Methylene Blue (MB) : PYR (G) based Dye Sensitized Solar Cells : Morphology and its Implications

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Abstract :- The performance of dye-sensitized solar cells based on 1:1 ratio of methylene blue (MB) and pyronin (G) dye was studied. ZnO nano-structures were grown on FTO/nc-ZnO substrate using two different approaches. The first approach (Device A) incorporated zinc nitrate Zn(NO3)2, which resulted in formation of disoriented nanorods of zinc oxide. The device exhibited an open circuit voltage (Voc) of 590mV, a short circuit current (Jsc) of 2.45 mA/cm2, a fill factor (FF) of 0.6 and a power conversion efficiency (η) of 0.86%. The lower value of short circuit current may be due to the high resistance path offered by unorganized ZnO nanorods to the photoexcited electrons. On the other hand devices prepared by second approach using zinc acetate, resulted in formation of ordered and oriented nanostructures which provides easy path to the photogenerated electrons to travel through the counter electrode which results in overall improvement in the performance of the device. The improved device exhibits an open circuit voltage (Voc) of 0.61mV, a short circuit current (Jsc) of 5.87 mA/cm2, a fill factor (FF) of 0.63 and power conversion efficiency (η) of 2.25%.

Key words : Dye sensitized solar cells, ZnO, Methylene Blue, PYR (G)

I. INTRODUCTION

Nanocrystalline dye-sensitized solar cells (DSSCs) are proving to be the potential alternatives of solar energy harnessing, due to their high-energy conversion efficiency, flexibility and low production cost [1–6]. DSSC possesses three major components: (a) dye acts as sensitizer which harvests solar energy and generate excitons [7], (b) nanostructured acceptor materials like metal oxides are used to transport electrons efficiently [8], and (c) redox electrolyte or hole transporting materials to regenerate dye molecules [9]. Various approaches towards loading more dye, improving charge transfer, optimization of different morphologies with high surface area, (like well oriented nanotube arrays) are proposed to increase cell efficiency [10-13]. Present communication deals with the improvement in power conversion efficiency, by growing ordered structures of zinc oxide from zinc acetate solution in controlled environment, which acts as an acceptor. ZnO is a well known wide band gap semiconductor used in DSSCs.

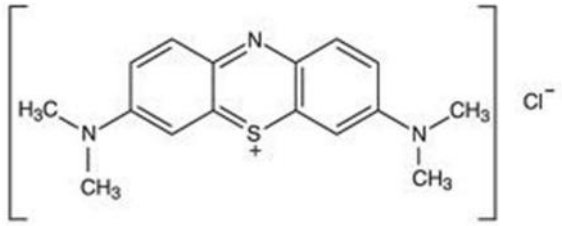
II. EXPERIMENTAL DETAILS :

Devices were fabricated on pre patterned fluorine doped tin oxide (FTO) glass substrates that were first cleaned by using ultrasonic bath in acetone and isopropanol respectively. A layer of colloidal nanocrystalline ZnO (nc-ZnO) was spin-coated over FTO, which acts as transparent electrode. ZnO nanorods were grown on FTO/nc-ZnO layer using two different methods. In first method (device A), the FTO/nc-ZnO substrate was submerged in an equimolar 25 mM aqueous solution of Zinc nitrate, Zn(NO3)2 and hexamethylene tetraamine, and heated at 90°C for two hours [14]. The substrate was then thoroughly rinsed with distilled water and annealed at 400°C for 30 minutes. In second method (Device B), zinc acetate solution in 2-methoxyethanol was used for the formation of thin film of zinc acetate [15], which was then subjected to thermal annealing for about 5 minutes at 3000C in air. The so formed ZnO film was rinsed with deionized water and ethanol. ZnO nanofibers were hydrothermally grown from the nucleation layer in 1mM solution of zinc nitrate in deionized water for 30 minutes at 750C [16]. The electrode was rinsed again with ethanol and dried in air for 15 minutes at 1500C. Both samples were dye sensitized by soaking the substrates for 24 hours in a dye solution consisting of Methylene blue MB) and Pyronin (G) dye in 1:1 ratio. Counter electrodes were prepared on florene doped tin oxide (FTO) coated glass substrate using the thermal platinum cluster catalyst method [17]. Few droplets of platinum solution consisting of 5mmol/dm3 PtCl4 in isoproponol was spread on the substrate and dried in ambient air. Finally the substrates were fired in an oven at 4000C for 15 minute and then cooled at room temperature.

The solar cells were assembled by placing the dye sensitized ZnO electrodes and the counter electrodes together in a sandwich structure using a spacer. An electrolyte solution consisting of 0.5 M LiI, 0.05 M I2 and 0.5 m tetra-butyl-pyridine (TBP) in methoxypropionitrile was applied between the electrodes.
All electrical measurements were taken in lab environment using a 1000 W halogen lamp as light source. Light intensity was measured using a lux meter. J-V characteristics were measured using a Keithley electrometer (Model 6514) and a stabilized power supply.

Result and Discussion

Figure 1 (a) and (b) shows the structure of sensitizing dye, Methylene blue (MB) and Pyronine (G). The absorption spectrum was recorded using uv-vis spectrophotometer, which marked their absorption peak (λmax) at 665nm and 547nm respectively.



$C_{16}H_{18}ClN_3S$ MW = 319.86

Fig.1(a) Structure of Methylene Blue (MB)

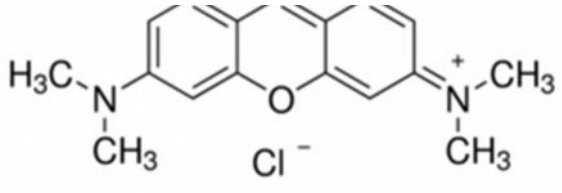


Fig.1 (b) Structure of Pyronin (G)

Figure 2 shows the absorption spectrum of the ZnO films (Device A and Device B) grown by two different solution phase hydrothermal methods, the spectra shows ZnO band gap transition at 375 nm (corresponds to band gap of about 3.3 eV), which is in agreement with bulk ZnO [18]. The absorption spectrum of both nano-structured substrates shows a broad tail due to light scattering from the ZnO film at higher frequencies.

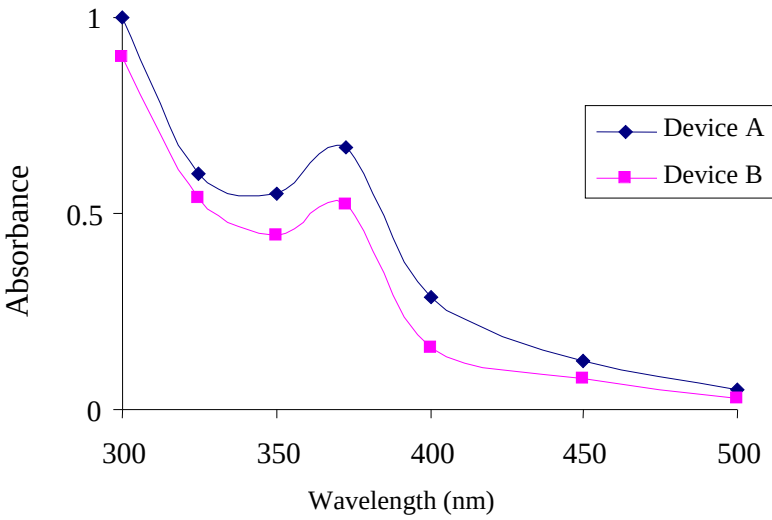


Fig.2 Absorption spectra of ZnO thin films

The J-V characteristics of device A and B are shown in figure 3. Device A exhibits an open circuit voltage (Voc) of 590mV, a short circuit current (Jsc) of 2.45 mA/cm^2, a fill factor (FF) of 0.6 and a power conversion efficiency (η) of 0.86%. It has been observed that the device prepared by first method using zinc nitrate $Zn(NO_3)_2$, shows lesser value of short circuit current (Jsc=2.45mA), this can be attributed to formation of disoriented ZnO nanorods and weak attachment to the FTO/*nc*-ZnO substrate which introduces series resistance in the acceptor material and therefore do not provide a good electrical pathway for the photo generated electrons to travel to the FTO back contact. Further disorganized orientation of ZnO nanorods creates various traps in acceptor material which acts as recombination centers and hence affects the performance of the device.

On the other hand device B prepared by second method using Zinc acetate shows a remarkable improvement in the performance of the device. It exhibits an open circuit voltage (Voc) of 0.61mV, a short circuit current (Jsc) of 5.87 mA/cm^2, a fill factor (FF) of 0.63 and power conversion efficiency (η) of 2.25%. The enhancement in the value of short circuit current may be due to the formation of highly ordered and suitably oriented ZnO nano-rods. The hydrothermal growth of ZnO nano-rods achieved by this method is found to be in the perpendicular direction to the plane of the substrate. Thus provides more dye loading area and contains lesser trapping sites for effective recombinations of charge carriers. Further due to enhanced surface area available for dye adheration on ZnO nano-rods, a large number of exiton dissociation sites contribute towards the process of charge separation. This type of morphology, hence provide good electrical path for the photo-exited electrons to traverse their way towards the back contact, which results in overall improvement in the performance of the device. The fill factors of devices are negligibly affected in both cases, which likely provide further scope to optimize their blend morphologies.

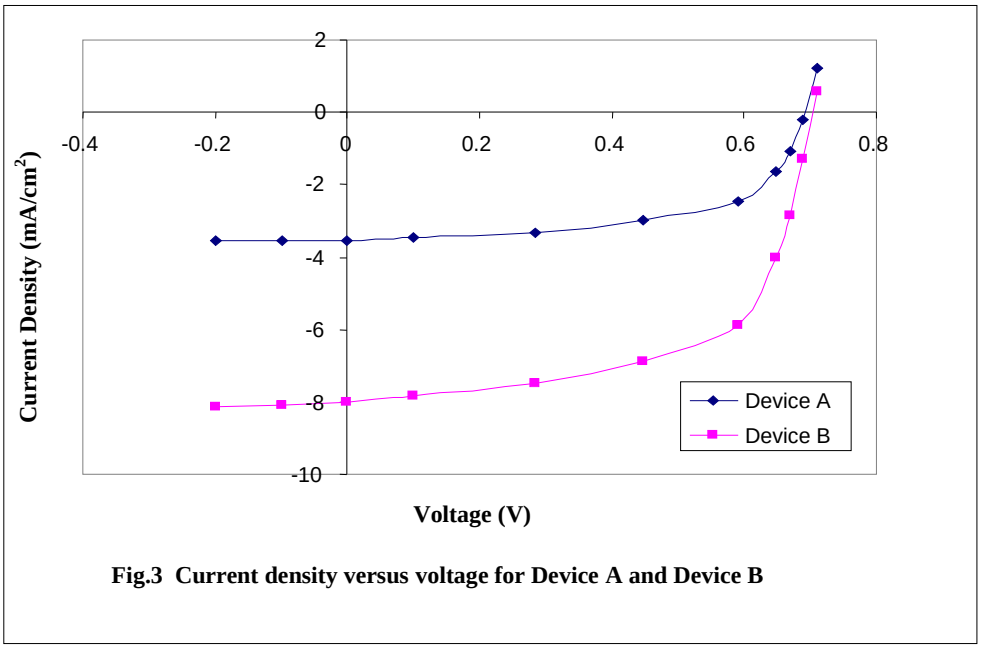


Fig.3 Current density versus voltage for Device A and Device B

III. Conclusion

It was found that orderly grown ZnO nano-rods acts as suitable structures to transport photo-generated electrons to the counter electrode resulting in increased value of short circuit current, which accounts to the increase in power conversion efficiency (η) of the solar cells. Further, losses due to recombination of charge carriers at trap centers can be minimized by growing well oriented nano-rods using wide band gap semiconductor materials.

References:

[1] Photoelectrochemical Cells. M. Grätzel. Nature (2001) 414, 338.
[2] Saito Y, Fukuri N, Senadeera R, Kitamura T, Wada Y, Yanagida S. Electrochem Commun (2004) 6,71–4.
[3] Furube A, Katoh R, Yoshihara T, Hara K, Murata S, Arakawa H, et al. J Phys Chem B (2004) 108,12583–92.
[4] Wu JH, Hao SC, Lan Z, Lin JM, Huang ML, Huang YF, et al. Adv Funct Mater (2007) 17, 2645–52.
[5] Marinado T, Hagberg DP, Hedlund M, Edvinsson T, Johansson EMJ, Boschloo G,et al. Phys Chem Chem Phys (2009) 11, 133–41.
[6] Kim S, Lee JK, Kang SO, Ko J, Yum JH, Fantacci S, et al.. J Am Chem Soc (2006) 128, 16701–7.
[7] H. Tian, F. Meng, Opt. Sci. Eng. 99 (2005) 313–329.
[8] M. Gratzel, Prog. Photovoltaics 14 (2006) 429–442.
[9] M. Gorlov, L. Kloo, Dalton Trans. (2008) 2655–2666.
[10] Na SI, Kim SS, Hong WK, Park JW, Jo J, Nah YC, et al Electrochim Acta (2008), 53,2560-6.
[11 Kang SH, Kim JY, Kim Y, Kim HS, Sung YE. J Phys Chem C (2007) 111, 9614-23.
[12] She GW, Zhang XH, Shi WS, Fan X, Chang JC, Lee CS, et al. Appl Phys Lett (2008) 92:053111-3.
[13] Xu L, Liao Q, Zhang J, Ai X, Xu D. J Phys Chem C (2007) 111:4549-52.
[14]Growth of Arrayed Nanorods & Nanowires of ZnO from Aqueous Solutions. L. Vassieres. Adv. Mater. (2003) 15, 464-466.
[15] M. Ohyama, H.Kozuka, T. Yoko, Thin Solid Films 306 (1997) 78.
[16] R.B.Peterson, C.L. Fields, B.A. Gregg, Langmuir 20 (2004) 5114.
[17] N. Papageorgiou, W.F. Maier, M.Gratzel, J. Electrochem. Soc.144 (1997) 876-884.
[18] On the optical band gap of zinc oxide. V. Srikant and D.R. Clarke. J. Appl. Phys. (1998), 83, 5447-5451.