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***Abstract*- Chlorophyll dye has been extracted from fresh leaves of Spinach (Spinacia *oleracea*). The extracted dye is grafted on the photo-anode prepared using zinc oxide polydisperse particles. These particles are synthesized through wet chemical precipitation route and characterized in terms of their phase formation behavior and micro-structural properties. The light absorption characteristics of the extracted dye and the dye soaked anode are carried out using UV-vis spectroscopy. Sandwiched type solar cell is prepared and the photo-voltaic parameters are estimated under simulated solar light.**

Keywords-Dye, Solar cell, Spinach, Zinc oxide

I. INTRODUCTION

Worldwide growing demand for fossil fuels has exerted pressure on the finite source of energy. The burning of fossil fuels also produces greenhouse gases that contribute to global warming [1-2]. As alternatives to fossil fuels, renewable energy resources produce abundant clean energy. In this context, recently, dye sensitized solar cells (DSSC) have attracted considerable academic and commercial attention as simple and cost effective renewable energy source. A typical DSSC is usually composed of a photo-anode, electrolyte and counter electrode [3]. A dye (sensitizer) grafted on meso-porous semiconducting oxide (e. g. TiO_2, ZnO) grown over transparent conducting glass acts as working electrode (photo-anode) and a platinized conductive glass or platinum foil is used as counter electrode. The photo-anode, sensitizer, electrolyte and cathode are sequentially arranged and then laminated to make sandwiched DSSC. Under the exposure of sunlight, the dye molecules become photo-excited and inject electron into the conduction band of the semiconductor electrode. The original configuration of the dye is then subsequently restored by electron donation from the electrolyte. The regeneration of the dye by the electrolyte intercepts the recapture of the conduction band electron and these electrons flow to the conducting surface of anode. The electrolyte is regenerated at the counter electrode when the circuit is completed through an external load [4-5]. The characteristics of all the constituents (semiconductor, dye, electrode, electrolyte etc) of a DSSC influence the solar to electrical power conversion efficiency of the cell. In particular, dye and photo-anode play important role for the harvesting of solar energy as well as injection, collection and transportation of photo excited electrons. Various metal complexes and organic dyes have been synthesized and used as sensitizers. Ruthenium (Ru) complexes are considered good sensitizers for DSSCs because of their intense charge-transfer absorption over the entire visible range and highly efficient metal-to-ligand charge transfer [6]. However, high cost and the complicated synthesis of ruthenium complexes often restrict their adaptability for DSSC application. Viewing in the same line, various natural and organic dyes have been studied as alternative photo-sensitizer for DSSC applications. The main features of natural dyes are their availability, ecological friendly and low in cost [7]. Among various natural dyes, chlorophyll is known as very common but important photo sensitizer for photosynthesis in green plants.

In the present work, chlorophyll dye has been extracted from fresh leaves of Spinacia *oleracea*. The extracted dye is grafted on the photo-anode prepared using zinc oxide polydisperse particles. These particles are synthesized through wet chemical precipitation route and characterized in terms of their phase formation behavior and micro-structural properties. The photo-absorption characteristics of the extracted dye and the dye soaked anode are carried out using UV-vis spectroscopy. Sandwiched type solar cell is prepared and the photo-voltaic parameters are estimated under simulated solar light.

The photon to electric conversion efficiency of the natural dye sensitized solar cell is found poor [8-10]. Since the natural dyes are low in cost and simple to extract, research work is indispensable to find their effective utility in sensitized solar cells. As revealed from the literature, various research groups are working with natural dye sensitizers for DSSC applications [11-14]. In most of the literatures, the dyes are mostly grafted on the popular TiO_2 based photo-anodes [11-13]. The chlorophyll sensitized ZnO photo anode based solar cells are hardly found in the literature. Therefore, the present study could be important to the researchers working on the sensitized solar cell related research issue.

II. EXPERIMENTAL

A. Extraction and characterisation techniques of dye

The procedure for the extraction of chlorophyll from Spinacia *oleracea* has been described in Fig. 1. Briefly, the fresh spinach leaves are washed well with distilled water, chopped into small pieces and dried at 60°C for an hour. The leaves are crushed using grinder machine. The crushed mass is kept in rotary evaporator at 50°C for 2h and thereafter ethanol is added into it. The ethanolic mass is then filtered and the filtrate is preserved at -4°C for further use. Fourier transformed infrared (FTIR) (IRPrestige-21, Shimadzu, Japan) spectroscopy is used to identify the characteristics peak of the extracted dye and the UV-vis (UV-3600, Shimadzu, Japan) spectroscopy is employed to know its light absorption characteristics.

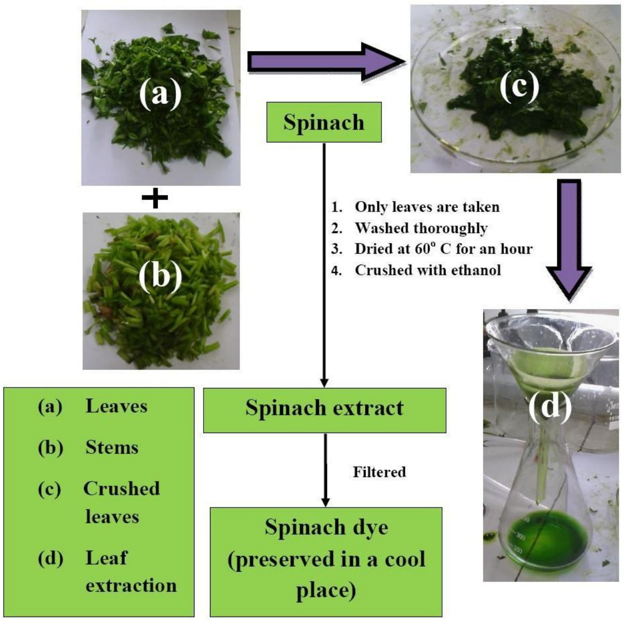

Figure 1. Flow diagram of the extraction of chlorophyll dye from

B. Preparation and characterisation techniques of zinc oxide

Zinc oxide particles are synthesized from zinc (II) nitrate through wet chemical precipitation method. Zinc nitrate is first dissolved in deionized water and ammonium hydroxide is added drop wise into it to form white precipitate. The precipitate is filtered and washed repeatedly with deionized water to make its pH neutral. The residue is then dried in oven at 80°C for 24h to prepare the dried particles. For further crystallization, the dried particles are calcined at 600°C for 2h in air. Thermal gravimetric analysis (TGA) (Jupiter STA 449 F1, Netzsch, Germany) are carried to know respective mass loss when the temperature of the dried particles are elevated from room temperature to 600°C with an increment of 10 °C/min. FTIR spectroscopy is used to identify the characteristics peak of dried and calcined particles of zinc oxide. The phase formation behavior of calcined particles is studied by analyzing the X-ray diffraction (PW 3040/60, Panalytical, Netherlands) recorded using CuK_α radiation.

C. Preparation and characterisation techniques of zinc oxide photo-anode before and after dye loading

In order to prepare the photoanode on tin doped indium oxide (ITO) substrate the calcined zinc oxide particles are grinded thoroughly and mixed with a binder (resulted by mixing ethyl cellulose and terpineol in 1:10 weight ratio) ultimately to prepare a paste. The paste is then coated on the ITO glass substrate using doctor blade technique. Prior to the coating, the ITO substrate is cleaned with water, ethanol and acetone in an ultrasonic bath. The ZnO film is then heat treated in four steps up to 300°C with an increment of 75°C and dwell time for ~ 30 min in each step. After final heating, the film is cooled down to room temperature for further use. Optical image analyzer has been used to measure the thickness of the film. The surface morphology and composition of the film has been investigated using a scanning electron microscope. The film is then soaked in the dilute ethanolic solution of extracted chlorophyll dye. Diffuse reflectance spectroscopy (DRS) has been carried out to know the visible light reflectance behavior of the photoanode before and after dye loading.

D. Fabrication of cell and measurement of photo-conversion efficiency

The developed dye loaded photo-anode is used to fabricate sandwiched type DSSC. Pt coated ITO substrates, spinach dye and I^-/I^{3-} electrolyte (Dyesol, Australia) are used as cathode, sensitizer and electrolyte respectively. To prepare the counter electrode, a thin layer of Pt paste (Dyesol, Australia) is coated on the conducting surface of the ITO substrate and heated at 350°C for 30 min. To make the electrical contact convenient, the Ag paste based electrode is extended from conducting to

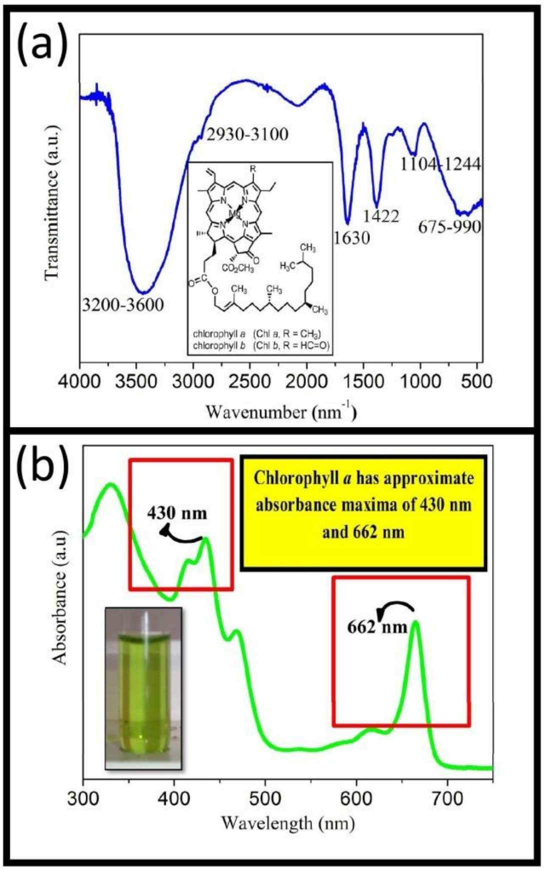

Figure 2: (a) FTIR spectra of ethanolic extract of Spinacia *oleracea* leaf (inset shows the chlorophyll structure), (b) visible light absorption spectra of the spinach extract.

non-conducting side of the transparent substrate. The anode and cathode are sandwiched to prepare the solar cell. Pressure probes have been used to take out the electrical contacts from the fabricated solar cell. The photo-current (I) and voltage (V) characteristics are carried out using an automated set-up (PTS-2-QE, Sciencetech, Canada) well equipped with solar simulator (incident light intensity = 100 mW from air mass 1.5 G), and source meter (2400, Keithley, USA). A standard Si solar cell is used as reference to verify the total system. The solar to electric power conversion efficiency (η) of solar cells is estimated using following formula

$$\eta = J_{SC} \times V_{OC} \times FF / P_{in} \qquad (1)$$

where, J_{SC}, V_{OC}, FF and P_{in} are the, short-circuit current density, open-circuit voltage, fill factor and incident power respectively [14].

III. RESULTS AND DISCUSSIONS

A. *Characterisation of chlorophyll dye*

Fig. 2 (a) shows the FTIR of the extracted chlorophyll dye. The chemical formula of the chlorophyll is shown in the inset of Fig. 2 (a). The characteristic peaks of chlorophyll are present in the FTIR spectrum. The broad peak at a wave number range of 3200-3600 cm^{-1} corresponds to the OH stretching vibration due to the presence of ethanol. The remaining peaks at ν ~ 2930-3100 cm^{-1}; ν ~ 1630 cm^{-1}, ν ~ 1422 cm^{-1} and ν ~ 1104-1244 cm^{-1} may arise due to $-CH_2$ stretching of aliphatic groups, -NH stretching of secondary amines, C=O groups from pyrrole ring having conjugation, bending vibrations of the C–OH alcoholic group and C–O single bond vibrations respectively [15-16]. The broad medium peak in the range 675-990 illustrates the ~C-H bending frequency. The UV-vis absorption spectrum of the dye has been shown in Fig. 2 (b). The digital image of the green colored chlorophyll dye is shown in the inset of Fig. 2 (b). The spectrum indicates the distinct absorption maxima at 430 and 662 nm which match well with the light absorption characteristics of chlorophyll reported elsewhere [17-19].

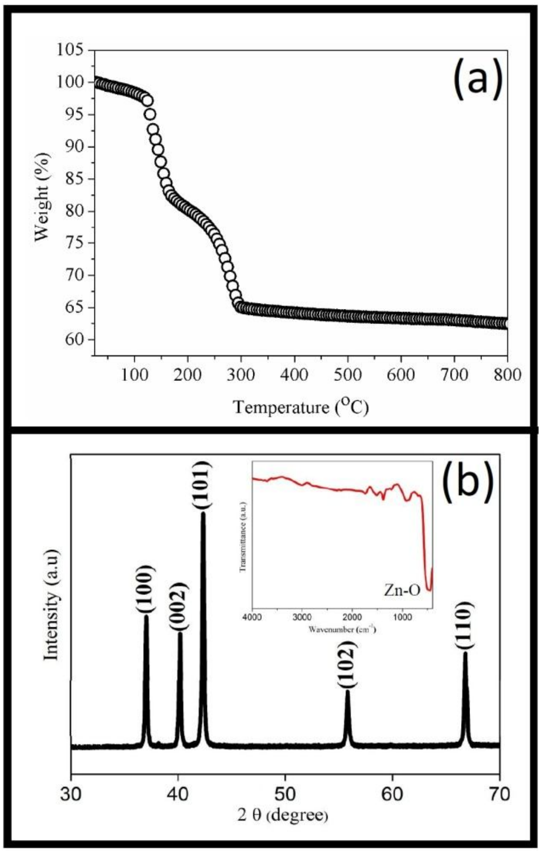

Figure 3: (a) TGA plot of crude ZnO, (b) X-ray diffraction pattern of the ZnO particles calcined at 450°C (inset shows the FTIR spectra of ZnO calcined at 450°C)

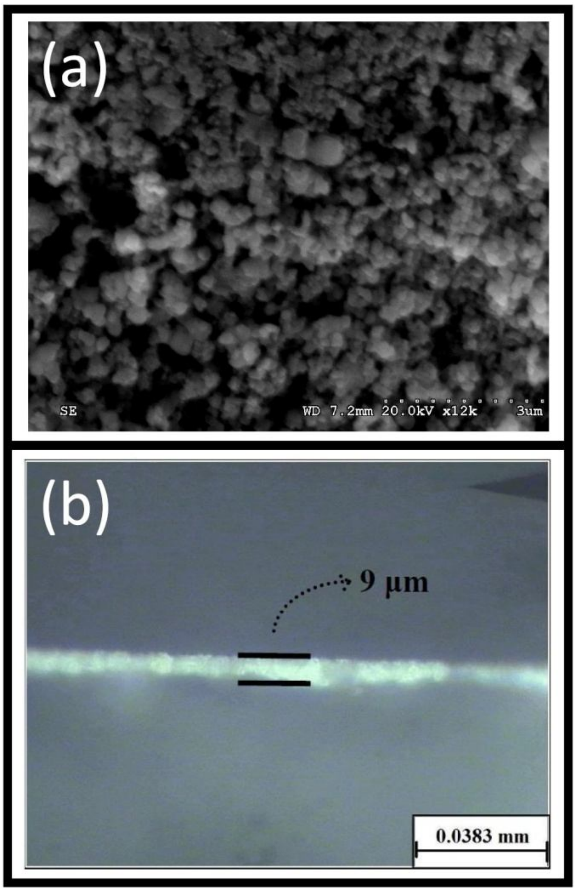

Figure 4: (a) SEM image of the zinc oxide film, (b) Optical image for cross-section of zinc oxide film

B. *Characterisation of zinc oxide particles*

The TGA plot of the dried zinc oxide particles have been shown in Figure 3 (a). As envisaged from the figure no significant mass loss is observed beyond 150°C. Figure 3 (b) shows the X-ray diffraction (XRD) pattern of the ZnO particles calcined at 600°C. The XRD pattern is in good agreement with standard JCPDS data (card no.36-1451) of zinc oxide. For the calcined particles, the distinct metal-oxygen (Zn-O) bond is also found in the FTIR spectra shown in the inset of Fig. 3 (b) [20].

C. Characterisation of zinc oxide photo-anode before and after dye loading

The SEM image of the ZnO photo-anode is shown in Figure 4 (a). As revealed from the figure, the surface of anode is film is composed of nano and submicrometer size zinc oxide particles. Owing to such morphology, the photo-anode can absorb the dye and scatter the incident light efficiently. From the optical microscope image (shown in the Figure 4 (b)), the thickness of the film is estimated to be ~09 µm. To verify the dye uptake as well as the light scattering behaviour, the photo-anode (before and after dye loading) is further characterised using UV-vis reflectance spectra shown in Figure 5. In the visible region, high diffused reflectance (~80%) is achieved for ZnO anode before dye loading. The dye loading however decreases the diffused reflectance value of the film due to the absorbance of light by the dye.

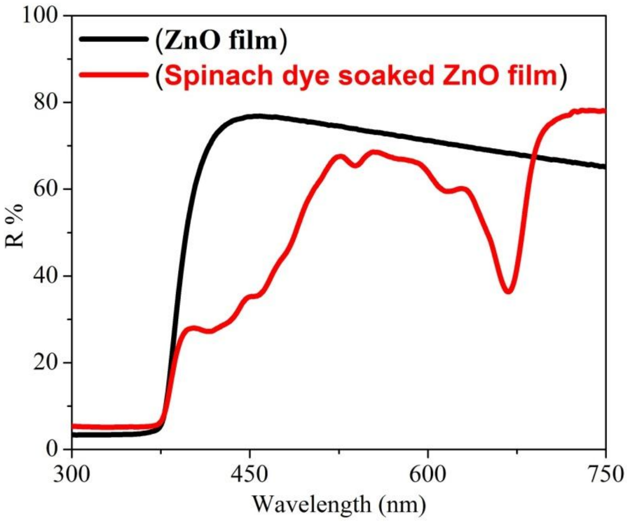

Figure 5: UV-vis reflectance spectra of ZnO film before and after dye loading

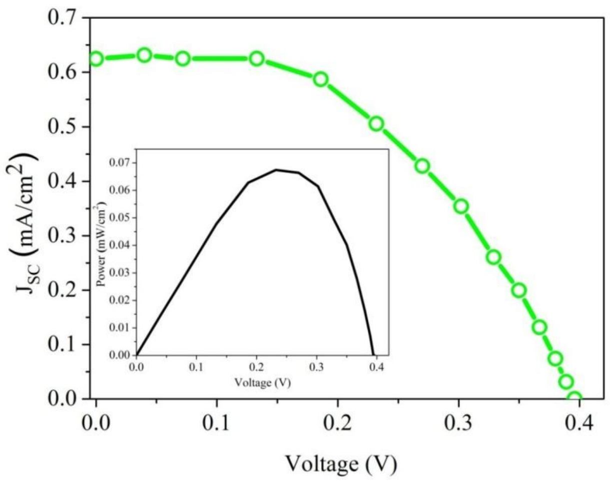

Figure 6: I-V characteristics of the fabricated dye sensitized solar cell (Inset shows the power-voltage relationship)

D. Photovoltaic performances of the developed dye sensitized solar cell

Figure 6 shows the current density and voltage plot of the developed DSSC. The maximum power obtained by varying the open circuit voltage is shown in inset of Figure 6. The estimated photovoltaic parameters (J_{SC}, V_{OC}, FF, η) are summarised in the TABLE I.. The power conversion efficiency of the developed solar cell is found ~ 0.142 %.

TABLE I. PHOTOVOLTAIC PERFORMANCE OF THE DEVELOPED SOLAR CELL SENSITIZED WITH CHLOROPHYLL DYE

Cell area(cm^2)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	*η %*
0.16	0.395	0.624	0.575	0.142

IV. CONCLUSION

In the present work, zinc oxide particles synthesized through wet chemical precipitation route is used to prepare photo-anode for dye sensitized solar cell. Chlorophyll dye extracted from Spinach (Spinacia *oleracea*) is used as sensitizer. The synthesized zinc oxide particles are characterised in terms of its phase formation behaviour and micro-structural features. The light absorption characteristics of the extracted dye are investigated using UV-vis spectroscopy. The developed cell shows ~0.142% solar to electric conversion efficiency under the simulated solar light (power of incident light 100 mW cm^{-2} from Air Mass 1.5G). The estimated values of short circuit current density, open circuit voltage and fill factor are found 0.395 mA/cm^2, 0.624V and 0.575 respectively.

ACKNOWLEDGMENT

The authors would like to express their gratitude to Director, CSIR-CMERI for his kind permission to publish the paper. The support and help rendered by the scientific and technical staffs of Centre for Advanced Materials Processing (CAMP), CSIR-CMERI, are sincerely acknowledged. Mr. D. Sengupta is grateful to Council of Scientific and Industrial Research (CSIR), Govt. of India for providing his research fellowship. Dr. K. Mukherjee wishes to acknowledge Department of Science and Technology, Govt. of India for providing him Inspire Faculty fellowship (Ref. DST/ IFA12-CH-43). Ms. P. Das thanks Department of Science and Technology, Govt. of India for supporting her research fellowship from the research grant of DST-Inspire Faculty award.

REFERENCES

1. H. S. Jung and J. K. Lee "Dye sensitized solar cells for economically viable photovoltaic systems," J. Phys. Chem. Lett., 4 (10), pp 1682-1693, 2013
2. N. S. Lewis, "Toward cost-effective solar energy use," Science, 315, pp 798-801, 2007
3. M. Gratzel. "Dye-sensitized solar cell," J Photoch Photobio C, 4, pp 145-153, 2003
4. B. O'Regan and M. Gratzel, "A low-cost, high efficiency solar-cell based on dye sensitized colloidal TiO_2 films," Nature 353, pp 737-740, 1991

5. A. Zaban, A. Meier and B. Gregg, "Electric potential distribution and short-range screening in nanoporous TiO_2 electrodes," J. Phys. Chem. B, 101 (40), pp 7985-7990, 1997
6. S. Hao, J. Wu, Y. Huang and J. Lin, "Natural dyes as photosensitizers for dye-sensitized solar cell," Sol. Energy 80, pp 209-214, 2006
7. H. Kim et al., "Curcumin dye extracted from Curcuma longa L. used as sensitizers for efficient dye sensitized solar cells," Int. J. Electrochem. Sci., 8, pp 8320-8328, 2013
8. G.P. Smestad and M Grätzel, "Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nanocrystalline energy converter," J. Chem. Educ.; 75(6), pp 752-756, 1988
9. A. C. Nwanya, P.E. Ugwuoke, P. M. Ejikeme, O.U Oparaku and F.I. Ezema, "Jathropha Curcas and Citrus Aurantium leaves dye extract for use in dye sensitized solar cell with TiO_2 films," Int. J. Electrochem. Sci., 7, pp 11219 -11235, 2012
10. H. Chang, H.M. Wu, T.L. Chen, K.D. Huang, C.S. Jwo and Y.J. Loa, "Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea," J Alloys Compd 495, pp 606–610, 2010
11. H. Zhou, L. Wu, Y. Gao and T. Ma "Dye-sensitized solar cells using 20 natural dyes as sensitizers," J Photoch Photobio A, 219(2-3), pp 188-194, 2011
12. S. A. Taya, T. M. El-Agez, H. S. El-Ghamri and M. S. Abdel-Latif, "Dye-sensitized solar cells using fresh and dried natural dyes"; International Journal of Materials Science and Applications," 2(2), pp 37-42, 2012
13. M. R. Narayan, "Review: Dye sensitized solar cells based on natural photosensitizers"; Renew Sust Energ Rev, 16, pp 208-215, 2012
14. H. Kim et al., " Natural dye extracted from Rhododendron species flowers as a photosensitizer in dye sensitized solar cell"; Int. J. Electrochem. Sci., 8, pp 6734 – 6743, 2013
15. R.K Das et al., "The synthesis of gold nanoparticles using Amaranthus spinosus leaf extract and study of their optical properties"; Advances in Materials Physics and Chemistry, 2, pp 275-281, 2012
16. S. Mukherjee et al., "Green chemistry approach for the synthesis and stabilization of biocompatible gold nanoparticles and their potential applications in cancer therapy"; Nanotechnology 23, pp 455103, 2012
17. Q. Wu et al., "Natural dye -sensitized mesoporous ZnO solar cell"; Seventh International Conference on Thin Film Physics and Applications SPIE Vol. 7995, pp 799532, 2011.
18. A. L. P. Nery, R. M. Liegel and C. Fernandez, "Fluorescence and chemiluminescence: teaching basic principles by simple demonstration experiments." J. Chem. Educ., Vol. 13, No. 2, 2010
19. G. Wu et al., "Dye-sensitized solar cell using natural dyes extracted from spinach and amaranth"; http://dx.doi.org/10.1364/ACP.2009.WL43
20. A. Heidari, H. Younes and A.A.L. Zinatizadeh, "Controllable synthesis of flower-like ZnO nanostructures with hydrothermal method", IJE Transactions B: Applications, Vol. 22, No. 3, pp 283-289, October 2009

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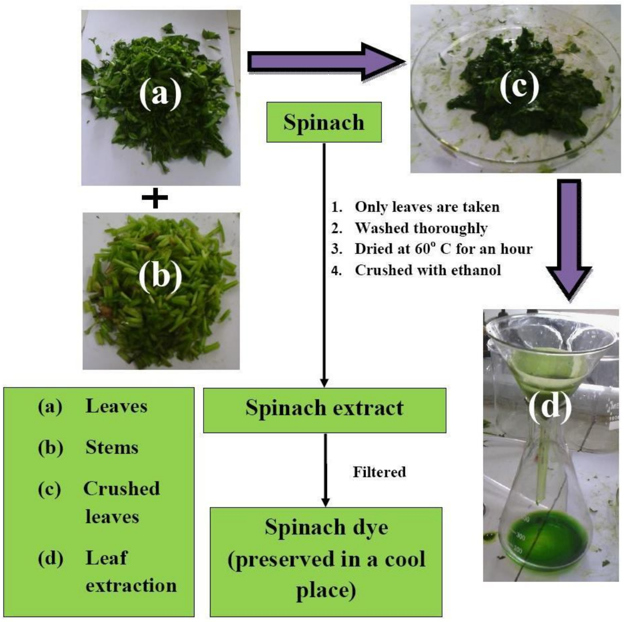

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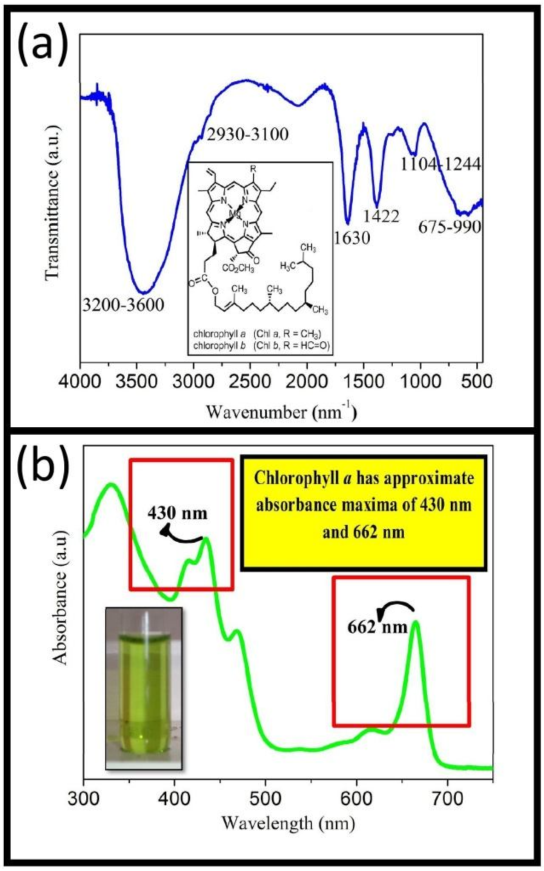

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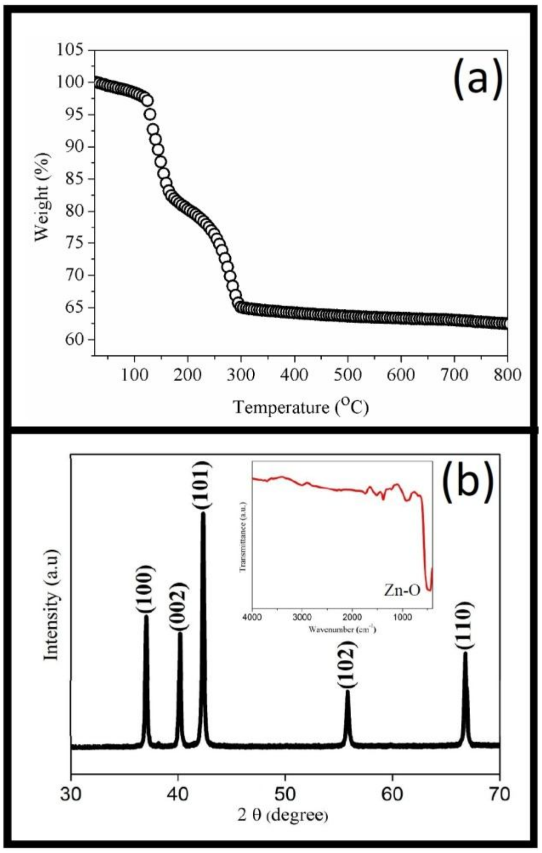

Figure 3: (a) TGA plot of crude ZnO, (b) X-ray diffraction pattern of the ZnO particles calcined at 450°C (inset shows the FTIR spectra of ZnO calcined at 450°C)

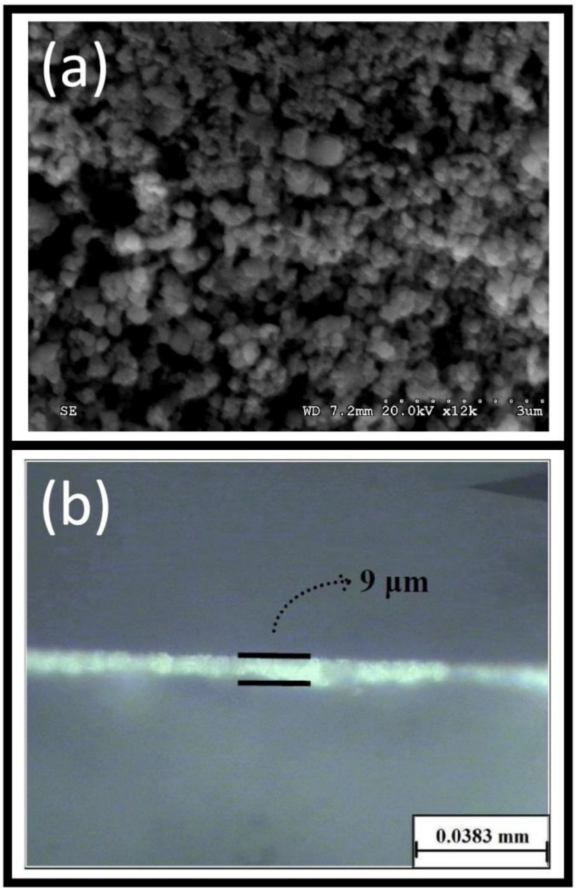

Figure 4: (a) SEM image of the zinc oxide film, (b) Optical image for cross-section of zinc oxide film

B. Characterisation of zinc oxide particles

The TGA plot of the dried zinc oxide particles have been shown in Figure 3 (a). As envisaged from the figure no significant mass loss is observed beyond 150°C. Figure 3 (b) shows the X-ray diffraction (XRD) pattern of the ZnO particles calcined at 600°C. The XRD pattern is in good agreement with standard JCPDS data (card no.36-1451) of zinc oxide. For the calcined particles, the distinct metal-oxygen (Zn-O) bond is also found in the FTIR spectra shown in the inset of Fig. 3 (b) [20].

C. Characterisation of zinc oxide photo-anode before and after dye loading

The SEM image of the ZnO photo-anode is shown in Figure 4 (a). As revealed from the figure, the surface of anode is film is composed of nano and submicrometer size zinc oxide particles. Owing to such morphology, the photo-anode can absorb the dye and scatter the incident light efficiently. From the optical microscope image (shown in the Figure 4 (b)), the thickness of the film is estimated to be ~09 µm. To verify the dye uptake as well as the light scattering behaviour, the photo-

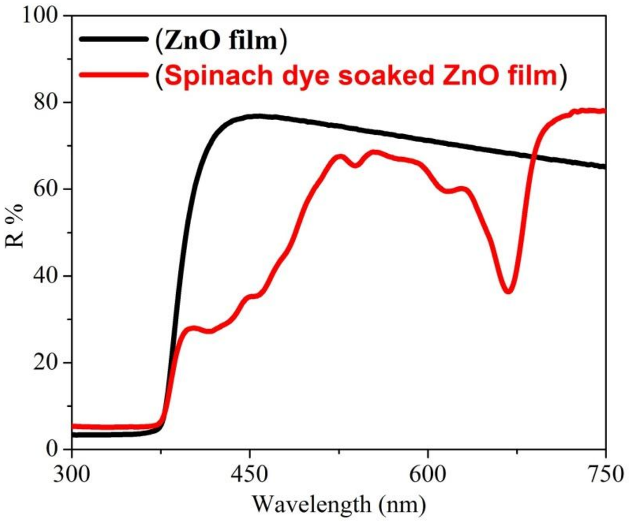

Figure 5: UV-vis reflectance spectra of ZnO film before and after dye loading

anode (before and after dye loading) is further characterised using UV-vis reflectance spectra shown in Figure 5. In the visible region, high diffused reflectance (~80%) is achieved for ZnO anode before dye loading. The dye loading however decreases the diffused reflectance value of the film due to the absorbance of light by the dye.

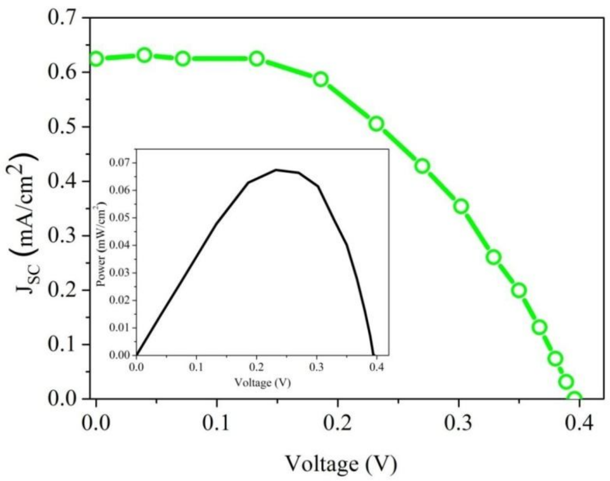

Figure 6: I-V characteristics of the fabricated dye sensitized solar cell (Inset shows the power-voltage relationship)

D. Photovoltaic performances of the developed dye sensitized solar cell

Figure 6 shows the current density and voltage plot of the developed DSSC. The maximum power obtained by varying the open circuit voltage is shown in inset of Figure 6. The estimated photovoltaic parameters (J_{SC}, V_{OC}, FF, η) are summarised in the TABLE I.. The power conversion efficiency of the developed solar cell is found ~ 0.142 %.

TABLE I. PHOTOVOLTAIC PERFORMANCE OF THE DEVELOPED SOLAR CELL SENSITIZED WITH CHLOROPHYLL DYE

Cell area(cm^2)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	*η %*
0.16	0.395	0.624	0.575	0.142

IV. CONCLUSION

In the present work, zinc oxide particles synthesized through wet chemical precipitation route is used to prepare photo-anode for dye sensitized solar cell. Chlorophyll dye extracted from Spinach (Spinacia *oleracea*) is used as sensitizer. The synthesized zinc oxide particles are characterised in terms of its phase formation behaviour and micro-structural features. The light absorption characteristics of the extracted dye are investigated using UV-vis spectroscopy. The developed cell shows ~0.142% solar to electric conversion efficiency under the simulated solar light (power of incident light 100 mW cm^{-2} from Air Mass 1.5G). The estimated values of short circuit current density, open circuit voltage and fill factor are found 0.395 mA/cm^2, 0.624V and 0.575 respectively.

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REFERENCES

1. H. S. Jung and J. K. Lee "Dye sensitized solar cells for economically viable photovoltaic systems," J. Phys. Chem. Lett., 4 (10), pp 1682-1693, 2013
2. N. S. Lewis, "Toward cost-effective solar energy use," Science, 315, pp 798-801, 2007
3. M. Gratzel. "Dye-sensitized solar cell," J Photoch Photobio C, 4, pp 145-153, 2003
4. B. O'Regan and M. Gratzel, "A low-cost, high efficiency solar-cell based on dye sensitized colloidal TiO_2 films," Nature 353, pp 737-740, 1991

5. A. Zaban, A. Meier and B. Gregg, "Electric potential distribution and short-range screening in nanoporous TiO_2 electrodes," J. Phys. Chem. B, 101 (40), pp 7985-7990, 1997
6. S. Hao, J. Wu, Y. Huang and J. Lin, "Natural dyes as photosensitizers for dye-sensitized solar cell," Sol. Energy 80, pp 209-214, 2006
7. H. Kim et al., "Curcumin dye extracted from Curcuma longa L. used as sensitizers for efficient dye sensitized solar cells," Int. J. Electrochem. Sci., 8, pp 8320-8328, 2013
8. G.P. Smestad and M Grätzel, "Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nanocrystalline energy converter," J. Chem. Educ.; 75(6), pp 752-756, 1988
9. A. C. Nwanya, P.E. Ugwuoke, P. M. Ejikeme, O.U Oparaku and F.I. Ezema, "Jathropha Curcas and Citrus Aurantium leaves dye extract for use in dye sensitized solar cell with TiO_2 films," Int. J. Electrochem. Sci., 7, pp 11219 -11235, 2012
10. H. Chang, H.M. Wu, T.L. Chen, K.D. Huang, C.S. Jwo and Y.J. Loa, "Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea," J Alloys Compd 495, pp 606–610, 2010
11. H. Zhou, L. Wu, Y. Gao and T. Ma "Dye-sensitized solar cells using 20 natural dyes as sensitizers," J Photoch Photobio A, 219(2-3), pp 188-194, 2011
12. S. A. Taya, T. M. El-Agez, H. S. El-Ghamri and M. S. Abdel-Latif, "Dye-sensitized solar cells using fresh and dried natural dyes"; International Journal of Materials Science and Applications," 2(2), pp 37-42, 2012
13. M. R. Narayan, "Review: Dye sensitized solar cells based on natural photosensitizers"; Renew Sust Energ Rev, 16, pp 208-215, 2012
14. H. Kim et al., " Natural dye extracted from Rhododendron species flowers as a photosensitizer in dye sensitized solar cell"; Int. J. Electrochem. Sci., 8, pp 6734 – 6743, 2013
15. R.K Das et al., "The synthesis of gold nanoparticles using Amaranthus spinosus leaf extract and study of their optical properties"; Advances in Materials Physics and Chemistry, 2, pp 275-281, 2012
16. S. Mukherjee et al., "Green chemistry approach for the synthesis and stabilization of biocompatible gold nanoparticles and their potential applications in cancer therapy"; Nanotechnology 23, pp 455103, 2012
17. Q. Wu et al., "Natural dye -sensitized mesoporous ZnO solar cell"; Seventh International Conference on Thin Film Physics and Applications SPIE Vol. 7995, pp 799532, 2011.
18. A. L. P. Nery, R. M. Liegel and C. Fernandez, "Fluorescence and chemiluminescence: teaching basic principles by simple demonstration experiments." J. Chem. Educ., Vol. 13, No. 2, 2010
19. G. Wu et al., "Dye-sensitized solar cell using natural dyes extracted from spinach and amaranth"; http://dx.doi.org/10.1364/ACP.2009.WL43
20. A. Heidari, H. Younes and A.A.L. Zinatizadeh, "Controllable synthesis of flower-like ZnO nanostructures with hydrothermal method", IJE Transactions B: Applications, Vol. 22, No. 3, pp 283-289, October 2009