

Short Communication

Development of Flexible Dye-sensitized Solar Cell Based on Pre-dyed Zinc Oxide Nanoparticle

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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 TiO₂. It is known that ZnO has higher electron mobility than TiO₂ [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 colored nanoporous 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

2.1 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 (I₂), 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.⁻¹, Touki Co. Ltd., Japan) was used as the substrate for the ZnO photoanode.

a) Preparation of single pd-ZnO paste: Eosin Y 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.

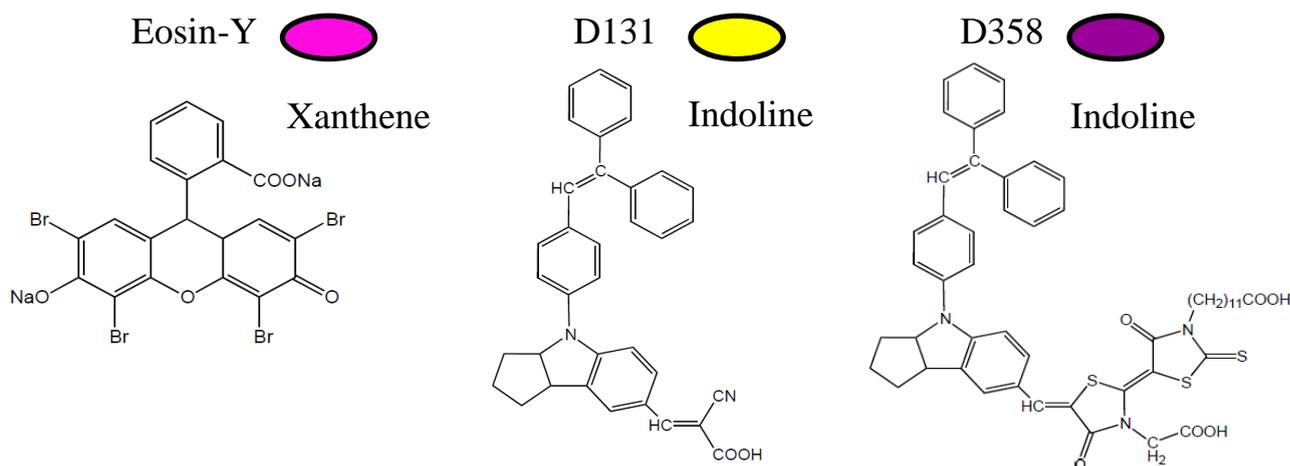


Figure 1. The structures of dyes used. Eosin Y: C₂₀H₈Br₄Na₂O₅, Mol. Wt. is 693.87; D131 dye: C₃₅H₂₈N₂O₂, Mol. Wt. is 508.61 and D358 dye: C₅₂H₅₃N₃O₆S₃, Mol. Wt. is 912.19.

2.2 Fabrication of the dye sensitized solar cells

Eosin Y 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 I₂ 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 cm².

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.

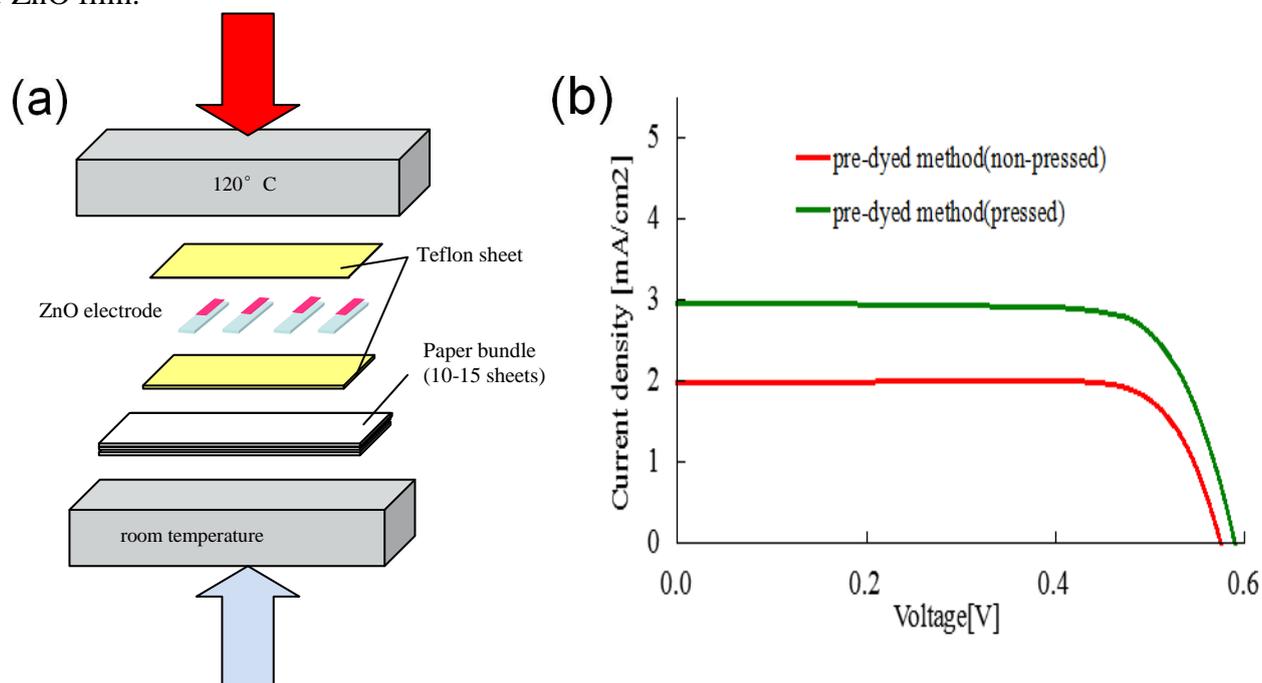


Figure 2. (a) The hot-press process of pd-ZnO film on ITO/PET substrate, (b) I-V characteristics of DSSCs with or without hot-press process. The total active area of the cell was 0.25 cm². Dye: Eosin Y.

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] ^{a)}	Jsc [mA/cm ²] ^{b)}	FF ^{c)}	Eff [%] ^{d)}
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 $FF = P_{max}/(J_{sc}V_{oc})$.

Since the amount of dye adsorption on ZnO particle can greatly affect the performance of DSSCs, the concentration of dye solution was optimized using D149 dye. Although the organic dyes have relative narrow absorption wavelength range, they have high light absorbance ability in their absorption wavelength range [28, 29]. In conventional dyeing process, nanoporous ZnO film on ITO/PEN substrate was immersed in the dye solution, and 0.5 mM of dye concentration was satisfactory. In the case of pre-dyeing, ZnO nanopowder (Finex50, ca. 20 nm) was dispersed in the dye solution, and 0.5 mM was not best dye concentration as shown in figure 3. When dye concentration was increased from 0.5 mM to 1.25 mM, short circuit current (J_{sc}) increases with the increase of dye concentration. J_{sc} was not increased further at higher concentration (1.6 mM). Best performance ($J_{sc} = 9.49 \text{ mA cm}^{-2}$, $V_{oc} = 0.67 \text{ V}$, $FF = 0.67$ and $\eta = 4.24\%$) was achieved at 1.25 mM.

Absorption of photon in wide wavelength region is an important requirement for the enhancement of photoconversion efficiency of DSSCs. Some researchers reported that a mixture of two kinds of dye which has different wavelength absorption show the better performance to DSSCs by virtue of the absorbing the light of wider wavelength range [30, 31]. By employing pre-dyeing method, simple mixture of pd-ZnO powders adsorbed different dye was prepared and applied to DSSCs. Three kinds of dyes D131, D358 and EosinY show yellow, purple and pink color, respectively. Mixed pd-ZnO paste was easily prepared by simple mixed two kinds of pd-ZnO powder in 1:1 ratio. In the DSSC community, another basic measurement of performance is called incident photon to current conversion efficiency (IPCE). IPCE is defined as the ratio of the number of electrons generated in the circuit inside and outside the unit time and the number of incident monochromatic photons the unit time as

shown in following equation. IPCE values can provide practical information about the monochromatic quantum efficiencies of a solar cell.

$$IPCE\% = \frac{I_{sc}(A)}{P(W)} \times \frac{1240}{\lambda(nm)} \times 100$$

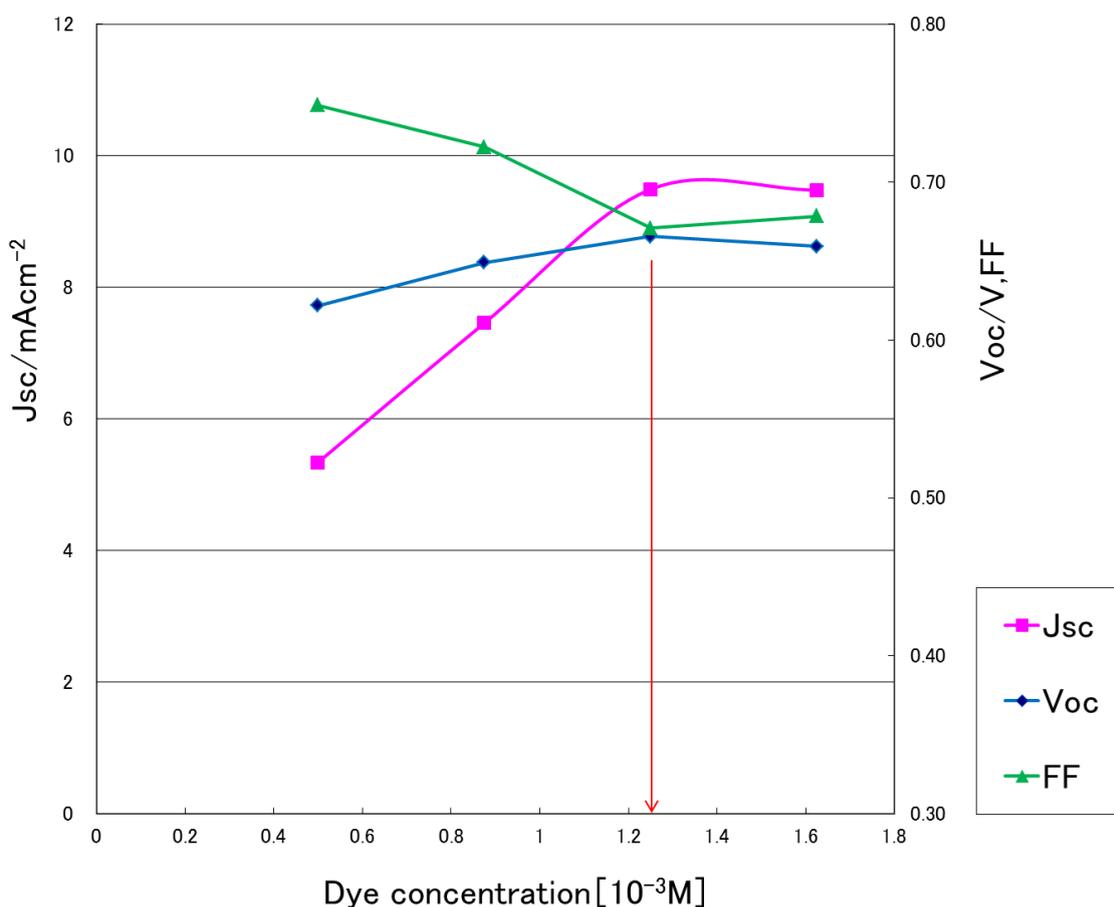


Figure 3. Variation of photovoltaic parameters, i.e., Jsc, Voc, FF depended on dye concentration. The best performance was achieved at 1.25 mM of concentration: Jsc = 9.49 mA cm⁻², Voc = 0.67 V, FF = 0.67 and η = 4.24%

In figure 4, due to the pigment wavelength characteristics, D358 DSSC's performance is better than the other two single pigments. A variety of mixed dye systems were compared with a single dye to observe changes in the absorption spectra for DSSCs using multiple dyes [32]. Efficiency improvements are observed in three kinds of DSSC made of pd-ZnO mixed film.

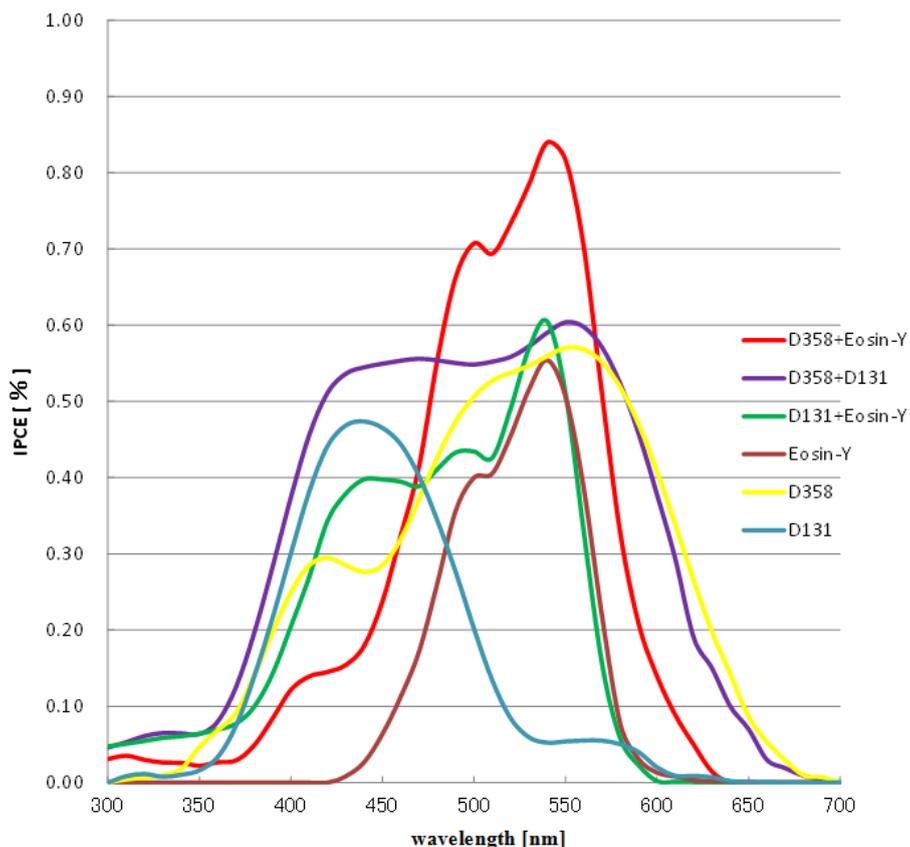


Figure 4. IPCE of mixed pigment and single pigment. Single pigment were Eosin Y, D131 and D358. Mixed pigment were D358 and Eosin Y; D358 and D131; D131 and Eosin Y.

Table 2. Photovoltaic performance of DSSCs based on pd-ZnO. The upper three rows are single pigments and lower three rows are mixed pigments.

Dye on Pd-ZnO	Voc [V]	Jsc [mA/cm ²]	FF	Eff [%]
Eosin Y	0.59	2.97	0.75	1.31
D131	0.65	3.85	0.70	1.76
D358	0.64	6.20	0.60	2.37
D131+EosinY	0.60	6.91	0.64	2.66
D358+D131	0.61	8.75	0.57	3.03
D358+EosinY	0.57	6.08	0.69	2.38

For example, DSSC based on mixture of D131 and Eosin Y pd-ZnO (green line) shows appreciable increase of IPCE at 400 nm wavelength region compared with single Eosin Y pd-ZnO based DSSC (brown line). The photoenergy conversion efficiency of mixed pd-ZnO based DSSCs are higher than that of single pd-ZnO based DSSCs except for the case of D358 and Eosin Y combination because light absorption wavelength ranges of D358 and Eosin Y are overlapped each other. In our successive investigation for various dye combination, the best results was obtained by purple D149 and D131 combination (Figure 5). The photovoltaic parameters of the best DSSC were $J_{sc} = 9.73 \text{ mA cm}^{-2}$, $V_{oc} = 0.71 \text{ V}$, $FF = 0.68$ and $\eta = 4.56\%$. It is notable that not only J_{sc} improvement but also

higher Voc contribute the improvement of efficiency. Although the reason of this Voc improvement is unclear yet, it is suggested that multiple dye combination using pre-dyeing method has some potential for improving not only Jsc by expanding absorption wavelength range but also other photovoltaic parameters such as Voc.

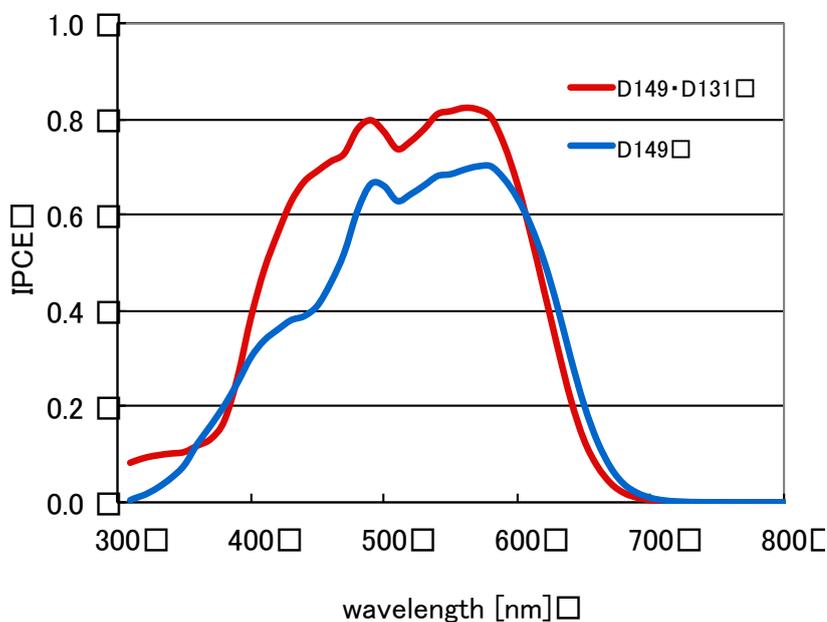


Figure 5. IPCE of DSSCs using pd-ZnO with mixed pigment and single pigment. Single pigment is D149. Mixed pigment is D149 and D131: $J_{sc} = 9.73 \text{ mA cm}^{-2}$, $V_{oc} = 0.71 \text{ V}$, $FF = 0.68$ and $Eff = 4.56\%$.

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^{-2} to 2.97 mA cm^{-2} . The results suggests that jsc 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 Jsc 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.

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