



INSTITUTE OF PHYSICS - SRI LANKA

Research Article

Properties of solid-state ZnO|dye|CuCNS solar cell

P.M. Sirimanne^{*a,b}, and J.B. Zhang^b

^aNano-Science Laboratory, Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

^bEnvironmental and Renewable Energy Systems Division, Graduate School of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

Abstract

Hybrid ZnO films were prepared via a single-step electrochemical process. Extraction of organic component from the hybrid films resulted tiny ZnO columns perpendicular to the substrate. A Semiconductor hetero Junction was prepared by depositing CuSCN on ZnO films. The maximum photocurrent of 0.36 mAcm^{-2} and photovoltage of 290 mV were observed for the solid-state cell fabricated by sandwiching organic dye mercurochrome in between ZnO and CuSCN films.

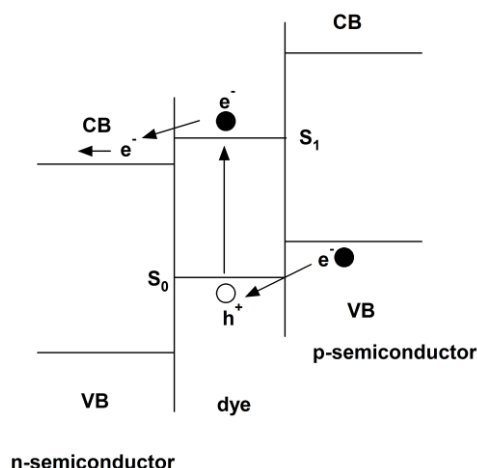
1. INTRODUCTION

Recently, semiconductor hetero-junctions have been aroused considerable interest all over the world due to capability of fabrication of various solid-state devices. An appropriate coupling of semiconductors with semiconductors, polymers with polymers or semiconductors with polymers results simplified models of solid-state junctions. Various techniques have been employed in fabrication of hetero-junctions [1-5]. Preparation of semiconductor junction by a simple deposition technique is a scientific challenge. Semiconductor junctions exhibit exciting phenomenon. For example, a simple solid-state solar cell was firstly demonstrated by Tennakone *et al* by sandwiching a natural pigment cyandin in between CuI and TiO₂ films [6]. A higher photocurrent generation was observed on TiO₂|dye|CuI (n-semiconductor|dye|p-semiconductor) so-called NDP type solar cells prepared by adding a molten salts to the CuI solution [7]. However, band

*corresponding author, Email: psirimanne@hotmail.com

Present address: Department of Materials Engineering, Monash University, Clayton 3800, Victoria, Australia

structures of n-semiconductor and p-semiconductor play an important role in NDP type solid-state solar cells. Charge generation of a NDP type solar cell is illustrated in Scheme 1.



Scheme 1 Charge generation of a NDP type cell

Under illumination, dye molecules attached to the semiconductor get excited from its singlet state (S_0) to the excited singlet state (S_1) and electrons are injected into the lower lying conduction band (CB) of the n-type semiconductor from dye molecules. The vacancy exists in the dye molecule is immediately neutralized from accepting an electron from the inner band of the p-type semiconductor and resulting a photocurrent in the cell. Several natural pigments [6, 8–11], synthesized dyes [4, 12–14], conjugated polymers [5, 15] and low band gap semiconductor [16] have been identified as suitable sensitizers for fabricating NDP type solar cells. So far, only few semiconductor-semiconductor or semiconductor-polymer pairs have been identified to fabricate NDP type solar cells [6, 17]. In this article, we report characteristics of CuSCN|ZnO hetero-junction fabricated by electrochemically at low temperature and a solid-state solar cell fabricated by sandwiching mercurochrome in between CuCNS and ZnO films.

2. EXPERIMENTAL

Fluorine doped indium oxide (FTO) coated glass substrates are not completely active for deposition of ZnO by electrochemically at oxygen saturated atmosphere. Activation of these substrates was carried out in 0.1 M KCl by applying a constant potential of -1.0 V vs SCE. ZnO was deposited on activated FTO as follows; $ZnCl_2$ was added to the electrolytic bath (until concentration reach 5 mM) and electrolysis was carried out for 20 min by replacing Pt counter electrode used for pre-electrolysis from a pure Zn wire, under similar potentiostatic conditions. Resulted compact ZnO film is used as a template for deposition of hybrid films. Hybrid ZnO films were prepared by adding eosin Y to the electrolytic bath (until concentration reach to 45 μ M) and by continuing

electrolysis for further 20 min. All electrochemical process were carried out in a single compartment cylindrical cell, at a constant temperature of 70°C, in an aqueous medium by using three electrode configuration, at oxygen saturated atmosphere (bubbling rate 100 ml/min). The working electrode was kept at electrolyte|air interface and was rotated at a constant speed of 500 rpm through out the experiment. Hybrid ZnO-eosin Y films were then rinsed with water dried under air stream and kept at atmospheric condition for over night. Extraction of eosin Y from hybrid films was carried out by immersing them in a KOH solution (pH=10.5). Characteristics of ZnO films are studied by using a UV-Visible spectrometer (Hitachi U4000), a scanning electron micrograph (Jeol) and an x-ray diffractometer (Rigaku).

A member of a xanthenes dyes, mercurochrome used as the sensitizer for ZnO films, since mercurochrome strongly chelates with ZnO and their by much higher photocurrent is predicted. CuSCN was then deposited on sensitized ZnO electrodes as follows, a constant potential of + 0.2 V vs Ag/AgCl was applied on sensitized ZnO electrodes at a constant temperature at 15°C in ethanolic 0.1M Cu(ClO₄)₂ and 0.025M LiSCN electrolyte. A Pt wire was used as the counter electrode and working electrode was placed horizontally almost at the surface of the electrolyte and was rotated at a constant rate of 300 rpm throughout the electrochemical deposition. Further filling of pores of ZnO film was carried by depositing CuCNS by spreading a small amount from a solution prepared by digesting CuCNS in propylsulfide until photovoltage of the cell reaches its maximum. A thin layer of graphite was then carefully applied on the top of CuCNS layer by painting smoothly from graphite granular.

3. RESULTS AND DISCUSSION

Chronoamperograms for a) pre-electrolysis of FTO and b) deposition of compact ZnO films are shown in Fig. 1. As is shown, current generated due to reduction of molecular oxygen initially increases gradually with time and reach a saturation level (curve a, Fig. 1). Saturation of current indicates activation of FTO for oxygen and seems to be due to limitation of diffused oxygen in the electrolyte [18]. We have firmly maintained physical parameters such as temperature of electrolytic bath, applied potential, oxygen concentration in the bath and rotating speed, since they are strongly influenced on current across the electrodes. Reduction of molecular oxygen takes place via four electron reduction process in aqueous media and can be summarized as follows [18,19],



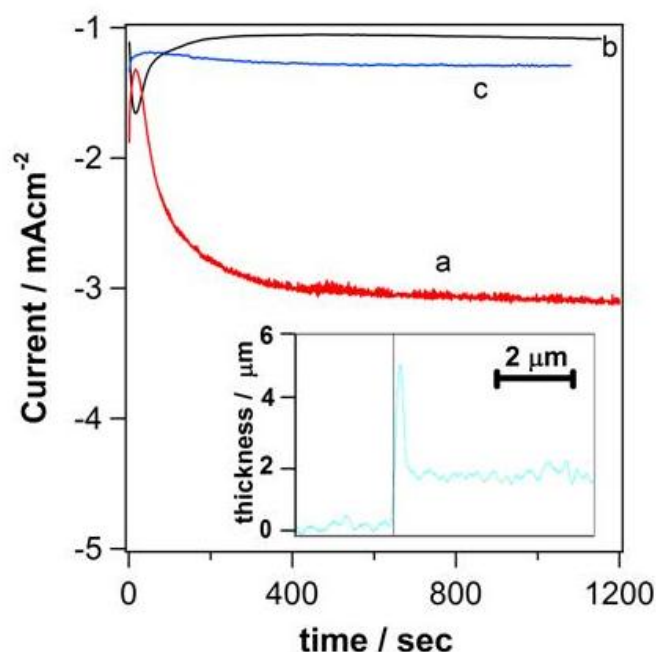
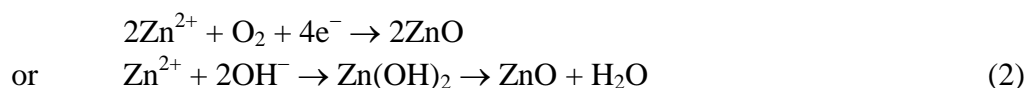


Fig. 1 Chronoamperograms for (a) pre-electrolysis, (b) deposition of ZnO on FTO and (c) deposition of hybrid ZnO|Eosin Y films on ZnO. Inset shows the variation of the thickness of the compact ZnO film.

Addition of Zn^{2+} into the electrochemical bath changes kinetics in the system and forms ZnO on FTO. Formation of ZnO nucleus exhibits peculiar variation of current as soon as ZnCl_2 is added to the electrolyte (curve b, Fig. 1). However, overall process of formation of ZnO seems to be kinetically controlled process and takes place via following process [18]



Electrolysis results fairly uniform ZnO layer on FTO as is observed (insert of Fig. 1). Thickness of the film can easily be controlled by changing deposition time and strength of reactance. These films exhibit transmittance over 90% for visible light (curve a, Fig. 2) and highly compact structure, Fig. 3(a). Several organic molecules have been identified as competent for fabrication of hybrid films with ZnO by electrochemically [18, 20, 21]. We have chosen eosin Y to fabricate hybrid films since mechanism of hybrid ZnO-eosin Y films is well understood [20]. However, in brief, $E^{1/2}$ potential of eosin Y is located at -0.9 vs SCE which is close to externally opposed potential on ZnO electrode. At this voltage eosin Y get reduces and reduced form is coupled with ZnO to form hybrid films [22]. Chronoamperogram for deposition of hybrid ZnO|eosin Y film is shown as curve c in Fig. 1. These hybrid ZnO|eosin Y films exhibit almost color less nature or slightly reddish color as deposition is completed and become dark reddish color due to aerial oxidation being aged. Absorption spectra for b) ZnO and c) ZnO|eosin Y hybrid films are shown in Fig. 2.

The onset of optical absorption of thin ZnO films reflects band gap energy is about 3.4 eV. Hybrid ZnO-eosin Y films absorb light in two regions of wavelengths where ZnO and eosin Y absorb light. As is observed, ZnO-eosin Y hybrid films exhibit a saturation of absorbance in the wavelength range of 475-550 nm (curve c). This situation is contrast with that of without ZnO (curve d). Eosin Y in ethanol exhibits two predominant electronic transitions at 520 (maximal) and 480 (shoulder) nm. This shoulder and maximum are correlated with dimers and monomers of eosin Y and common characteristic for xanthene dyes [23]. Enhancement and broadening of absorption in shorter wavelengths are due to chelation of eosin Y with ZnO and a peculiar property for H-type aggregation [24]. Observation of absorption maximum and a shoulder with almost equal intensities suggests equilibrium of eosin Y aggregates and monomers on ZnO. In addition, ZnO-eosin Y hybrid films exhibit a red shift of absorption onset in wavelength shorter than 400 nm (curve c). This red shift is due to the enhancement of grains by encapsulation of eosin Y in ZnO. Morphology of ZnO-eosin Y hybrid films is also studied. Scanning electron micrographs for a (a) ZnO, (b) hybrid ZnO-eosin Y and (c) after extracting eosin Y from hybrid ZnO film are shown in Fig. 3. As is observed, ZnO grains exhibit hexagonal highly compact structure in nature and hybrid films exhibit grains with a round headed top. However, highly porous structure is observed after extracting eosin Y from hybrid films. These films exhibit higher degree of porosity than compact and hybrid films.

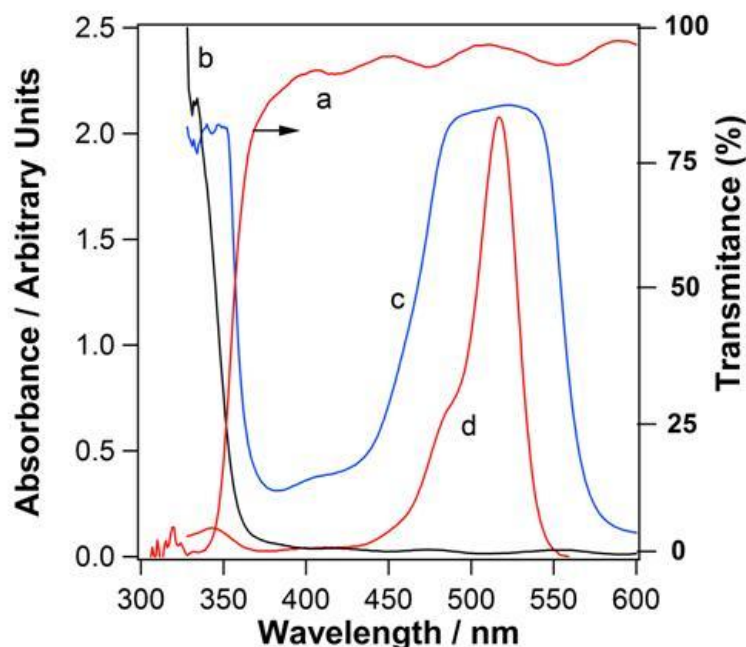
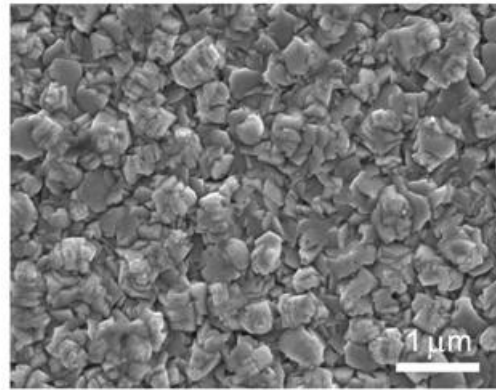
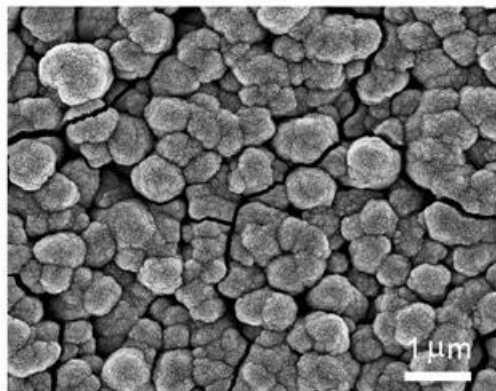


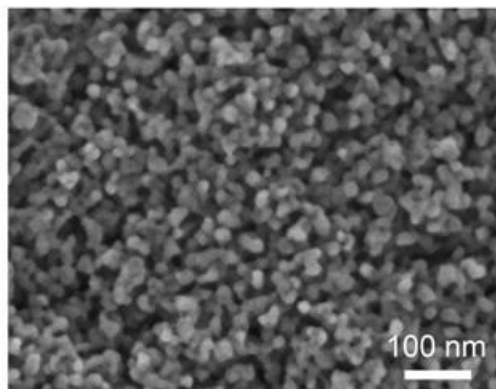
Fig. 2 (a) transmittance spectrum of ZnO film and absorption spectra for (b) ZnO film, (c) hybrid ZnO|Eosin Y film, (d) aqueous solution of eosin Y in water (50 μ M)



(a)



(b)



(c)

Fig. 3 Morphology of (a) ZnO film and hybrid ZnO/Eosin Y film (b) before and (c) after dye extraction

We have made a semiconductor hetero-junction by depositing CuSCN on ZnO films. The optical and electrical properties of CuCNS are reported elsewhere [25,26]. Deposition of CuSCN seems to occur via following intermediate reactions.



Fig. 4 illustrates chronoamperogram for deposition of CuSCN on a compact ZnO film. However, a slight deviation of chronoamperogram is observed when ZnO contains eosin Y. Formation of CuSCN electrodes seems to be controlled by diffusion of Cu(SCN)^+ toward the electrode. Formation of CuCNS by this technique was confirmed by XRD and SEM measurements. X-ray diffractogram of CuSCN|ZnO hetero-junction is also shown as the insert in Fig. 4. Characteristics peaks are identified due to CuSCN, ZnO and SnO_2 . As is observed CuSCN films (on ZnO) exhibit high degree of crystallinity with the orientation parallel to (0,0,3) axis. Growth of thin films with a preferred orientation is a specific feature of thin films [27]. However peaks belonging to other lattice planes are also observed at higher angles. In addition, morphology of junction also studied. Cross sectional views of (a) hybrid ZnO and (b) after extraction of eosin Y from the hybrid film are shown in Fig. 5.

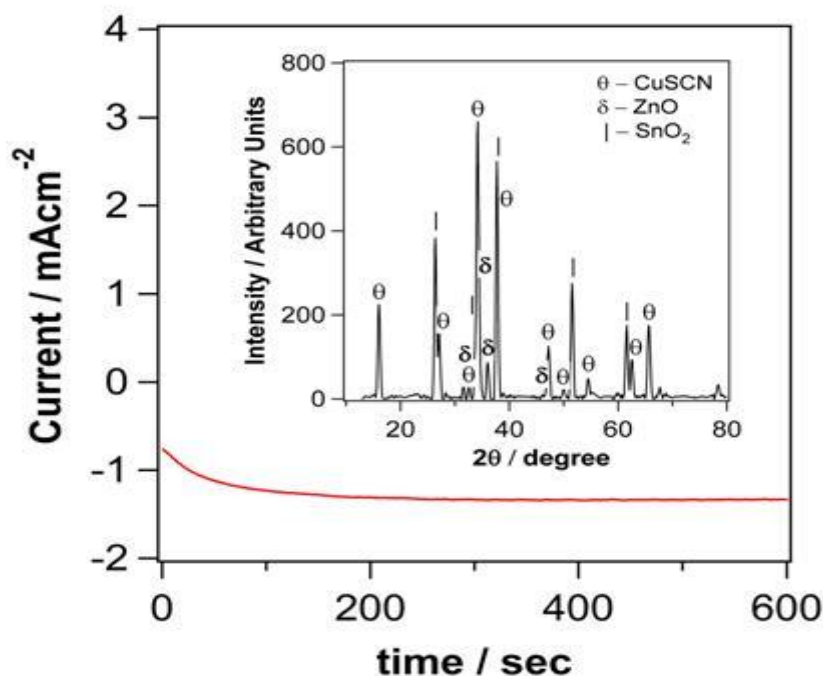


Fig. 4 Chronoamperograms for deposition of CuSCN on ZnO film. Ethanol is used as the electrolyte. Inset shows the x-ray diffractogram of ZnO|CuCNS hetero-junction on FTO.

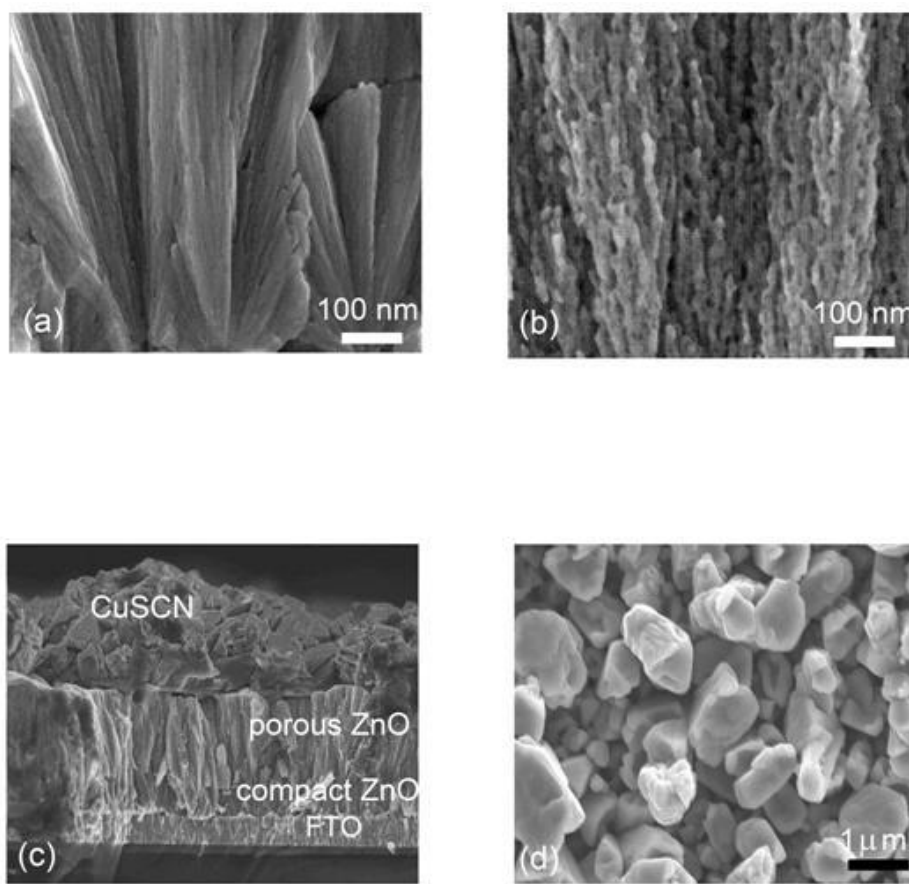


Fig. 5 Cross sectional images of hybrid ZnO/eosin Y film a) before and (b) after dye extraction, (c) p-CuSCN/n-ZnO hetero-junction on FTO and (d) morphology of the surface of CuSCN layer

Hybrid ZnO exhibits cracks and pinholes free structure. However, highly porous structure is observed after extracting eosin Y from hybrid films. Cross sectional view of CuSCN/ZnO hetero-junction is also shown in Fig. 5. Several physically different layers are observed in the image c and are recognized as FTO, compact ZnO, porous ZnO and CuSCN from the characteristics features of each layer. The surface of CuSCN layer is also shown in the same figure (image d). CuSCN films exhibit wide distribution in grains. XRD and SEM measurements reveal formation of physical contact between ZnO and CuSCN layers. Formation of semiconductor hetero-junction electronically is confirmed by current-voltage measurements.

Dark current-voltage characteristics of CuSCN/ZnO hetero-junction are shown in Fig. 6 (curve a). As is observed, a sudden rise of current is observed when the CuSCN layer is anodically polarized from the equilibrium. Such significant current flow is generally observed on p-n junctions close to the breakdown potential. However, we did not observe any significant change in current flow when the applied potential is increased toward more negative direction from the equilibrium. The observed rather poor current

flow is due to migration of minority carriers (ie. electron in the CuCNS layer toward ZnO layer due to high potential gradient at the space charge layer). A significant positive shift of current-voltage characteristics toward more positive direction is observed in the presence of organic dyes molecules (eg. mercurochrome) on ZnO films (curve b). Similar a positive shift of current-voltage characteristics has been generally observed on sensitized n-type semiconductors due to change of flat band position of host material compare to bare semiconductor [28]. A feeble charge generation is observed for hetro-junction prepared by using sensitized ZnO films and CuSCN, under illumination.

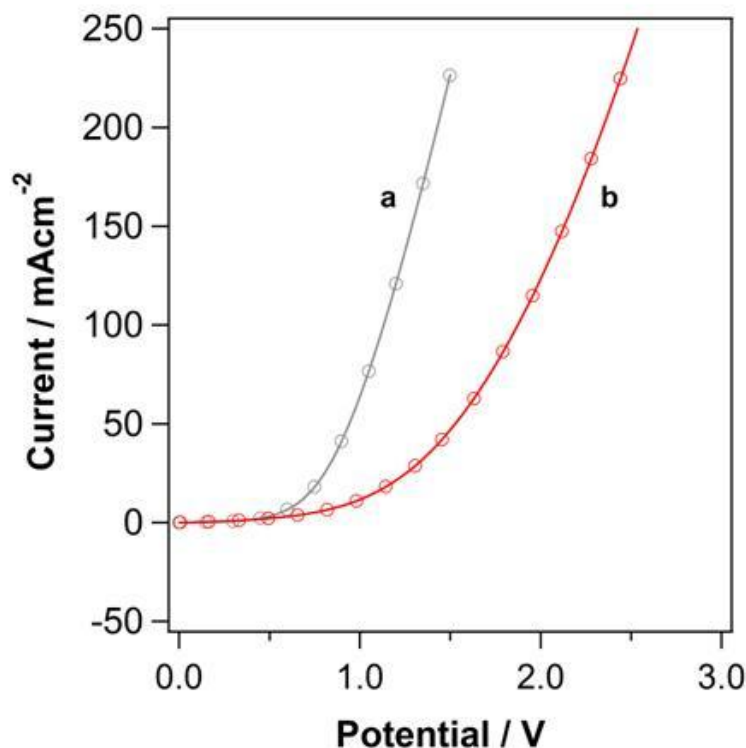


Fig. 6 Current-voltage characteristics of a) p-CuSCN|n-ZnO hetro-junction, b) p-CuSCN|mercurochrome|n-ZnO device, at dark

Current-voltage characteristics of ZnO|mercurochrom|CuSCN cell under illumination are shown in Fig. 7. The maximum photocurrent of 0.36 mAcm^{-2} and photo-voltage of 290 mV are observed from this device. Absorption spectrum of mercurochrome is also shown as the inset of the same figure. However, photo-properties of this device is not comparable with other sensitized solid-state devices [3, 4, 11]. Poor performance of this device may be due to inefficient charge separation at the interface caused due to penetration of fewer amounts of CuSCN into the ZnO films. Lose of excited energy of dye molecules via quenching of dye aggregates may be another reason.

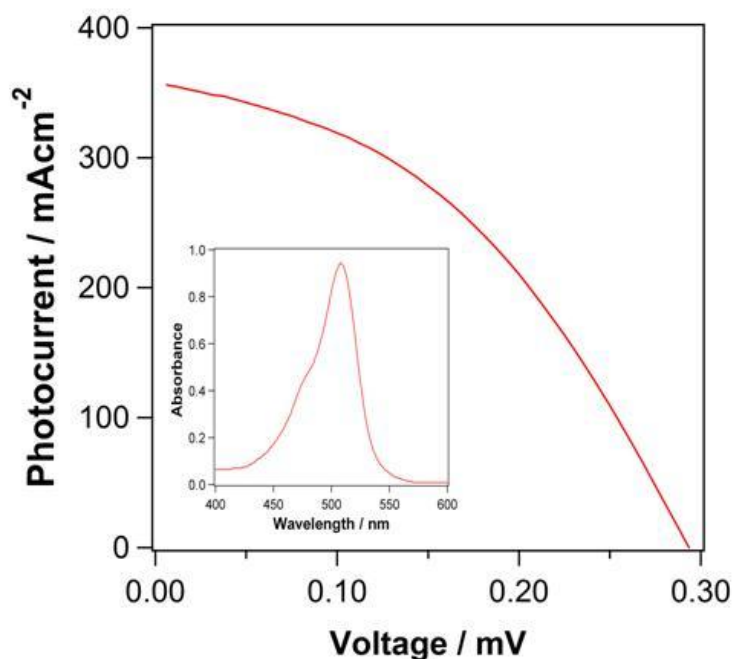


Fig. 7 (a) Current-voltage characteristics of CuSCN|mercurochrome|ZnO device under illumination, light intensity 100 mWcm^{-2} and inset shows the absorption spectrum of mercurochrome.

4. CONCLUSION

A simple low temperature electro-chemical technique is developed to fabricate a semiconductor hetero-junction. p-CuSCN|n-ZnO hetero-junction exhibits excellent rectification effect under polarization. Capability of usage of ZnO as an alternative for titania film in dye-sensitized solid state cells is demonstrated.

REFERENCES

1. D. G. Baik, and S.M. Cho, *Application of sol-gel derived films for ZnO/n-Si junction solar cells*, Thin Solid Films, **354**, (1999) 227-231
2. B.R. Sankapal, A. Ennaoui, T. Guminskaya, Th. Dittrich, W. Bohne, J. Rorich, E. Strub M.Ch. Lux-Steiner, *Characterization of p-CuI prepared by the SILAR technique on Cu-tape/n-CuInS₂ for solar cells*, Thin Solid Films, **480-481**, (2005) 142-146
3. M. Rusop, T. Shirata, P.M. Sirimanne, T. Soga, T. Jimbo, and M. Umeno, *Study on the properties and charge generation in dye-sensitized n-TiO₂/dye/p-CuI solid state photovoltaic solar cells*, Applied Surface Sci. **252**, (2006) 7389-7396.

4. P.M. Sirimanne, T. Shirata, T. Soga, and T. Jimbo, *Charge generation in a dye sensitized solid-state cell under different modes of illumination*, J. Solid State Chem. 166, (2002) 142-147.
5. P.M. Sirimanne, E.V.A. Premalal, P.K.D.D.P. Pitigala, and K. Tennakone, *Utilization of MEH-PPV as a sensitizer in titania based photovoltaic cells*, Sol. Energy Mater. & Solar Cells, 90, (2006) 1673-1679.
6. K. Tennakone, G. R. R. A. Kumara, A. R. Kumarasinghe, K. G. U. Wijayantha, and P. M. Sirimanne, *A dye sensitized nano-porous solid-state photovoltaic cell*, Semicond. Sci.Technol. 10(12), (1995) 1689–1693.
7. G.R.A. Kumara, A. Konno, K. Shiratsuchi, J. Tsukahara, and K. Tennakone, *Dye-Sensitized Solid-State Solar Cells: Use of Crystal Growth Inhibitors for Deposition of the Hole Collector*, Chem. Mater. 14, (2002) 951–955.
8. K. Tennakone, G.R.R.A. Kumara, K.G.U. Wijayantha, I.R.M. Kottegoda, V.P.S. Perera, and G.M.L.P. Aponsu, *Semicond. Nano-porous solid-state photovoltaic cell sensitized with tannin*, Sci. Technol. 13(1), (1998) 134–138.
9. K. Tennakone, G.R.R.A. Kumara, I.R.M. Kottegoda, V.P.S. Perera, and P.S.R.S. Weerasundara, *Sensitization of nano-porous films of TiO₂ with santalin (red sandalwood pigment) and construction of dye-sensitized solid-state photovoltaic cells*. J. Photochem. Photobiol. A, Chem. 117(2), (1998) 137–142.
10. P.M. Sirimanne, and T. Soga, *Fabrication of a solid-state cell using vitamin C as sensitizer*, Sol. Energy Mater. and Sol. Cells, 80 (2003) 383–389.
11. G.R.A. Kumara, S. Kaneko, M. Okuya, B. Onwona-Agyeman, A. Konno, and K. Tennakone, *Shiso leaf pigments for dye-sensitized solid-state solar cell*, Solar Energy Mater and Solar Cells, 90 (2006) 1220-1226.
12. P.M. Sirimanne, and H. Tributsch, *Generation of inhomogeneous photocurrent in solid-state TiO₂/dye/CuI cells and effect of ligands attached to surfactant on morphology of CuI films*, Sol. Energy, 81 (2007) 535–539
13. P.M. Sirimanne, M.K.I. Senevirathna, E.V.A. Premalal, and P.K.D.D.P. Pitigala, *A solid-state solar cell sensitized with mercurochrome*, Curr. Sci., 90 (2006) 639–640.
14. B. Onwona-Agyeman, S. Kaneko, G.R.A. Kumara, M. Okuya, K. Murakami, A. Konno, and K. Tennakone, *Sensitization of Nanocrystalline SnO₂ Films with Indoline Dyes*, Jpn. J. Appl. Phys. 44 (2005) L731–L733.
15. G.K.R. Senadeera and W.M.T.C. Pathirathne, *Utilization of conducting polymer as a sensitizer in solid-state photocells*, Curr. Sci., 87(3) (2004) 339–342.
16. K. Tennakone, G.R.R.A. Kumara, I.R.M. Kottegoda, V.P.S. Perera, and G.M.L.P. Aponsu, *Nanoporous n- TiO₂/selenium/p-CuCNS photovoltaic cell*, J. Phys. D, Appl. Phys., 31, (1998) 2326–2330.
17. P.M. Sirimanne, and E.V.A. Premalal, *Optical properties of Poly-[2-methoxy-5-(2-ethyl-hexyloxy)-phenylene vinylene and its application in photovoltaic cells*, Sri Lankan J. of Physics, 8 (2007) 29-37.

18. A. Goux, T. Pauporte, T. Yoshida, and D. Lincot, *Mechanistic study of the electrodeposition of nano-porous self assembled ZnO/eosin Y hybrid thin films: effect of eosin Y concentration*, *Langmuir*, 22(25) (2006) 10545-10553
19. A. Goux, T. Pauporte, T. Yoshida, and D. Lincot, *Oxygen reditton on electrodeposited Zinc oxide electrodes in KCl solution at 70 °C*, *Electrochimica Acta*, 51(15), (2006) 3168-3172
20. T. Yoshida, T. Pauporte, D. Lincot, T. Oekermann, and H. Minour, *Cathodic electrodeposition of ZnO/eosin Y hybrid thin films from oxygen saturated aqueous solution of ZnCl₂ and eoysin Y*, *J. Electrochem. Soc.*, 150 (2003) C608-C615.
21. T. Oekermann, T. Yoshida, D. Schlettwein, T. Sugiura, and H. Minoura, *Photoelectrochemical properties of ZnO/tetrasulfophthalocyanine hybrid thin films prepared by electrochemical self-assembly*, *Phys.Chem.Chem.Phys.*, 3 (2001) 3387-3392.
22. J. B. Zhang, T. Yoshida, D. Komatsu and H. Minoura, *Electrocatalytic role of eosin Y during electrodeposition of Zinc oxide/eosin Y hybrid thin films*, 16th International Conference on Photochemical Conversion and Storage of Solar Energy, July 2-7, 2006, Uppsala, Sweden, IPS-16 Book of Abstract W7-P-21.
23. K. Hara, T. Hoguci, T. Kinoshita, K. Sayama, H. Sugihara, and H. Arakawa, *Highly efficient photon-to-electron conversion with mercurochrome-sensitized nanoporous oxide semiconductor solar cells*, *Solar Energy Matter and Solar Cells*, 64 (2000) 115-134
24. R.F. Khairutdinov, and N. Serpone, *Photophysics of Cyanine Dyes: subnanosecond relaxation dynamics in monomers, dimers, and H- and J-aggregates in solution*, *J. Phys. Chem.*, B 101 (1997) 2602-2610.
25. D.L. Smith and V.I. Saunders, *Preparation and structure refinement of the 2H-poly type of CuSCN*, *Acta. Crystallogr. B*, 38 (1982) 907-909.
26. K. Tennakone, A.H. Jayatissa, C.A.N. Fernando, S. Wickramanayake, S. Punchihewa, L.K. Werasena and W.D.R. Premasiri, *Semiconducting and Photoelectrochemical Properties of n- and p-Type β-CuCNS*, *Phys. Stat. Solidi (a)*, 103 (1987) 491-497.
27. J. Hinze, and K. Ellmer, *In situ measurement of mechanical stress in polycrystalline zinc-oxide thin films prepared by magnetron sputtering*, *J. Appl. Phys.* 88 (5) (2000) 2443-2449
28. P.M. Sirimanne, I. Senevirathna, and K. Tennakone, *An enhancement of photoproperties of solid-state TiO₂/dye/CuI type cells by coupling mercurochrome with natural juice extracted from pomegranate fruits*, *Chem. Lett.*, 34-11 (2005) 1568-1569