In this chapter, transparent ZnO nanorod arrays on FTO glass substrates and used them as the wide band gap semiconductor in dye-sensitized solar cells. Dye sensitized solar cells (DSSC’s) were fabricated using natural dyes extracted from Amla. The ZnO nanostructured working electrode has been prepared by hydrothermal method on ITO coated glass substrate. The crystallinity and morphology of the prepared working electrode has been studied using X-ray diffraction and scanning electron microscopy (SEM) techniques. Here we have used carbon coated ITO as counter electrode instead of the conventional Platinum electrode and Iodine compounds acts as a good electro catalyst for the redox reaction. The nanorods length can be highly controlled by adjusting the reaction time interval. The lengths of the nanorod mainly determine the short circuit current density and cell performance. The increasing in the nanorod length provides larger amount of surface area, more adsorbed dyes, and resulting in higher conversion efficiency. The photovoltaic properties are examined, under A.M 1.5 irradiation as a function of open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$), Fill-Factor (FF) and efficiency ($\eta$) aiming to determine the conditions that lead to the production of natural dye DSSCs with different solvents. The effects of natural dye extract temperature, pH of the dye and the solvent used for dye preparation on the solar cell Characteristics have been studied. The efficiency of Amla extract sensitized ZnO nanorod solar cells are found to be value of 0.71% at 75°C in ethanol better than the other solvents using methanol.
8.1. Introduction

Natural Dye Sensitized Solar Cell (DSSC) is very simple to construct and is made of low-cost materials. Fabrication costs will therefore be less than that for conventional dye solar cells [1, 2]. Coumarin, merocyanine derivatives and polyene dyes have been designed successfully as organic-dye Photosensitizers in DSSCs, and high solar energy to electricity conversion efficiencies of up to 8% under AM 1.5 irradiation have been attained [3]. The lower performance of DSSCs based on organic dyes compared to those based on Ru complexes is probably due to the lower open-circuit voltage (Voc) that is generated in the DSSCs based on organic dyes, rather than the performance of the short-circuit photocurrent density (Jsc), which is almost the same [4]. Novel iminocoumarin dyes having carboxyl and hydroxyl anchoring groups have been investigated. The IPCE value for iminocoumarin dye sensitized solar cell was 21.38%. The overall low efficiency of the dyes is ascribed to the lack of light harvesting ability at longer wavelength region [5]. Fruit dyes like mulberry and others have also been tested for DSSC. Fill factor values of 0.40 to 0.61 have been achieved on dye sensitization of dye extracts from mulberry, chaste tree fruit and cabbage palm fruit [6].

Amla (Emblica officinalis Gaertn, family Euphorbiacea) is a native of India, Ceylon, Malaya and China (Fig.8.1). The fruit is used as a major constituent in several Ayurvedic preparations such as Chyavanprash and Rasayana that promotes health and longevity [7]. Amla is one of the richest sources of Vitamin C known (Fig.8.2). In addition to this, potent antioxidant, several active tannoid principles (EmblicanninA, Emblicannin B, Punigluconin and Pedunculagin) have been identified which appear to account for its health benefits [8, 9]. Amla has been reported to posse’s expectorant, purgative, spasmolytic, antibacterial, hypoglycemic [10, 11], hepatoprotective and hypolipidemic activity [12]. The aqueous extract has been reported to have anti-pyreticlaxative and tonic properties and also showed antibacterial activity [13]. The ascorbic acid content of fresh Amla fruit can range up
to 950/100 gm which is said to highest among all fruits next only to Barbados cherry [14]. The fruits of Emblica officinalis are rich in tannins. The fruits have 28% of the total tannins distributed in the whole plant. The fruit contains two hydrolysable tannins Emblicannin A and B, which have antioxidant properties, one on hydrolysis gives gallic acid, ellagic acid and glucose wherein the other gives ellagic acid and glucose. The fruit also contains Phylllemblin [15, 16]. The fruits, leaves and barks are rich in tannins. The root contains ellagic acid and lupeol and bark contains leucodelphinidin. This seeds yield a fixed oil (16%) which is brownish-yellow in colour. It has the following fatty acids: linolenic (8.8%), linoleic (44.0%), oleic (28.4%), stearic (2.15%), palmitic (3.0%) and myristic (1.0%) [17].

Zinc Oxide (ZnO) nanostructures are an important and promising class of nanoscale building blocks for environment-friendly and cost-effective solar cells [18]. These nanostructures and their hybrids provide excellent functions for solar cells benefiting from their large surface area, uniform carrier transport, and improved light scattering. It is worthy to note that ZnO is one of the first materials employed in DSSCs [19]. Despite many efforts, which have put into improving the conversion efficiency of these DSSCs, it remains lower than that for TiO₂-based cells. Up to now, the best efficiency for a ZnO DSSC is 6.5% [20], which is around half of the best efficiency obtained for TiO₂ (12%) [21]. To further improve the efficiency, the majority of studies regarding ZnO solar cells focus on two main aspects: (i) developing facile methods to synthesize ZnO nanowires/rods [22] with outstanding conductive properties and (ii) searching for new dye molecules to solve the stability problem of ZnO in electrolyte. To overcome these problems, eco-friendly natural pigments like fruits and flowers has been used as photosensitizes to replace artificial chemical dyes. Colourful and transparent solar cells can be made using various kinds of dyes, depending on the use of the cell. For example, transparent solar cells could be used in place of windowpanes. Additionally, the use of a plastic substrate, rather
than glass, is possible if low temperature processing of the TiO$_2$ film preparation (< 250°C) is available and would expand the use of DSSC [23-25].

In the present work, we have synthesized ZnO nanorods on FTO coated SLG Substrate and fabricated solar cells using Amla (Phyllanthus Emblica) dye extract. Here we have used carbon coated FTO as counter electrode instead of the conventional Platinum electrode and Iodine compounds acts as a good electro catalyst for the redox reaction. The photovoltaic properties are examined, under A.M 1.5 irradiation as a function of open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$), Fill-Factor (FF) and efficiency ($\eta$) aiming to determine the conditions that lead to the production of natural dye DSSCs with different solvents [10].

### 8.2. Experimental

#### 8.2.1. Deposition of Fluorine Doped Tin Oxide Thin Films (FTO)

100 cc of 2 M Fluorine chloride solution was prepared in doubled distilled water and 14.285 gm of Fluorine chloride was dissolved in it, to obtain the 20% doping concentration of Fluorine. A few drops of oxalic acid were added in it for removal of whitish precipitate from the above mixture, 10 cc solution was taken as a precursor solution and 10 cc of propane 2-ol was added in it which gives the 20 cc spraying solution [26]. The final solution was sprayed through the specially designed glass nozzle at the spray rate of 5 cc per minute. The substrate temperature was maintained at 475°C. It is found that, the conducting glasses have 13 $\Omega$/cm$^2$ sheet resistance and about 90% transparency [27].The Conducting glasses prepared from Spray pyrolysis technique and it have 15-20 S/cm$^2$ sheet resistance and about 92% transparency. The substrate cleaning process was discussed in previous chapter – VI.

#### 8.2.2. Preparation of Working Electrode

In our experiment, Zinc Oxide photo anode was deposited on Fluorine doped tin oxide (FTO) coated glass substrate. Initially, the FTO glass substrates were
ultrasonically soaked in acetone and ethanol, and then dried at 100 °C in an oven. To synthesize ZnO nanorods, two step chemical methods have been used. In the first step, ZnO seed layer has been prepared by simple sol-gel method [30].

To prepare ZnO seed layer, 0.3 M of zinc acetate dehydrate (Zn (CH₃COO)₂·2H₂O) was dissolved in a mixture of 10 ml ethanol and 0.25 ml water. FTO coated glass substrates were dipped in the prepared solution and this resulted in the formation of seed layer, these seed layer films are annealed at 300 °C for 30 minutes. In the second step, ZnO nanorods have been prepared by hydrothermal method [31]. To prepare ZnO nanorods, an aqueous precursor solution was prepared by dissolving 0.02 M zinc nitrate (Zn (NO₃)₂·6H₂O) and 0.2M hexamethylenetetramine ((CH₂)₆N₄) in 20 mL deionized water. The solution was transformed into Teflon coated stainless steel autoclave and the seed layer coated substrate was vertically dipped in the aqueous solution and it was maintained at a bath temperature of 85 °C for 4 hrs. After the growth period, the substrates were removed from the solution and were thoroughly washed with deionized water to remove the residual salt from the surface of the film. Now the prepared film was annealed at 450 °C for 30 minutes and this resulted in the formation of ZnO nanorods [32-34].

8.2.3. Preparation of Natural Dye Sensitizer

For Amla extract preparation, the cleaned fruits were cut into small pieces and put into two different beakers. Chopped fruits were soaked in 200 ml of ethanol at different temperatures. Then the residual parts were removed by filtration and the filtrate was washed with hexane several times to remove any oil or chlorophyll present in the extract. This was directly used as dye solution for sensitizing ZnO nanorod electrodes. The Amla extract was extracted from the ethanol solvent at different temperatures such as room temperature, 50 °C, 75 °C and 100 °C. To study the effect of pH on the performance of solar cell, the pH of the Amla extract solution
was changed by adding dilute HCl and dye solution with three different pH values 1.0, 2.0 and 3.0 have been used as sensitizer. To study the effect of extracting solvent on the performance of solar cell, the Amla extract was also extracted by using methanol. [35].

8.2.4. Assembling the Solar Cell

To assemble the natural dye sensitized ZnO nanorod based solar cell, the prepared ZnO nanorod electrode were immersed in the synthesized dye solution at room temperature for 24 h, after that period the film was rinsed in anhydrous ethanol and then dried [36]. A carbon-coated FTO electrode was then placed over the dye-adsorbed ZnO nanorod electrode. A redox electrolyte was prepared using 0.5 mol KI, 0.05 mol I2, and 0.5 mol 4-tert-butylpyridine and a drop of electrolyte solution was injected into the into the cell [37].

8.2.5. Characterization

The structure of the prepared films has been studied by X-ray diffraction studies using a Rigaku X-ray diffractometer (XRD) using Cu Kα irradiation. The surface morphology of the films were studied using scanning electron microscopy (SEM;VEGA 3 TE SCAN), The photocurrent-voltage (J-V) characteristics of the devices were measured using white light from a xenon lamp (max.150 W) using a sun 2000 solar simulator (Sponsor: MHRD &IIT-BOMBAY). Light intensity was adjusted using a Si solar cell to ~AM-1.5. Incident light intensity and active cell area were 100 mWcm⁻² (one sun illumination) and 0.4 cm² (0.5 × 0.8cm), respectively.

8.3. Results and discussion

8.3.1. Structural and Morphological Analysis

Fig.8.3 shows the X-ray diffraction patterns for the film. The diffraction peaks observed at 35.91°, 48.09°, 55.880°, and 62.35° are attributed to the (101), (102), (110), and (103) planes, respectively, of hexagonal wurtzite structure, as can be seen
in comparison with the JCPDS card nos. 00-003-0752. The films are polycrystalline in nature and highly oriented along (101) plane. The crystallite sizes were calculated using Scherrer’s formula using information on broadening of diffraction peak (\(\beta\)), X-ray wavelength (\(\lambda\)), and incident X ray angle with crystal plane (\(\theta_B\)). The average crystallite size for the (100), (002), and (101) XRD peaks was found to be 17 nm and the calculated lattice parameter \(c\) was 0.5124 nm.

Figure 8.4(a) is the scanning electron microscope image of ZnO nanorods. The SEM image shows that the prepared films have rod like structure. The columnar structure was more uniformly developed with a well-developed faceted and needle capsuliform surface morphology. The surface and cross-sectional morphology of films were closely related to their preferred orientation.

Figure 8.4(b) shows a nanoscale system with a uniform morphology with bright rod-shaped agglomerates of grains. When the metal precursors Zn/O combination is increased the film exhibited dense layers with fine grains. The grain size revealed from SEM pictures was found to increase with the increase in the power, which is also confirmed by the increase in the nano rod size (16.87 nm) revealed from x-ray diffraction data.

8.3.2. Fourier Transform Infrared Analysis (FT-IR)

Infrared spectroscopy (IR) is an analytical tool that can be used in the determination of chemical compound of a dye. It can also be used for the elucidation of the structure of both organic and inorganic components of the dye. It usually reveals the functional groups present in a sample [38]. Figure 8.5 shows the Infrared spectra was recorded on a Perkin –Elmer 1600 series-FTIR Spectrometer as KBr discs. The IR spectrum of all samples show broad peaks in region of 3300 – 3600 Cm\(^{-1}\) could be assigned to OH stretching frequency of coordinated water. Absorption peaks at 1600 – 1750 Cm\(^{-1}\) have been assigned to the carbonyl C=O stretching modes, suspected for the metal chelates. 1300-1365 Cm\(^{-1}\) for C=C stretching and
1150 - 1230 Cm⁻¹ medium weak C-O stretching. The 1367 Cm⁻¹ from the raw dye sample can be assigned to C=C chelate ring of some metal chelate complexes within the sample.

8.3.4. Optical properties of the Photosensitizers

Optical properties of the Amla fruit extracted with two different solvents and it adsorbed on ZnO film surface studied from UV–Vis spectra. The absorption spectra that Amla extract adsorbed on ZnO is obviously wider and red shift compared with that in ethanol and methanol solutions. When the dyes adsorbed on the ZnO film, the average value of the shift is 13 nm, which means that the interaction formed through the C–O–Zn chemical bond.

Fig. 8.6-8.9 shows the absorbance and transmittance spectrum of biosensitizer extracted from Amla fruit with different pH and temperatures respectively. A major observation from Fig.8.7 and 8.9 is that the Amla fruit sensitizer shows higher average transparency in the visible range (400-750 nm) of the optical spectrum. The average transmittance value of sensitizer at 100°C was 84% while that of 75°C and a room temperature condition has 85% and 89 % respectively. Dye extract temperature at 50°C shows the highest transparency of 97 % throughout the spectrum. The absorption characteristic is a very important property in DSSC as it directly reflects the optical transition probability [39]. Absorption spectral characteristics of all dyes are shown in Fig.8.6 and 8.8. It can be seen that all dyes show absorption in the visible region, 400-750 nm. Dye molecules absorb light and transfer that light energy by resonance energy transfer to a specific chlorophyll pair in the reaction centre of the photo systems. Molecules absorbs strongly in the blue and red regions of the absorption spectrum while reflecting green [40]. From the above figures, it can be seen that both pH and temperatures has the absorbent peaks in the red region at the wavelengths of about 657 nm. No blue peaks were observed in this study. Even though Amla extract at pH=3 and 75°C has broad absorption
range, the adsorption on the working electrode is higher than the other pH and temperatures. The reason may be the pigments present in the Amla (tannins) extracts do not attach to ZnO by the same amount. The adsorption coefficient or the amount of dye molecules adsorbed on the surface of ZnO working electrodes were determined by spectroscopic measurement of the dye desorbed from the surface.

The ZnO working electrodes were soaked in an ethanol solution containing dye solutions (0.1 M) at room temperature for 24 h. After sensitizing ZnO electrodes with the dye molecules the electrodes were sequentially washed with water/ethanol and dried in the air. In order to analyze the amount of dye loading in ZnO electrode, the dye was desorbed from the electrode into NaOH solution in water/ethanol (1.0 M, 50:50, V/V). A UV-Vis spectrophotometer was employed to measure the dye concentration in the desorbed-dye solution. The calculated values are $6.1 \times 10^{-7} - 3.9 \times 10^{-8}$ mol/cm$^2$ for Amla extracts at different pH and temperatures [41]. This result indicates that the amount of dye adsorbed is remarkably different, even though the same concentration was maintained for both the dyes. This is due to the difference in the adsorption rate of the dye on the film. The low amount of adsorption of betanin is due to the weak bond between the dye molecule and the surface of ZnO film. Whereas the dye molecules present in pH=1 and 50$°$C were easily interacts with the ZnO surface, so large amount of dye molecules are adsorbed on the surface. Due to these extracts sensitized electrode shows broader absorption than the other extract sensitized electrodes [42].

8.4. Photo current density – Voltage (J-V) Characteristics of the Solar Cell

8.4.1. J-V characterization of the Solar Cell using ZnO / Amla Dye

Fig.8.10 shows the photocurrent density-voltage (J-V) characteristics of natural dyes (prepared at room temperature) sensitized ZnO nanorod based solar cells. The conversion efficiency ($\eta$) of the Amla dye extract sensitized solar cell is 0.20% with short circuit current density of 0.65 mA/cm$^2$, open circuit voltage 0.46V,
fill factor of 0.68 and it is shown in Table 8.1. The pH of the dye extract has an important effect on the performance of Amla natural dye sensitized solar cells and it is shown in Table 8.2. The solar cells fabricated using ZnO nanorod sensitized dye with pH values 1, 2 and 3 show efficiency values of 0.20%, 0.25%, 0.28 % respectively (Fig.8.11). The dyes synthesized at pH = 3 shows good interaction with the working electrode, the reason is at pH = 3, the tannins existed as *Emblica officinalis* which is stable form of Amla, an increasing pH hydrated this ion to tannoid bases. However, the cell deterioration by acid leaching is expected as the pH goes lower (pH = 1), which results in a lower efficiency.

The effect of dye extracting temperature on the performance of dye sensitized solar cells is shown in Table 8.3. Solar cell sensitized using dye extracted at 50 °C shows a power conversion efficiency of 0.52%, with Voc of 0.45 V, Jsc of 1.43 mA/cm² and FF of 0.82. Solar cell sensitized using the dye extracted at 75 °C shows power conversion efficiency of 0.71%, with Voc of 0.47 V, Jsc 1.79 mA/cm² and FF of 0.85. Solar cell sensitized using dye extracted at 100 °C shows a conversion efficiency of 0.47% with Voc of 0.41 V, Jsc of 1.52 mA/cm² and FF of 0.47(Fig.8.12). The photocurrent density-voltage (J-V) characteristics of natural dye (extracted using different solvent) Sensitized ZnO nanorod based solar cells. As shown in Table 8.4, the solar cells prepared using natural dye extracted in ethanol shows a higher efficiency than that of Solar cells prepared using natural dye extracted in methanol. The Fig.8.13 clearly shows that the dye extracted using methanol absorbs less light compared to that of the dye extracted using ethanol.

**8.4.2. J-V characterization of the Solar Cell using TiO₂ / Amla Dye**

In addition, the J-V characteristics of the Amla Dye Solar Cell using TiO₂ photo anode. TiO₂ working electrode was prepared via doctor blade method. Thoroughly concerning the preparation of TiO₂, photo anode was discussed in previous Chapter -VI (section 7.2.3). The above procedure for TiO₂ films repeated
several times in order to make films with thickness around 1.5 microns TiO₂ films were sensitized in a dye solution of Amla bio- dye for 24 h at room temperature. Carbon paste coated on an ITO substrate was used as a counter electrode. The Dye sensitized solar cell (DSSC) was fabricated by clamping the dye-sensitized TiO₂ photo electrode against carbon counter-electrode.

The conversion efficiency (η) of the Amla extract sensitized TiO₂ nanostructure based solar cell is 0.19% with short circuit current density 1.09 mA/cm², open circuit voltage of 0.34 V and fill factor of 0.52. It clearly shows that the Amla dye extract based DSSC performs lower efficiency with TiO₂ photo anode as compared to that of the ZnO nanostructured photo anode.

Solar cells sensitized using the dyes extracted at higher temperatures (50°C and 100 °C) also gives lower efficiency than that of the solar cell sensitized using the dyes extracted at 75 °C. This is due to the lighter colour of the extract, which is due to restriction of tannins ion solubility [43]. It shows that, the optimum extracting temperature is 75 °C. To confirm the effect of dye synthesizing temperature on the performance of solar cell, UV-Vis absorption spectra was recorded for synthesized dye and dye sensitized working electrode. The dye synthesized at 75°C shows greater absorbance of light than the dye synthesized at other temperatures. The reason is the dye extracted at 75 °C resulted in deep coloured solution. The extracts absorb visible light and sensitize the oxide semiconductor to low-energy irradiation. The broadening of the absorption band of the coloured photo anode is related to the charge transfer interaction responsible for the binding of the dye to the oxide surface [44]. A good dispersion of dye molecules on the oxide surface could in fact improve the efficiency of the system.

Finally, DSSCs as promising alternatives to the conventional silicon based solar cells require specific modifications and inspired connections before they can be applied to a production line. The electrolyte thickness, the efficient current collection,
and effective isolation of the cells to the module are of the main issues to be solved before.

8.5. Summary

Low-cost natural dyes have been prepared from Amla fruit extract to study their effect on the performance of ZnO nanostructured DSSCs. Carbon-based materials were found to be a good CE material for DSSCs and such a cell with graphite as CE produced the best efficiency value of 0.71% at 75°C, with the highest photocurrent density and alternative CE material for expensive Pt. X-ray diffraction patterns for ZnO nanorods shows hexagonal wurtzite structure, as can be seen in comparison with the JCPDS card no. 00-003-0752. The films are polycrystalline in nature and highly oriented along (101) plane. The average crystallite size for the XRD peaks was found to be between 17 nm. The SEM image shows that the prepared films have rod like structure. The ZnO nanorods are needle in shape and the distribution is closely packed giving rise to little porosity and voids. The efficiency of the Amla dye sensitized solar cells can be enhanced by changing the solvent used in the preparation of the dye, changing the temperature and pH of the extract. Ethanol is found to be the suitable solvent for natural dye, the optimum dye extracting temperature is found to be 75 °C and the suitable value of pH is found to be 3.

The conversion efficiency (η) of the Amla extract sensitized TiO₂ nanostructure based solar cell is 0.19 % with short circuit current density 1.09 mA/cm², open circuit voltage of 0.34 V and fill factor of 0.52. It clearly shows that the Amla dye extract based DSSC performs lower efficiency with TiO₂ photo anode as compared to that of the ZnO nanostructured photo anode. Further optimization of the cell is possible for achieving higher efficiencies.
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