# Facile Fabrication of ZnO Nanofibers Based Photoanode for Cost Effective Metal–Free Organic Dye–Sensitized Solar Cells

**P. Rameshkumar, A. Pandikumar**

***Abstract*: A facile substrate grown method was employed to fabricate zinc oxide nanofibers (ZnO Nfs) modified photoanode on fluorine-doped tin oxide (FTO) substrate. The modified ZnO Nfs photoanode was used to fabricate dye sensitized solar cell (DSSC), sensitized with a cheap metal free organic dye, eosin yellow (eosin-Y). The efficiency of solar to electrical energy conversion was achieved as 1.51% with simulated AM 1.5 G solar irradiation of 100 mW cm$^{-2}$. The better efficiency is ascribed to the effective diffusion of electrons within the one dimensional (1D) ZnO Nfs and the efficient interfacial contact between the electrolyte and the ZnO photoanode through pinholes and pores present in the twisted nanofibers. These facilitated the improved interfacial charge transfer. The result demonstrates the promising route of substrate grown ZnO nanofibers for the application of photoanode material in DSSCs.***

***Keywords*: ZnO nanofibers; Eosin Yellow; ZnO nanostructures; Dye-sensitized solar cells; Photoelectrochemical cells**

## I. INTRODUCTION

Zinc oxide (ZnO) is a semiconductor exhibiting large band-gap energy (~3.37 eV) and large exciton binding energy (60 meV) [1]. The excellent optical and electron mobility make ZnO is an ideal candidate for photoanode material in dye sensitized solar cells (DSSCs) [2]. Nanostructured is commonly used to modify the photoanode surface in DSSCs, owing to their tunable morphology, which shows better performance in the conversion of solar energy to electrical energy [3]. ZnO nanostructures have different morphologies like nanoparticles, nanorings, nanotubes, nanoflowers, nanowires, nanobelts, nanocages and nanofibers [4]. Hence, the practical task existing in decreasing the surface area of photoelectrode is to preserve light-harvesting efficiency and consequently to reach higher photocurrents. One such approach is to develop DSSCs because dyes present larger absorption cross-sections [5, 6].

Organic dye sensitizers are much cheaper than the ruthenium-metal complexes and also have several merits, such as, higher absorption coefficient, larger conservation of limited precious metal resources and user friendly for cell reusage [7–10]. Among them, eosin-Y is actively explored as sensitizer in ZnO coupled organic dye in DSSCs due to its low-cost, water solubility and better performance. Remarkably, the efficiency of converting the solar energy with ZnO/eosin-Y system is greater than that of $TiO_2$/eosin-Y system [7–10]. In this study, we explore the facile fabrication of ZnO nanofibers (ZnO Nfs) modified photoanode by seed mediated growth on the substrate and its application DSSC using eosin-Y dye.

**Revised Manuscript Received on July 22, 2019.**

***** Correspondence Author

**P. Rameshkumar**[a], Department of Chemistry, School of Advanced Sciences, Kalasalingam Academy of Research and Education, Krishnankoil – 626 126, India. Email: rameshkumar0212@gmail.com

**A. Pandikumar**[b]*****, Functional Materials Division, CSIR-Central Electrochemical Research Institute, Karaikudi-630003, India*Corresponding Author: pandikumarinbox@gmail.com

## II. MATERIALS AND METHODS

### A. Chemicals

High pure zinc acetate dihydrate ($Zn(OAc)_2.2H_2O$), zinc nitrate hexahydrate ($ZnNO_3.6H_2O$), sodium hydroxide (NaOH) and silver nitrate (Ag NO3) were procured from Merck. Hexamethylenetetramine (HMT) and eosin yellow (eosin–Y) was obtained from Alfa-aesar. Chemicals and reagents with analytical grade were used in this work.

### B. Growth of ZnO nanofibers on FTO

Prior to the growth of ZnO nanofibers (ZnO Nfs) on fluorine-doped tin oxide (FTO), ZnO seeds were prepared by follwing procedure. Breifly, 2.5 mM of NaOH was slowly introduced into methanol containing 1 mM of $Zn(OAc)_2.H_2O$ at 80 °C and allowed to stir for 45 min. A cleaned FTO conducting glass was coated with 100 µL of ZnO seed solution by spin coating at ~3000 rpm. The coating process was repeated thrice to obtain uniform coating with desired thickness. The ZnO Nfs were grown by adopting the following procedure. A 2.5 mM of $ZnNO_3.6H_2O$ and 2.5 mM of HMT were mixed together in aqueous medium, heated to 90 °C and then stirred for 30 min. The ZnO coated substrate was horizontally placed inside the growth solution, which was allowed to grow the nanofibers for 30 min at 90 °C. The substrate was withdrawn from the growth solution and washed using double distilled water many times. It was then vacuum dried at 100 °C for 2 h to remove the water molecules.

### C. Fabrication of DSSCs

The dye was adsorbed on ZnO Nfs modified photoanode by soaking the hot film (80 °C) in ethanolic 0.5 mM eosin-Y and it was reserved at room temperature for overnight. Under $N_2$ atmosphere, the dye-adsorbed photoanode was taken out from the solution. A counter electrode was prepared by depositing Pt on FTO using 7 mM $H_2PtCl_6.6H_2O$ in 2-propanol. The $Pt^{4+}$ ions were thermally reduced to $Pt^0$ at 425 °C. Finally, the electrode was kept in a sealed device using a hot-melted double layer parafilm having the thickness of ~50 µm. The redox electrolyte containing 0.3 M KI and 0.03 M $I_2$ in ethylene glycol (Solaronix) was introduced into the space available between the photoanode and counterelectrode.

### D. Characterization techniques

Diffuse reflectance spectra of ZnO Nfs and eosin-Y adsorbed ZnO Nfs thin films were collected through Shimadzu UV-2550 UV–vis spectrophotometer assembled with ISR-2200 DRS accessory. PL spectra of the samples were obtained with a JASCO-FP-6500 spectrofluorimeter. SEM micrographs and EDX spectrum were collected using FEI Quanta FEG 200 scanning electron microscopic instrument fixed with EDX accessory. Crystalline property of ZnO Nfs was analyzed by obtaining X–ray diffraction (XRD) pattern using Bruker AXS D8 Advance instrument with Cu Kα radiation (λ = 1.54178 A°). Light source was Oriel class-A solar simulator (91195A, Newport) with ozone free 450 W xenon lamp for DSSC application. Current-voltage (J-V) curves were obtained using a Autolab PGSTAT302N electrochemical workstation.

## III. RESULTS AND DISCUSSION

### A. Optical characteristics of photoanode

Fig. 1 displays the UV-vis diffuse reflectance spectra of ZnO Nfs and eosin-Y adsorbed ZnO Nfs thin films. A characteristic absorption feature of ZnO was observed below 390 nm for ZnO Nfs [11]. It is obvious that the eosin-Y adsorbed ZnO Nfs thin film absorbed more than 50% incident light in the region covering from 494 to 530 nm. This suggests that the ZnO Nfs based photoanode can be applied in DSSCs because of its light harvesting efficiency in the visible region. The photoluminescence (PL) spectrum of ZnO Nfs show two major peaks; an near-UV peak around 410 nm, a green emission peak in between 520 and 540 nm (Fig. 2a) [12, 13]. The ionized oxygen vacancies created by the exciton combination of ZnO caused a sharp intense UV emission [14], which illustrates the formation of good quality and high stoichiometry of the ZnO Nfs. The near-UV peak and the broad visible bands are ascribed to the band-edge emission and the deep-level defects in ZnO crystal, such as vacancies and interstitials of zinc and oxygen, respectively. The broad visible emission of ZnO Nfs at 550 nm (2.25 eV) was attributed to the transition between the electron present near the conduction band and the hole at vacancy associated with the surface defects [15]. PL spectrum of eosin–Y sensitized ZnO Nfs is shown in Fig. 2b. The dye-adsorbed ZnO Nfs exhibit an emission peak at 530 nm (2.30 eV) indicating a great fraction of sensitization by eosin-Y. A large surface-to-volume ratio provided by the thinner nanofibers favours the formation high degree surface and subsurface oxygen vacancies.

### B. X-ray diffraction and morphology analysis

Fig. 3 shows the XRD pattern of the ZnO Nfs. In the XRD pattern, nine typical diffraction peaks such as (100), (002), (101), (102), (110), (103), (200), (112) and (201) at the 2θ value in the range of 30-70° can be matched to the fiber like-ZnO. All the diffraction peaks are perfectly matched to the ZnO with hexagonal wurtzite structure (JCPDS, 80-0075). The XRD pattern specifies that the ZnO Nfs contain well-faceted crystals ends along the (c-axis) [16]. The (101) plane is having greater intensity than (002) and (100) planes of ZnO Nfs. Fig. 4 (a and b) displays the SEM images of the ZnO Nfs thin film. From the SEM images, it is seen that the core diameter of the ZnO Nfs is in the range of 20-50 nm. The ZnO Nfs surface exhibits random, porous and rough nature. This rough and porous surface is much beneficial for dye loading [17]. This distinctive structural feature may be beneficial, as this porous morphology offers large numbers of pinholes for promoting the permeability of electrolytes into the inner structure of ZnO Nfs [18]. The presence of O and Zn elements present in the nanofibers was confirmed through EDX analysis (Fig. 4c). The emission peaks matching to the elements O, and Zn were identified at 0.52 (O), and 1.12, 8.60, 9.63 (Zn), respectively. It clearly revels that the ZnO Nfs contains only O, and Zn elements.

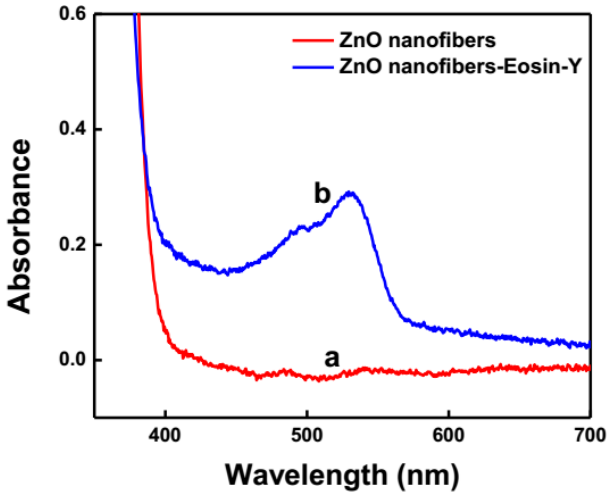


**Fig. 1. Diffuse reflectance spectra of ZnO Nfs (a) and eosin-Y adsorbed ZnO Nfs thin films.**

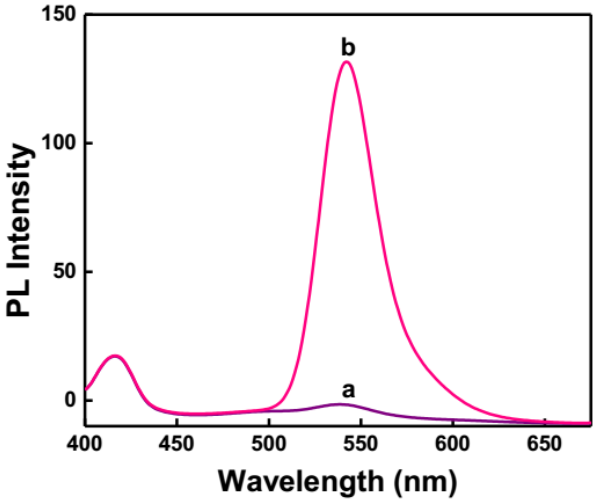


**Fig. 2. PL spectra of ZnO Nfs (a) and ZnO Nfs mixed with 1 µM eosin-Y in ethanol (b) at λexc = 375 nm.**

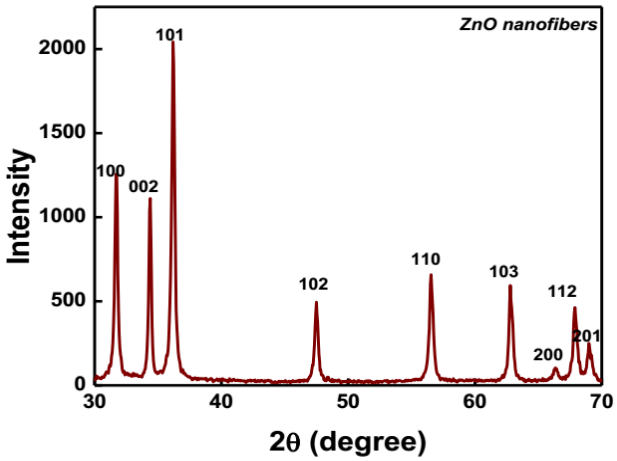


**Fig. 3. XRD pattern of ZnO Nfs.**

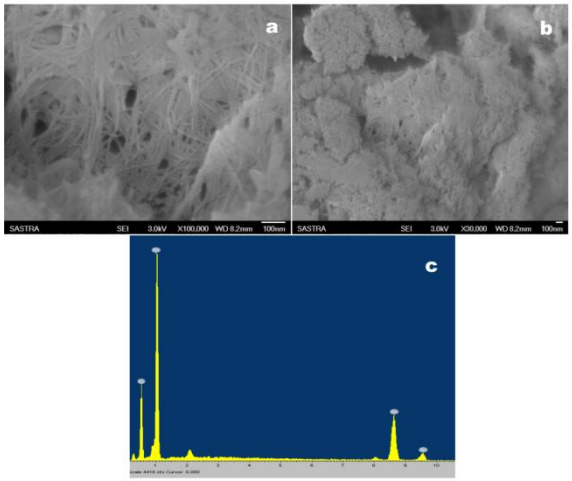


**Fig. 4. SEM micrograph of ZnO Nfs thin film (a & b) and EDX spectrum of ZnO Nfs (c).**

### C. Photovoltaic performance of DSSCs

The DSSC was assembled using the substrate grown ZnO Nfs photoanode and its photovoltaic performance was evaluvated under simulated AM 1.5G solar irradiation of 100 mW $cm^{-2}$. The efficiency of solar to electrical conversion of the DSSC was studied by evaluating the cell parameters such as open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), photocurrent-photovoltage (J-V) characteristics, fill factor (FF) and efficiency (η) using the standard equations.

$$FF = \frac{V_{max} \cdot j_{max}}{V_{oc} \cdot J_{sc}}$$

$$\eta(\%) = \frac{V_{OC} \cdot J_{SC} \cdot FF}{P_{in}}$$

where, $V_{max}$ and $J_{max}$ are the photovoltage and photocurrent density, respectively at the maximum power point and $P_{in}$ is the power of the incident light (100 mW/$cm^2$).

The short circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF), and overall conversion efficiency (η) of the DSSC with ZnO Nfs photoanode was obtained to be 3.89 mA/cm2, 0.69 V, 0.56, and 1.51%, respectively (Fig. 5a). The applicability of the ZnO Nfs in DSSC confirms the efficient electrolyte penetration into the ZnO photoelectrode through pinholes and nanopores present in the twisted nanofibers matrix. This can be explained by the fact that, pinholes and pores present in the ZnO nanofibers provide advantages like higher loading of eosin-Y dye, improved light absorption, higher photocurrent and increased exposed surface area to the electrolyte [17, 18]. This leads to rapid electron transport within the nanofibers in uni-directional and thereby minimizing the charge recombination process thus increase the cell performace [17,18].

The stability and reproducibility of ZnO Nfs based DSSC were studied and the data are presented in Fig. 5b. The photocurrent-time (I-T) profile obtained for ZnO Nfs based DSSC is in good agreement with its J-V characteristics. In the ZnO Nfs modified photoanode based DSSCs, the photocurrent rises rapidly to a maximum value and attains a steady–state current immediately after the light is turned 'on'. A sudden decrease in the photocurrent happens when the light is turned 'off' and there is no current response in the dark. The steady-state photocurrent-maximum remains same even after performing several 'on-off' cycles. This characteristic of ZnO Nfs/eosin-Y revealed good stability of the cell.

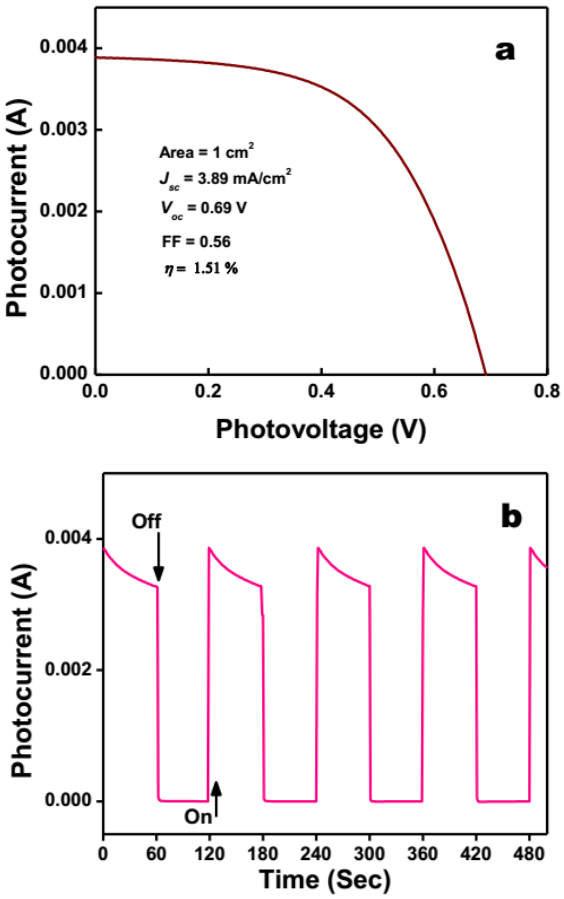


**Fig. 5. Photocurrent-photovoltage (J-V) curve (a) and photocurrent-time (I-T) profile (b) recorded for DSSC with ZnO Nfs modified photoanode sensitized with eosin-Y. Area of the cell was 1 cm2.**

## IV. CONCLUSION

The ZnO nanofibers (ZnO Nfs) modified photoanode for DSSC was fabricated by a simple solution mediated substrate grown method. The optical properties of the ZnO Nfs gives an idea that it can be used as photoanode for DSSC. The sharp and intense red emission due to the ionized oxygen vacancies, which is increased further when quenching with eosin-Y. The SEM micrographs reveals that the presence of fiberous nature of ZnO with 25-50 nm diameter. The photovoltaic performance of the DSSC containing ZnO Nfs modified photoanode sensitized with eosin-Y was evaluated and the overall efficiency of solar to electrical energy conversion (η) of the ZnO Nfs modified DSSC was 1.51%. This higher effciency is due to the quick diffusion of electrons within the nanofibers in uni-directional to the photoanode, and also increased interfacial conatct between the photoanode and electrolyte. The simplicity and flexibility of this technique is believed to provide promising opportunity in the designing of various nanostructured materials with enhanced surface activity for high performance solar cells.

## ACKNOWLEDGMENT

APK thanks SERB-DST for financial support through Early Career Research Award (ECRA) (SERB File No.: ECR/2017/001758).

## REFERENCES

[1] B.Weintraub, Z. Zhou, Y. Li, Y. Deng, Solution synthesis of one-dimensional ZnO nanomaterials and their applications. Nanoscale, 2010, 2, 1573–1587.
[2] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells. Chem. Rev. 2010, 110, 6595–6663.
[3] Q. Zhang, C. S. Dandeneau, X. Zhou, G. Cao, ZnO nanostructures for dye-sensitized solar cells. Adv. Mater. 2009, 21, 4087-4108.
[4] S. Suresh, A. Pandikumar, S. Murugesan, R. Ramaraj, Samuel Paul Raj. Photovoltaic performance of solid-state solar cells based on ZnO nanosheets sensitized with low-cost metal free organic dye. Solar Energy, 2011, 85, DOI:10.1016/j.solener.2011.04.016.
[5] Z. L. Wang, Zinc oxide nanostructures: growth, properties and applications. J. Phys.: Condens. Matter, 2004, 16, R829–R858.
[6] T. W. Hamann, R. A. Jensen,A. B. F. Martinson, H. Van Ryswyk, J. T. Hupp, Advancing beyond current generation dye-sensitized solar cells, Energy Environ. Sci. 2008, 1, 66–78.
[7] W. J. Lee, H. Okada, A. Wakahara, A. Yoshida, Structural and photoelectrochemical characteristics of nanocrystalline ZnO electrode with eosin-Y. Ceramics International 2006, 32, 495–498.
[8] H. Graaf, C. Maedler, M. Kehr, T. Oekermann, Structural changes of electrodeposited ZnO matrices for dye-sensitized solar cells during preparation. J. Phys. Chem. C 2009, 113, 6910–6912.
[9] T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura, H. Minoura, Electrochemical self-assembly of nanoporous ZnO/Eosin Y thin films and their sensitized photoelectrochemical performance. Adv. Mater. 2000, 12,1214–1217.
[10] Suri, P.; Panwar, M.; Mehra, R. M. Photovoltaic performance of dye-sensitised ZnO solar cell based on Eosin-Y photosensitizer. Materials Science-Poland 2007, 25 137–144.
[11] A. B. Djurišić,Y. H. Leung, Optical properties of ZnO nanostructures, Small, 2006, 2, 944-961.
[12] V. A. L. Roy, A. B. Djurišić, W. K. Chan, J. Gao, H. F. Lui, C. Surya, C. Luminescent and structural properties of ZnO nanorods prepared under different conditions. Appl. Phys. Lett. 2003, 83,141-143.
[13] S. Rakshit, S. Vasudevan. Trap-state dynamics in visible-light-emitting ZnO:MgO nanocrystals. J. Phys. Chem. C, 2008, 112 (12), pp 4531–4537.
[14] J. F. Scott, UV resonant raman scattering in ZnO. Phys. Rev. B, 1970, 2, 1209-1221.
[15] A.V. Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, The kinetics of the radiative and nonradiative processes in nanocrystalline ZnO particles upon photoexcitation. J. Phys. Chem. B 2000, 104, 1715 1723.

## AUTHORS PROFILE

**Dr. Perumal Rameshkumar** is currently working as an Assistant Professor of Chemistry at Kalasalingam University, India. He obtained his M.Sc. (chemistry) (2009) from Madurai Kamaraj University. He joined as Junior Research Fellow (2010) at the same University and subsequently promoted as Senior Research Fellow (2012). His doctoral thesis focused on “polymer encapsulated metal nanoparticles for sensor and energy conversion applications. He worked as Post-Doctoral Research Fellow (2014) at University of Malaya, Malaysia in the field of “graphene-inorganic nanocomposite materials for electrochemical sensor and energy conversion applications”. His current research interests include synthesis of functionalized nanomaterials, optical sensors, energy-related electrocatalytic processes, electrochemical sensors and supercapacitors. His research outcomes were documented in 25 peer reviewed journals including 01 review article and he edited 01 book under Elsevier publication.

**Dr.Alagarsamy Pandikumar** obtained his Ph.D in Chemistry (2014) from the Madurai Kamaraj University, Madurai. His doctoral research focused on synthesis, characterization of plasmonic nanocomposite materials and its application of photo-physical/chemical properties in photocatalysis, photoelectrocatalysis and dye-sensitized solar cells. He successfully completed his post-doctoral fellowship tenure (2014-2016) at the University of Malaya, Malaysia under high Impact Research Grant. During post-doctoral research, he has developed several graphene based metal, metal oxide, polymeric nanocomposites for electrochemical sensors and dye-sensitized solar cells applications. He was appointed as a Research Assistant Professor in Research Institute at SRM University, India. His current research involves development of novel materials with graphene, graphitic carbon nitrides, transition metal chalconides in combination to metals, metal oxides, polymers and carbon nanotubes for photocatalysis, photoelectrocatalysis dye-sensitized solar cells and electrochemical sensor applications. His results outcomes were documented in 108 in peer reviewed journals including 9 review articles; Among them Five of the key articles have been cited more than 50 times and also have 1750 citations with the h−index of 33. On other side, he served as Guest Editor for a special issue in Materials Focus journal and edited 8 books for Wiley, Elsevier, and TransTech Publishers.