Chapter-5

Fabricated Dye Sensitized Solar Cells (DSSCs)
5.1. Dye Sensitized Solar Cell with Curcumin Dye

5.1.1. Introduction

The DSSC is a solar cell whose working is based on the sensitization of wide band gap semiconductors. The state of art for the solar cell fabrication based on dye sensitization is already mentioned in the first chapter. The efficiency of the DSSC depends on mainly two factors: the absorption spectrum of the dye and the anchorage of the dye to the surface of TiO$_2$ [214]. Recent studies reveal that the photovoltaic conversion efficiencies obtained for DSSCs based on natural dyes were not more that 1%.

In the present study, a natural, eco-friendly and cost-effective curcumin 1, 7-bis-(4-hydroxy-3- methoxyphenyl)-1, 6-heptadiene-3, 5-dione, yellow-orange dye found in turmeric root is used as photo-sensitizer and PEDOT:PSS film developed over graphite coated FTO is used as counter electrode for making dye-sensitized solar cell. DSSC with curcumin dye has been reported by En Mei Jin et al [216] but the efficiency was limited to 0.6 % only. Our aim was to increase the efficiency with surface modification of nc-TiO$_2$ electrode. We studied the effect of the polarity of solvents in sensitization process by dissolving the dye in different solvents such as Acetone, DMF, DMSO and Ethanol. Using cyclic voltametry, the effect of solvents on diffusion and injection process is determined by recording the change in HOMO-LUMO position. By taking SEM and doing Kelvin probe analysis, the effect of HCl and TiCl$_4$ treatment on the performance of TiO$_2$ working electrode was also analyzed. It is found that TiCl$_4$ treatment of nc-TiO$_2$ surface imparts surface roughness, and ultimately an increase in dye-loading capacity resulting in enhanced photocurrent. The reduction in the recombination rate is attributed to the increase in $V_{oc}$ due to accumulation of greater concentration of electrons.

5.1.2. Materials

Fluoride doped tin oxide-coated glass substrate having resistance of 10Ω/cm$^2$ is purchased from Solaronix, Switzerland. Titanium dioxide nano crystalline Degussa P-25 is from Orion Chem. Pvt. Ltd, India. Curcumin dye of 98% purity is purchased from Akey Flavours & Aromatics Pvt. Ltd., Pathanamthitta. For electrolyte preparation, polyethylene glycol (PEG) (MW 400), Potassium/ Lithium Iodide and Iodine from
Aldrich are procured and used as such. Poly ethylene dioxy thiophene : Poly styrene sulfonate (PEDOT:PSS) is also from Aldrich. Other chemicals such as Dimethyl Sulfoxide (DMSO), Dimethyl formamide (DMF), Acetone, Ethyl alcohol, 2-Propanol, Acetylacetone, Titron X-100 and Acetonitrile are from Merck, India.

![Fig.5.1. Structure of Curcumin dye](image)

5.1.3. Preparation of TiO$_2$ electrode and its counter electrode

The conducting glass substrates (FTO) were firstly cleaned with de-ionized water followed by 2-Propanol and then dried in air. To prepare TiO$_2$ colloidal solution, the TiO$_2$ (P25 Degussa) powder was grinded with 2 ml of distilled water and Acetyl acetone for 30 minutes and then 1ml of Triton X-100 is added with continuous mixing. This paste of TiO$_2$ was coated over FTO by screen printing technique. After air-drying, the TiO$_2$-coated FTO film was sintered at 450°C for 1 hour in electronic furnace. The so prepared TiO$_2$ film was immersed in a 0.1M HCl solution for an hour and then washed with de-ionized water. Now the device was kept in TiCl$_4$ solution for an hour, rinsed with de-ionized water and then dried at room temperature. The TiO$_2$-coated FTO substrate was then dipped into the solution of Curcumin dye for 12 h, followed by rinsing with organic solvent. In order to ascertain the effect of Organic solvents over the diffusion process, polar aprotic solvents like Acetone, DMF, DMSO were taken. Polar protic solvent i.e. ethanol was taken for dye diffusion.

The preparation of counter electrode is as follows: A thin layer of graphite is coated on the FTO using a pencil tip. The PEDOT:PSS aqueous solution and the organic solvent DMSO is mixed by the volume ratio 3:1. The mixed solution is filtered and stirred.
continuously for 6 h at room temperature. The DMSO treated PEDOT:PSS films are formed on FTO by spin coating technique. The film was dried at 200°C for 30 min.

5.1.4 Assembling of the DSSC:

The curcumin dye sensitized photo-electrode is clamped with the DMSO-treated PEDOT:PSS coated FTO counter electrode to form a sandwiched type structure. The electrolyte solution is prepared with 30 ml PEG, 4.12 g LiI, 7.6 ml Acetonitrile, 2ml Propyline carbonate and 0.45 g Iodine and is injected into the inter space between the photo-electrode and the counter electrode. The schematic diagram of the device is shown in Fig.5.2. Now the device is ready for characterization.

![Schematic diagram of DSSC](image)

**Fig.5.2.** Schematic diagram of DSSC
5.1.5. Surface analysis of the device

5.1.5.1. Surface roughness analysis

Surface imaging via non-contact surface work function determination is generally done using Kelvin Prob which is based on a vibrating capacitor and measures the work function difference, or the surface potential, between a conducting specimen and a vibrating tip.

We evaluated the surface work function of bare nc-TiO$_2$, TiCl$_4$ treated TiO$_2$ and finally the one sensitized with Curcumin using Kelvin Probe System (Model SKP5050P). It is found that the work function of bare TiO$_2$ is 4.988 eV, and that of TiCl$_4$ treated one has 4.659 eV. This means that the porosity of the substrate is increasing with TiCl$_4$ treatment. After dye adsorption the work function increases which indicates that the substrate surface became smooth by the adsorption of dye.

5.1.5.2. Surface roughness imaging.

The surface roughness imaging is done with SEM and the images of the nc-TiO$_2$, TiCl$_4$ treated nc-TiO$_2$ and Dye-sensitized TiCl$_4$ treated nc-TiO$_2$ surface were recorded with SEM (Model JSM-6390) at 15 V and 20,000 MAG using 1 micron marker. The images are as shown in Fig.5.3. The figure reveals that treatment with TiCl$_4$ imparts surface roughness and generation of more bindings sites which is responsible for enhanced dye loading leading to an increase in $J_{sc}$ and conversion efficiency.
Fig. 5.3. SEM images of (a) TiO$_2$ fired at 450°C (b) TiO$_2$ Treated with TiCl$_4$ and (c) Curcumin adsorbed TiCl$_4$ treated TiO$_2$. 
5.1.5.3. Surface analysis through Raman Spectroscopy

Additionally to ascertain the impact of TiCl₄ treatment over the phase & particle size of nc-TiO₂, we recorded Raman Spectra of bare nc-TiO₂ sintered at 450°C & TiCl₄ treated nc-TiO₂ respectively. It is shown in figure Fig.5.3 (d) and (e). Treatment with TiCl₄ imparts generation of rutile phase peaks at 443.2 cm⁻¹ & 619.7 cm⁻¹ that means the photo electrode made of ncTiO₂ contains mixture of both anatase as well as rutile phase which is ultimately responsible for enhancement in surface roughness and increase in dye loading leading to improved photocurrent.

(d)

(e)

Fig.5.3. Raman Spectra of (d) bare nc-TiO₂ sintered at 450°C (e) TiCl₄ treated nc-TiO₂
5.1.6. Optical properties of photo-electrode

5.1.6.1 UV-Vis spectroscopy

The optical absorption of the photo-electrode, recorded by a Photodiode array spectrophotometer (Model SPECORD, Analytic Jena) is shown in Fig.5.4. The absorption spectra of photo electrode sensitized with Curcumin dye in Acetone, DMF, DMSO and Ethanol are reflected for the absorption ranges from 300-500 nm.

![Absorption Spectra of photo electrode fabricated with Curcumin dye in Acetone, DMF, DMSO and Ethanol in bare TiO$_2$](image)

A decrease in the intensity of absorption as we go from Acetone to Ethanol is observed. It appears that the selection of appropriate solvent plays a role in improving the efficiency of the cell. The polar aprotic solvents like acetone, DMF and DMSO were found to be more effective for dye diffusion whereas ethanol being polar protic in nature was not suitable for dye diffusion. The acetone (0.306 cP) is found to be more effective in comparison to DMF (0.92 cP) and DMSO (1.996 cP) amongst the polar protic solvents.
5.1.6.2. Absorption spectra after surface treatment of nc-TiO$_2$:

Fig.5.5 shows the absorption spectra of photo electrodes i.e. (i) bare, (ii) HCl treated and (iii) TiCl$_4$ treated TiO$_2$. The absorption peaks associated with dye ranges from 200-500 nm. The intensity of absorption is larger for TiCl$_4$ and HCl-treated photo-electrode than the bare TiO$_2$.

This change in the UV–Vis absorption indicates that the amount of adsorbed dye in TiCl$_4$ and HCl-treated photo-electrode is larger than that of the bare photo-electrode. The enhancement in dye adsorption may be attributed to surface protonation in HCl treated TiO$_2$ film [218, 219]. The acid treatment changes the surface of TiO$_2$ nanoparticles to positively charged. The increase in surface roughness of TiCl$_4$ treated TiO$_2$ film is justified from the SEM images shown in Fig.5.3. The diameter of nc-TiO$_2$ in modified TiCl$_4$ treated layer was found to be larger and that makes the layer as a scattering layers restricting the loss of light and enabling connection of particle grains [220].

From the Kelvin prob analysis it is clear that the treatment with TiCl$_4$ results variation in surface potential (work function) which may be due to generated roughness. In other words, it is concluded that TiCl$_4$ treatment of ncTiO$_2$ surface imparts generation of more binding sites and thereby increases in dye adsorption leading to increase in photocurrent and total conversion efficiency. The SEM images reveals that treatment with
TiCl₄ imparts surface roughness and generation of more binding sites which is responsible for enhanced dye loading, leading to an increase in J_{sc} and conversion efficiency.

5.1.7. Photovoltaic properties

Current density vs. voltage characteristics of DSSC made with curcumin dye in different solvents such as Acetone, DMF, DMSO and Ethanol are plotted and shown in Fig.5.7. The photo voltaic parameters are determined and tabulated in Table 5.1. It is clear from the analysis that curcumin dye in Acetone solvent is more efficient than others solvents because the density of the dye molecule adsorbed to the TiO₂ electrode was more in the presence of Acetone. The J-V plots of DSSC made with different electrodes are also plotted and shown in Fig.5.8 and estimated parameters are summarized in Table 5.2. The effect of counter electrode/electrolyte can be neglected because the same counter electrode is used for different DSSC’s. TiCl₄-treated TiO₂ photo-electrode shows the best solar cell performance. HCl treatment also shows the improvement in efficiency. The short circuit photocurrent (J_{sc}) for the TiCl₄-treated photo-electrode increases up to 3.04 mA/cm², while in the bare photo electrode it is 1.36 mA/cm². The J_{sc} of HCl-treated photo-electrode is 1.76 mA/cm², lying in-between the bare and TiCl₄-treated one. These results indicates that the increase in J_{sc} is responsible for the improvement in the overall energy conversion efficiency and that the TiCl₄ treatment is more effective in improving the solar cell performance than the HCl treated one. IPCE expand represents the percentage of incident photons that are converted to electrons at a certain wavelength and is defined by the formula (5.1)

\[
IPCE(\lambda) = \left( \frac{1240}{\lambda} \right) \times \left( \frac{J_{sc}}{\phi} \right)
\]  

(5.1)

where \(\lambda\) is the wavelength (in nanometers), \(J_{sc}\) is the short circuit current in mA.cm⁻² and \(\phi\) is the incident radiative flux (in units of mW.cm⁻²). The spectrum is relatively broad, showing the electron injection in the TiO₂ conduction band, which is characteristic of the dye absorption spectrum. It is shown in Fig.5.6.
Fig. 5.6. Photo action curve of DSSC’s made of bare, HCl and TiCl₄-treated TiO₂ photo-electrodes.

Fig. 5.7. Photocurrent–voltage curve of DSSC’s with Curcumin dye in Acetone, DMF DMSO and Ethanol in bare TiO₂ photo electrode
Fig. 5.8. Photocurrent-voltage curves of DSSC’s fabricated with Curcumin, in bare HCl and TiCl$_4$ treated TiO$_2$ photo-electrodes

Table 5.1. Photovoltaic parameters of DSSC fabricated with Curcumin dye in Acetone, DMF, DMSO and Ethanol in bare TiO$_2$.

<table>
<thead>
<tr>
<th>Solvent of Dye</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
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<tr>
<td>ACETONE</td>
<td>1.35</td>
<td>0.43</td>
<td>0.517</td>
<td>0.63</td>
</tr>
<tr>
<td>DMF</td>
<td>0.95</td>
<td>0.42</td>
<td>0.526</td>
<td>0.44</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.89</td>
<td>0.42</td>
<td>0.482</td>
<td>0.38</td>
</tr>
<tr>
<td>ETHANOL</td>
<td>0.68</td>
<td>0.42</td>
<td>0.525</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 5.2. Photovoltaic parameters of DSSC fabricated with bare TiO$_2$, HCl and TiCl$_4$-treated electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Short circuited current ($J_{sc}$) (mA/cm$^2$)</th>
<th>Open circuit voltage ($V_{oc}$) (V)</th>
<th>Fill factor (FF)</th>
<th>Power conversion efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare TiO$_2$</td>
<td>1.36</td>
<td>0.45</td>
<td>0.49</td>
<td>0.625</td>
</tr>
<tr>
<td>HCl- TiO$_2$</td>
<td>1.76</td>
<td>0.48</td>
<td>0.54</td>
<td>0.947</td>
</tr>
<tr>
<td>TiCl$_4$-TiO$_2$</td>
<td>3.04</td>
<td>0.51</td>
<td>0.44</td>
<td>1.420</td>
</tr>
</tbody>
</table>

The improvement in conversion efficiency after treatment of nc-TiO$_2$ with TiCl$_4$ is justified by the experimental observations. Its sensitization with curcumin in Acetone solvent accelerates diffusion of dye into nc-TiO$_2$ surface masked with more binding sites and thereby increases in dye adsorption leading to increase in photocurrent and total conversion efficiency.

5.1.8. Conclusion

The fabricated DSSC having configuration FTO/nc-TiO$_2$ (Treated with TiCl$_4$): curcumin-Electrolyte ($I^3/I^-$ system)/PEDOT: PSS-Graphite/FTO was characterized for its
photo-voltaic response. The effect of TiCl$_4$ treatment of nc-TiO$_2$ photo-electrode and of polar aprotic and polar protic solvents in the sensitization process, are investigated. It is found that treatment of nc-TiO$_2$ with TiCl$_4$ and further its sensitization with Curcumin dye in Acetone solvent imparts accelerated diffusion of dye into nc-TiO$_2$ surface having more binding sites and thereby increases in dye adsorption leading to increase in photocurrent and total conversion efficiency.
5.2 Dye sensitized solar cell incorporated with Multi Walled Carbon Nanotubes (MWCNTs)

5.2.1. Introduction

Dye-sensitized solar cells have attracted much attention for more than a decade since reported first time by Gratzel and coworkers [222]. Attempts are going on to increase the adsorption of dyes for harvesting the solar spectrum, smoothen the function of transport of photo-excited electrons and encourage the diffusion of an electrolyte ion. The process involves the injection of electrons from the photo-excited dye into the conduction band of the semiconductor oxide (TiO$_2$), from where they pass through the transparent conducting oxide fluorine-doped tin oxide (FTO) current collector and finally into the external circuit. Further, the sensitizer is regenerated by electron transfer from a donor, typically iodide ions, which are dissolved in the electrolyte that is present in the porous semiconductor. The tri iodide ions formed during the reaction diffuse to the counter electrode, where they are reduced back to iodide by the conduction band electrons that have passed though the external circuit that performs the electrical work.

Now a days PEDOT:PSS coated FTO glass is used as counter electrode instead of costly platinum sputtered FTO glass to catalyze the reduction of I$^{3-}$ to I$^-$ in redox electrolyte[223-225]. Recently, it was reported that conductivity of the PEDOT:PSS film is enhanced if a liquid organic compound such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) or tetrahydrofuran (THF) is added to the PEDOT:PSS aqueous solution[226, 227]. Besides the choice of preparation method for depositing conducting polymers on the conducting glass is significant for the determination of efficiency of DSSC. A few methods, such as spin coating [228] and chemical polymerization [224] were employed in order to form a conductive polymers deposited counter electrode, which posses good electrochemical stability. W.J.Lee et al [229] modified the counter electrode by using Multi wall carbon nanotubes and they could replace the costly platinum electrode by it without much change in efficiency of the cell.

Modification of working electrode is also important. Vincent et al. [230] reported the inclusion of carbon nanotubes in an inorganic TiO$_2$ sol-gel matrix. Huang and Gao studied the growth behavior of Multi wall carbon nanotubes (MWCNTs) by incorporating
it on immobilized rutile TiO$_2$ (R-TiO$_2$) [231]. Photovoltaic devices are fabricated by Ago and colleagues using composites of MWCNTs and conjugated polymers [232]. Ionic gel electrolytes are prepared by Usui et al. by dispersing MWCNTs into ionic liquid electrolytes. They achieved higher energy conversion efficiency with corresponding dye-sensitized solar cells (DSSCs), relative to those using bare ionic liquid electrolytes [233]. It has been reported that the DSSCs fabricated with anatase and r-TiO$_2$ are comparable in their photo voltaic properties at one-sun intensity (100 mW cm$^{-2}$) [234, 235]. It has been proved that r-TiO$_2$ has superior light scattering properties compared to anatase TiO$_2$, because they are cheaper to produce, have higher refractive index and is chemically more stable [236]. However, the electron transport is slower in the rutile layer than in the anatase layer because of the interparticle connectivity associated with particle packing density and is evident from the data suggested by intensity modulated photocurrent spectroscopy along with scanning electron microscopy [234]. Stephan et al. reported that the introduction of MWCNTs in poly (methyl methacrylate) polymers increased the conductivity of the composite by 9 orders of magnitude [237]. On treating carbon nanotubes with a concentrated acid mixture of H$_2$SO$_4$ and HNO$_3$ [238-241] or of H$_2$SO$_4$ and KMnO$_4$ [242], carboxylic acid groups can be introduced in the nanotubes in addition to shortening them [243]. It is assumed that MWCNTs attached with carboxylic acid groups can adhere more strongly to TiO$_2$ particles than untreated MWCNTs due to which a strong covalent bond is formed between the dye molecule and the TiO$_2$ which will results in efficient DSSCs.

In the present study, Rose Bengal, an organic dye whose molecular structure is shown in Fig.5.9 is used as photo-sensitizer and graphite coated DMSO-treated PEDOT:PSS as counter electrode for dye sensitized solar cell. In the present research we have preferred MWCNTs and studied their beneficial influence, with and without modification, when incorporated in P25 TiO$_2$ films, on the photovoltaic properties of the DSSCs. Three types of investigations are presented in this paper. First, MWNTs are incorporated in P25 TiO$_2$ films and sensitized with Rosebengal dye. In the second investigation, P25 TiO$_2$ films are sensitized with Rosebengal dye and f-MWNTs (MWCNTs functionalized with –COOH) and in the third one, f-MWNTs are incorporated in P25 TiO$_2$ films, and then sensitized with the dye.
5.2.2. Materials

Multi Wall Carbon nanotubes (MWCNTs) of length 1-2 micrometers and diameter 10-30 nm prepared by CVD process is purchased from Intelligent Materials Pvt. Ltd. Fluoride doped tin oxide-coated glass substrate having resistance of $10\,\Omega/cm^2$ is purchased from Solaronix, Switzerland. Titanium dioxide (Degussa P-25) and RB dye were procured from Orion Chem. Pvt. Ltd, India and Hi-Media Laboratories Pvt. Ltd. Mumbai, respectively. For electrolyte preparation, Polyethylene glycol (PEG) (MW 400) Potassium iodide and Iodine from Aldrich are procured and used as such. Poly ethylene dioxy thiophene : Poly styrene sulfonate (PEDOT:PSS) is also from Aldrich. Other chemicals such as Dimethyl Sulfoxide (DMSO), Nitric acid, Dimethyl formamide (DMF), 2-Propanol, Acetylacetone, Titron X-100 and Acetonitrile are from Merck, India.

5.2.3. Preparation of photo-electrodes

The conducting glass substrates (fluorine-doped tin oxide) (FTO) are cleaned and rinsed with de-ionized water and 2-propanol, and then soaked in Propanol for 12 h. The FTO substrates are dried in air prior to film preparation. The TiO$_2$ colloidal solution is prepared by grinding the TiO$_2$ (P25 Degussa) powder purchased from Aldrich with 2ml of distilled water and Acetylacetone for 30min. Finally the 8.0 ml of distilled water and 0.1ml of Triton X-100 are added with continuous mixing for 10min and is coated over FTO by doctor blade technique. Functionalisation of Multi Walled Carbon Nanotubes (MWCNTs) is done as follows- 10 mg of MWCNTs are mixed with 70% concentrated HNO$_3$ and is refluxed for 8 h at 140$^0$C. The resulting product is cooled and centrifuged at 4500 rpm for 30 minutes, followed by washing with distilled water at 3000 rpm for 45 minutes. MWCNTs and functionalized Multi Walled Carbon Nanotubes (f-MWCNTs) in DMF (Dimethyl Formamide) are shown in Fig.5.10. It is seen that f-MWCNTs disperse well in organic liquids. Final product is dried at 80$^0$C, designated as f-MWCNTs and is characterized using Fourier Transform Infrared (FTIR) and Raman Spectra.
At first standard electrode- P25 is prepared as follows- TiO$_2$ is coated on fluorine doped SnO$_2$ (FTO) conducting glass, fired at 450$^\circ$C for 30 minutes and Rose Bengal dye is adsorbed after 12 hours sensitization. The other electrodes PE1, PE2 and PE3 are prepared as follows. PE1:- MWCNTs (0.5mg) were incorporated in P25 TiO$_2$ (1.2 g) by direct mixing to form a colloidal paste, coated on FTO conducting glass, fired at 450$^\circ$C and dye is adsorbed after 12 hours sensitization. PE2 is made by sensitizing fired TiO$_2$ coated FTO glass with a mixture of dye and f-MWCNTs. PE3 is made by sensitizing the Rose Bengal dye on fired FTO glass coated with a mixture of P25 TiO$_2$ and f-MWNTs. Nearly the same TiO$_2$ film thickness is maintained in all four cases, this being 15 $\mu$m. The reason for these thick films is to prevent MWCNTs from protruding from the films, which otherwise could have caused a short circuit in the DSSCs.

5.2.4. Preparation of counter electrode

PEDOT:PSS aqueous solution (1:3 wt.% dispersion in water) is purchased from Aldrich. The preparation of counter electrode is as follows: A thin layer of graphite is coated on the FTO using a pencil tip. The PEDOT:PSS aqueous solution and the organic solvent DMSO is mixed by the volume ratio 3:1. The mixed solution of PEDOT:PSS and DMSO is filtered and stirred continuously for 6 h at room temperature. The DMSO treated PEDOT:PSS films are formed on FTO by spin coating technique. The film was dried at 200$^\circ$C for one hour.
5.2.5. Assembling of DSSC

The dye sensitized solar cell is assembled by clamping dye sensitized photo-electrode with a DMSO-treated PEDOT:PSS coated FTO counter electrode to form a sandwiched type structure. Electrolyte solution is prepared as reported in [244], by taking the proportionate quantity of 0.5 mol KI and 0.05 mol of iodine and PEG (MW 400) (0.14 mol) in 50 ml acetonitrile solvent. The conductivity of the electrolyte solution is recorded with conductivity bridge meter and it is found to be 13.6mScm$^{-1}$. One drop of this electrolyte solution is injected into the inter space between the photo-electrode and the counter electrode. The schematic diagram of the device is as shown in Fig.1 of our previous published report [244].

The absorption spectrum of the fabricated device is recorded using a Photodiode array (Analytic Jena) or Perkin-Elmer spectrophotometer (Lambda35). FTIR spectra are obtained using IRAffinity-1 Shimadzu 01080 FTIR Spectrophotometer to identify the formation of carboxylic acid groups on f-MWNTs. Raman spectra are obtained using a Avalon Instruments Raman station R3 purchased from Ireland UK in which green laser of $\lambda=532$ nm is used. The scanning range is from 200 – 4000cm$^{-1}$ to identify the attachment of TiO$_2$ to f-MWNTs. AFM images are taken using Digital Instruments Veeco, USA, Model- Nanoscope 111A, software version 5 and the tips used are contact mode tips. Photocurrent–voltage curves are measured using a Keithley electrometer 6517 A. A 300 W Xe lamp with an AM 1.5 with input power 100 mW per cm$^2$ is used to illuminate an active area of 1 cm$^2$ of the TiO$_2$ electrode.

5.2.6. Results and discussion

An FTIR spectrum of MWCNTs is shown in Fig.5.11. It is then compared with FTIR spectrum of f-MWCNTs shown in Fig.5.12 (a) and (b). The attachment of carboxylic acid groups to acid treated MWCNTs (f-MWCNTs) is identified. FTIR spectra of f-MWCNTs showed a C=O peak of the COOH groups at 1730 cm$^{-1}$ and a broad OH peak around 3400 cm$^{-1}$, in addition to a C=C peak of MWCNTs nearly at 1600 cm$^{-1}$. On the basis of these results, the presence of COOH groups in the f-MWCNTs is confirmed. As a result of the shortening and simultaneous functionalization with COOH groups by
nitric acid, f-MWCNTs dispersed well in water [245] and DMF shown in Fig 5.10. Their good miscibility with water is beneficial for the fabrication of TiO$_2$ film electrodes.

**Fig.5.11.** FTIR spectra of MWNTs

**Fig.5.12.** FTIR Spectra of f-MWNTs (a) within the range 500-2000 cm$^{-1}$ and (b) within the range 3000-3700 cm$^{-1}$

The AFM images of the prepared film such as TiO$_2$ film, (Fig. 5.13 (a)), MWCNTs incorporated TiO$_2$ film, (Fig. 5.13 (b)) and f-MWCNTs incorporated TiO$_2$ film, (Fig. 5.13 (c)) are taken and analyzed
Fig. 5.13. AFM images of (a) TiO$_2$ film (b) MWNTs incorporated TiO$_2$ (C) f-MWNTs incorporated TiO$_2$

Fig. 5.14. Raman Spectra of the prepared film
Interestingly the calculated RMS roughness values are 117, 153 and 103 nm respectively. By the introduction of MWNTs the roughness value found to be increased because the MWCNTs are not exactly filling the gap between the TiO$_2$ nano particles. But when it is functionalized the RMS roughness value found to be decreased. This reduction in roughness is attributed to the smoothing effect induced by the f-MWCNTs as it fills exactly the gaps between the TiO$_2$ nano particles. This means that there is more favorable cluster formation in P25 TiO$_2$ films in the presence of f-MWCNTs. Also there is an increased surface area of the films fabricated in the presence of f-MWCNTs.

![Absorption spectra of different Photo electrodes](image1)

**Fig.5.15.** Absorption spectra of different Photo electrodes

![Current- Voltage characteristics of DSSCs having different photo electrodes](image2)

**Fig.5.16.** Current- Voltage characteristics of DSSCs having different photo electrodes
Fig. 5.14 is the Raman spectra of the TiO$_2$ film which is compared with the TiO$_2$ film in presence of MWCNTs and f-MWCNTs. It is found that the MWCNTs incorporated film shows blue-shifts by 4 cm$^{-1}$ and f-MWCNTs shifts by 7 cm$^{-1}$. These blue-shifts can be attributed to the strain effects at the f-MWCNT/TiO$_2$ interfaces, which may influence the vibration frequencies [254]. The difference in the Raman spectra between f-MWCNTs versus MWCNTs is due to the increased adherence of r-TiO$_2$ particles to f-MWCNTs.

The optical absorption spectra of the P25 (the standard electrode), PE1, PE2 and PE3 are shown in Fig. 5.15. It is seen in the Fig. that for all the photoelectrodes the absorption band extend from 320 to 600nm but the intensity of absorption is different in different electrodes. This means that the dye absorption in PE3 is more than that of other electrodes. This is due to the increased surface area of the films fabricated in the presence of f-MWCNTs.

Fig. 5.16 shows the J–V curves of DSSCs made by incorporating MWCNTs, with and without functionalization, in the TiO$_2$ films, compared with that of a cell fabricated with P25 film only. The results are summarized in Table 5.3. Compared to a cell fabricated with P25 film only, the cell with PE1 shows a higher $J_{sc}$ by about 4%. Similarly the cells with PE2 and PE3 show $J_{sc}$ improvements of about 15 and 40%, respectively. However, there are hardly any changes in open circuit voltage ($V_{oc}$) of the four cells. As a result of mainly $J_{sc}$ enhancements, the overall energy conversion efficiency ($\eta$) has increased by 7, 32, and 60% for the cells prepared with Films PE1, PE2, and PE3 respectively, with

<table>
<thead>
<tr>
<th>Photo Electrode</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
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<tr>
<td>P25</td>
<td>6.72</td>
<td>0.68</td>
<td>0.50</td>
<td>2.3</td>
</tr>
<tr>
<td>PE1</td>
<td>6.97</td>
<td>0.68</td>
<td>0.51</td>
<td>2.5</td>
</tr>
<tr>
<td>PE2</td>
<td>7.72</td>
<td>0.68</td>
<td>0.57</td>
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</tr>
<tr>
<td>PE3</td>
<td>9.44</td>
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</tbody>
</table>
respect to that of the cell made with P25 film only. The surface area of the TiO$_2$ films is increased in the presence of f-MWCNTs which is the reason for the enhanced $J_{sc}$. This is evident from the absorption spectra of the photo electrodes (Fig 5.15). Enhanced quantity of dye adsorption in the presence of f-MWCNTs is the indicative of enhanced surface area of TiO$_2$ film. This suggests that the surface area of TiO$_2$ films for dye adsorption has increased in the order of surface area of P25<PE1<PE2<PE3. It may be due to additional adsorption sites gained from the adherence of TiO$_2$ particles to f-MWCNTs. The $J_{sc}$ increases are consistent with this order of increase of surface area. The increased surface area of TiO$_2$ films with the incorporation of f-MWCNTs those are otherwise not available when TiO$_2$ particles aggregate themselves in the P25 film. Because of the fine distribution of f-MWCNTs in the TiO$_2$ films, as can be understood from AFM images (Fig.5.13), a better dispersion of TiO$_2$ particles in the PE3 can be visualized and hence additional adsorption sites for the dye. The $J_{sc}$ increase also arises from enhanced light scattering by the TiO$_2$ films with f-MWCNTs. The reason for this may be favorable TiO$_2$ cluster formation induced by f-MWCNTs in the films in the order of that of P25<PE1<PE2<PE3, again in agreement with the order of the $J_{sc}$ increase. The enhanced light scattering of PE2 and PE3, compared to that of the film P25 and PE1 can be accounted for the higher light scattering properties of TiO$_2$ on f-MWNTs and is clear from the AFM studies of the photo electrodes. The $J_{sc}$ enhancement can also be explained by the increase in interconnection among the TiO$_2$ particles in the TiO$_2$ films prepared with f-MWCNTs. Formation of f-MWCNT-induced clusters, as mentioned already, enables increase in interconnection among the TiO$_2$ particles in the film, relative to that among the particles in the film without f-MWCNTs. The increased interconnectivity in turn increases the electrical conductivity of the film in the presence of f-MWCNTs. In addition to improved interconnectivity among TiO$_2$ particles in the films in the presence of MWCNTs, the anchoring of TiO$_2$ particles to nanotubes can promote charge separation, owing to the fact that carboxylic acid groups of f-MWCNTs are also able to attach themselves to TiO$_2$ particles. Since absorbance is proportional to the free electron density in the conduction band of TiO$_2$, the implication is a higher electron transport in Films PE1, PE2 and PE3. This suggests that the surface electron trap sites are possibly blocked by the improved interconnectivity among TiO$_2$ particles. The absorbance pattern of Films P25, PE1, PE2 and PE3 are consistent with their respective $J_{sc}$ enhancements. The figure shows the rise and fall of the $J_{sc}$ recorded during one on-off cycle of illumination at (100 mW cm$^{-2}$).
Electrons trapped in the surface states appear to be responsible for the slower photocurrent response in the case of the DSSC with bare P25 film [246, 247]. It is to be emphasized here that the performance of the cell is not optimized with regard to film thickness, dye purification and device architecture. This study focused on the influence of MWCNTs and TiO$_2$/f-MWCNTs, when incorporated in P25 TiO$_2$ film, on the photovoltaic properties of the corresponding DSSCs. Comparative measurements are made in this regard with reference to a cell without f-MWCNTs.

5.2.7. Conclusions

Incorporation of acid-treated multi-wall carbon nanotubes that is functionalized (f-MWCNTs) in P25 TiO$_2$ films yields considerably increased $J_{sc}$ about 40% with the same open-circuit voltage and fill factor for the pertinent dye-sensitized solar cells, with respect to the unmodified cell. The enhanced essential $J_{sc}$ is attributed to increased surface area of the films fabricated in the presence of f-MWCNTs. The $J_{sc}$ enhancement also arises from more favorable cluster formation in P25 TiO$_2$ films in the presence of f-MWCNTs than that in the absence of them. Improved interconnectivity among TiO$_2$ particles in the presence of the f-MWNTs is seen as another reason for the $J_{sc}$ enhancements. The $J_{sc}$ enhancements are consistent with the increase in dye adsorption, light scattering and potential-dependent optical absorbance of the respective cells. The efficiency of the fabricated devices is compared in Table.5.3. It is observed that the efficiency of the functionalized MWCNT incorporated photo electrode in DSSC shows an efficiency of 3.7%.