

# FLEXIBLE DYE-SENSITIZED SOLAR CELL BASED ON PRE-DYED ZINC OXIDE NANOPARTICLE

Priya Chandan Satpathy<sup>1</sup> and Chandrakanta Nayak<sup>2</sup>

<sup>1</sup>Aryan Institute of Engineering & Technology, Bhubaneswar, Odisha

<sup>2</sup>NM Institute of Engineering and Technology, Bhubaneswar, Odisha

---

**Abstract:** Dye-sensitized solar cells (DSSCs) based on dyed zinc oxide (ZnO) nanoparticles made by simple pre-dyeing method have been developed. Nanoporous ZnO film has been fabricated on transparent conducting oxide plastic polymer substrates. In order to improve lower porosity and bad interparticle connectivity, hot-press method was applied to pre-dyed ZnO film on the plastic substrate photoelectrode. The result that the hot-press treatment greatly improved the short circuit current of DSSCs based on pre-dyed ZnO, indicates electrical contact of nanoparticles plays crucial role. In order to increase conversion efficiency, one of important points is how to enhance absorption of photon in wide wavelength region. We have successfully demonstrated that DSSCs based on two different kinds of pre-dyed ZnO composite film can expand absorption wavelength region and showed remarkable improvement of short circuit current.

---

**Keywords:** Pre-dyeing method, Hot-press treatment, Pre-dyed zinc oxide nanoparticle, Mixed dye sensitization, Flexible plastic substrate

## 1. INTRODUCTION

Many researchers throughout the globe have focused on developing highly efficient and low-cost photovoltaic devices to endure the present and future energy crisis issues. However, the relatively high production costs of ordinary solar cells have limited their widespread commercialization. In this regard, dye-sensitized solar cells (DSSCs) reported by O'Regan and Grätzel in 1991 are one of the promising candidates for the next-generation solar cell because of their relatively easy fabrication procedures, high energy conversion efficiency (~ 13%), low production cost [1, 2]. In particular, with the growing demand for daily electricity, based on extensive research on solar cells, flexible solar cells have more advantages [3]. Flexible solar cells can be applied to different shapes of buildings or equipment surfaces, such as portable solar modules. In flexible substrates based on plastics, paper or metal foils, flexible DSSCs using thin and lightweight conductive plastic substrates are more advantageous for industrial production through roll-to-roll processes and their potential has attracted wide attention. In conventional preparation, the mesoporous photoelectrode of the DSSCs require a heat treatment higher than 450°C so that the photoelectrode can achieve good adhesion between the particle - particle and particle-substrate. However, flexible plastic substrates can only be endured at temperatures below 150°C [4, 5]. In order to overcome this limitation, several low-temperature techniques [6, 7], microwave sintering [8, 9], including chemical sintering [10], mechanical

compressing [11-14], electrophoretic deposition (EPD) [15], hydrothermal necking [16, 17] and ultrasonic spray-coating [18] have been reported. Even though these successful fabrication of DSSCs on plastic substrate, another problem is the dyeing process. It usually takes several hours. The time-consuming dyeing process will obscure the merit of high speed production such as swift-running roll-to-roll process. We have studied the alternative ZnO based on conventional mesoporous TiO<sub>2</sub>. It is known that ZnO has higher electron mobility than TiO<sub>2</sub> [19, 20], which makes it an ideal choice.

In addition, when the under standard AM1.5G illuminated conditions and tested, the display efficiency of more than 7%. The solution-processing of the ZnO layer is simple and economical, and can be carried out at room temperature, which is more advantageous than other battery designs [21]. From these viewpoints, we developed a simple method in which dyeing process is applied to ZnO nanoparticle then pre-dyed ZnO (pd-ZnO) paste is applied to transparent electrode substrate to form colorednanoporous ZnO photoelectrode. We call this process as pre-dyeing method. By employing this method, time-consuming dyeing process can be removed from roll-to-roll process. Another advantage of this method is facile preparation of multiple dye pd-ZnO film. Mixed dye paste is easily prepared by mixing two kinds of pd-ZnO in a solvent. We have attempted to improve the efficiency of DSSCs based on the combination of different pd-ZnO, which absorb the light of different wavelength region. Possible drawback of pre-dyeing method is inadequate connection of ZnO nanoparticles. In this work, nanoporous ZnO photoanode have been successfully formed on the ITO/PEN conductive flexible substrate by hot-press method [22]. The calcination or sintering step can be omitted by employing this method. The method produces relatively compact ZnO layer, the thickness may be changed by hot press treatment [23].

## 2. EXPERIMENTAL

### *Preparation of pre-dyed ZnO paste*

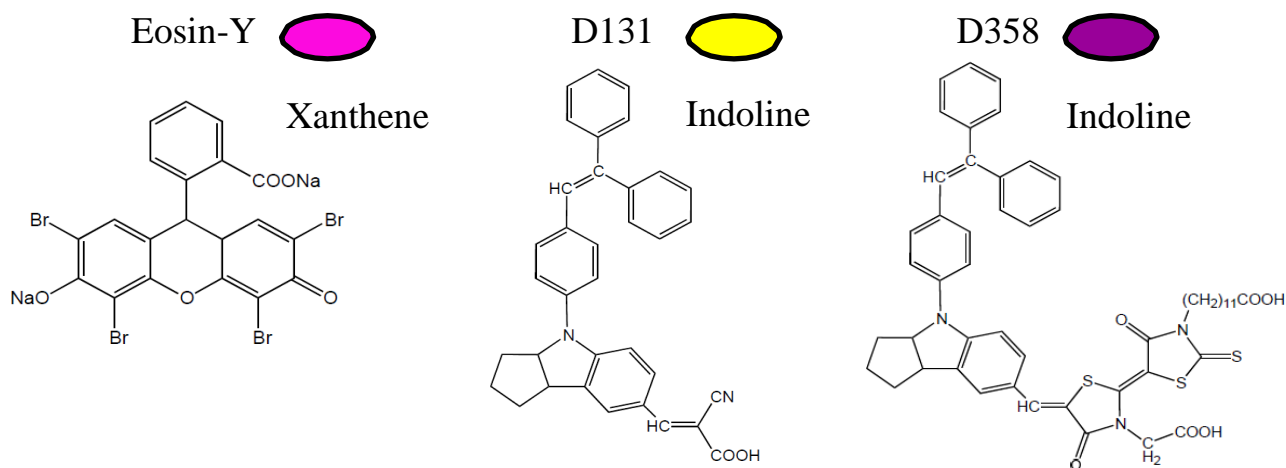
Ethanol and EosinY (2',4',5',7'-Tetrabromofluorescein) dye were obtained from Aldrich. D131 dye (2-Cyano-3-[4-[4-(2,2-diphenylethenyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopent[b]indol-7-yl]-2-propenoic acid) was obtained from Mitsubishi Paper Mills Ltd., D149 dye (5-[[4-[4-(2,2-Diphenylethenyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopent[b]indol-7-yl]methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-3-thiazolidineacetic acid) and D358 dye (5-[3-(Carboxymethyl)-5-[[4-[4-(2,2-diphenylethenyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopent[b]indol-7-yl]methylene]-4-oxo-2-thiazolidinylidene]-4-oxo-2-thioxo-3-thiazolidinedodecanoic acid) were also obtained from Mitsubishi Paper Mills Ltd. Chenodeoxycholic acid was obtained from Wako Pure Chemical Industries, Ltd. Iodine (I<sub>2</sub>), Acetonitrile (ACN) and tert-butyl alcohol were obtained from Kanto Chemical Co. Inc. and their water molecules were removed by molecular sieves (4A). ZnO powder (Finex50, ca. 20 nm) was obtained from Sakai Chemical Industry Co. Ltd. Indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrate (30~50 Ωsq.<sup>-1</sup>, Touki Co. Ltd., Japan) was used as the substrate for the ZnO photoanode.

a) Preparation of single pd-ZnO paste: EosinY dye in ethanol solution of 40 ml, adjusted to 2.5

mM, 5.0 mM, 7.5 mM, 1.25 mM, 1.75 mM, dye solution, adding 1 g of ZnO powder into the above solution, respectively. Under airtight and shading conditions, the solution was stirred for 24 hours by magnetic stirrer at room temperature. After filtration, pre-dyed ZnO powder (pd-ZnO) was dried in air. Finally, pd-ZnO paste was prepared by adding ethanol (3 ml) and sonicated before use. These processes are depicted in scheme 1. In the case of the other dyes, pd-ZnO paste was prepared as follows. The D131 dye (25.6 mg) / chenodeoxycholic acid (1:2 by molar ratio) were dissolved in the mixture of acetonitrile (20 ml) and tert-butanol (20 ml) to form dye solution. As the same method above, we were obtained dye solution and synthesized pd-ZnO pastes.

b) Preparation of mixed pd-ZnO paste: Added 0.5 g ZnO powders into the above dye solution to prepare pd-ZnO powders, then mixed two kinds of them (1:1 by weight ratio) to produce hybrid .

slurry for the preparation of film layer. The structures of dyes (Eosin Y, D131 and D358) are shown in figure 1.



**Figure 1.** The structures of dyes used. Eosin Y:  $C_{20}H_8Br_4Na_2O_5$ , Mol. Wt. is 693.87; D131 dye:  $C_{35}H_{28}N_2O_2$ , Mol. Wt. is 508.61 and D358 dye:  $C_{52}H_{53}N_3O_6S_3$ , Mol. Wt. is 912.19.

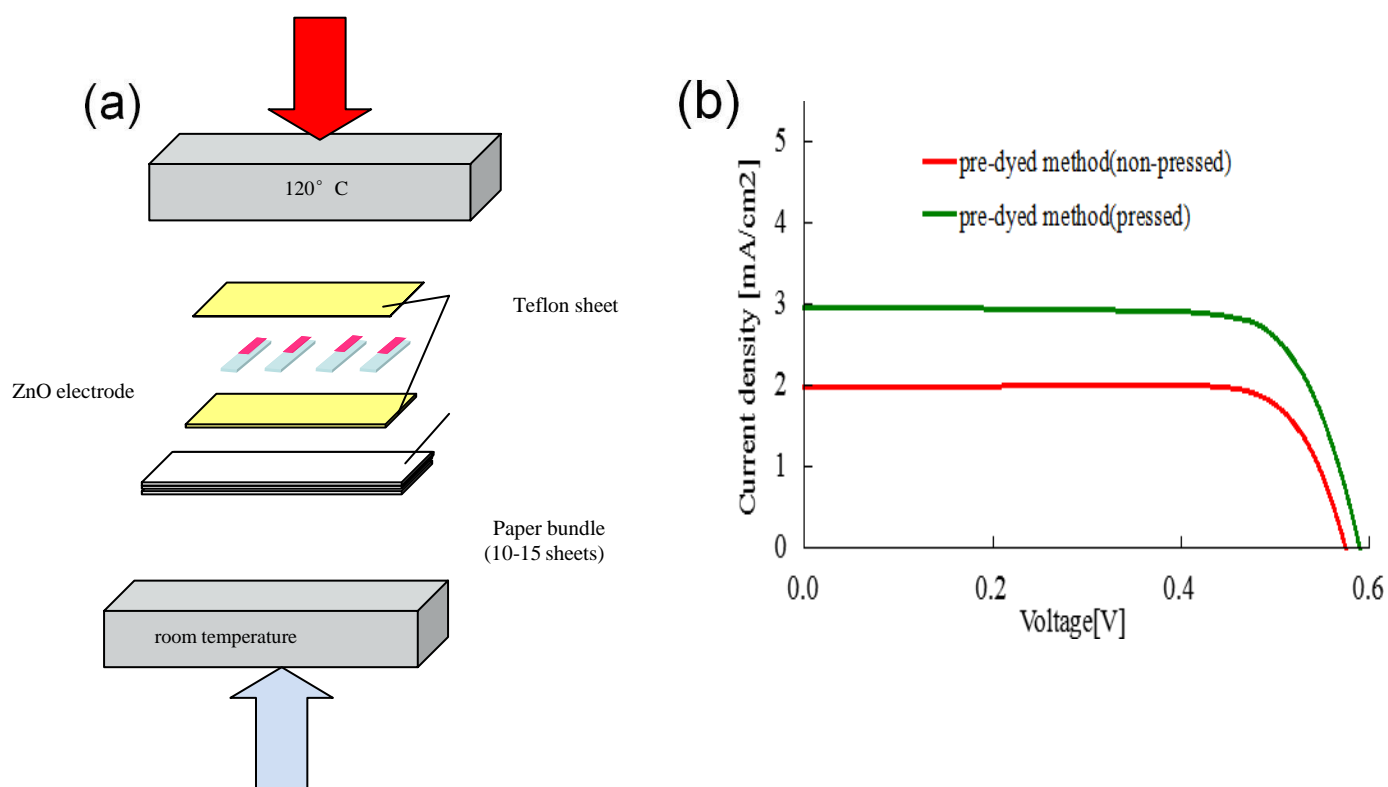
#### *Fabrication of the dye sensitized solar cells*

EosinY dye in ethanol solution of 40 ml, adjusted to 1.25 mM dye solution, adding 1 g of ZnO powder into the above solution, respectively. Under airtight and shading conditions, the solution was stirred for 24 hours by magnetic stirrer at room temperature. After filtration, obtained pre-dyeing ZnO powder (pd-ZnO) was dried under air. Finally, 1 g of pd-ZnO was dispersed in ethanol (3 ml) using homogenizer to prepare pd-ZnO paste. Indium tin oxide/polyethylene terephthalate (ITO/PET) plastic substrates were washed with ethanol. The paste was sonicated for 15 min in an ultrasonic bath to form a viscous pd-ZnO paste. Then, the ZnO paste was applied onto ITO/PET substrates using squeegee method. The prepared films were pressed under 20 Mpa conditions of pressure and 120°C for 20 s, and in the meantime adhesion of the coating were improved by hot-press conditions. To evaluate their photovoltaic performance, the dye-sensitized ZnO/PET films were sandwiched with Pt counter electrode. The electrolyte, mixture of 3.1 g tetra-n-propyl ammonium iodide, 0.25 g  $I_2$  in 20 ml solution of acetonitrile/ethylene carbonate (1:4 by volume), was injected into the space between the

sandwiched cells. The active area of the dye coated ZnO film was  $0.25 \text{ cm}^2$ .

### 3. RESULTS AND DISCUSSION

In the case of pd-ZnO, it is conceivable that the whole surface of ZnO particle could be covered with dye, resulting in deterioration of the contact between the ZnO particles and reduction of the electrical conductivity [24]. In order to solve this problem, hot-press treatment was applied to Eosin Y pd-ZnO film.



**Figure 2.** (a) The hot-press process of pd-ZnO film on ITO/PET substrate, (b) I-V characteristics of DSSCs with or without hot-press process. The total active area of the cell was  $0.25 \text{ cm}^2$ . Dye: Eosin Y.

Figure 2(b) and table 1 show the photovoltaic performance of DSSCs based on pd-ZnO with or without hot-press treatment. Without hot-press:  $J_{sc} = 1.97 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.57\text{V}$ ,  $FF = 0.80$  and  $\eta = 0.90\%$ ; with hot-press:  $J_{sc} = 2.97 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.59 \text{ V}$ ,  $FF = 0.75$  and  $\eta = 1.31\%$ . As for the conventional method, almost no change due to hot press treatment was found. This is regarded to improve the contact between the particles by pressing, but at the same time, the pores of the porous thin film are buried, the surface area decreases, lead to the amount of dye adsorption decreases. After

hot-press treatment, adhesion of pd-ZnO film to the flexible substrate can be improved, and the compact layer becomes more homogeneous [25-27]. The lower charge transfer resistance, higher photocurrent,  $J_{sc}$  is about 50% improved. The ZnO surface to crushed and exposed ZnO nanoparticles not adsorbed the dye by applying a hot press treatment, it is expected that compact contact between the particles is improved and movement of electrons becomes smooth. ZnO film thickness was reduced from 10-15m to 4-5m. This implies that both of the connection between ZnO nanoparticles and the electrical contact between ITO/PEN substrate and ZnO nanoparticles are improved. Therefore, the hot-press treatment is essential for fabricating efficient pd-ZnO based DSSCs.

**Table 1.** Photovoltaic performance of pd-ZnO based DSSCs with or without hot-press process used Eosin Y.

	Hot-press	Voc [V] <sup>a)</sup>	Jsc [mA/cm <sup>2</sup> ] <sup>b)</sup>	FF <sup>c)</sup>	Eff [%] <sup>d)</sup>
pd-ZnO (Eosin Y)	without	0.57	1.97	0.80	0.90
	with	0.59	2.97	0.75	1.31

a) Open-circuit voltage, b) short-circuit photocurrent density, c) fill factor, and d) light-

to-electricity conversion efficiency of pd-ZnO based DSSCs. The fill factor can assume values between 0 and less than 1 and is defined by the ratio of the maximum power ( $P_{max}$ ) of the solar cell per unit area divided by the Voc and Jsc according to  $FF = P_{max}/(J_{sc}V_{oc})$ .

#### 4. CONCLUSIONS

DSSCs based on pre-dyed ZnO nanoparticle were fabricated on flexible plastic substrate. The performance of DSSCs was remarkably improved by the hot-press treatment of pd-ZnO film on ITO/PEN substrate. For example, in the case of Eosin Y pd-ZnO based DSSC, short circuit current density was increased from 1.97 mA cm<sup>-2</sup> to 2.97 mA cm<sup>-2</sup>. The results suggests that  $j_{sc}$  was improved about 50% by hot press treatment. It is considered that pre-dyeing method with ZnO adsorbs in advance dye on the particle surface, so that the compact contact between the ZnO particles deteriorates, the conductivity becomes poor, and  $J_{sc}$  decreases. However, the hot press treatment improved both of the connection between ZnO nanoparticles and the electrical contact between ITO/PEN substrate and ZnO nanoparticles. By changed the dye concentration, we found that the dye concentration of 1.25mM, ordinary ZnO prepared flexible DSSC efficiency similar basically. In addition, the solar-to-electric conversion efficiency of 4.56% under 1 sun illumination was achieved in DSSC based on the combination of D149 and D131 pd-ZnO. Wide range wavelength light absorption by virtue of dye combination contribute the improvement of short circuit current. To the best of our knowledge, this is first successful example of colored paint (pd-ZnO paste) based DSSCs. Pre-dyeing method is promising especially for the production of flexible DSSCs made by roll-to-roll process.

## References

1. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, *Chem. Rev.*, 110, (2010) 6595.
2. B. O'Regan, and M. Grätzel *Nature.*, 353 (1991) 737.
3. C. Hasitha, Weerasinghe, F. Z. Huang, Y. B. Cheng, *Nano Energy.*, 2 (2013) 174.
4. K. M. Lee, W. H. Chiu, M. D. Lu, and W. F. Hsieh, *J. Power Sources*, 196 (2011) 8897.
5. H. W. Chen, C. Y. Lin, Y. H. Lai, J. G. Chen, C. C. Wang, C. W. Hu, K. C. Ho, *J. Power Sources*, 196 (2011) 4859.
6. J. M. Ball, M. M. Lee, A. Hey and H. J. Snaith, *Energy Environ. Sci.*, 6 (2013) 1739.
7. M. J. Carnie, *Chem. Commun.*, 49 (2013) 7893.
8. S. Uchida, M. Tomiha, H. Takizawa, M. Kawaraya, *J. Photochem. Photobiol. A.*, 164 (2004) 93.
9. S. Uchida, M. Tomiha, N. Masaki, A. Miyazawa, H. Takizawa, *Sol. Energy Mater. Sol. Cells.*, 81 (2004) 135.
10. N. G. Park, K. M. Kim, M. G. Kang, K. S. Ryu, S. H. Chang, Y. J. Shin, *Adv. Mater.*, 17 (2005) 2349.
11. H. Lindstrom, A. Holmberg, E. Magnusson, L. Malmqvist, A. Hagfeldt, *J. Photochem. Photobiol. A.*, 145 (2001) 107.
12. H. Lindstrom, A. Holmberg, E. Magnusson, S.E. Lindquist, L. Malmqvist, A. Hagfeldt, *Nano Lett.*, 1 (2001) 97.
13. G. Boschloo, H. Lindstrom, E. Magnusson, A. Holmberg, A. Hagfeldt, *J. Photochem. Photobiol. A.*, 148 (2002) 11.
14. S. A. Haques, E. Palomares, H. M. Upadhyaya, L. Otley, R. J. Potter, A. B. Holmes, J. R. Durrant, *Chem. Commun.*, (2003) 3008.
15. T. Miyasaka, Y. Kijitori, *J. Electrochem. Soc.*, 151 (2004) A1767.
16. D.S. Zhang, T. Yoshida, K. Furuta, H. Minoura, *J. Photochem. Photobiol. A.*, 164 (2004) 159.
17. D.S. Zhang, T. Yoshida, H. Minoura, *Adv. Mater.*, 15 (2003) 814.
18. H. G. Han, H. C. Weerasinghe, K. M. Kim, J. S. Kim, Y. B. Cheng, D. J. Jones, A. B. Holmes, T. H. Kwon, *Sci. Rep.*, 5 (2015) 14645.
19. Q. Zhang, C. S. Dandeneau, X. Zhou and G. Cao, *Adv. Mater.*, 21 (2009) 4087.
20. R. Vittal, K. C. Ho, *Renew Sust Energ Rev.*, 70 (2017) 920.
21. M. Liu, M. B. Johnston and H. J. Snaith, *Nature.*, 501 (2013) 395.
22. C. Kim, S. Kim, and M. Lee, *Appl. Surf. Sci.*, 270 (2013) 462.
23. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science.*, 338 (2012) 643.
24. J. Shao, F. Liu, W. Dong, R. Tao, Z. Deng, X. Fang, and S. Dai, *Mater. Lett.*, 68 (2012) 493.
25. S. H. C. Mohammad, K. Naoki, S. Tetsuo, *Mater. Res. Bull.*, 80 (2016) 135.
26. S. H. C. Mohammad, K. Naoki, S. Tetsuo, *J. Alloys Compd.*, 656 (2016) 476.
27. S. Y. Lin, J. J. Wu, *Electrochim. Acta.*, 152 (2015) 61.
28. M. Peng, B. Dong X. Cai, W. Wang, X. M. Jiang, Y. H. Wang, Y. Yang, D. H. Zou, *Solar Energy.*, 150 (2017) 161.
29. D. Kumar, K. Y. Wong, *Materials Today Energy* 5 (2017) 243.
30. M. A. Green, K. Emery, Y. Hishikawa and W. Warta, *Prog. Photovolt: Res. Appl.*, 17, (2009) 320.
31. Y. Ogomi, S. S. Pandey, S. Kimura, and S. Hayase, *Thin Solid Films.*, 519 (2010) 1087.
32. Y. J. Chae, S. J. Kim, J. H. Kim, E. Kim, *Dyes Pigm.*, 113 (2015) 378.