ORIGINAL RESEARCH PAPER

Chemistry

PHOTOELECTROCHEMICAL(PEC) STUDY OF THE DYE SENSITIZED HIGH BAND GAP STRUCTURE OF ZNO SEMICONDUCTOR ELECTRODES PREPARED BY THE SOL-GEL METHOD

KEY WORDS: Solar cell, PEC cell, ZnO/TiO2, dye sensitized cell and high band gap semiconductor etc.

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ABSTRACT

The goal of this present work gives an overview of present generation solar cells – dye sensitized high band gap ZnO semiconductor electrodes have been synthesized by wet chemical (sol-gel) methods by mixing zinc nitrate hexahydrate [Zn (NO3)2.6H2O] solution with glycerol with continuous stirring at the temperature ~900C. The synthesized ZnO have been characterized by X-ray diffraction analysis (XRD) method. The obtained ZnO powder has been converted in the form of pellets of thickness 1.46 mm, 1.76 mm and 1.25 mm. Then electrodes have been prepared by developing electrical contact on the surface of the pellet. The synthesized electrodes have been studies for photoelectrochemical (PEC) measurements under darkness and illumination. The dye sensitized electrodes are chemically stable and do not photodegrade easily. The performance of dye-impregnated ZnO electrodes were found up to 6-8 cycles. This research work to serve futuristic application as a solar energy for humankind.

INTRODUCTION

A dye sensitized solar cell is a photoelectrochemical (PEC) system, which is most cases, involves use of some high band gap n-type semiconductor, such as ZnO and TiO_2. In such system the operation is based on the photo-injection of electrons from dye molecules into the conduction band of the semiconductor and hole transfer to a redox mediator. The photo-injected electrons then reach the external circuit through the semiconductor network, whereas the holes, in the form of oxidized ions, transit through the electrode pores towards the counter electrode. The effect of dye sensitization in PEC cell with a p-type semiconductor is scantily studied[8]. Besides the low light absorption by a dye mono-layer and the low injection efficiencies of dye multilayers necessitate the use of a high surface area electrode, and in this regard, nanostructured semiconductors can play a very significant role. Why?....used high band gap electrodes. The wide gap oxide semiconductors are most suitable to perform the functions in the DSSC. ZnO and TiO_2 are the semiconductor material in a dye sensitized solar cell [DSSC]. ZnO and TiO_2 have same electron affinities and almost the same band gap energies but ZnO has much higher election diffusivity than TiO_2, a high electron mobility, a large excitation binding energy, is available at low cost, and stable against photo-corrosion[21]. They are transparent because their wide gap and therefore path most of the solar radiation to the active Die material which is active material is main absorber of the incident solar-radiation.

It is also n type with high carrier concentration and so can act as an electron transport layer especially that it has a conduction band edge that matches the lumo level of the Die where it must extract the photo generated electrons from the Die. These materials are also chemically stable and inert against the environmental effects[18-20].

ZnO is a high band gap (E_G = 3.2 eV) n-type semiconductor[2] that possesses optical properties which rander it important industrially as a phosphor in field emissive display and in other cathodoluminescent devices as a photocatalyst and as the gain medium in UV semiconductor losers. In this paper ZnO electrodes with the particle size (~ 54 nm) have been prepared by sol-gel method[12].

METHOD AND MATERIAL

1. Sol-Gel synthesis of ZnO

All samples of ZnO were synthesized by a sol-gel method[9] involving the use of glycerol as key reagent. Zn $(NO_3)_2.6H_2O$ was dissolved in double distilled water to get precursor solution with zinc concentration 0.5, 0.1 & 0.2N. Precursor solution was then placed on a hot plate at 60-70˚C & a fixed amount of glycerol was added drop by drop with continuous stirring.

The resulting dark brown gel was further heating at 250˚C for 2hrs. to get ZnO powder. The obtained samples of ZnO powder were suspended in alcohol and sonicated for 30 minutes. Following this content dried in oven at 60˚C then calcinated at 600˚C. By pressing ZnO powder in a uniaxial cold pressing KBr press, employing 1.3 cm. diameter die, pellets of thickness (1.46mm, 1.77mm & 1.25mm) were obtained. The pellets were again sintered in muffle furnace (separately at 600˚C, 700˚C & 1100˚C) for 1hr. After grinding & polishing with alumina powder, pellets were analyzed for density and electrical resistance.

2. Preparation of working electrode

To form working electrode an electrical contact (back) was developed from one surface of the pellet. To form the contact, two drops of silver paste were put one side of the pellet and then a Cu wire was prepared over it, gently, and then dried at 60 ˚C for 30 minutes to ensure complete drying[4]. The contact, so prepared, was examined for its ohmic nature and then all the sides of the pellet except 1 cm^2 area the centre of the other side (i.e. front side) of the pellet was sealed with epoxy resin. Epoxy coating was cured for 2 hour at 70°C.

3. The treatment of ZnO electrode with Dye solution

The ZnO working electrodes, prepared as above, were dipped vertically, through a hanger, in the alcoholic solution of the chosen dyes[13], for 16 hours, duration at 24±2 ˚C. Following this, the electrodes were dried in oven at 60 ˚C for 30 minutes. The different concentrations of dyes under which this study has been conducted, were 10^{-4}, 10^{-3} & 10^{-2}M.

4. Photoelectrochemical (PEC) Studies

The PEC measurements were carried out in PEC cell in three electrodes configuration. The working electrodes were ZnO semiconductor, electrodes, while counter electrode was a Pt mesh electrode. Saturated calomel electrode (SCE) was used as reference electrode. The PEC cell was filled with nearly 30 cm^3 of electrolyte (pH = 7, 10^{-1} M NaOH) solution.

The current-voltage characteristics of the cell were determined both under darkness and illumination employing a Potentiostat (Model: EG&G VERSASTAT II). For illumination 150 W xenon are source, (Driel, USA) was used. A comparison of the data, recorded under darkness and illumination, revealed the level of photoactivity of the electrode towards the splitting of water[6].

RESULTS AND DISCISSION

The prepared ZnO samples were subjected to X-ray diffraction analysis at solid state physics laboratory, New Delhi. The observed X-ray diffractogram indicated major peaks corresponding to miller indces (101), (100), (002), (110), (103) and (102) with relative intensities as 100, 59.04, 44.47, 32.78, 27.82 and 20.40 %.

This set of diffraction peaks, with their relative intensities resembles very closely to ZnO phase. Hence, the formula of polycrystalline ZnO phase in the in the samples of confirmed.

Employing the X-ray diffraction analysis data[1], the average particle/grain size of crystalline solids calculated by use of Scherrer's. equation i.e. B = 0.9%. □/t cos □ is lies in the range 54 nm, which suggest the formation of a nanostructured ZnO.

Electrical resistance[11] of the ZnO pellets of all the samples were highly resistive, with resistively > few KΩ. Density values of ZnO pellets were found in the range 7.07 – 7.04 g/cm^3 for samples sintered at 600 – 700^{0}C and slightly increased were of the order 7.32 g/cm^3 samples sintered at 1100^{0}C.

The observed current was recorded in PEC cell, comprising ZnO working electrode, under darkness and illumination. The obtained curves clearly suggest (by comparing the dark current with current recorded under illumination) that the ZnO is photosensitive[14-17]. But, in presence of dyes there is significant gain in photo-current, compared to the values recorded, when no dyes were used. The only exception to this is, probably, eosin, in presence of which, there is no significant gain in photocurrent.

Further when crystal violet/rose Bengal dye is used, the photocurrent was highest, when dye concentration is raised, initially, there is gain in photocurrent, but beyond a certain concentration (with different dyes), probably, the photocurrent decreases.

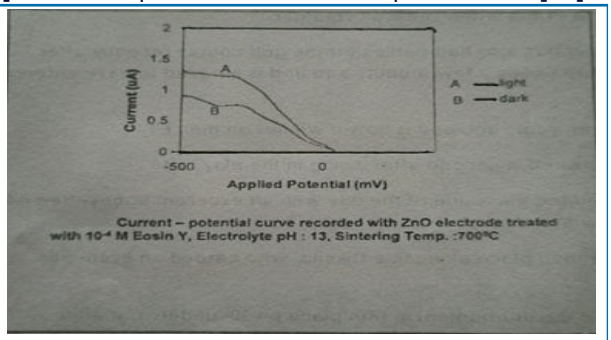
A possible reason for this is that at low dye concentration, the light absorption cross-section is small, but, with the increases in dye amount, the probability od deexcitation of excited the drop in photocurrent generation at higher dye concentration[3].

From fig. 1-4, from current - Voltage curves, the ZnO samples are behaving like a p-type material as photocurrent is seen only under cathodic bias[10]. Hence, in the studied dye densitized PEC cells comprising p-type ZnO working electrode, the dye molecules may serve as, (i) additional light absorbing units attached to ZnO electrode and (ii) mediators facilitating the transfer of electrons from the conduction band of the ZnO to H^+ ions present in the electrolyte.

In the investigated dye molecules, apart from lone pair of electrons at N, O ans I in the attached peripheral functional groups, the carboxylate group is also present, the absorption of the dye molecules with ZnO is likely through the formation of Zn-linkages with these centers. The injection of photogenerated holes from dye molecules to ZnO conduction band may, thus, smoothly occur via such linkage[5].

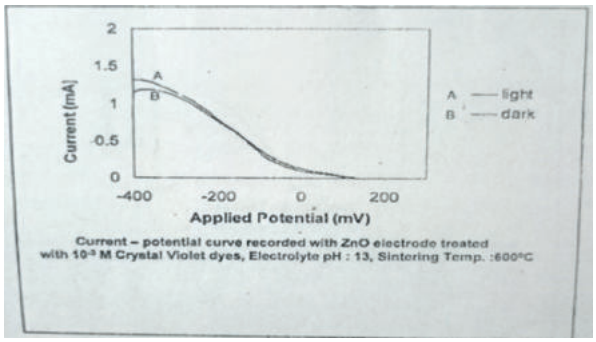
The success of the dye, with p-type ZnO, will largely depend upon how quickly electrons is transferred from the photoexcited dye molecule to the H^+ ions. The oxidized dye molecule must also swiftly return to its original state, by accepting electrons from the conduction band of the ZnO, in order to avoid photodegradation of dye[7], itself.

To achieve high stability of PEC cell and significant photocurrent generation a proper alignment of energy levels of dye system, H^+/H^2 redox level and ZnO band edges is thus, very crucial. To this effect the use of rose bengal nd crystal violet, at appropriate concentration, looks promising.



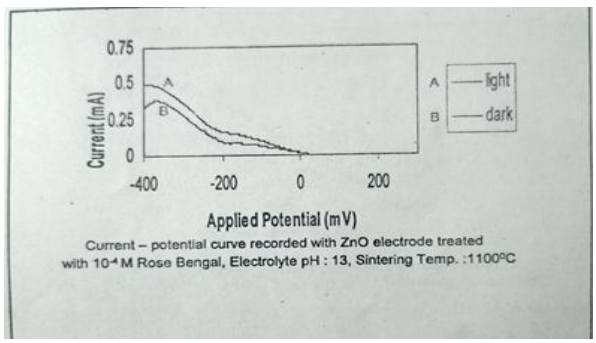
Current – potential curve recorded with ZnO electrode treated with 10^{-4} M Eosin Y, Electrolyte pH : 13, Sintering Temp. :700^{0}C

Fig. 1



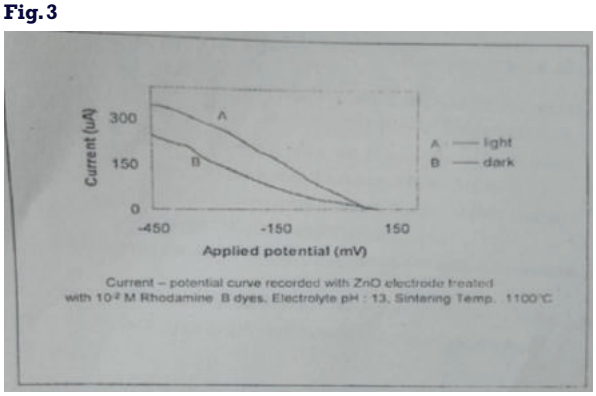
Current – potential curve recorded with ZnO electrode treated with 10^{-5} M Crystal Violet dyes, Electrolyte pH : 13, Sintering Temp. :600^{0}C

Fig. 2



Current – potential curve recorded with ZnO electrode treated with 10^{-4} M Rose Bengal, Electrolyte pH : 13, Sintering Temp. :1100^{0}C

Fig. 3



Current – potential curve recorded with ZnO electrode treated with 10^{-3} M Rhodamine B dyes, Electrolyte pH : 13, Sintering Temp. 1100^{0}C

Fig. 4

Conclusion

The dye sensitized ZnO electrode has been prepared by sol-gel method through the zinc nitrate hexa hydrated [$ZnO(NO_3)_2.6H_2O$]. It has been found the particle size of prepared ZnO electrode is 54nm. There is definite advantage of employing, dye sensitized ZnO electrode in the PEC study. The dye investigated here are chemically stable and do not photo-degrade easily. The performance of dye impregnated ZnO electrodes were tested in repeated cycles, the observed photo-current values were found reproducible only up to 6-8 cycles, after which the values recorded a regular decrease.

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REFERENCES

1. Gordillo, G. and Calderon, C.; *J. Advan. In Material sci. and Tech.*, **Vol. 1**, 01(1996).
2. Nyffenegger, R.M., Craft, B., Shaaban, M., Gorer, S., Erley, G., and Penner, R.M.; *Chem. Matter*, **Vol. 10**, 1120 (1998).
3. S. Chwarzburg, K. and Frank, W.; *J. Phys. Chem.*, **Vol. 103 (B)**, 28(1999).
4. Jongh, P.E., Meulenkamp, E.A., Vanmaekelbergh, D. and kelly, J.J.; *J. Phy. Chem.*, **Vol. 104(B)**, 7686(2000).
5. Sayama, K., Hara, K., Mori, N. and Arakawa, H.; *J. Chem. Common*, 1173(2000).
6. Bandara, J. and TennaKone, K.; *J. Appl. Catalysis A : General*, **Vol. 208**, 335(2001).
7. Tokumoto, M.S., Smith, A., Santilli, C.V., Pulcinelli, S.H., Craievieh, A.F., Elkaim, E., Traverse, A. and Briois, V.; *Thin Solid Flims*, **Vol. 416**, 284(2002).
8. Bandara, J., TennaKone, K. and Binduhewa, P.; *New J. Chem.*, **Vol. 25**, 1302 (2003).
9. Kitazawa, N., Sakaguchik, A.M., Watanabe, Y.; *J. of Materials Sci.*, **Vol. 38**, 3069(2003).
10. Wang, L.G. and Zunger, A.; *Phys. Review Letter*, **Vol. 25**, 256401(2003).
11. Kaur, R., Singh, A.V. and Mehra, R.M.; *Internet Article*.
12. Mishra, P.R., Singh, A.K., and Srivastava, O.N.; *Indian J. Phys.*, **Vol. 78A(A)**, 81(2004).
13. Clifford, J.N.; J.A.M. *Chem. Soc.*, **Vol. 126**, 5670(2004).
14. Grätzel, M.; *Philos Trans A Math Phys Eng Sci.*, **Vol. 365(1853)**, 993(2007).
15. Zhang, Q., Christopher, S., Xiaoyuan Zhou, D. and Cao, G.; *Advanced Materials*, **Vol. 21(41)**, 4087(2009).
16. Huang, J., Yin, Z. and Zheng, Q.; *Energy Environmental Science*, **Vol. 4**, 3861(2011).
17. Sakai, N., Miyasaka, T. and Murakami, T. N.; *J. Phop Chom. C,* **Vol. 117**, No. 21, 10949(2013).
18. Vittal and Kuo Chuan H.; *Renewable and Sustainable Energy Reviews.* **Vol. 70**, 920(2017).
19. Siwatch, S., Kundu, V. S., Kumar, A., Kumar, s., Chauhan, N. and Kumari, M.; *Optik*, **Vol. 194**, 163117(2019).
20. Bhati, K, A., Khan, M, I., Saleem, M., Alvi, F., Raza, R. and Rehman, S.; *Materials Research Express*, **Vol. 6**., No.7, 075902(2019).
21. Ram Kumar, P., Agith Bosco Raj, T. and Sahaya Shajan, X.; *Materials today communications*, **Vol. 33**, 104818(2022).