites in the partially crystallized TONTs formed by their methods like water annealing method, water incubation and water vapor treatment. A comparative study of the DSSCs constructed using amorphous TONTs and room temperature crystallized TONTs performed by Liu et al., yield Jsc 0.077 mA/cm² and Voc 0.5 V for the latter which is nearly equal to Jsc 0.035 mA/cm² and V_{oc} 0.571 V for the former.

In the present study, Jsc and Voc values for the P-TONT and A-TONT DSSC [Figure 7.2] are 2.01 mA/cm², 0.63 V and 0.11 mA/cm², 0.3 V showing that pulsed crystallized TONT based DSSCs have much improved performance rate when compared to that of amorphous TONT based cells. Moreover the present cell (P-TONT) manifests an efficiency two orders higher than that reported for room temperature crystallized TONTs by other researchers [Table 7.2]. This might be attributed to the high crystallinity of the anatase TONTs obtained here by the superfast crystallization.

Table 7.2
Solar cell parameters of dye sensitized solar cell fabricated using as-prepared and pulsed crystallized TONTs

<table>
<thead>
<tr>
<th>Sample description</th>
<th>J_{sc} (mA)</th>
<th>V_{oc} (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>0.11</td>
<td>0.3</td>
<td>0.53</td>
<td>0.17</td>
</tr>
<tr>
<td>Pulse crystallized</td>
<td>2.01</td>
<td>0.63</td>
<td>0.33</td>
<td>0.41</td>
</tr>
</tbody>
</table>

### 7.2.3 DSSC using Copper doped TiO₂ nanotubes

Copper doped nanotubes are fabricated by the electrochemical doping method mentioned earlier in Chapter 5. These doped nanotubes are used to fabricate DSSCs. The performance of the DSSCs fabricated using TiO₂ nanotubes with different copper percentage is compared. The I-V characteristics is shown in Figure 7.3.

The short circuit current increases
Figure 7.3
I-V characteristics of dye sensitized solar cell fabricated using as prepared and Cu doped T0NTs

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Isc (mA)</th>
<th>Voc (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>0.61</td>
<td>0.66</td>
<td>0.48</td>
<td>0.19</td>
</tr>
<tr>
<td>2.6 % Cu doped</td>
<td>0.35</td>
<td>0.58</td>
<td>0.49</td>
<td>0.11</td>
</tr>
<tr>
<td>3.2 % Cu doped</td>
<td>1.07</td>
<td>0.68</td>
<td>0.38</td>
<td>0.25</td>
</tr>
<tr>
<td>5.2 % Cu doped</td>
<td>1.15</td>
<td>0.68</td>
<td>0.38</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Table 7.3  Solar cell parameters of dye sensitized solar cell fabricated using as-prepared and pulsed crystallized T0NTs
from 0.35 mA to 1.14 mA as the doping percentage increases from 2.6 to 5.2 at % and open circuit voltage increases from 0.58 V to 0.68 V. The increase in the short circuit current may be due to the increase in the nanotubular conductivity through doping. The efficiency of the solar cell also increases with the doping concentration (Table 7.3).

7.2.4
DSSCs using Zn doped TONTs

The performance comparison of the as prepared TONT, Zn doped TONT and the heterostructure Zn-TONT/ZnO nanoflake in DSSC application is done by fabricating three types of cells. The I-V characteristics of the Zn-TONT/ZnO nanoflake heterostructure and Zn doped TONTs is compared with that of the as-prepared titanium dioxide nanotubes. While the improvement in the open circuit voltage ($V_{oc}$) with the DSSC using heterostructure is only about 70 mV, the short circuit current for the heterostructure $I_{sc}$ 4 mA is about an order of magnitude higher than that with the pure TONT ($I_{sc}$ 0.6 mA). The Voc and $I_{sc}$ of DSSC with Zn doped TONT shows a slight increase 30 mV and 0.6 mA respectively. This has produced a considerable increase in the efficiency of the heterostructure cell over the pure TONT based cell that has been fabricated and operated under the same conditions while the efficiency of DSSC with doped TONT over that of pure TONT is ~2 times in magnitude. The result shows that though efficiency is slightly increased in DSSC with Zn doped TONT in comparison to that with pure TONT, the DSSC fabricated with Zn-TONT/ZnO nanoflake heterostructure shows still a significant enhancement when compared to either of them.

Zn-TONT/ZnO nanoflake heterostructure shows solar cell conversion efficiency of 1.35%. Hence, it can be concluded that the improved performance is due to the combined effect of ZnO nanoflake and preferential [001] orientation of the anatase TONT explained in Chapter 7.
<table>
<thead>
<tr>
<th>Sample description</th>
<th>Isc (mA)</th>
<th>Voc (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>0.35</td>
<td>0.58</td>
<td>0.49</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn doped</td>
<td>1.7</td>
<td>0.68</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>Zn doped TONT/ZnO heterostructure</td>
<td>4.01</td>
<td>0.71</td>
<td>0.47</td>
<td>1.35</td>
</tr>
</tbody>
</table>

**Table 7.4**
Solar cell parameters of dye sensitized solar cell fabricated using as-prepared TONTs, Zn doped TONTs and Zn-TONT/ZnO heterostructure

The improvement in the efficiency of DSSC could be explained based on the more effective processes of carrier production and transport in the heterostructure-based DSSC whose band alignment is illustrated in **Figure 7.5**. In TONT based DSSC’s when the solar...
radiation falls on the dye molecules through the transparent platinum FTO window and the electrons from the HOMO (Highest Occupied Molecular Orbital) of the N719 dye are excited to the LUMO (Lowest Unoccupied Molecular Orbital), the photo generated electrons are injected into the conduction band of the TONT and are collected by the titanium metal back contact. In this process, there is a large possibility for the charge recombination of the electrons in the conduction band of the TONT and holes present in the HOMO of the dye, which may reduce the efficiency of the device. In the Zn-TONT/ZnO nanoflake heterostructure based DSSC, the presence of ZnO nanoflakes [band gap 3.37 eV with CB and VB positioned slightly above that of the corresponding bands in TONT] on the top of the TiO₂ nanotubes [band gap 3.2 eV] decreases the recombination rate of the electrons owing to the small energy barrier created by them. In addition, ZnO lattice is reported to provide electron mobility almost 3 times larger compared to the TONT which facilitates faster transport of the generated electrons to the back metal contact. This increased mobility thus acts as an additional factor that further reduces the recombination rate of the photo generated charge carriers. This synergetic property of Zn-TONT/ZnO nanoflakes in promoting efficient separation of carriers may be the reason for improved solar cell efficiency.

### 7.3 SUMMARY

Dye Sensitized Solar Cells (DSSCs) are fabricated using as fabricated, pulsed crystallized and doped TiO₂ nanotubes and their performance characteristics are assessed. An enhancement in efficiency is observed for cells fabricated with TONTs prepared by innovative methods when compared to the as-prepared, with the highest efficiency of 1.35% for Zn doped TONT/ZnO nanoflake heterostructure.