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TiO_2 -ZnO-Based Dye-Sensitized Solar Cells using Natural Sensitizers

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Abstract: The TiO_2 –ZnO based composites using natural dyes extracted from Spinach as Chlorophyll by varying composite ratio as 40% wt:60% wt (sample “a”) and 60% wt:40% (sample “b”) were used for fabrication of Dye-sensitized solar cells (DSSCs).For the fabrication of PV Cell, AR grade (make Loba, India) chemicals were used for experimentation. The effect of surface morphology composite structure has been studied using XRD characterizations. The structural property of the TiO_2 -ZnO film sample “a” shows good behaviour with preferred (103) orientation and “b” with preferred (101) orientation. The UV-Vis spectroscopy, for composite sample “a” recorded in the range from 206 nm to 347 nm, while for sample “b” is between 229 nm to 982 nm. Different PV parameters of the fabricated PV cells were measured at room temperature under incandescent light of 100 W/m^2.The fabricated PV cells exhibited I_{SC} 0.46 mA (for Sample “a”) 0.51 mA (for Sample “b”), the V_{OC} is 0.72 V and 0.84 V, with power conversion efficiency of 0.18% and 0.21% for Sample “a” and “b” respectively.

Keywords: *Dye-Sensitized Solar Cells, Power Conversion Efficiency, Natural Sensitizers*

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are one of the most actively researched next generation silicon-based solar cells because of its versatile uses, transparency, simple structure, and cheap cost.DSSCs are expected to be greatly reduced compared with conventional silicon solar cells. However, before they are put on the market, many things need to be done on DSSCs, such as increasing efficiency, achieving better durability and avoiding electrolyte loss caused by the leakage and or volatility of the electrolyte solution. Today, many efforts have been focused on improving the solar conversion efficiency. One of the important factors in efficiency of DSSCs is the dye which is used as sensitizer in DSSC. Many different dye groups, such as organic dyes, organic metal complexes and natural dyes, are currently employed in DSSCs. Synthetic and natural sensitizer can be compared on the basis of various parameters such as cost of cell, environment issues, stability problem, maximum absorbance, efficiency of the DSSC. The metal complex sensitizer synthesized from complex fabrication method while natural sensitizers are prepared from flowers, leaves and roots etc using simple ethanol, methanol or water extraction process thus less costly as compared to synthetic dyes [2].The natural dyes that have been used in DSSCs which should provide reasonable light harvesting efficiency, sustainability, low cost and easy waste management. Promising natural compounds are carotenoids, polyphenols and chlorophylls [3]. The architecture of DSSCs consists of transparent conducting oxide substrate [fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO)][4], different semiconductors [zinc oxide (ZnO), TiO2active or absorbing material (organic, inorganic dyes [5]), electrolyte (iodide/triiodide (I/I3-), copper) and counter electrode(graphene-based carbon)[6,7].The optical performance of dye in DSSCs influences the overall performance of the cell. Natural and synthetic dyes are classifications of dyes. Plant, animal, and mineral dyes belong to natural dyes [8].N. Gokilamani et al. fabricated TiO_2 dye-sensitized solar cell natural dye extracted from rose petals using the red rose power conversion efficiency of 0.81 %[9].Rodriguez et al. researched on red Bougainvillea glabra, violet Bougainvillea glabra, red Bougainvillea spectabilis, violet Bougainvillea spectabilis, and purifified red Bougainvillea glabra. The most prominent performance characteristic has been shown using red Bougainvillea spectabilis with an efficiency of 0.48%[10].A.B.Kashyout et al. fabricated zinc films using colloidal method from zinc oxide. It has been observed that the grain size was inversely proportional to the centrifugal speed. It decreased from 150 nm to 50 nm by increasing centrifugal speed from 6,000 to 15,000 rpm. The cell was sensitized from artificial and natural dye both. Natural dye has shown high open circuit voltage of 0.6 V [11].P.M.Sirimanne et al. extracted juice from pomegranate fruits containing cyanine (flavylium) utilized as natural dye sensitizer. The solid-state TiO2 (n type semiconductor)/pomegranate pigment (natural dye)/CuI (p type) solar cell has shown maximum absorbance at the wavelength of 570 nm that caused highest efficiency of the cell as compared to other natural pigments (cyanidin, tannin, santalin and vitamin C)[12].Chang et al. extracted natural dye from spinach and ipomoea extracts. Maximum absorbance found by ipomoea and spinach at wavelength 410 nm and 437 nm respectively. The highest efficiency of 0.278% was achieved from ipomoea extract. It has been also observed that raise in temperature affect the performance of DSSC remarkably [13].Diah Susanti fabricated DSSC from TiO_2 and tamarillo fruit extract as a dye with the highest efficiency of 0.043%.Plastic wrapping helped to slightly reduce the power drops, although it could not stabilize the power performance [14].Reena Kushwaha et.al.worked on four natural pigments extracted from leaves of teak (Tectona grandis), tamarind (Tamarindus indica), eucalyptus (Eucalyptus globulus), and the flower of crimson bottle brush (Callistemon citrinus) that were used as sensitizer for DSSC. The leaves of teak (Tectona grandis) showed best photosensitization effects. The extract from leaves of teak (Tectona grandis) has shown absorption in broad range of the visible region (470–662 nm) of the solar spectrum [15].In this paper, TiO_2 -ZnO films based dye sensitized solar cell is fabricated on the ITO substrate using doctor blade technique. The prepared samples were characterized through XRD, UV–Vis absorption spectra. The chlorophyll dye extracted from spinach is used as sensitizer.

2. EXPERIMENTAL

2.1. Materials

Ethanol was used for extracting dye from Spinach, Chemicals of analytical reagent (AR) grade (Loba, India), iodide/triiodide solution as electrolyte and the sealing tape. ITO-coated (Indium-doped tin oxide) conductive glass slides (surface resistivity 10 ohm/Sq, thickness 1.1 mm) were used as substrates for preparing TiO_2-ZnOthin film electrode and Aluminium foil as a counter electrode.

2.2. Extraction of Natural Dye Solutions

The natural dyes Chlorophyll were extracted from Spinach with ethanol. The Spinach is chopped into fine pieces and mashed uniformly into paste using the mortar and further mixed with ethanol. The mixture of mixture of spinach and ethanol solution is stirred using magnetic stirrer for an hour at speed of 450 rpm. Afterward the solution was left at room temperature for 24 hours and filtered with Whatman paper.

2.3.Photo-anode preparation

- ITO Cleaning: ITO glass substrates were cleaned using detergent solution beaker and ultrasonication treatment was given for 10 min, then ITO glass was rinsed with water and dipped into distilled water beaker followed by ethanol and acetone dipping for few seconds and, kept for the drying.

- TiO_2-ZnO Paste: The TiO_2-ZnO Paste was prepared with varying composite ratio as 40% wt:60% wt (sample "a") and 60% wt:40% (sample "b") as reported by Diah Susanti et.al.[14]. Initially, for sample "a"2.4 gm of TiO_2 and 1.6 gm of ZnO powder was mixed with 15 ml ethanol and stirred using a magnetic stirrer for 30 minutes to form TiO_2-ZnO Paste. The TiO_2-ZnO paste was dropped using an eye-pipette on top of ITO conductive glass of 50 mm x 25 mm by doctor blade technique. The TiO_2-ZnO coated ITO was then annealing at 450^{o}C for 30 min. Subsequent to this step the substrate immersed within natural extracted chlorophyll dye for
- 24 hours. The dye-coated substrate were dried to air and used as photo-electrode in the cell. The aluminium counter electrode was prepared on simple glass substrate.The photo-electrode (dye-coated TiO_2-ZnO film) was put over Aluminium counter electrode in such a way that the conductive side of both the electrodes faced each other and sealed with clip. Thereafter the electrolyte solution was injected within the sandwich layered and tightly sealed with sealing tape as shown in the schematic fig.1.

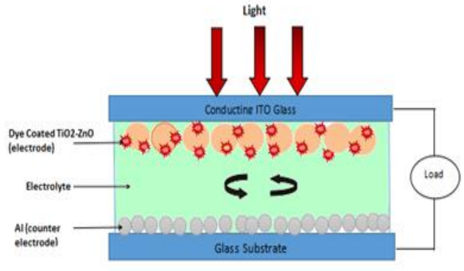

Fig.1: Side View of PV Cell

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Figure 2 shows the XRD patterns of the TiO_2-ZnO composites. The XRD patterns of the samples were recorded using a Rigaku Miniflflex-II in the 2θ range from 10 to 80.In the XRD pattern, both for sample "a" and "b" shows anatase phase for TiO_2, well-known as stables phases, while for ZnO shows corundum phase. The diffraction peaks for sample “a” is at 37.78°, 47.53° and 48.02° are indicating anatase phase while the diffraction peaks at 36.93°,38.52°and 66.37° indicating corundum phase. The sample “b”shows dominating antase phase of TiO_2.The diffraction peaks at their corresponding planes are (100),(101) and (103). The existence of many peaks indicates that TiO_2-ZnO film deposited is polycrystalline in nature.

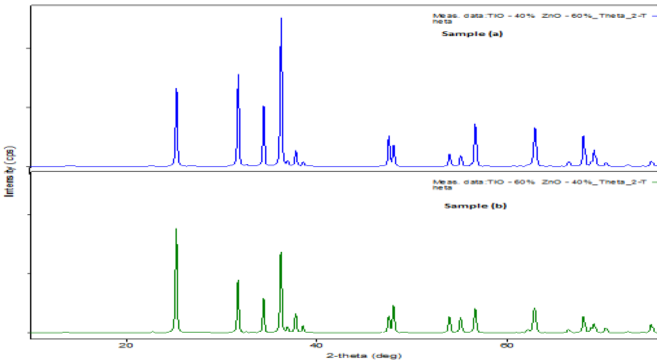

Fig.2: XRD patterns of the TiO_2-ZnO Composites

3.2 UV–Vis Analysis

UV–Vis absorption spectra were expose information on the electronic structure and absorption behaviour of composites materials. Figure 3 presents the UV–Vis spectra of the TiO_2-ZnO composites for sample “a” and “b”. The TiO_2-ZnO composites showed concentrated and broad absorption bands in the UV region. The absorption spectra for sample “a” show broad absorption over the wavelength range from 206 nm to 347 nm. Beyond 350 nm, the absorption decreased smoothly up to 600 nm. However, the absorption at 257 nm was found to be maximum. Furthermore for sample “b” show broad absorption over the wavelength range from 229 nm to 982 nm, beyond that absorption spectra increasing gradually as increasing in the Ti content in the composite. Thus, the absorption edge at around 330 nm may be countered due to absorption by Ti clusters incorporated with ZnO composite. Overall present of broad picks within the absorption spectra in the UV region confirm that the material hold PV action and can be utilized as a PV material.

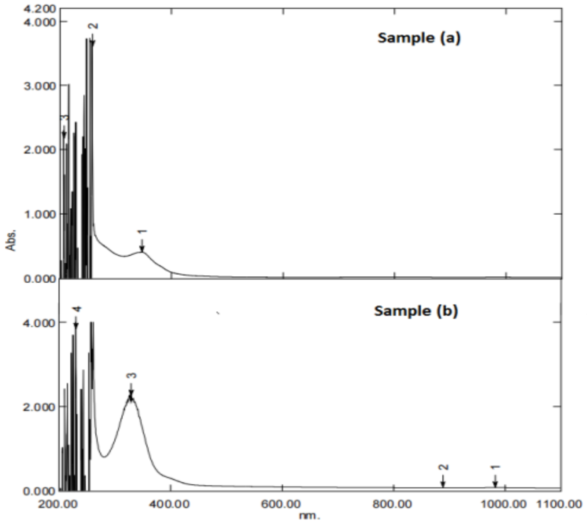

Fig.3: UV–visible spectra of the TiO_2-ZnO composites

3.3 PV Performance

The performance of fabricated cell is determined on the basis of photovoltaic parameters, i.e.,
fill factor (FF) and power conversion efficiency as follows:

$$FF = V_{max} \times I_{max} / I_{sc} \times V_{oc} \quad (1)$$

$$\eta = (I_{sc} \times V_{oc}) \times FF/P_{in} \quad (2)$$

Where, Pin is the input power

The digital nanoammeter and microvoltmeter was used to measure the current and voltage, as shown in Fig. 4. The I–V characteristic DSSC’s is determined by measuring the photocurrent–photo voltage under irradiation and obtained I–V curve is used to present typical diode behaviour of the fabricated DSSC’s.The short-circuit current (Isc) and open-circuit voltage (Voc) is obtained by keeping voltage, current zero and vice-versa. In both cases there is no power produce from the cell as VI = 0.The I–V characteristic curves of the fabricated DSS cells are shown in Fig.4.Also it is noted that the product VI is maximum resembles maximum power (Pmax) from cell. The values of Imax and Vmax is calculated on the basis of I–V curve.

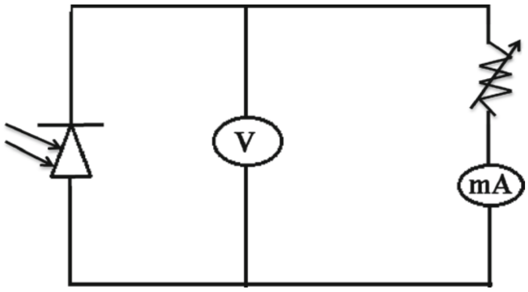

Fig.4 Circuit for DSSC’s for I-V Characteristics

The current conversion efficiency is a function of the incident light absorption wavelength. The fabricated DSSC’s absorbed incident light was within region from

350 nm to 200 nm within the photoactive layer, which is responsible for the creation of excited charge carriers and bound electron–hole pairs. The PV parameters such as Voc, Isc, and FF corresponding to the fabricated DSSC's are listed in Table I. In the present work, the power conversion efficiency (ɳ) was found to lie in the range between 0.18 % and 0.21%, while the fill factor was between 0.56 and 0.50.

Sample	Ratio in wt%	V_{oc} (V)	I_{sc} (mA)	FF	Efficiency, ɳ (%)
a	40:60	0.72	0.46	0.56	0.18
b	60:40	0.84	0.51	0.50	0.21

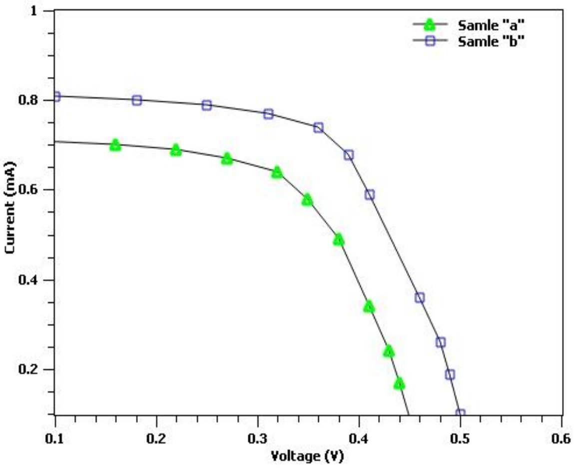

Fig. 5 I–V characteristics for PV cells with (a) 40 wt.%:60wt.%, (b) 60 wt.%:40 wt.%

4. CONCLUSIONS

DSSC's were constructed from natural dyes as Chlorophyll extracted from the Spinach. The ITO thin films used as conductive substrates for DSSC's and TiO_2-ZnO films were deposited on ITO conductive layers by the doctor-blade technique along with aluminium counter electrode as ITO/TiO_2-ZnO/Al architecture. The performance of PV cells was studied successfully. The semi-crystalline nature of composite exposed using XRD analysis. The composite materials possessed high absorption within UV region than visible region. The sample "b" shows optimum power conversion efficiency of 0.21% comparatively sample "a" this may be due to increases in the content of Ti.

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