UGC MAJOR RESEARCH PROJECT

FINAL REPORT

FABRICATION OF DYE SENSITIZED SOLAR CELLS WITH NANOCRYSTALLINE ZnO THIN FILMS

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UNIVERSITY GRANTS COMMISSION

BAHADUR SHAH ZAFAR MARG

NEW DELHI – 110 002

PERFORMA FOR FINAL REPORT OF THE WORK DONE ON THE PROJECT

1. TITLE OF THE PROJECT : FABRICATION OF DYE SENSITIZED SOLAR CELLS WITH NANOCRYSTALLINE ZnO THIN FILMS

2. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR:

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4. UGC APPROVAL LETTER NO. AND DATE:

F.No. 42-860/2013 (SR) Dated: 22.03.2013

UGC EXTENSION LETTER NO. AND DATE:

F.No. 42-860/2013 (SR) Dated: 26.03.2016

5. DATE OF IMPLEMENTATION : 01.04.2013

6. TENURE OF THE PROJECT : 01.04.2013 to 31.03.2017

7. TOTAL GRANT ALLOTTED : Rs. 11,26,163.00/-

8. TOTAL GRANT RECEIVED

1st Installment : Rs.8,77,300.00/-

2nd Installment : Rs.1,92,327.00/-

9. FINAL EXPENDITURE : Rs. 10,67,346.00/-

10. TITLE OF THE PROJECT : FABRICATION OF DYE SENSITIZED SOLAR CELLS WITH NANOCRYSTALLINE ZnO THIN FILMS

11. OBJECTIVES OF THE PROJECTS

a) The objective is to use porous nanocrystalline ZnO films in DSSC to replace costly TiO_2 electrodes. ZnO presents comparable band gap values as well as conduction band position and higher electronic mobility than TiO_2. The exciton binding energy of ZnO (60 meV) is higher than TiO_2 (40 meV) and higher electron mobility (200 cm^2 v^{-1} s^{-1}) over TiO_2 (30 cm^2 v^{-1} s^{-1}). Therefore it is aimed to improve the efficiency of ZnO solar cells.

b) Identification and effective utilization of natural dyes to increase the efficiency of the solar cells.

c) Fabrication of DSSC with suitable dyes.

d) Effort to improve efficiency of the fabricated DSSC with metal (Sn, Al, Ti, In) doped ZnO as photoanode. Also using photoanodes with different morphology (nanoparticles, nanorods, nanowires, nanoflowers etc.) to improve the efficiency.

12. WHETHER OBJECTIVES WERE ACHIEVED (GIVE DETAILS)

YES. DSSC were fabricated using spray deposited ZnO thin films on ITO as photoanode and natural dyes (extract from Flowers and leaves) as sensitizer. Efficiency has been improved using doped (Sn^{4+}, Ga^{3+}, Al^{3+}, In^{3+}) ZnO films as photoanode in DSSC.

13. ACHIEVMENTS FROM THE PROJECT

As per the objective, DSSC were fabricated with ZnO film as photoanode and natural dyes as sensitizer and cell efficiency were measured. The cell efficiency were found to be higher than the previously reported values. Also as per objective DSSC with different doped ZnO films on ITO as photoanode were tested. Among the cells, the one with Ga doped ZnO as photoanode found to have higher efficiency. Similarly the cell with pomegranate dye gave an efficiency of 1.21%.

- ZnO nanorods were prepared by combining two methods (spray pyrolysis and hydrothermal method) on ITO glass plate and is used as photoanode in DSSC. The cell efficiency of 1.75% was achieved with ZnO nanorods as photoanode and pomegranate dye as sensitizer.
- As per the objective, the work was carried out and the obtained results were published in reputed journals with good impact factor.
- Project Fellow got best paper award in the national conference for the paper entitled "Dye sensitized solar cell sensitized using natural dyes and ZnO nanorods on ITO glass substrate as photoanode" (certificate enclosed).
- Also, the project fellow submitted the part of the work as thesis and has been awarded Ph.D degree.

14. SUMMARY OF THE FINDINGS

In the present work, Pure and doped Zinc Oxide (ZnO) thin films were deposited on Glass substrate / Indium coated tin oxide glass substrates (ITO) using spray pyrolysis technique. The performance of DSSCs prepared using the deposited film on ITO glass substrate as photoanode and natural dye as sensitizer were studied. The structural, morphological, optical and electrical properties of the films were characterized by different analytical tools such as, XRD, FESEM with EDX, AFM, UV-Visible, PL and Hall Effect measurement. The current – voltage characteristics of DSSC were measured using Keithley 2450 source meter.

Pure ZnO films deposited at 350 ^{o}C exhibited better crystalline structure, hexagonal grains with porous nature, increased surface roughness, higher transmittance value and n-type conductivity, which makes a promising candidate for DSSC. A maximum power conversion efficiency of 0.60% was observed for the prepared DSSC using the extract of *pomegranate* dye. Doping of ZnO nanostructured thin films was significant interest for a variety of practical applications. Various dopants (Sn, Al, Ga & In) were used to tune the optical and electrical properties inorder to enhance the performance of the DSSC. The different natural dye extracts has been used as to improve the DSSC efficiency. Pure and doped films exhibited preferential orientation along c-axis direction. FESEM images showed different surface morphologies such as, flake-like (Sn doped ZnO), Nanosheets, (Al doped ZnO), Spherical (Ga doped ZnO) and Wringle-network Structure (In doped ZnO). EDX analysis confirmed the presence of Sn, Al, Ga, In, Zn and oxygen only. A very high transmittance value of 90% was observed for 1.5 at.% of Ga doped ZnO thin films. Also, the lowest resistivity (0.23×10^{-3} Ω cm) and high conductivity values were noticed for

1.5 at.% of Ga doped ZnO. The UV-Vis observations confirm the incorporation of dye into doped ZnO mesoporous film. The observed diffraction peaks in UV-Vis at different positions are due to the presence of different types of flavonoids and colors. Among the various dyes used as the sensitizer, a broad absorption peak with high light harvesting nature and enhanced efficiency was observed for the pomegranate. The maximum power conversion efficiency was 0.75%, 1.02%, 1.21% and 1.07% for Sn doped ZnO (SZO 1.0 at.%), Al doped ZnO (AZO 1.5 at.%), Ga doped ZnO (GZO 1.5 at.%) and In doped ZnO (IZO 1.0 at.%) respectively.

As a pilot study, ZnO nanorods was prepared by combining two methods (Spray pyrolysis, and hydrothermal method) showed the highest optical transmittance and lowest resistivity along with the power conversion efficiency value of 1.75%. The enhanced cell efficiency can be attributed to the improvement in short circuit current density (Jsc). The improvement of short circuit current density is due to the higher dye loading in the available larger surface area of the ZnO nanorods. As a result of higher dye loading, more electrons are injected from the dye molecule to the conduction band, which results the enhanced cell efficiency. The above results were published in standard International reputed journals with good impact factor.

15. CONTRIBUTION TO THE SOCIETY

Dye-sensitized solar cells (DSSCs), also known as Gratzel cells, are new inventions in thin-film solar cells. The dye used as a sensitizer in DSSC plays a major role in cell performance. Though, the maximum conversion efficiency of 11-12% is achieved with Ru complexes having an intense charge-transfer absorption and efficient metal-to-ligand charge transfer; the major disadvantages of Ru complexes are its cost, toxicity, rarity and systems complexity. Researchers have focused their attention on natural dye as an alternative to artificial dye because of its easy availability, low cost, easy preparation, environmental friendly and biodegradable. Several natural dye sensitizers have been used as sensitizer. DSSCs main advantages can be summarized as follows: Good performance under standard reporting conditions; Stable performance at non standard conditions of temperature, irradiation and solar incidence angle; Low cost; Available environmental-friendly raw materials; Semi-transparency and multi-color range possibilities.

In our present work the prepared photoanode (ZnO nanocrystalline film on ITO) and the dye (natural dyes extracts from plant) used are cheap as well as non toxic and environmental friendly. Most of the materials used in DSSC are of low cost. Of the fabricated DSSC's the one with Ga doped ZnO as photoanode and pomegranate as sensitizer showed enhanced efficiency of 1.21%. The fabricated DSSCs, the one with ZnO nanorod formation as photoanode and pomegranate extract as sensitizer shows appreciable efficiency which could be used large scale production with slight modifications.

In addition to that ZnO nanorods as photoanode (prepared using spray and hydrothermal technique) and natural dye (pomegranate extract) shows on the improved efficiency of 1.75%. Although its conversion efficiency is less than the best thin film cells, in theory its price / performance ratio should be good enough to allow than to compete with fossil fuel electrical generation. Large scale production of DSSC with natural dyes will leads to high power efficiency and meets green energy concepts of government of India.

16. WHETHER ANY Ph.D. ENROLLED/PRODUCED OUT OF THE PROJECT

Yes. Ph.D degree awarded to Mr. P.Dhamodharan, project fellow on 24.07.2017.

17. NO. OF PUBLICATIONS OUT OF THE PROJECT

1. R. Sridhar, **C. Manoharan**, S. Ramalingam, S. Dhanapandian, M. Bououdina, "Spectroscopic study and optical and electrical properties of Ti-doped ZnO thin films by spray pyrolysis" **-** Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol.120 (2014) pp.297–303.
2. P. Dhamodharan, **C. Manoharan,** S. Dhanapandian, P. Venkatachalam, "Dye-Sensitized Solar Cell using sprayed ZnO nanocrystalline thin films on ITO as photoanode" **-** Spectrochimica acta A: Molecular and Biomolecular Spectroscopy, Vol.136 (2015) pp.1671–1678.
3. **C. Manoharan,** G. Pavithra, S. Dhanapandian, P. Dhamodharan and B. Shanthi "Preparation of Spray Pyrolysized ZnO:Sn Thin Films and their Antibacterial Activity" - Spectrochimica acta A: Molecular and Biomolecular Spectroscopy, Vol.141 (2015) pp.292–299.
4. P. Dhamodharan, **C. Manoharan,** S. Dhanapandian, S. Ramalingam, M. Bououdina, "Preparation and characterization of spray deposited Sn doped ZnO thin film on ITO subtracts as photoanode in dye sensitized solar cell" **–** Journal of Materrials Science: Materials in Electronics, Vol.26 (7) (2015) pp.4830-4839.
5. **C. Manoharan,** G. Pavithra, S. Dhanapandian, P. Dhamodharan "Effect of In doping on the properties and antibacterial activity of ZnO films prepared by spray pyrolysis" - Spectrochimica acta A: Molecular and Biomolecular Spectroscopy, Vol.149 (2015) 793-799.

6. **C. Manoharan**, G. Pavithra, S. Dhanapandian, P. Dhamodharan and A. Arunachalam, "Properties of spray pyrolysed ZnO: Al thin films and its antibacterial activity" **-** Applied Nanoscience, Vol. 6 (6) (2016) pp.815-825.
7. P. Dhamodharan, **C. Manoharan,** M. Bououdina, R. Venkadachalapathy, S. Ramalingam, "Al-doped ZnO thin films grown onto ITO substrates as photoanode in dye sensitized solar cell" - Solar Energy, Vol. 141 (2017) pp.127–144.
8. P. Dhamodharan, **C. Manoharan,** M. Bououdina, "Tuning the properties of ZnO thin film on ITO substrates with Ga dopant for dye sensitized solar cell applications" - Journal of Materials Science: Materials in Electronics, (2018) pp.1-12, ***DOI: 10.1007/s10854-018-9366-8.***