Application of pre-dyeing method to flexible dye-sensitized solar cell based on zinc oxide nanoparticle

静岡大学博士論文

Application of pre-dyeing method to flexible dye-sensitized solar cell based on zinc oxide nanoparticle

酸化亜鉛ナノ粒子に基づくフレキシブル色素増感太陽電池における先染法の応用

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Abstract

With the global warming and the increasing demands for energy, the necessity of suppression increases in carbon dioxide emissions. Thus, it has become quite essential to develop renewable energy sources and to develop non-polluting, clean sources of energy are becoming increasingly crucial. Solar energy holds the possibility of solving these energy problems. However, the relatively high production costs of ordinary solar cells have limited their widespread commercialization. But the original paper by O'Regan and Grätzel in 1991 reported that dye-sensitized solar cell (DSSC) is one of the next-generation solar cells because of their relatively easy fabrication procedures, high energy conversion efficiencies (~15%) and low production cost. Especially, with the increasing of the requirement for the portable and convenient applications, flexible substrates have been extensively investigated to be used for the solar cells. Flexible solar cells based on plastic, paper or metal foil possess more advantages than the glass-based ones. In particular, flexible DSSCs using thin and light-weight conducting plastic substrates have attracted much interest for their potential of mass production by the roll-to-roll process. In the traditional preparation of the mesoporous photoelectrode of the DSSCs, a thermal treatment higher than 450 ºC is necessary, with which the photoelectrode can have a good adhesion between the particle-particle and particle-substrate. However, the plastic substrate can only bear the temperature lower than 150 ºC. In this study, 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. However, the efficiency of DSSC made by pre-dyeing method was much lower than traditional method. 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. In order to improve lower porosity and bad interparticle connectivity, hot-press method was applied to photoelectrode on plastic substrate (ITO/PEN). This is regarded to improve the contact between the particles by pressing. However, at the same time, the pores of the porous thin film are buried, resulting in decreases of the surface area and the amount of dye adsorption. After hot-press treatment, adhesion of pd-ZnO film to the flexible substrate can be improved, and the compact layer becomes more homogeneous. It was possible to

prepare a dye-sensitized solar cell with a conversion efficiency of 1.97% by adjusting the proper quantities of dye to the zinc oxide and subjecting it to a hot press treatment using EosinY dye. In order to reach higher efficiency, D149 dye was used which has broader absorption wavelength range than EosinY dye. The solar-to-electric conversion efficiency of 4.56% under 1 sun illumination was achieved by utilizing the hot-press technique on the low-temperature preparation of nanostructured ZnO films.

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. 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. Efficiency improvements are observed in three kinds of DSSC made of pd-ZnO mixed film. For example, DSSC based on mixture of D131 and Eosin Y pd-ZnO shows appreciable increase of IPCE at 400 nm wavelength region compared with single Eosin Y pd-ZnO based DSSC. 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 yellow D131 combination. The photovoltaic parameters of the best DSSC were Jsc = 9.73 mA cm^{-2}, Voc = 0.71 V, FF = 0.68 and η =4.56%. It is notable that not only Jsc 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. Wide range wavelength light absorption by virtue of dye combination can 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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CHAPTER 1

Introduction

1.1 Energy resources and structure

Energy is the material basis of human survival and economic development. Since the industrial revolution, coal, petroleum, natural gas, hydropower, nuclear power and renewable energy have massively entered the field of human activity. The evolution of the energy structured to promote and reflect the world's economic development and social progress, but also greatly influenced the global carbon dioxide emissions and global climate. In developed countries, energy consumption is lower than that of developing countries. The reason, on the one hand, is that the economic development of developed countries has entered the later stage of industrialization, i.e. economic development of the industrial structure to low energy consumption. High yield, high energy consumption of the manufacturing industry gradually shifted to developing countries. On the other hand, the developed countries attach great importance to energy saving and improve energy efficiency. The current world energy consumption is mainly based on fossil resources. Although USA, China and some Asian countries are based mainly on coal, most of the other countries are based mainly on oil and natural gas [1]. Over the past 30 years, North America, central and South America, Europe, the Middle East, Africa and Asia Pacific region, the total energy consumption of the six regions have increased, especially, Asia will account for about 40% of the world's total in 2030 [2,3]. However, the main energy resources could dry up in a few decades, i.e. coal about 130 years, nuclear power generation fuel uranium about 70 years, natural gas about 60 years, oil about 40 years, and reserves of oil producer by task about 20 years will be dried up (**Figure 1.1**). Therefore, no matter what kind of conventional energy structure, the energy crisis that human beings are facing becomes increasingly serious. With the excessive exploitation of natural resources and grave pollution of environment, energy problem and environment problem have become the world's major problem. Then, energy supply and demand contradiction has become increasingly prominent. Since energy problem is not just in the competition for resources, more attention should be attracted in the process of fossil energy development and utilization. Furthermore, negative impact is difficult to eliminate,

such as environmental pollution, the greenhouse effect and a series of environmental issues on the agenda. Therefore, energy development using natural resources such as solar, wind, tidal power, geothermal energy and other renewable energy is the inevitable trend.

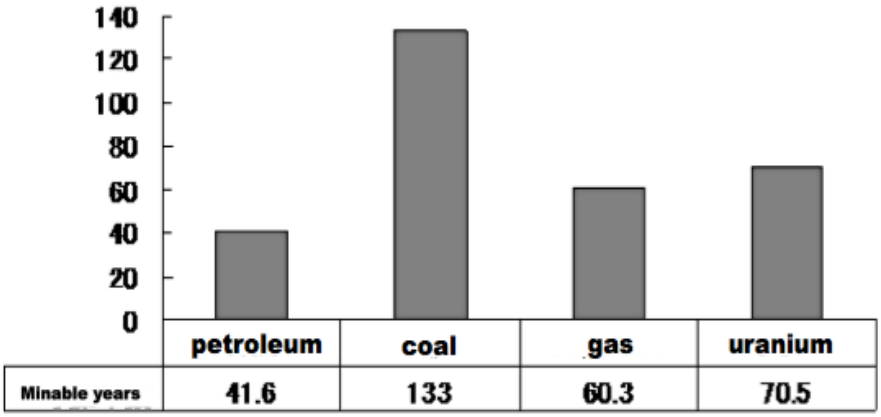

Fig.1.1 The minable years of each resource.

The pollutant and thermal pollution to the environment is small which toward the use of renewable energy. In addition, renewable energy can reduce carbon emissions from generation of electricity. Renewables contributed 19.2% to humans' global energy consumption and 23.7% to their generation of electricity in 2014 and 2015, respectively. This energy consumption is divided as 8.9% coming from traditional biomass, 4.2% as heat energy (modern biomass, geothermal and solar heat), 3.9% hydroelectricity and 2.2% is electricity from wind, solar, geothermal, and biomass. Worldwide investments in renewable technologies amounted to more than US$ 286 billion in 2015, with countries like China and the United States heavily investing in wind, hydro, solar and biofuels. Globally, there are an estimated 7.7 million jobs associated with the renewable energy industries, with solar photovoltaics being the largest renewable employer. Especially the wind and photovoltaic, because the cost is reduced continuously, import volume in 2015 hit a record high. Wind power, wind turbine generator set land prices decreased by 45% in 2010 after the new import volume in 2015 for 63GW, the cumulative increase over 17% in 2010. Solar panel also lowered the price 80% during this period, the new import amount of photovoltaic power generation in 2015 for 47 GW, the cumulative increase over 26% in 2010 be reported [3-5]. By the end of 2015, the cumulative installed capacity of renewable

energy equipment for hydro power 1209 GW, the largest share of the rest of the wind (432 GW) and photovoltaic (227 GW). The details are as follows. The area of renewable energy power generation equipment capacity was the fastest growing emerging market countries, Central American and Caribbean cumulative growth compared to 14.5% and Asia accumulated more than 12.4% growth in 2014 (**Figure 1.2**).

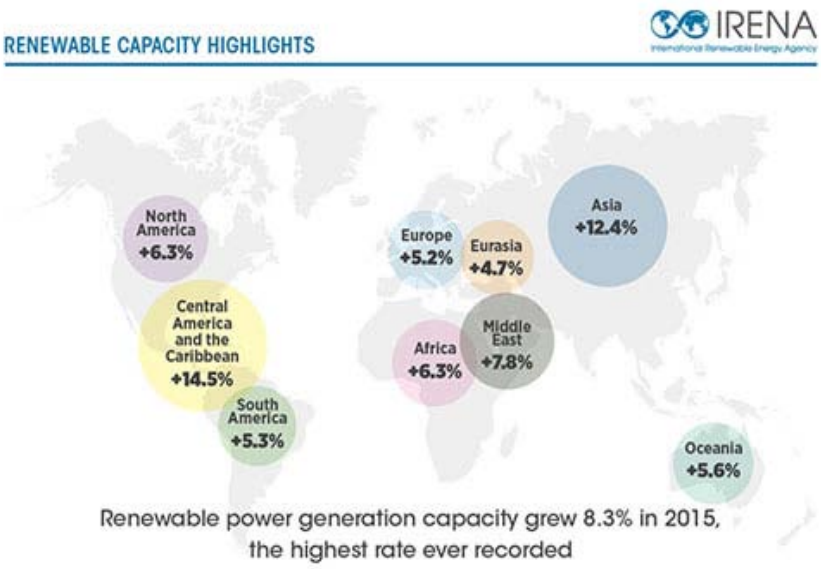

Fig.1.2 Renewable energy equipment capacity growth in the global market
Recourse: Prepared by IRENA [3].

1.2 Solar cell

A solar cell is a device that converts sunlight into electrical energy through a photovoltaic effect. Depending on the material used, there are several types of solar cells. The first generation cells also called conventional, traditional or wafer-based cells. Currently, solar cell has used the high purity silicon cells. High-performance monocrystalline cells is based on high quality single crystal silicon materials and related on the basis of thermal processing technology. Monocrystalline silicon battery technology has nearly mature in battery production, the general method of surface texture, doping emitter passivation, partition technology, such as the main battery development are plane monocrystalline cells and grooving buried gate electrode monocrystalline silicon cells. Improve the processing efficiency is mainly rely on

monocrystalline silicon surface microstructure and partition doping technique. Monocrystalline silicon solar cell conversion efficiency is undoubtedly the highest, in the large scale application and industrial production is still dominant, but due to the monocrystalline silicon material price and the corresponding cumbersome battery technology, the cost of single crystal silicon prices high, to reduce the cost of its is very difficult. In order to save high quality materials, looking for single crystal silicon battery replacement products, development of the thin film solar cells, polycrystalline silicon thin film solar cells and amorphous silicon thin film solar cells is the typical representative. At present, monocrystalline silicon cell efficiency was 25.0%, polycrystalline silicon cell efficiency was 20.4% [6-9].

Second generation cells are thin film solar cells, that include amorphous silicon, Cadmium telluride (CdTe) and CIGS cells and are commercially significant in utility-scale photovoltaic power stations, building integrated photovoltaics or in small stand-alone power system. CIGS solar cells from four elements constitute the best proportion of chalcopyrite crystal as the absorption layer, the absorption spectrum wavelength range. The CIGS thin film battery efficiency up to 20%, CdTe thin film battery efficiency up to 20%. It is currently the most efficient thin-film solar cell [10, 11].

The third generation of solar cells includes a number of thin-film technologies often described as emerging photovoltaics—most of them have not yet been commercially applied and are still in the research or development phase. Many use organic materials, often organometallic compounds as well as inorganic substances. Despite the fact that their efficiencies had been low and the stability of the absorber material was often too short for commercial applications, there is a lot of research invested into these technologies as they promise to achieve the goal of producing low-cost, high-efficiency solar cells. At present, the dye-sensitized solar cell efficiency can be stabilized at 10% or more [12-14].

1.3 Dye-sensitized solar cell

Dye sensitized solar cell mainly imitate the principle of photosynthesis, developed a new type of solar cell. Its main advantage is that raw material is rich, the cost is low, the technology is relatively simple, has great advantages in the large area of industrial production, at the same time, all raw materials and production process is non-toxic, non-polluting, part of the material can be fully recycled, to protect the human environment has important significance [15]. The structure of the DSSC is a kind of "sandwich" structure, the principle of operation of the dye-sensitized solar cell. Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of a semiconductor oxide film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load as shown in **Figure 1.3**, mainly from the following several parts: the conductive glass, dye photosensitizer agent and porous structure of TiO_2 semiconductor nanocrystals film, electrolyte and platinum electrode. The adsorption of dye semiconductor nanocrystals film called light anode, platinum electrodes called the electrode or photocathode. The TiO_2 band gap in the battery is 3.2 eV [16-19], which can only absorb the sunlight in the ultraviolet region. The visible light cannot

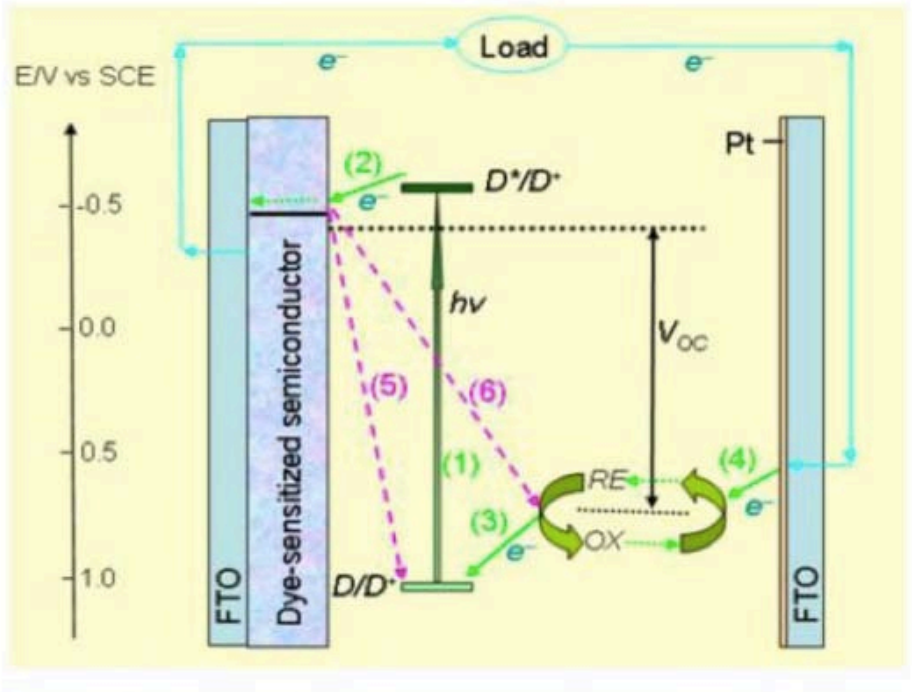

Fig.1.3 The principle and structure of dye sensitized solar cell.

excite it, so the TiO_2 film is covered with a layer of dye photosensitizer to absorb the wider visible light. When the sunlight is irradiated on the dye, the electrons in the dye molecules are excited to the excited state [10]. Because the excited state is unstable and the dye is in contact with the TiO_2 film, the electrons are injected into the TiO_2 conduction band, and the dye molecules themselves become oxidized. The electrons injected into the TiO_2 conduction band enter the bottom of the conduction band, and finally flow through the external circuit to the counter electrode to form photocurrent. The dye molecules in the oxidized state are reduced to the ground state by the I^- in the electrolyte solution, and the I_3^- in the electrolyte is reduced to I^- by the electrons entering from the cathode, thus completing a photo-electrochemical reaction cycle. This new type of solar cell is more widely used than silicon battery: such as lightweight, can be made of plastic or metal sheet made of thin film; it can use different colored dyes to colorful; in addition, also can be designed into a variety of solar cells of various shapes. The dye-sensitized solar cell total it has a broad prospect of industrialization, is a new type of solar cell has a very broad application prospect.

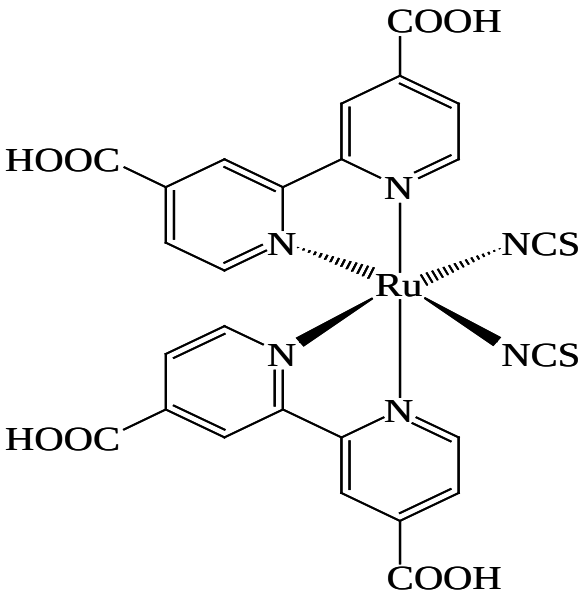

Fig.1.4 Chemical structure of Ruthenium complex dye N3 molecule.

Grätzel cell realized high conversion efficiency of 13% is that porous titanium oxide and Ru(II)$L_2(NCS)_2$,L=2,2'-bipyridyl-4,4'-dicarboxylicacid dye [4,20], so-called N3 dye(**Figure1.4**). TiO_2 is the n-type semiconductor material having high energy gap, and can absorb only ultra-violet light below 388 nm wavelength, but ultraviolet accounts for only 6% of the sun [21-24]. Dye can absorb visible light. When dyes absorb light, excited electrons transfer to TiO_2 electrodes, at the same time oxidized dye also can accept electrons from iodide in the electrolyte, so as to achieve a kind of feedback balance effect. Using Ru complexes dye-sensitized solar cells, can accept more than 10^8 times of redox reaction, so the durability, make this kind of solar cell efficiency can be promoted to more than 10% [25-27]. N3 dye absorption of light on a wide range, and photoelectric conversion efficiency is relatively high. Its carboxyl (COOH) group can form a stable bonding with TiO_2, and its NCS bond can promote the absorption of visible light. The maximum absorption peak of N3 dyes for visible light occurs at a wavelength of 540 nm. The absorption wavelength can be extended to about 750 nm [28]. However, N3 dye is due to the use of this rare metal ruthenium, which has a disadvantage that the price is high. Also because of the limited resources, there is also a worry that the depletion in the future. Thus as, ideal is the use of low cost, resource rich dye to make the battery [29-31]. At this point, D149 as one of the typical organic dye as shown in **Figure 1.5**. The D149 dye has an absorption wavelength range similar to that of the N3 dye, and also has a COOH group in the

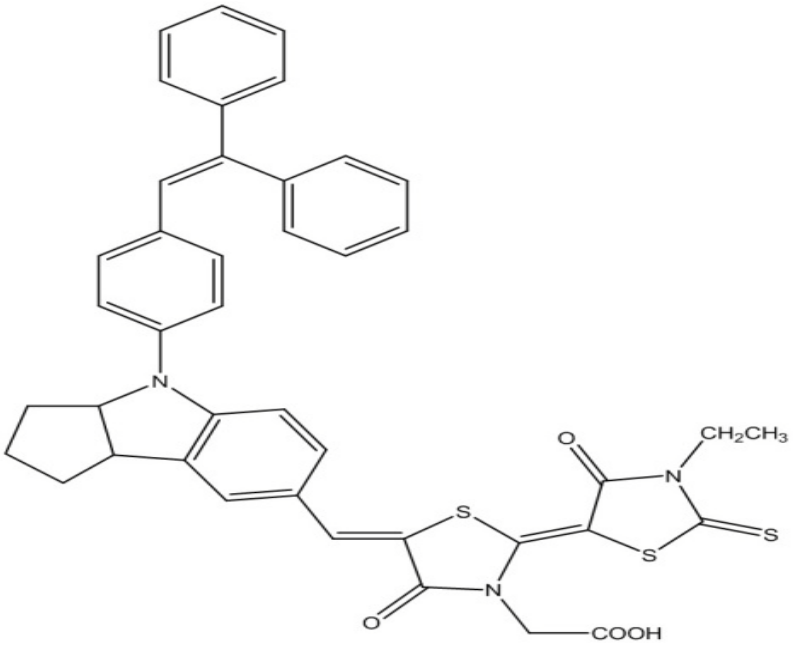

Fig.1.5 Chemical structure of the D149 dye molecule.

molecule, which can be easy to combined with TiO_2 surface, this seems to be the expected high photoelectric conversion efficiency [32-37].

1.4 The purpose of this study

Since the Grätzel type dye sensitized solar cells (DSSCs) was developed, the research on the DSSCs has been promoted continuously. However, there are still some practical obstacles. One of them is the durability of the battery. Although silicon solar cell has life of about 20 years, the dye-sensitized solar cell has life of only a few years. One reason for this is the use of TiO_2 oxide semiconductor material. TiO_2 is an excellent material for cost and durability. Due to its high photocatalytic activity, it absorbs the ultraviolet light contained in the sunlight and causes the decomposition of organic components in the dye and electrolyte. Therefore, there is a possibility that the solar battery life is shortened. Therefore, various metal oxide semiconductors instead of titanium oxide were researched. ZnO, SnO_2, Nb_2O_5, WO_3, In_2O_3, ZrO_2, Ta_2O_5 and so on carries on the discussion. Among of them, ZnO is cheap, non-toxic substances, and have 60 meV free exciton binding energy, a wide range of 10^{-4}~10^{12} Ωcm resistance rate, characteristics of 200 $cm^2V^{-1}S^{-1}$ high electron mobility, so it is used in a wide variety of uses in technology [38-42]. In addition, ZnO (3.37eV) has similar band gap with TiO_2 (3.2 eV), and the injection rate of excited electron from the dye to ZnO has been known to be comparable to TiO_2. Furthermore, photocatalytic activity of ZnO is lower than TiO_2. At present, the dye-sensitized solar cells are in general using glass substrate. High conversion efficiency of dye-sensitized solar cells has been achieved using glass substrates, but the glass substrate is heavy and fragile [41-43]. Therefore, a plastic substrate is used to reduce the weight. In addition, the plastic substrate is cheaper than the glass substrate, and not easy to crack. Since the application of roll-to-roll process [44] for DSSCs fabrication is expected to reduce production cost, the introduction of plastic substrates in the future will become very important. In traditional DSSC fabrication process, mesoporous TiO_2 thin film on the substrate is immersed in the dye solution. However, the dye adsorption process usually takes a few hours or even a day, which would reduce production efficiency and increase manufacturing cost. Then, the merit of roll-to-roll production process which has high speed and high efficiency is lost. A possible solution to this problem is preparing the dyed paste and applying it to make colored mesoporous thin film on

plastic substrate. By adsorbing dye to ZnO nanopowder in advance and then forming a thin film on the substrate (hereinafter referred to pre-dyeing method). By this method, it is possible to omit the step of dye adsorption to the porous thin film, which takes about 1 to 2 hours each time. Therefore, the electrode can be manufactured in a short time, and it can be said it is more suitable for the roll-to-roll manufacturing method. On the other hand, in the pre-dyeing method, since the surface of the ZnO particles is covered with the dye, the adhesion between the ZnO particles deteriorates when the film formation and the cell efficiency may decrease. The solution to this problem, through the hot pressing process ITO/PET substrate [35-38, 45] membrane of the ZnO porous membrane, improved tackiness between ZnO particles, thus to improve the performance of electronic transport paths have certain effect. The solution to this problem, the ZnO porous film on the ITO/PET substrate through the hot press treatment in the adhesiveness between the ZnO particles by is improved and has an effect on the increase of the electron transport path. Nanocrystal ZnO film, redox electrolyte and dye are inevitable constituent in preparing DSSC. Among these constituents, dye is key component since it absorbs light and generates electrons. Since typical dye can absorb only a part of sunlight wavelength region, the combination of different dye makes broad absorption wavelength absorption possible, leading to an increase in Jsc and thus, enhanced power conversion efficiency for DSSC based on plastic substrate. It is expected that the photovoltaic performances of the cell improve by multiple dye combination.

1.5 Conclusion

The current world energy consumption is mainly based on fossil resources. However, as the main energy resources and dependence of fossil fuels is considered could dry up in a few decades. Therefore, no matter what kind of conventional energy resources are used, the energy crisis that human beings are facing becomes increasingly serious. With the excessive exploitation of natural resources and grave pollution of environment, global warming. A large amount of carbon dioxide in the air, dust content has serious impact on people's health and the natural environment to the survival of humans. Thus solar, wind, tidal power, geothermal energy and other renewable energy development is the inevitable trend. Solar energy is the most widely used. Solar energy is radiant light and heat from the Sun that is harnessed using a

range of ever-evolving technologies such as solar heating, photovoltaics, solar thermal energy, solar architecture, molten salt power plants and artificial photosynthesis. Considering solar energy utilization, solar cell is one of the important options. Representative solar cells have silicon solar cell, CdTe and CIGS thin film solar cells and dye-sensitized solar cell. At present, the DSSC in general uses TiO_2 and glass substrate. TiO_2 has high photocatalytic activity, it absorbs the ultraviolet light contained in the sunlight. Therefore, there is a possibility that the durability of solar cell becomes bad. As a candidate for TiO_2 alternative, ZnO is cheap, non-toxic substances, and it has almost the same band gap, the comparable electron transfer rate. Concerning substrate material, the DSSC are in general use glass substrate. But the glass substrate is heavy and fragile. On the other hand, a plastic substrate is used to reduce the weight. In addition, the plastic substrate is cheaper than the glass substrate. By virtue of flexibility of plastic substrate, the use of roll-to-roll process for DSSCs fabrication is expected to reduce production cost, the introduction of plastic substrates will become very important. In traditional method, mesoporous TiO_2 thin film on the substrate is immersed in the dye solution. However, the dye adsorption process usually takes a few hours or even a day, which would reduce production efficiency and increase manufacturing cost. Also, the merit of roll-to-roll production process which has high speed and high efficiency is lost. The solution to this problem is pre-dying method. It is possible to omit the step of dye adsorption to the porous thin film. Therefore, the electrode can be manufactured in a short time, and it can be said it is more suitable for the roll-to-roll manufacturing method.

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CHAPTER 2

Experimental

2.1 Introduction

DSSC usually use TiO_2 and glass substrate. TiO_2 has very high photocatalytic activity [1], which can absorb ultraviolet rays from the sun. So that, the solar cell life will be shortened. At the same time, the glass substrate is very heavy and easy to crack. So we use other materials to replace them. ZnO [2, 4-6] is a cheap material, non-toxic substance, it has almost the same band gap and the same electron transfer rate with TiO_2. In addition, the plastic substrate is cheaper and lighter than the glass substrate, and not easy to crack. Because of its flexibility, we can expect the roll to roll process will be widely used in the future, and the use of plastic substrate will become very important. In the traditional method, a porous film is made on the substrate, then immersed in a dye solution and adsorbed the dye. The process of dye adsorption usually takes a few hours or even a day, which reduces productivity and increases manufacturing costs. Moreover, it is praised as the high speed and the high efficiency of roll to roll process has lost its advantage [3]. The solution to this problem is to have ZnO nanoparticles adsorbed dye in advance, and then make the film on the substrate (hereafter called pre-dyeing method). This can omit the process of adsorbing the dye to the porous film. Therefore, the electrode can be made in a short time, which is more suitable for the roll to roll manufacturing process.

2.2 Preparation of ITO/PET sheet

PET sheet coated with ITO (indium tin oxide) (30～50 $\Omega sq.^{-1}$, Touki Inc., Japan) was cut to about 10 × 25 mm, the ITO surface was washed with ethanol and dried.

2.2.1 Preparation of pre-dyeing ZnO Paste (pd-ZnO)

3.0 ml of ethanol, 0.1 ml of acetylacetone (KANTO CHEMICAL CO., INC.) and 0.1 ml of acetic acid (KANTO CHEMICAL CO., INC.) were measured with an automatic pipette and were mixed in a small sample bottle. ZnO paste was prepared as follows.

1g of ZnO powder (FINEX-50, SAKAI CHEMICAL INDUSTRY CO., LTD (Japan), surface untreated, average particle size 20 nm) was added and the dispersed solution was sonicated by homogenizer for about 5 minutes.

2.3 Preparation of dye solution

2.3.1 Preparation of EosinY dye solution

13g of EosinY (2′,4′,5′,7′-Tetrabromofluorescein disodium salt) [4] dye (Aldrich) added to ethanol of 40ml, ultrasonically stirred for 30 minutes under light-shielding conditions to prepare EosinY dye solution of 5.0×10^{-4} mol/l. **Figure 2.1** shows the structure of EosinY.

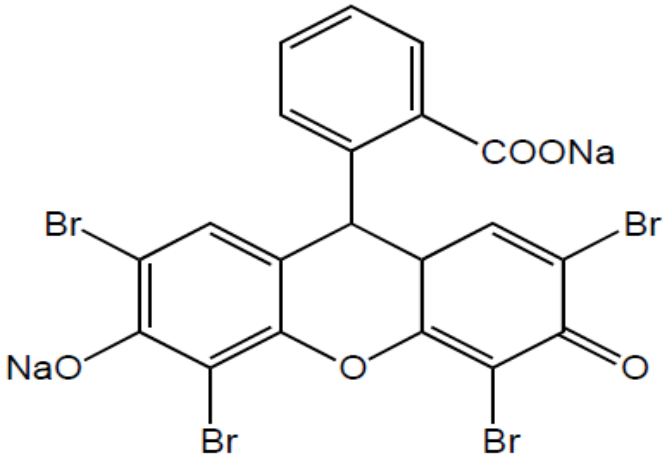


Fig.2.1 Chemical structure of the EosinY dye molecule.

2.3.2 Preparation of D149 and D131 dye solution

a)Weigh out 14.8 mg of 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) (MITSUBISHI PAPER MILLS LTD.) [4, 5] with an electronic balance and added to mixed solution of 40ml of acetonitrile: tert-butanol (KANTO CHEMICAL CO., INC.) in volume ratio of 1:1. Dye solution was sonicated for 30 minutes under light-shielding conditions. The concentration of D149 dye solution was 5.0×10^{-4} mol/l.

b)Weigh out 25.6mg of 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) (MITSUBISHI PAPER MILLS LTD.) [7-9] with an electronic balance and added to mixed solution of 40ml of acetonitrile: tert-butanol in volume rate of 1: 1. Ultrasonically stirred for 30 minutes under light-shielding conditions to prepare D131 dye solution of 5.0×10^{-4} mol/l. **Figure 2.2** shows the structure of D131 dye.

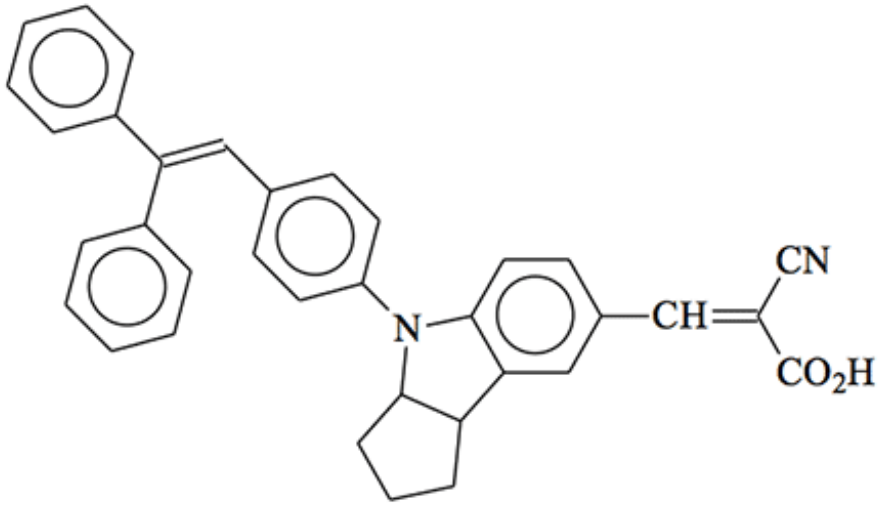


Fig.2.2 Chemical structure of the D131 dye molecule.

2.3.3 Preparation of mixed dye solution

The D149 dye was weighed out with a 7.4mg by electronic balance and added to the acetonitrile and tert-butanol mixed solution 20 ml with the volume ratio of 1:1. Then ultrasonically agitated for 30 minutes under light shielding conditions, we can get 12.5×10^{-4}mol/l D149 dye solution. At last, 15.7 mg of chenodeoxycholic acid (Wako Pure Chemical Industries, Ltd.) was added to the D149 dye solution to prepare a solution. The molar ratio of D149: chenodeoxycholic acid =1: 4. The D131 dye was weighed out with a 12.8 mg by electronic balance and added to the acetonitrile and tert-butanol mixed solution 20 ml with the volume ratio of 1:1. Then ultrasonically agitated for 30 minutes under light shielding conditions, we can get 12.5×10^{-4}mol/l D131 dye solution. At last, 19.6 mg of chenodeoxycholic acid (Wako Pure Chemical Industries, Ltd.) was added to the D131 dye solution to prepare a solution. The molar ratio of D131: chenodeoxycholic acid =1: 2. The two solutions were mixed to obtain 40ml solution with the volume ratio of 1: 1. **Figure 2.3** shows mixed dye adsorption.

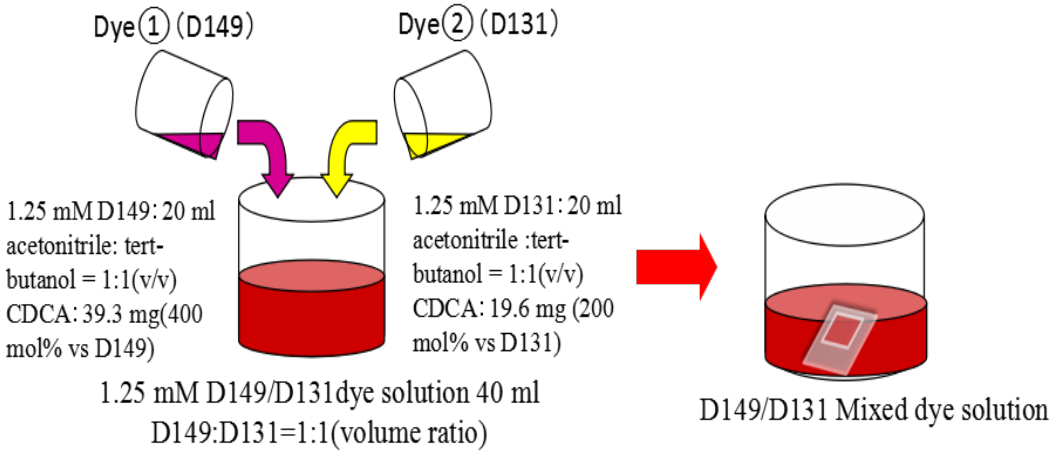
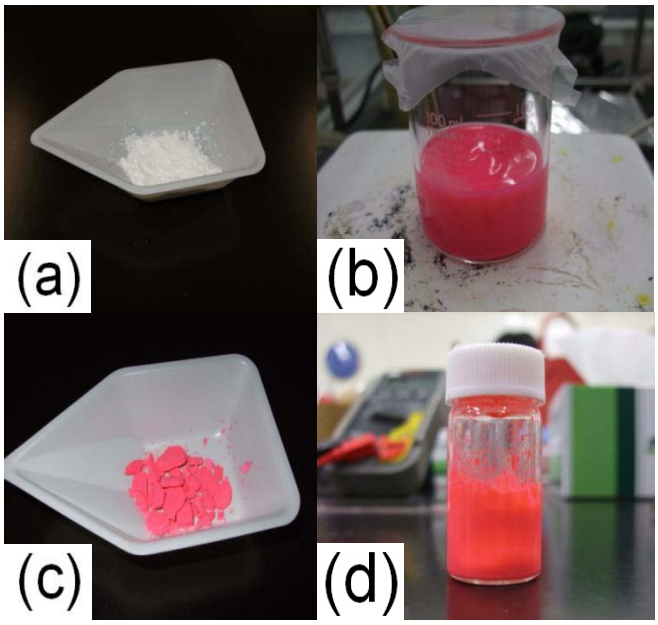


Fig.2.3 The mixed dye adsorption conditions.

2.4. Preparation of pd-ZnO powder

2.4.1 Preparation of pd-ZnO with EosinY dye

EosinY dye in ethanol solution of 40ml, adjusted to 1.25mM dye solution, adding 1g of ZnO powder into the above solution, respectively. In an airtight and shade conditions, stirred and filtered them. Then, dried them to obtain pre-dyeing ZnO powders. Finally, ethanol (3ml) blend with pd-ZnO powders use homogenizer to prepare pd-ZnO paste. As shown in **Scheme1**, to prepare pd-ZnO paste.



Scheme 1 Schematic representation for fabrication of pd-ZnO paste. (a) ZnO powders blend with (b) ethanol solution and dye, (c) after filtered, drying to obtain pd-ZnO powder and (d) pd-ZnO paste mixed water by homogenizer.

2.4.2 Preparation of pd-ZnO with D149 dye

The D149 powder (37mg)/chenodeoxycholic acid (1:4 by molar ratio) were ground for volume ratio of 1:1 in the mixture of acetonitrile (20ml) and tert-butanol (20ml) to form dye solution, As the same method above, we were obtained dye solution and synthesized pd-ZnO paste.

2.4.3 Preparation of pd-ZnO with D131 dye

The D131 powder (25.6mg)/chenodeoxycholic acid (1:2 by molar ratio) were ground for volume ratio of 1:1 in the mixture of acetonitrile (20ml) and tert-butanol (20ml) to form dye solution. As the same method above, we were obtained dye solution and synthesized pd-ZnO paste.

2.4.4 Preparation of pd-ZnO with D358 dye

D358(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) [10] powder (45.6mg)/chenodeoxycholic acid (1:4 by molar ratio) were ground for volume ratio of 1:1 in the mixture of acetonitrile (20ml) and tert-butanol (20ml) to form dye solution. As the same method above, we were obtained dye solution and synthesized pd-ZnO paste.

2.4.5 Preparation mixed dye of pd-ZnO

Added 0.5g ZnO powders into the above dye solution to prepare pd-ZnO powders, then mixed two kinds of them to produce hybrid paste for the preparation of film layer, respectively. The **Figure 2.4** is shown mixed pigments of pd-ZnO.

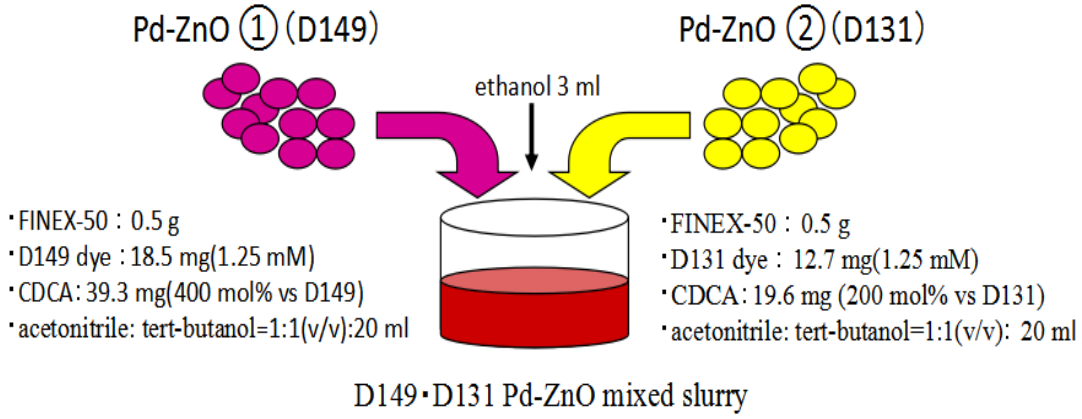


Fig.2.4.Mixed pd-ZnO paste production conditions.

2.5 Fabrication of ZnO thin electrode film

Indium-Tin Oxide / polyethylene terephthalate (ITO / PET) plastic substrates were washed with ethanol for removing dirt. Two sheets of cellophane tape were adhered as a spacer to the long side of the ITO / PET sheet. The 2.1.1 prepared paste was sonicated for 15 min in an ultrasonic bath. Then, the ZnO paste was pasted onto ITO / PET substrates using squeegee method. The tape was peeled off after drying, after the substrate was placed on a hot plate and heating at 150°C for 15 minutes to remove the organic substances. After hot press treatment, cut out the electrode area, the use of platinum back electrode as sandwiches combined and injected into the electrolyte shows in **Figure 2.5**. The hot press process is an important part of pre-dyeing method.

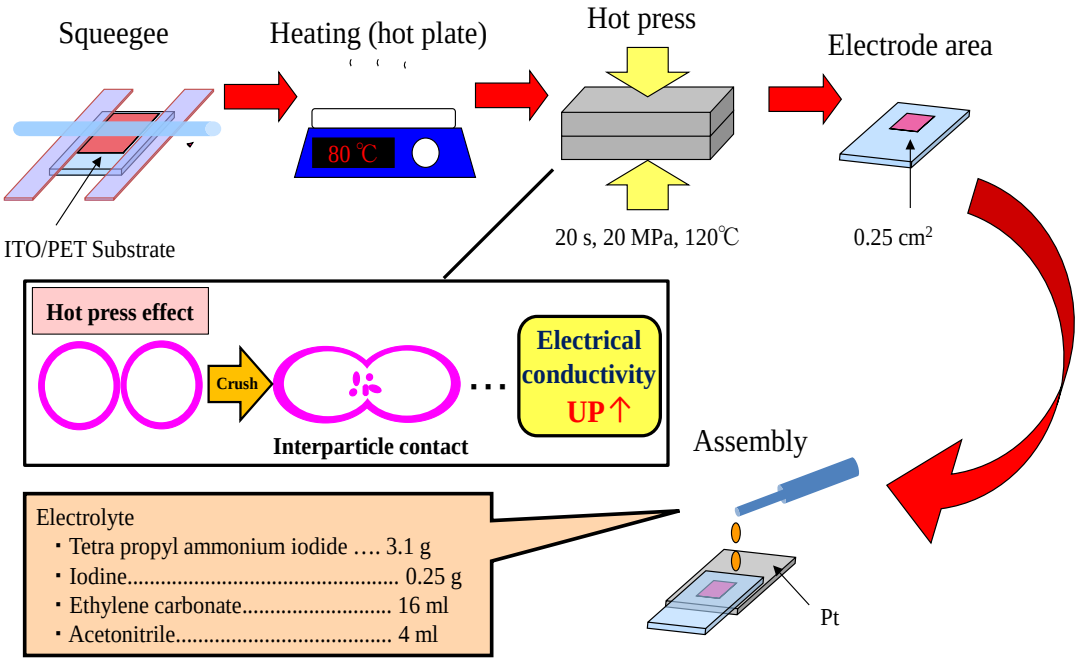


Fig.2.5 Fabrication process of dye sensitized solar cells.

2.6 Preparation of electrolyte

The electrolyte was a mixture of 3.1g tetra-n-propylammonium iodide, 0.25g I_2 in 20ml solution of acetonitrile/ethylene carbonate (1:4 by volume) was injected from a hole made on the counter electrode into the space between the sandwiched cells. The area of the ZnO electrode prepared in the previous section was scraped to 0.25cm^2 (0.5cm × 0.5cm). In order to prevent direct contact between the counter electrode and ITO, a polymer film (Surlyn, film thickness 25μm) as a spacer was cut into a concave shape and placed on the electrode. An electrolytic solution was dropped on the surface of the electrode and allowed to permeate into the porous thin film by capillary action. Finally, FTO glass substrate sputtered with the counter electrode of platinum was stacked and fixed with a clip, and a dye sensitized solar cell was assembled. The dimensions and assembly drawing are shown in **Figure 2.6**.

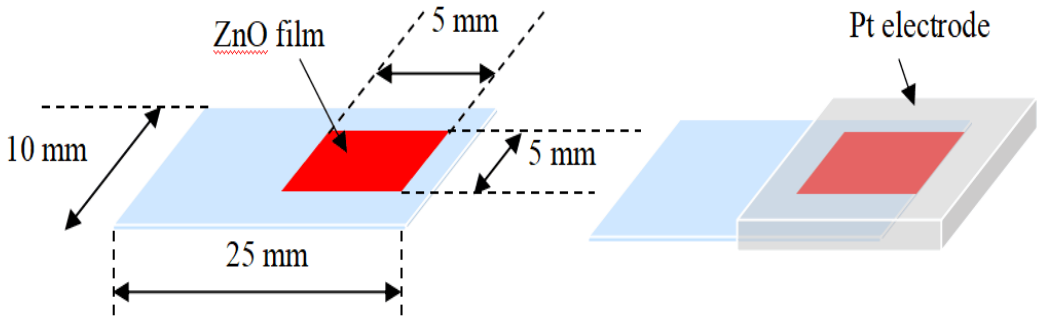


Fig.2.6 Dimensions and assembly draw of ITO/PET sheet cell.

UV-1600PC) of solar cells is AM 1.5 G. Conversion efficiency can be calculated by performing the following calculation as shown in **Figure 2.7**.

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$

The overall solar-toelectrical energy conversion efficiency, η, for a solar cell is given by the photocurrent density measured at short-circuit (Jsc), the open-circuit photovoltage (Voc), the fill factor of the cell (FF), and the intensity of the incident light (P_{in}) [11-13].

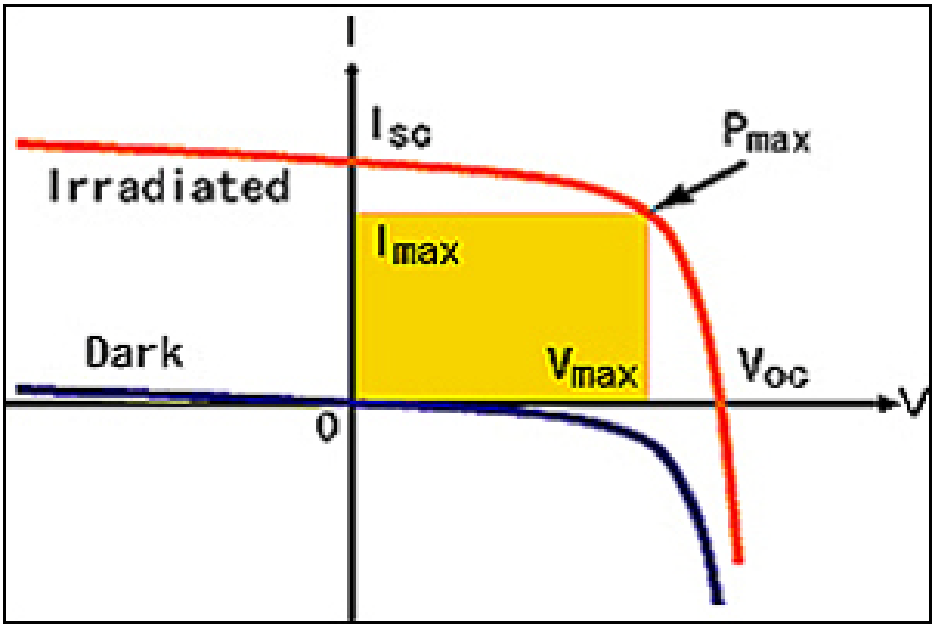


Fig.2.7 I-V curve of typical solar cell.

The fill factor can define by the ratio of the maximum power (Pmax) of the solar cell per unit area divided by the Voc and Jsc.

$$\mathrm{FF} = P_{\max}/(J_{\mathrm{sc}}V_{\mathrm{oc}})$$

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CHAPTER 3

Improve efficiency of DSSCs made by pre-dyeing method

3.1 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 (~ 14%), 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. In order to overcome this limitation, several low-temperature techniques [4, 5], microwave sintering [6], including chemical sintering [7], mechanical compressing [8-10], electrophoretic deposition (EPD) [11], hydrothermal necking [12, 13] and ultrasonic spray-coating [14] 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_2. It is known that ZnO has higher electron mobility than TiO_2 [15, 16], 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 [17-19]. In this study, 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. However, the efficiency of DSSC made by pre-dyeing method was much lower than traditional method. 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. In order to improve lower porosity and bad interparticle connectivity, hot-press method was applied to photoelectrode on plastic substrate (ITO/PEN). 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. It was possible to prepare a dye-sensitized solar cell with a conversion efficiency of 1.97% by adjusting the proper quantities of dye to the zinc oxide and subjecting it to a hot press treatment using EosinY dye. In order to reach higher efficiency, D149 dye was used which has broader absorption wavelength range than EosinY dye. The solar-to-electric conversion efficiency of 4.24% under 1 sun illumination was achieved by utilizing the hot-press technique on the low-temperature preparation of nanostructured ZnO films.

3.2 Comparison of performance by difference in particle diameter

FINEX-30 with an average particle size of 40μm was used as the ZnO powder, and FINEX-50 (average particle size 20μm) with a smaller particle diameter than the above could be obtained. Compared with FINEX-30, FINEX-50 has smaller particle diameter, and it increases about two times as the surface area [20]. Therefore, the amount of the dye adsorption can be increased, and short-circuit current (Jsc) is expected to be improved more than the cell using FINEX-30. The performance comparison of the cell fabricated by the conventional method using FINEX-50 and FINEX-30 is shown in **Figure 3.1** and **Table 3.1** (dye used: EosinY).

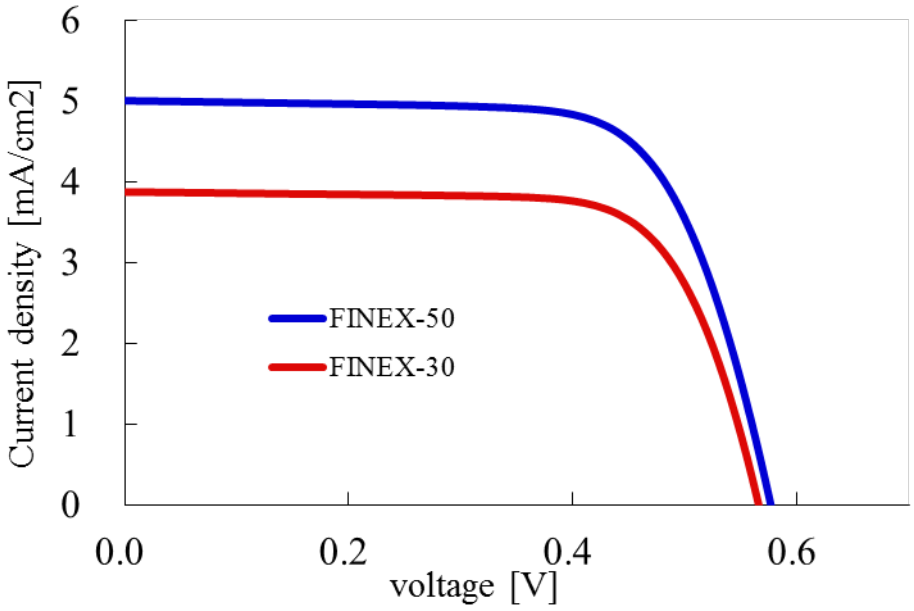

Fig.3.1 I-V curves of cells used FINEX-50 and FINEX-30.

The cells fabricated using FINEX-50 have higher Jsc and more dye adsorption than FINEX-30. As expected from this result, it can be said that the Jsc was improved by increasing the surface area and the amount of dye adsorption as the particle size became smaller.

Table.3.1 Photovoltaic properties of cells using FINEX-50 and FINEX-30.

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]	amount of dye adsorption [10^{-8}mol/cm^2]
FINEX-30	0.57	3.87	0.72	1.58	5.1
FINEX-50	0.58	5.00	0.70	2.03	11.5

3.3 Viscosity change under different solvents

When preparing pd-ZnO paste used FINEX-30, ethanol was used as a solvent. However, with FINEX-50, the viscosity of the pd-ZnO paste was drastically reduced. When the viscosity of the paste is low, a sufficient film thickness cannot be obtained, the amount of dye adsorption decreases, and Jsc decreases. This is considered to be due to the cause that the particle diameter of ZnO is reduced. As the particle size becomes smaller, the surface area increases, ZnO particles tend to aggregate, and the viscosity of the paste decrease is expected. As a method for increasing the viscosity of the paste, it is conceivable to add a dispersant to prevent aggregation of ZnO particles, to add a binder, or the like. However, these methods have a possibility of leaving the solvent in the ZnO film and deteriorating the battery performance at a short time and low temperature in the pre-dyeing method produced. Previous studies have reported that when acetic acid and acetylacetone added with the ZnO paste of the conventional method also added to the pd-ZnO paste, the cell performance deteriorates, and in particular, acetic acid will lead to dye of pd-ZnO peeling off. Solvents other than ethanol were used to improve the viscosity of the paste. Since the Arakawa laboratory at the Tokyo University of Science has reported that the film thickness can be increased by changing the solvent of the titanium oxide paste from ethanol to water. In this laboratory as well, the case where the solvent of pd-ZnO paste was changed from ethanol to water was examined. As a result, it was possible to obtain paste with high viscosity by adding pd-ZnO powder to distilled water and mixing, then applying the mixture to a homogenizer. The reason why the viscosity of the paste has been raised is that ZnO is a substance that is easily compatible with water [21,22]. It is known that the surfaces of metal oxides such as titanium oxide and ZnO are covered with hydrophilic groups. Since the affinity of the hydrophilic group for water is high, ZnO particles are likely to be dispersed, so it is considered that a paste with high viscosity could be obtained. From these results, the ZnO surface of pd-ZnO is not completely covered with the dye, and there is a portion where ZnO is exposed, and this portion has affinity with water and improves dispersibility is considered.

3.4 Effect of hot press treatment

The hot press treatment conditions shows in **Figure 3.2**. On the top, heated at 120°C, then at pressured 20 MPa for 20 seconds. As for the hot press condition, heating was carried out only from the lower plate of the press machine at 150°C. And pressure was applied for 15 minutes. But, this condition has a problem that peeling of the ZnO film frequently occurs [23]. If the ZnO film is peeled off from the substrate as shown on the left side of **Figure 3.3**, it becomes impossible to manufacture the battery.

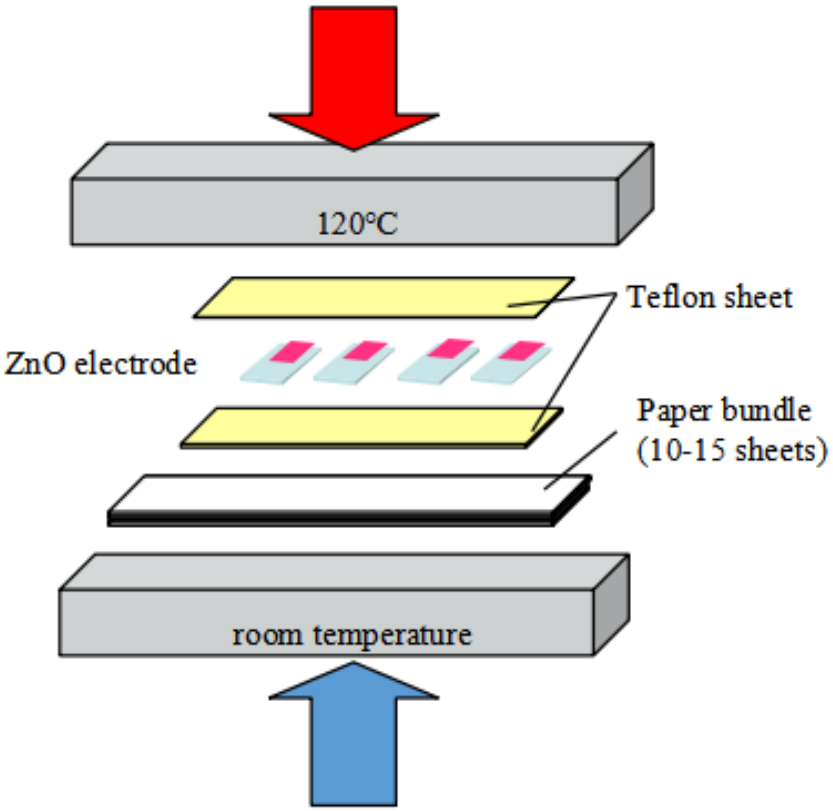

Fig.3.2 The graph is based on the hot-press process of pd-ZnO method.

Fig. 3.3 State of peeling after hot press.

As a cause of this, the order from the under side of heating, for a long time heated lead to distorts of PET substrate, so that the compactness of the ZnO and the substrate is deteriorated. Therefore, as in 3.5, heating was performed only from the upper plate of the press machine, and by placing the paper bundle as the heat insulating material, heat was not easily transmitted to the lower plate. Further, the pressing time was set to be 15 to 20 seconds in a shorter time. As a result, almost of the peeling of the ZnO film that has occurred so far has not occurred. From the above results, it is considered important to suppress the temperature rise of the PET substrate while heating the ZnO film in order to prevent peeling. The following experiment was conducted under this press condition.

The time of the hot pressing treatment is too long, the PET substrate was bended by heat and the ZnO film is liable to be peeled off. Therefore, the pressure time should not be longer than 30 seconds. As paper has a higher specific heat capacity than metal, temperature hardly rise, the minimum also need to place 10, can inhibit the temperature rise of PET substrate. Also, since the paper bundle is considered to act as a cushioning agent, it is 20MPa in the display of the press machine, but it is expected that the pressure actually applied is less than 20MPa.

3.5 Results of hot press treatment

Figure 3.4 and **Table 3.2** show the performance comparisons based on the with or without hot press treatment of the cell using a cell fabricated by a conventional method and pd-ZnO paste prepared with EosinY dye concentration of 5.0×10^{-4}M.

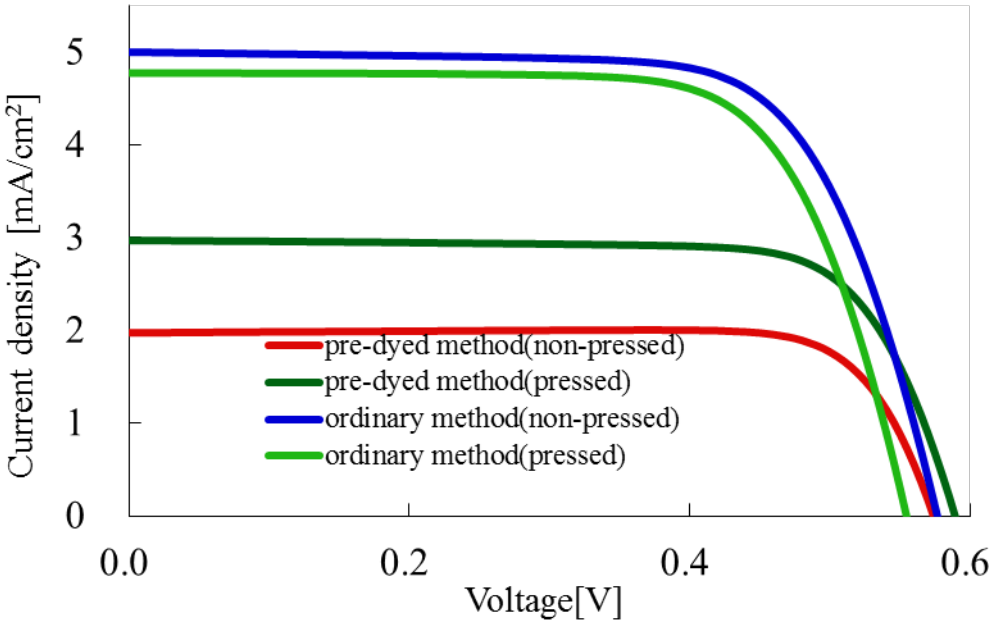

Fig.3.4 Photocurrent-voltage of DSSC with or without hot-press method.

Compare with the results, top lines used ordinary method, bottom lines used pre-dyeing method. In ordinary method, with or without hot press treatment, short-circuit current (Jsc) and efficiency have no obvious change. This is thought the pressure causes the pores of the porous film buried, the surface area reduced, and the absorption of the dye decreased. But in pre-dyeing method, the cells after treatment with hot press, look at the red and green line, Jsc improved 50%, lead to the efficiency improved. So we believed that the pre-dyeing method through out hot press treatment is efficient. However, efficiency still lags behind ordinary methods [24-27].

Table.3.2 The effect of based on traditional method and pre-dyeing method, with or without pressure treated.

	pressure	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
Traditional method	×	0.57	1.97	0.80	0.90
	○	0.59	2.97	0.75	1.31
Pre-dyeing method	×	0.58	5.00	0.70	2.03
	○	0.55	4.77	0.71	1.88

Therefore, it is considered that pd-ZnO method by the hot press treatment lead to Jsc was improved. **Figure 3.5** shows an image of the effect of hot press treatment in the pre-dyeing method.

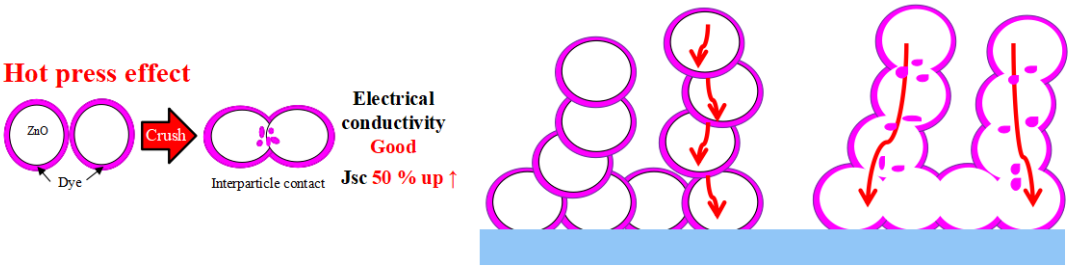

Fig.3.5 Image diagram of effect by hot press process treatment.

In case of pre-dyeing method, Jsc has increased about 50% by hot press treatment. It is considered that pre-dyeing method make ZnO adsorbs dye in advance on the particles surface, so that the compact contact between ZnO particles deteriorated, the

conductivity and Jsc decreased. However, by applying compression processing, the ZnO surface which adsorbed dye was crushed, the compact contact between the particles are improved and become smooth for the movement of the electrons. For the traditional method, there is little change caused by hot press treatment. This is thought the pressure improve the contact between particles, but at the same time, the pores of the porous film are buried and the surface area is reduced, lead to the amount of dye adsorption decreased.

3.6 Proper quantities of D149 dye to ZnO

In order to improve the efficiency of the pre-dyeing method, in next experiment ,we used the dye D149 to prepared the electrode. Photosensitive red-violet dye having excellent photoelectric conversion efficiency as a metal-free dye. D149 dye was used which has broader absorption wavelength range than EosinY dye [28-31]. **Figure 3.6** and **Table 3.3** show the comparison of the cell performance prepared by D149 dye and different method (pre-dyeing method and the traditional method).

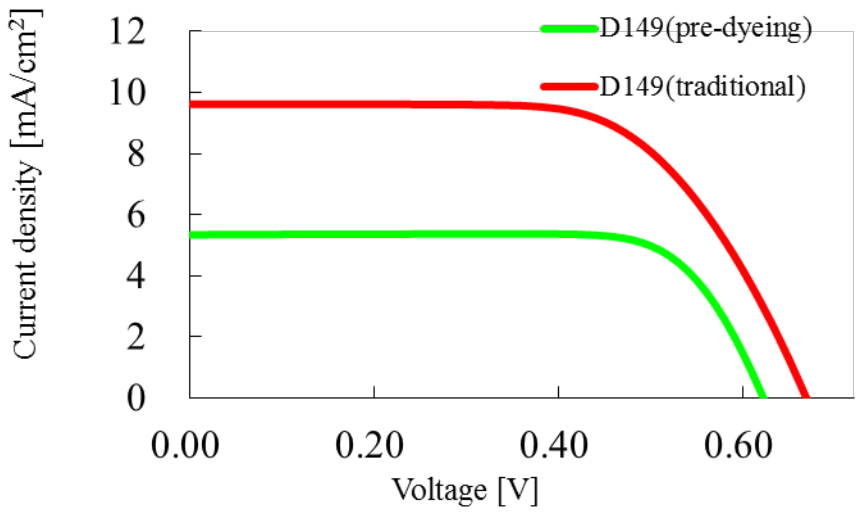

Fig.3.6 Comparison of performance with traditional method and pre-dyeing method.

Table.3.3 Effect of D149 dye by traditional method and pre-dyeing method.

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
Traditional method	0.62	5.34	0.75	2.48
Pre-dyeing method	0.67	9.61	0.64	4.10

The red line shows the traditional method, which has a higher Jsc, so the efficiency is relatively higher. In contrast to the traditional method, when the concentration of dye is 0.5mM, the pre-dyeing method is not ideal. Because in traditional methods, the amount of ZnO is relatively fixed and the dye concentration is sufficient, more pigments can make aggregation. So we investigated the dye concentration with the pre-dying method.

3.7 Influence of concentration on the pre-dyeing method

In order to improve the efficiency of the pre-dyeing method, we used the more efficient D149 pigment to prepare the electrode. With respect to the conventional method, Jsc and Voc were greatly improved by using D149 dye, and the conversion efficiency was obtained 4.10%. However, In contrast to the traditional method, when the concentration of pigment is 0.5mM, the pre-dyeing method is not ideal. This is because in traditional methods, the amount of ZnO is relatively fixed and the pigment concentration is sufficient. In pre-dying method, pigment was adsorbed in advance, only enough dye molecules can cover ZnO. With the amount change of dye concentration, Jsc changed obviously. When concentration reached to 1.25mM, performance showed the best. But when we increased concentration continue, there was no obviously changed, the concentration was saturated. This is the IV curve which used the traditional method and the pre-dyeing method in the optimum concentration condition. We can see that the efficiency has reached the same as the traditional method after the concentration increased from 0.5mM to 1.25mM. That means the pre-dyeing method is successful. The results are shown in **Figure 3.7** and

Table 3.4.

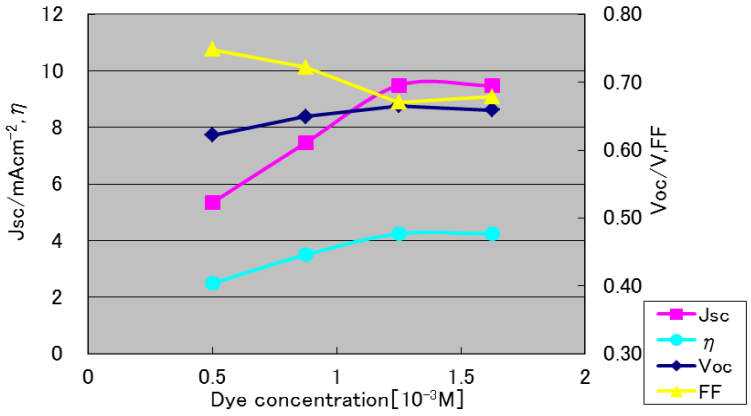

Fig.3.7 Variation of photovoltaic parameters, i.e., short-circuit photocurrent (Jsc),open-circuit voltage (Voc), fill factor (FF), and light-to-electricity conversion efficiency(η) ZnO-based DSSC, depending on dye concentration.

Table.3.4 Effect of D149 dye amount on Photoelectric Efficiency.

Dye concentration [10^{-3}M]	Amount of dye [10^{-5}mol-dye/g-ZnO]	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
0.5	2.0	0.62	5.34	0.75	2.49
0.875	3.5	0.65	7.46	0.72	3.50
1.25	5.0	0.67	9.49	0.67	4.24
1.625	6.5	0.66	9.48	0.68	4.24

With the amount change of dye concentration, Jsc and performance increases with the amount of dye increases. When the amount of dye was 5.0×10^{-5} mol/g-ZnO, the conversion efficiency showed a peak value, shows the efficiency almost equal to that with the traditional method. But when we increase concentration continue, there is no obviously change. From the above results, in the pre-dyeing method using the D149

dye, by adjusting the amount of dye to ZnO during dye adsorption, the dye adsorption amount was increased and the cell performance was improved, and the dye amount was 5.0×10^{-5} mol/g-ZnO. It can be said that it is optimum.

Table.3.5 Preparation methods of ZnO films, and corresponding photovoltaic parameters.

Method of prep.	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]	dye	Ref.
PD[a]	0.67	9.49	0.67	4.24	D149	
EPD[b]	0.57	10.82	0.65	4.04	D149	[5]
DCTP[c]	0.63	11.60	0.64	4.68	D149	[33]
CBD[d]	0.58	19.53	0.63	7.07	D149	[34]
CBD[d],DBT[e]	0.57	16.09	0.59	5.40	CYC-B1	[35]
S[f]	0.60	13.44	0.54	4.58	N719	[36]
DCM[g],CBD[d]	0.60	4.02	−	1.00	N3	[37]

a PD=Pre-dyeing method

b EPD=Electrophoretic deposition

c DCTP=Direct current thermal plasma

d CBD=Chemical bath deposition

e DBT=Doctor-blade technique

f S=Sputtering o E=Etching

g DCM=Dip coating method.

Table 3.5 gives various preparation methods of ZnO, photovoltaic parameters of their DSSCs [5, 33-37]. Through the comparison of various methods for low temperature preparation DSSCs, the performance of DSSCs based on pre-dyeing method is equivalent to the middle level. Although the performance is not very high, but for such a simple production process, it is worth studying. Since it is suitable for roll-to-roll process, it can be made cheaper and the production efficiency can be greatly improved.

3.8 Performance evaluation of D131 dye and D358

In previous studies, we have reported two dyes, EosinY and D149 dye. Depending on the combination of dyes, there is also the possibility of high efficiency. Therefore, as a dye other than EosinY and D149, D131 dye was paid to attention. Compare with D149 dye, the D131 dye has a simpler structure. The absorption maximum wavelength (420nm) of the light absorption spectrum is on the short wavelength region. When combined with ZnO, it has been reported that the absorption wavelength on the short wavelength side is efficiently converted into electric energy, and the conversion efficiency is as high as about 4%. At the same time, we used D358 dye with the same color as D149 dye and fabricated solar cells. **Figure 3.9** and **Table 3.5** show the DSSC performance compared with the traditional method and pre-dyeing method.

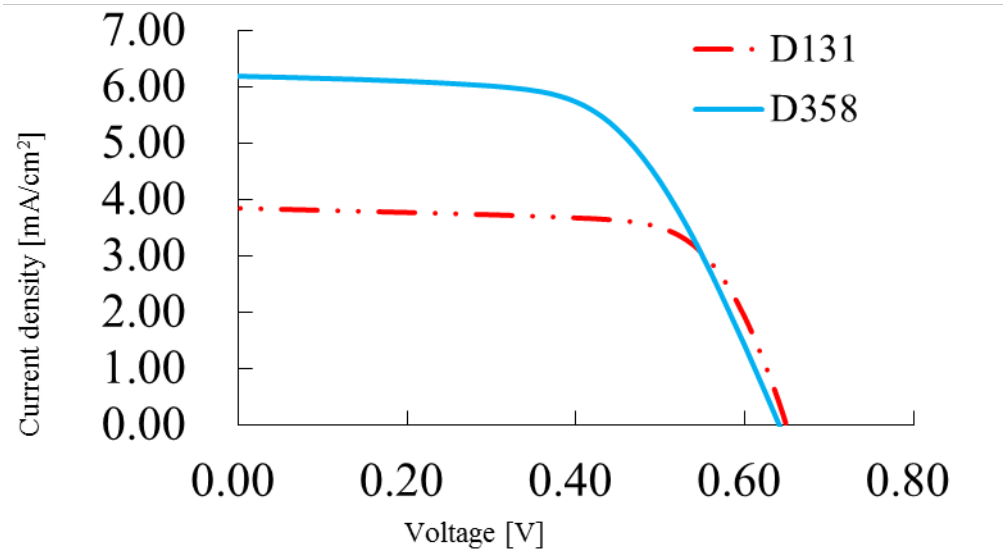

Fig.3.9 IV-curve of the pre-dyeing method with D131 dye and D358 dye.

Table.3.5 Performance of the pre-dyeing method with D131 dye and D358 dye.

Pre-dyeing method	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
D131	0.65	3.85	0.70	1.76
D358	0.64	6.20	0.60	2.37

As for the traditional method, we achieved conversion efficiency of 2.51% using D131 dye. For the pre-dyeing method, the performance is slightly lower than the traditional method.

3.9 Conclusion

We reported the photovoltaic performance of DSSCs based on pd-ZnO with or without hot-press treatment. Without hot-press: Jsc =1.97 mA cm^{-2}, Voc = 0.57V, FF = 0.80 and η = 0.90%; with hot-press: Jsc = 2.97 mA cm^{-2}, Voc = 0.59 V, FF = 0.75 and η = 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. The lower charge transfer resistance, higher photocurrent, Jsc is about 50% improved. By applying hot press to pd-ZnO thin film, some of pd-ZnO particles were crushed and bare surface of ZnO could be exposed. It is expected that compact contact between the particles is improved and movement of electrons becomes smooth. ZnO film thickness was reduced from 10-15 μm to 4-5 μm. 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. 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 relatively narrow absorption wavelength range, it has broad wavelength light absorption ability. 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. When dye concentration was increased from 0.5 mM to 1.25 mM, short circuit current (Jsc) increases with the increase of dye concentration. Jsc was not increased further at higher concentration (1.6 mM). Best performance (Jsc = 9.49 mA cm^{-2}, Voc = 0.67 V, FF = 0.67 and η = 4.24%) was achieved at 1.25 mM.

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CHAPTER 4

Performance Evaluation of DSSC made with Mixed Dye

4.1 Introduction

Absorption of photon in wide wavelength region is an important requirement for the enhancement of photo-conversion efficiency of DSSCs [1]. 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 [2-4]. 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. Efficiency improvements are observed in three kinds of DSSC made of pd-ZnO mixed film. For example, DSSC based on mixture of D131 and EosinY pd-ZnO shows appreciable increase of IPCE at 400 nm wavelength region compared with single EosinY pd-ZnO based DSSC. The photo-energy 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 yellow D131 combination. The photovoltaic parameters of the best DSSC were Jsc = 9.73 mA cm^{-2}, Voc = 0.71 V, FF = 0.68 and η =4.56%. It is notable that not only Jsc 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. Wide range wavelength light absorption by virtue of dye combination can 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.

4.2 Performance evaluation of DSSC made with the mixed dye solution

In the present study, we used some kinds of indoline in dye-sensitized DSCs based on pre-dyeing ZnO to extend their spectral range of light-harvesting to longer wavelengths [5]. There is a report recently that a mixture of two kinds of pigment which has different wavelength absorption shows the better performance to dye-sensitized solar cells, by the increase of density and more wide absorbing wavelength range [6-8].

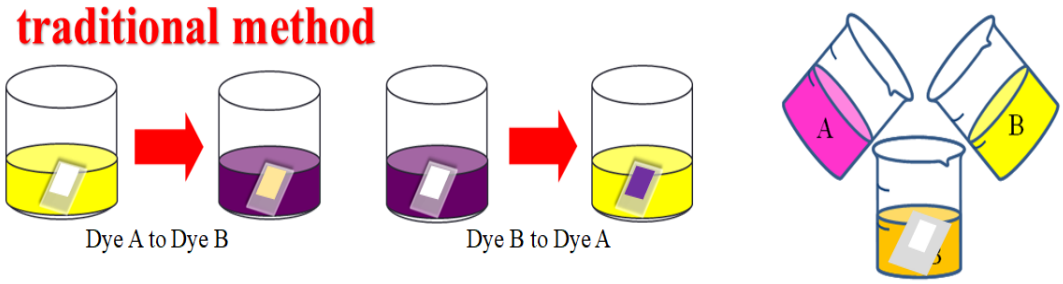

Fig.4.1 Dye adsorption modes of traditional method.

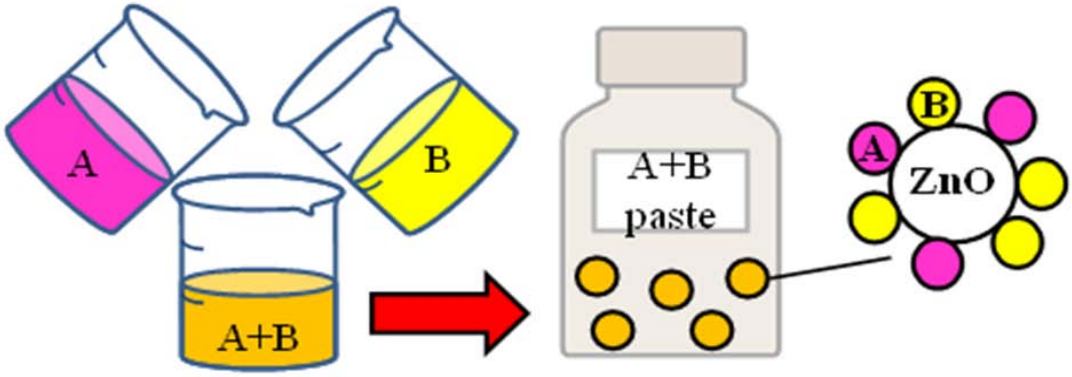

Fig.4.2 Dye adsorption mode of pre-dyeing method.

Dye sensitized solar cells using organic pigments because of each have different color, therefore they can absorb the light wavelength are different, generally from 400 ~ 700nm wavelength of visible light to obtain energy [9-12]. Two kinds of dyes having different absorption wavelength bands [13-18] were mixed to broaden the wavelength range of light that can be absorbed and at the same time the adsorption density of the dye to the ZnO surface was increased and the efficiency of converting the absorbed light to electricity was improved [19-23]. In order to absorb light in a wide wavelength band, two kinds of dyes "D149" or "D358" and "D131" are mixed. As a result, not only the wavelength band that can be absorbed is expanded but also the efficiency of converting the energy of the absorbed light into electricity can be improved as a whole [24-27]. In this study, we investigated the performance using two dyes by traditional method and pre-dyeing method. The dye adsorption of traditional method is shown in **Figure 4.1** and the dye adsorption of pre-dyeing method is shown in **Figure 4.2**.

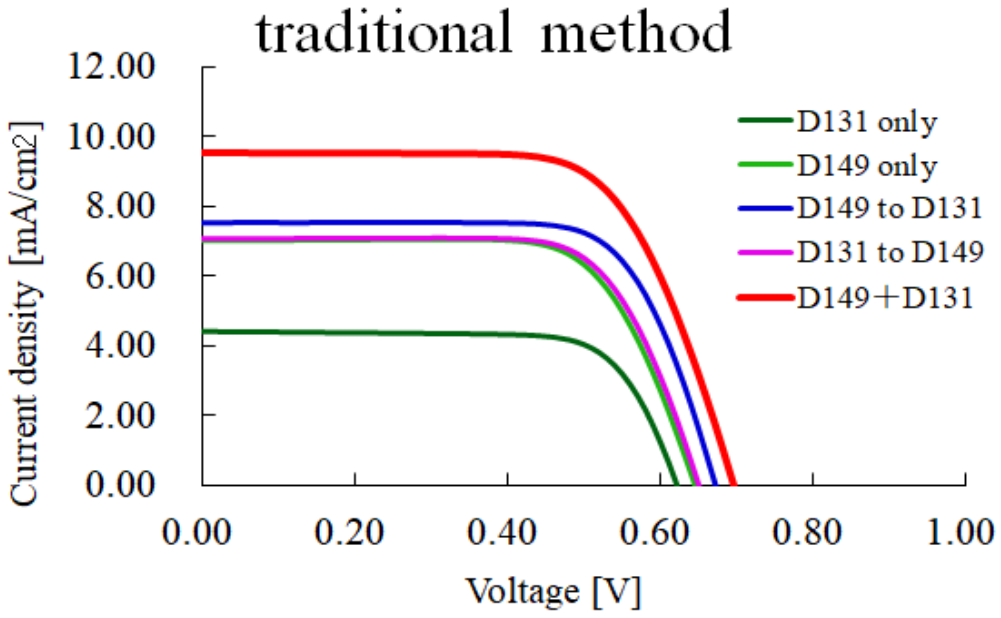

Fig.4.3 IV-curve of dye adsorption of traditional method.

Table.4.1 Performance of dye adsorption mode of traditional method.

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
D131	0.62	4.41	0.73	2.01
D149	0.65	7.02	0.70	3.18
D131 to D149	0.65	7.07	0.71	3.26
D149 to D131	0.67	7.53	0.72	3.65
D131+D149	0.69	9.70	0.70	4.69

The comparisons of performance are shown in **Figure 4.3 and Table 4.1**. Mixing two kinds of pigments increases the "absorption wavelength region", so the efficiency also increases. No matter traditional method or pre-dyeing method, the use of mixed pigments present the same results. The mixed pigment was better than a single pigment. The ordinary method due to second dye adsorption will become aggregation [28-30], the electron did not inject into conduction band of ZnO, lead to reduced conductivity. However, the efficiency of the two similar adsorption modes is almost the same.

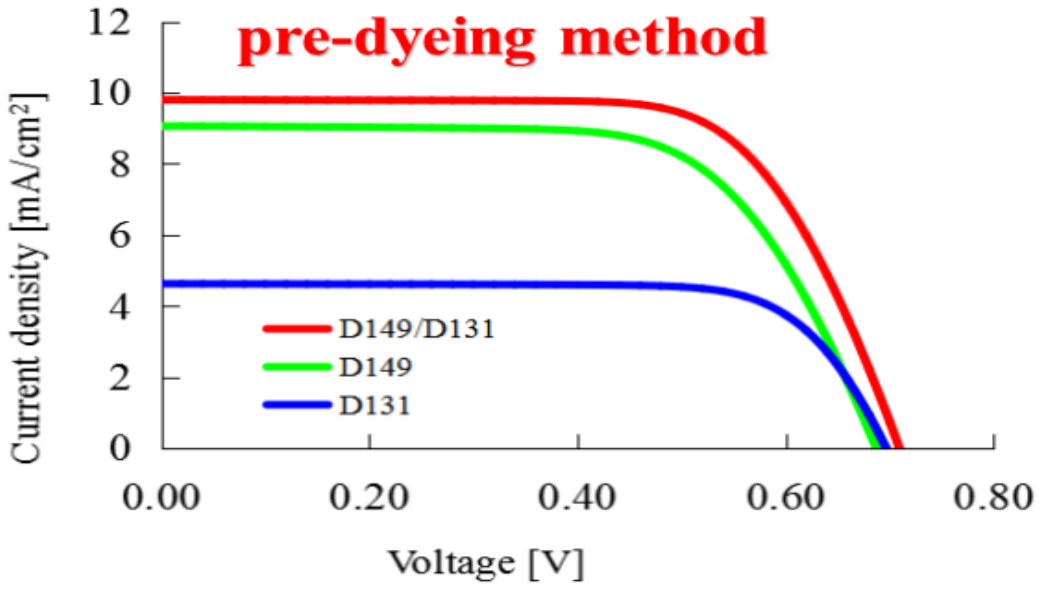

Fig.4.4 IV-curve of dye adsorption of mixed solution (pre-dyeing method).

Table.4.2 Performance of dye adsorption of mixed solution (pre-dyeing method)

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
D149/D131	0.70	9.80	0.68	4.66
D149	0.68	9.06	0.66	4.11
D131	0.69	4.98	0.72	2.44

In the mixed dye sensitization system by sequential dye adsorption, the performance was improved more than the single dye. In pre-dyeing method (**Figure 4.4 and table 4.2)**, ZnO powder into dye solution that had mixed A and B dye solution. Then make the paste. Two kinds of dyes in ZnO surface are adjacent to each other. In traditional method, ZnO paste coating on the substrate, then absorbed different dyes in turn. For sequential adsorption, Jsc was higher in D149 to D131 than in D131 to D149. The reason is that D149 with a wider absorption wavelength range is absorbed first, and the D131 farther away from the ZnO film absorbs less sunlight. In turn, D131 first absorbs sunlight, D149 while away from the ZnO film, but its wide absorption field and deep color, so obtained high efficiency. Through the I-V curve we can see no matter traditional method or pre-dyeing method, the use of mixed pigments present the same results. That is mixed pigment is better than a single pigment. Jsc was improved by combining a plurality of dyes in combination with D131 dye which at the short wavelength side having maximum absorption wavelength.

4.3 Performance evaluation of DSSC made with the mixed pd-ZnO powders

Three kinds of dyes have D131, D358 and EosinY show yellow, purple and pink hue, respectively. We used two kinds of pd-ZnO powders to produce dye-sensitized solar cells shown in **Figure 4.5**. Put ZnO powder into Dye A and Dye B solution separately, form pd-ZnO powder. Then mixed these two kinds of Pd-ZnO powder, and make the paste. By adopting mixed pigment, increase the absorption wavelength range. The IPCE spectrum is a plot of a ratio of number of output electrons (current) and input photons (irradiance) against wavelengths [31]. In theory, when two types of dye which have different wavelength range are mixed, the wavelength range will overlap or add up. Beside the increasing wavelength of the horizontal axis, the efficiency of incident light conversion current is also very important in vertical axis.

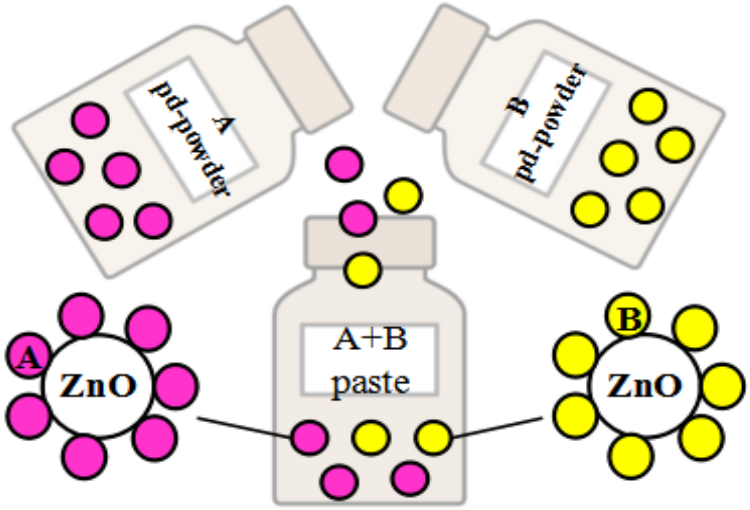

Fig.4.5 The adsorption dye pattern of two pd-ZnO powders

4.3.1 Dye combination of D131 and EosinY

In the first experiment, EosinY and D131 were used. The current–voltage characteristics under simulated solar light (AM1.5G) of solar cells are shown in **Figure 4.6**(right). The incident photon-toelectron conversion effciency (IPCE) spectra are shown in **Figure 4.6**(left). A variety of mixed dye systems were compared with a single dye to observe changes in the absorption spectra for DSSCs using multiple dyes. Through IPCE, the two kinds of pigments had different absorption wavelength range. DSSC based on mixture of D131 and EosinY pd-ZnO shows appreciable increase of IPCE at 400 nm wavelength region compared with single EosinY pd-ZnO based DSSC. According to IPCE, the absorption range of the mixed pigment was larger than that of a single pigment. Therefore, in the IV curve, the Jsc of the mixed pigment is higher, so its efficiency is better than that of the single pigment.

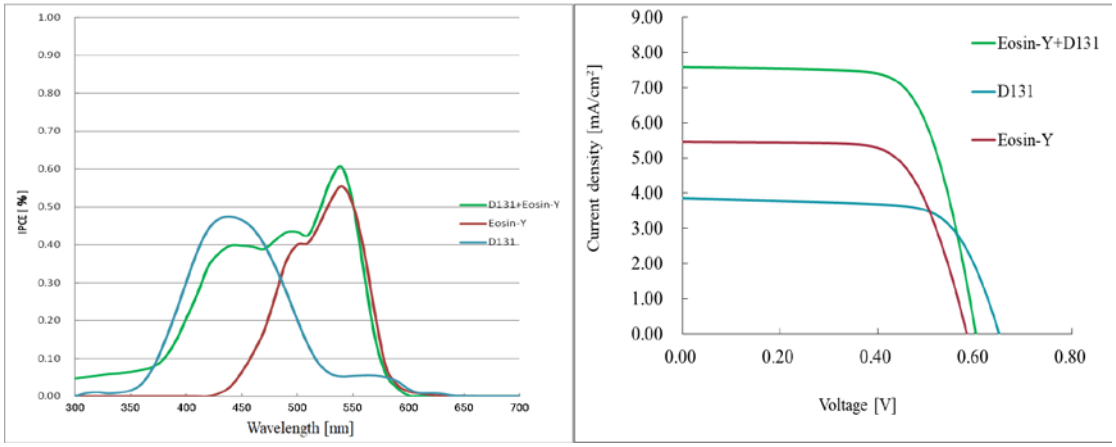

Fig.4.6 Spectral incident photon-to-electron conversion effciency (IPCE) of ZnO-DSCs sensitized with EosinY, D131, EosinY+D131(right). Current–voltage characteristics of DSCs built from ZnO films sensitized with di fferent dyes or dye combinations(left). (pre-dyeing method).

4.3.2 Dye combination of D131 and D358

In the second experiment, we chose D358 and D131. DSSC based on mixture of D131 and D358 pd-ZnO shows appreciable increase of IPCE at 400 nm wavelength region compared with single D358 pd-ZnO based DSSC. The current–voltage characteristics under simulated solar light (AM1.5G) of solar cells are shown in **Figure 4.7** (right). The incident photon-to-electron conversion efficiency (IPCE) spectra are shown in **Figure 4.7** (left). Through IPCE and IV curves, the same results showed that he photoenergy conversion efficiency of mixed pd-ZnO based DSSCs are higher than that of single pd-ZnO based DSSCs.

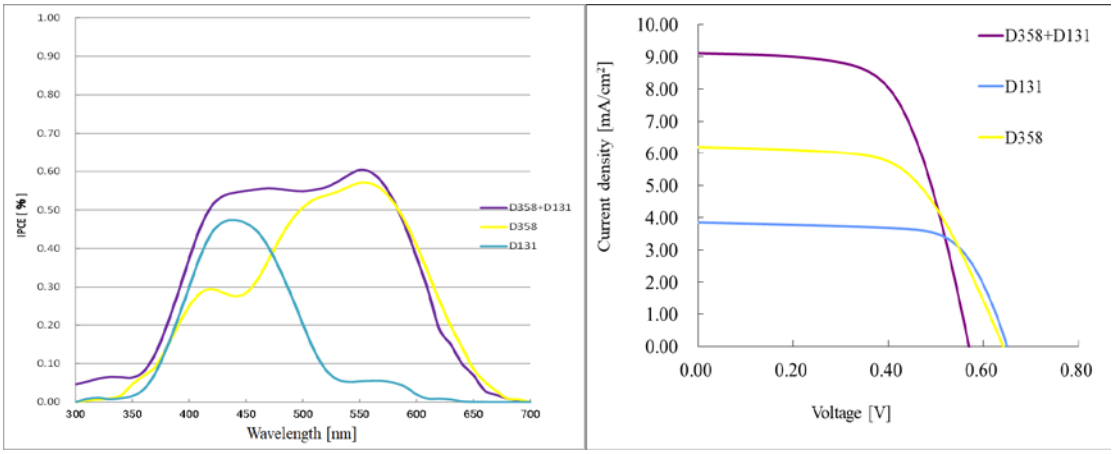

Fig.4.7 Spectral incident photon-to-electron conversion effciency (IPCE) of ZnO-DSCs sensitized with D358, D131, D358+D131(right). Current–voltage characteristics of DSCs built from ZnOfilms sensitized with di fferent dyes or dye combinations(left). (pre-dyeing method).

4.3.3 Dye combination of EosinY and D358

In the third group, we chose two red-colored item pigments D358 and EosinY. The incident photon-to-electron conversion efficiency (IPCE) spectra are shown in **Figure 4.8**(left). The current−voltage characteristics under simulated solar light (AM1.5G) of solar cells are shown in **Figure 4.8**(right). Although the mixed pigment efficiency is higher than that of the single D358 pigment, it is not obvious. The photo-energy 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.

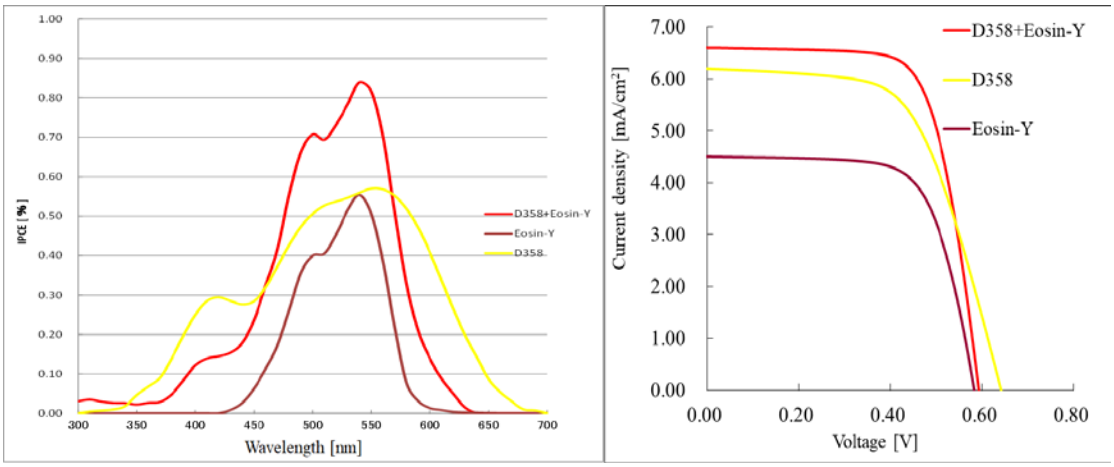

Fig.4.8 Spectral incident photon-to-electron conversion effciency (IPCE) of ZnO-DSSCs sensitized with EosinY, D358, EosinY+D358 (right). Current−voltage characteristics of DSSCs built from ZnOfilms sensitized with di fferent dyes or dye combinations (left). (pre-dyeing method).

4.3.4 Summary of three dyes combination

Figure 4.9 shows the incident photon-to-electron conversion efficiency (IPCE) with different pigment. In **Figure 4.10 and table 4.3**, 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. For example, DSSCs based on mixture of D131 and EosinY pd-ZnO (green line) shows appreciable increase of IPCE at 400 nm wavelength region compared with single EosinY 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 EosinY combination because light absorption wavelength ranges of D358 and EosinY are overlapped each other.

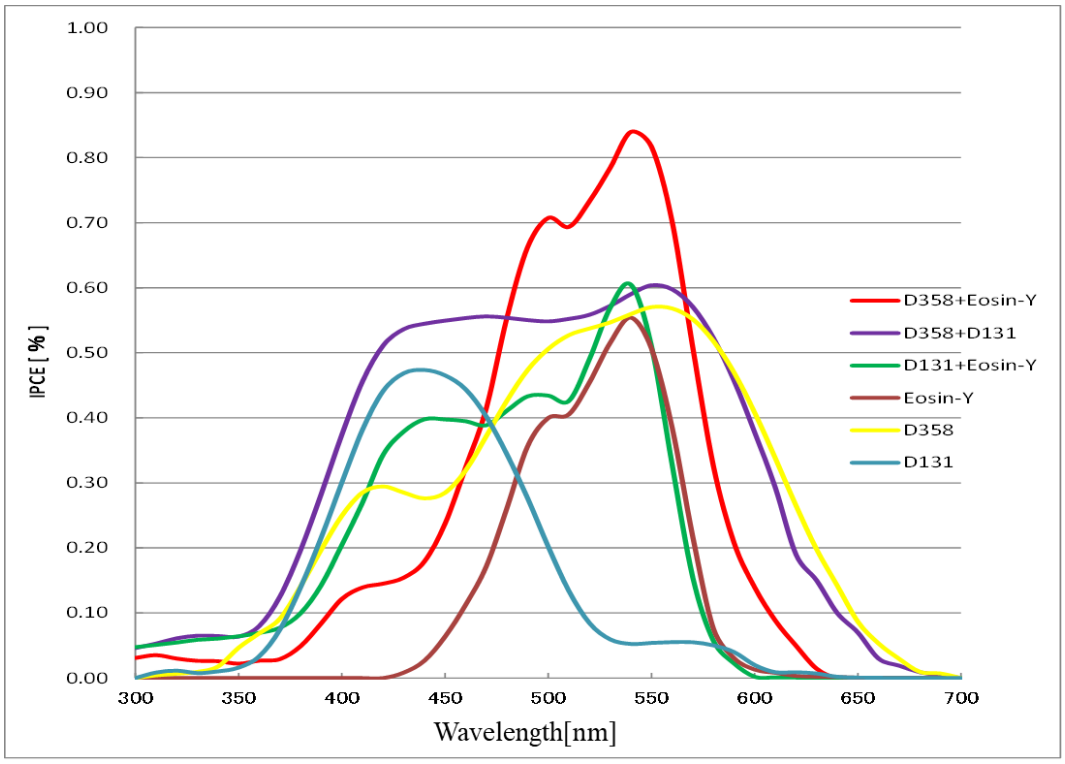

Fig.4.9 IPCE of mixed pigment and single pigment. Single pigment was Eosin Y, D131 and D358. Mixed pigment were D358 and Eosin Y; D358 and D131; D131 and Eosin Y.

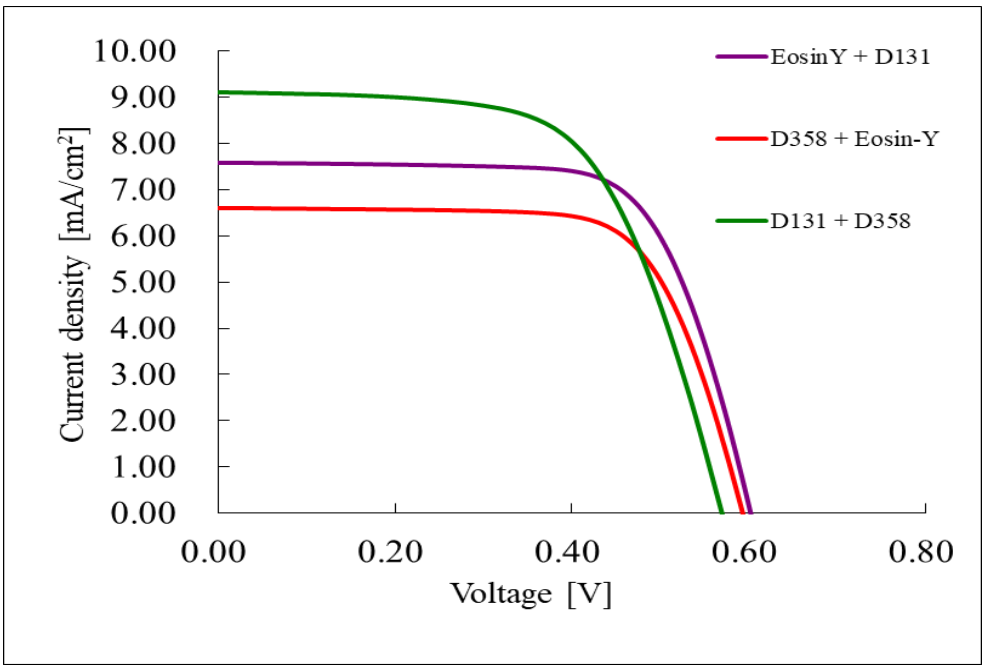

Fig. 4.10 The current–voltage characteristics of mixed pigment. Mixed pigment were D358 and Eosin Y; D358 and D131; D131 and Eosin Y.

Table. 4.3 Photovoltaic performance of DSSCs based on pd-ZnO. Mixed pigment were D358 and Eosin Y; D358 and D131; D131 and Eosin Y.

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
EosinY + D131	0.60	7.55	0.64	2.88
EosinY + D358	0.59	6.61	0.69	2.70
D131 + D358	0.57	9.10	0.66	3.42

4.3.5 The best performance DSSC made with dye combination of D131 and D149

In our successive investigation for various dye combination, the best results was obtained by D149 and D131 combination The incident photon-to-electron conversion efficiency (IPCE) spectra of DSSCs with mixed pigment and single pigment are shown in **Figure 4.11**. The current–voltage characteristics of DSSCs with single sensitizers and the combination D149/D131 are shown in **Figure 4.12**. **Table 4.3** shows the photovoltaic parameters of the best DSSCs were Jsc = 9.73 mA/cm^2, Voc = 0.71 V, FF = 0.68 and η =4.56%. It is notable that not only Jsc 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.

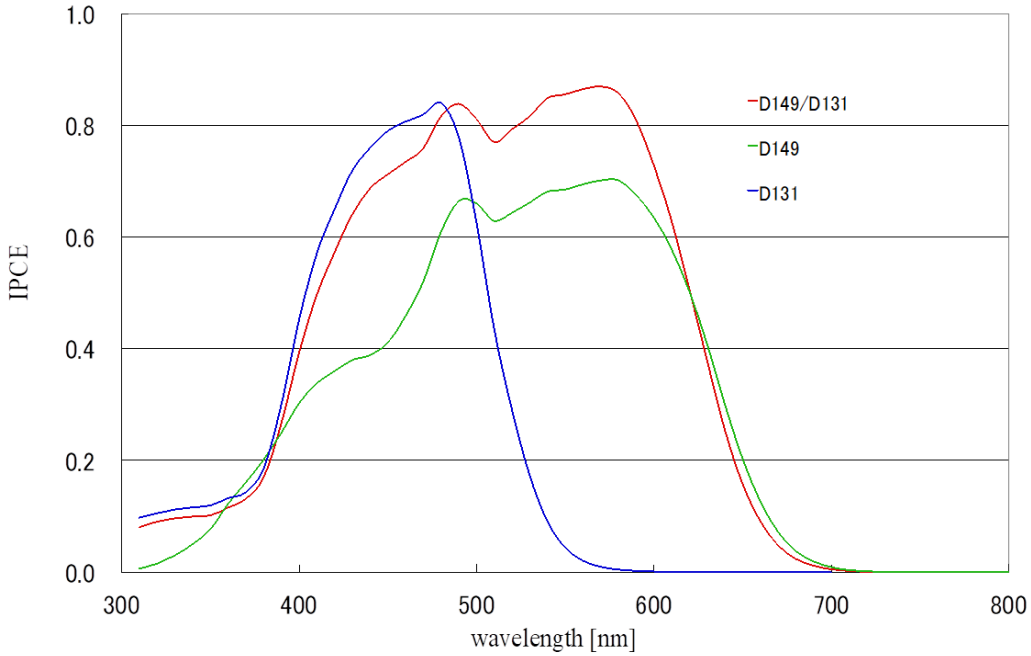

Fig.4.11 IPCE of DSSCs using pd-ZnO with mixed pigment and single pigment. Single pigment is D149. Mixed pigment is D149 and D131: Jsc = 9.73 mA cm−2, Voc = 0.71 V, FF = 0.68 and Eff =4.56%.

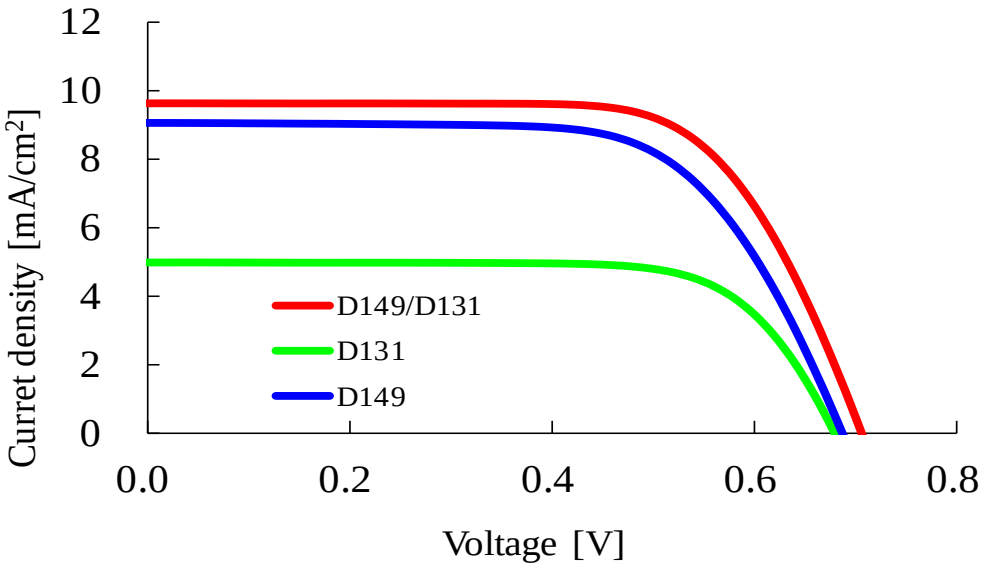

Fig. 4.12. Current−voltage characteristics of DSSCs with single sensitizers and the combination D149/D131.

Table.4.3 Photovoltaic performance of DSSCs based on pd-ZnO. The single pigments and mixed pigments.

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
D131+D149	0.71	9.73	0.68	4.56

4.4 Conclusion

For mixed dye solution systems, the traditional method and pre-dyeing method showed almost same results. That is, the performance of DSSCs with mixed pigment is higher than that of single pigment. Combined with D131, their IPCE has increased

in varying degrees, with significant changes in short-wavelength range. Although the absorption wavelength of D131 is only 500 nm at longest, it has absorption maximum at 430 nm. After mixing, the absorption efficiency increased in the short wavelength region. In the traditional method case, we did the two adsorption modes: the sequential adsorption pigments and the mixed solution. Either type of adsorption can produce a battery. However, because the secondary adsorption pigment can cause the pigment aggregation, the sequential adsorption pigment efficiency is not ideal, and there is no effect of the adsorption mode of the mixed pigment. In the traditional method, the sequence of absorption: D131 D149 Jsc = 7.07 mA/cm^2, Voc = 0.65 V, FF = 0.71 and η= 3.26%. D149 D131 Jsc = 7.53 mA/cm^2, Voc = 0.67 V, FF = 0.72 and η= 3.65%. The adsorption efficiency of the mixed solution was 4.69% (Jsc =9.70 mA/cm^2, Voc =0.69V, FF=0.70). The maximum efficiency of DSSC produced by pre-staining was 4.66% (Jsc =9 .80mA /cm^2, Voc = 0.70V, FF=0.68). These two similar adsorption modes are almost identical in efficiency.

Mixed pd-ZnO powder is the unique method for pre-dyeing method. 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. Efficiency improvements are observed in three kinds of DSSC made of pd-ZnO mixed film. For example, DSSC based on mixture of D131 and EosinY pd-ZnO shows appreciable increase of IPCE at 400 nm wavelength region compared with single EosinY pd-ZnO based DSSC. The photo-energy 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 EosinY combination because light absorption wavelength ranges of D358 and EosinY are overlapped each other. In our successive investigation for various dye combination, the best results was obtained by purple D149 and D131 combination. The photovoltaic parameters of the best DSSC were Jsc = 9.73 mA cm^{-2}, Voc = 0.71 V, FF = 0.68 and η =4.56%. It is notable that not only Jsc improvement but also higher Voc contribute the improvement of efficiency. Although the traditional method and pre-dyeing method have achieved almost the same efficiency, the pre-dyeing process is simpler and more suitable for roll-to-roll process.

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CHAPTER 5

Performance of DSSC made with pre-dyeing method (Double Layer)

5.1 Introduction

The absorption of photons in the wide wavelength region is an important condition for improving the efficiency of DSSCs. In order to obtain a larger absorption wavelength range, use the appropriate sensitizer to extend the absorption wavelength range beyond the D149 absorption range. The second indoline dye (D131) was introduced as a sensitizer to extend the light collection to the blue range of the visible spectrum [1]. In theory, the traditional method of making a double layer is like this. TiO_2 paste was coated on glass substrate. Then, sintered at 450 °C for 30 min to archive good adhesion of particles and glass substrate [2]. The substrate was immersed in a solution dye A at room temperature for 1 h. Make a double layer once again through the above process [3-5]. In fact, in the second sintering, the pigment is not resistant and decomposition in high temperature. Therefore, can't make a double layer film (**Figure 5.1**).

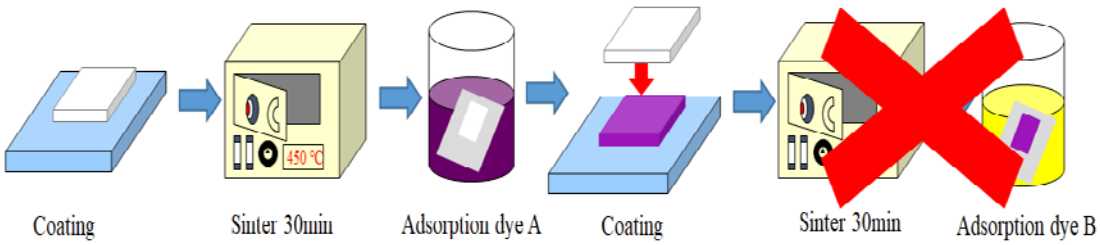

Fig.5.1 Fabrication of the double-layer electrode by traditional method.

There are some special methods [6-9] for the production of double layer film, such as Hayase group [10]. They made a titania layer was stained portion-selectively with two dyes under a supercritical condition of carbon dioxide to fabricate the double titania layers. Although a double layer of solar cell is produced, the technique is complex and

time-consuming [11-14], and it is not suitable for roll-to-roll process. In practice, the multiple layers of the dye-sensitizing films can extend the response wavelength range of light sensitizing and enhance the conversion efficiency of light to electric, when the ZnO and dye are uniform distribution in the interface between two layers. Therefore we propose a pre-dyeing method to fabricate the DSSC, in which the pre-dyeing process is carried out at the first stage, and the pd-ZnO paste with uniform density distribution of ZnO and dye is distributed by the dye adsorbed film making on plastic (ITO/PET) substrate [15-19]. Carrying out above process multiple times with different pd-ZnO, the multiple layers of pre-dyed ZnO can be formed with good conductivity at the interface between layers. Moreover in advance the pd-ZnO paste can be prepared, thus the processing time of the roll to roll making the flexible solar cell is much shorter than that of the traditional method.

5.2 Preparation of double-layer electrode

The double-layer film is difficult to achieve by traditional method, much less multi-layer. However, pre-dyeing method is a good solution to this problem. Due to the pre-made pd-ZnO paste, any pd-ZnO paste can be combined freely. Because this characteristics, multi-layer film is easy to make. In the case of the pre-dyeing method, since two types of pd-ZnO paste can be adjusted separately, it is possible to prepare double-layer electrode by continuously applying two kinds of dye adsorption layers. The advantage of this method is that the interaction between the two kinds of dyes is restricted only to the interface of the two layers and can be constituted of most of the porous ZnO alone.

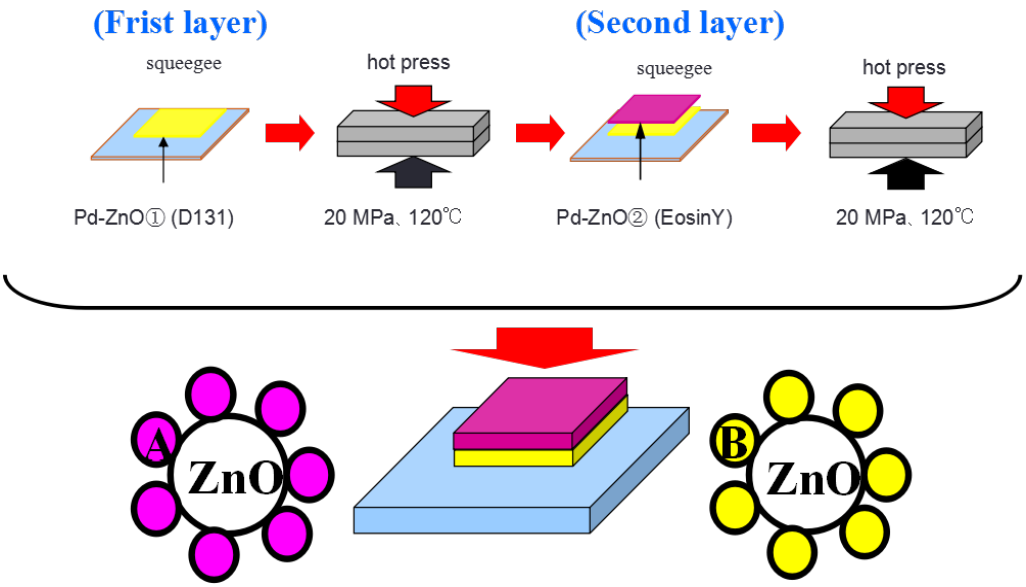

Fig.5.2 Fabrication of the double-layer electrode by pre-dyeing method.

The first layer was formed by pd-ZnO paste which adsorbed the pigment, and the second layer was formed by pd-ZnO paste which had been adsorbed by another dye after the hot-press treatment. Then, the second layer was heat-pressed again to form a double layer electrode. Hot press treatment after each coating. We need to make hot press twice. The double-layer is easy to make. The fabrication of the double-layer electrode shows in **Figure 5.2**. In our experiments, the two dyes were used in combination with D131, respectively, to make a double-layer electrode. In the EosinY and D131 production of double-layer electrode in the process, we use them as the first layer to the preparation of electrodes respectively. Through the results the two samples D131-EosinY and EosinY-D131 show high absorbance. We know that the first layer is D131 shows high efficiency (**Figure 5.3** and **Table 5.1**.), at the same time, mixed pigments are more efficient than single pigments. It may have been caused by particularly strong Rayleigh scattering of incident light at the nanoparticulate ZnO films, which becomes stronger towards smaller wavelengths and could have prevented a part of the transmitted light of shorter wavelengths from being detected [20, 21]. But in turn, the first layer is EosinY shows low efficiency, because of D131 is better than EosinY, the second layer is away from light, short-wavelength is absorbed at first. When the second layer is far away from the light source, the light transmittance is low and the electron capture efficiency is low [22].

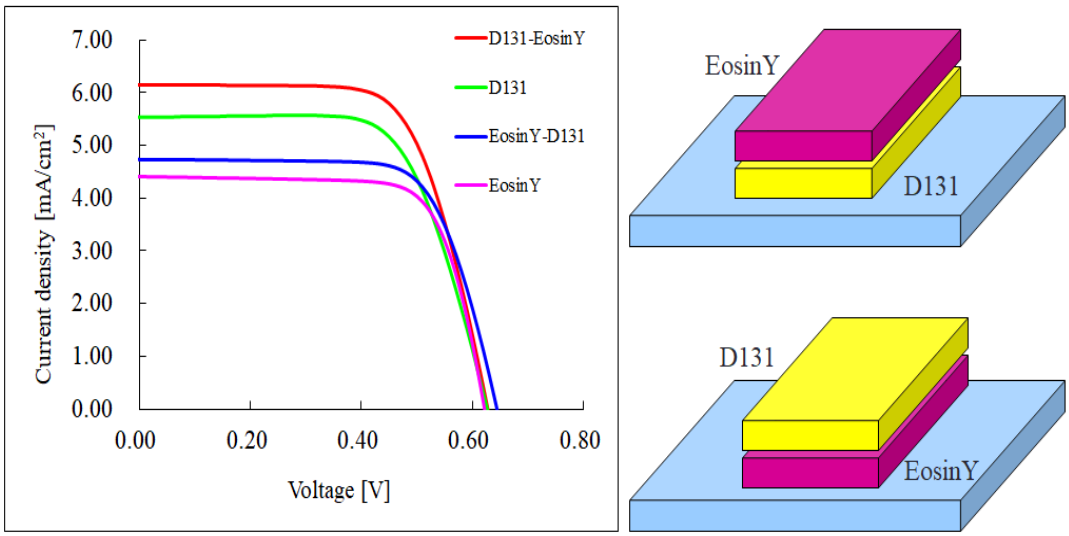

Fig.5.3 The IV curve of the double layer with EosinY and D131 case.

Table.5.1 Performance of DSSCs based on double layer and single layer made by pre-dyeing method (EosinY and D131).

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
D131-EosinY	0.69	6.16	0.67	2.62
EosinY-D131	0.65	4.83	0.69	2.17
D131	0.63	5.54	0.68	2.33
EosinY	0.62	4.41	0.73	2.01

Because of EosinY and D131, D131 shows high efficiency as the first layer. Therefore, we only use D131 as the first layer to prepare electrodes during the production of D149 and D131. The results are shown in **Figure 5.4** and **Table 5.2**. In the case of D149 and D131, although the light transmittance is affected due to the film thickness, the efficiency of the double-layer electrode and the single-layer electrode is almost the same. But it is also more efficient than DSSCs that only use a single pigment. Using this phenomenon, the photoelectric conversion efficiency is improved. From the results of the experiment, the most efficient: Jsc = 10.04 mA/cm^2, Voc = 0.68v, FF = 0.67 and η= 4.57%. We have proposed the pre-dyeing method to fabricate the flexible solar cells, which is suitable to mass production. This method can realize the multiple-layer structure of the pre-dyeing films to obtain the response of a wide wavelength range and achieve the enhancement of the photovoltage performance. The experiment of pd-ZnO method showed that desired results have been achieved.

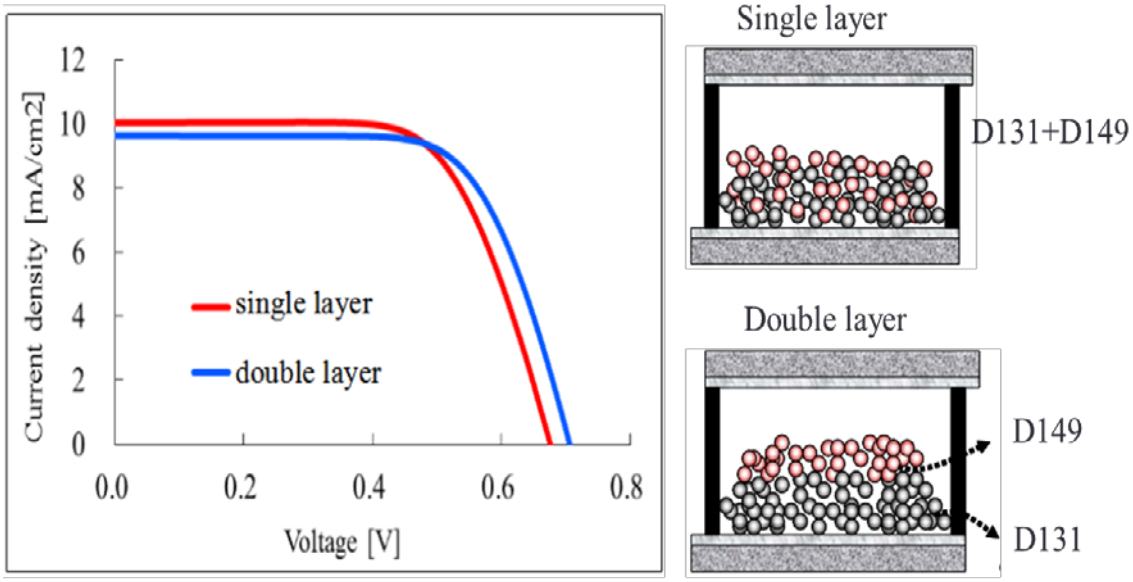

Fig.5.4 The IV-curve of double layer and single layer based on pre-dyeing method (D149 and D131).

Table.5.2 Performance of double layer and single layer based on pd-ZnO method (D149 and D131).

	Voc [V]	Jsc [mA/cm^2]	FF	Eff [%]
Single layer	0.69	9.81	0.67	4.54
Double layer	0.68	9.99	0.67	4.57

5.3 Conclusion

The double-layer electrode can be easily prepared by the pre-dyeing method, and the efficiency is substantially the same as the single-layer electrode. Overall, compared with the traditional method, the performance of pre-dyeing method was almost same. In EosinY and D131 double-layer case, D131 as the first layer shows higher efficiency. Because of D131 is better than the EosinY. At the same time, the second layer away from the light, short-wavelength is absorbed at first. While the second layer away from the light source, electron capture efficiency is low. However, when D131 in the second layer, it will become difficult to absorbed, because the short wave is difficult to pass. D131-EosinY was Jsc =6.16 mA/cm^2, Voc =0.69 V, FF=0.67 and η=2.62%. EosinY-D131 was Jsc =4.83 mA/cm^2, Voc =0.65 V, FF=0.69 and η=2.17%. In the case of D149 and D131, as with the previous results, double-layer electrodes are efficient. Jsc =10.04 mA/cm^2, Voc =0.68 V, FF=0.67 and η=4.57%. Pre-dyeing method achieves the same effect as traditional method.

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CHAPTER 6

Conclusions

In this thesis the photovoltaic performance of dye-sensitized solar cells based on the pre-dyeing method ZnO in combination with different kinds of dyes has been studied in detail.

Glass substrates are mainly used as materials for dye-sensitized solar cells, but by using a plastic substrate, weight reduction, diversification of installation location, cost reduction by introduction of roll-to-roll manufacturing method, etc. can be achieved. Dye-sensitized solar cell is generally produced by a procedure of forming an oxide semiconductor thin film on a substrate and adsorbing a dye. However, since dye adsorption takes time from several hours or even a day, the production efficiency is lowered and the manufacturing cost rises, and the merit of introducing the roll-to-roll production method of high speed and high efficiency is lost. In view of this, the dye-adsorbing step after film formation was omitted by using the pre-dyeing method in which the dye was previously adsorbed on the ZnO nanopowders so that the electrode could be produced in a short time. In this study, we examined optimization of paste and dye adsorption condition when FINEX-50 with a particle diameter of 20nm was used, and improvement of hot press processing condition was examined. By setting the conditions of the hot pressing treatment only from the upper plate and by setting the paper bundle as the heat insulating material on the bottom plate, at the same time, the pressing time to be as short as 20 seconds, it is possible to manufacture the electrode without peeling off the ZnO film from the substrate. The dye adsorption amount can be increased by replacing the FINEX-50 having an average particle diameter of 40nm with the ZnO nanopowders FINEX-50 having an average particle diameter of 20nm. The conversion efficiency improved from 1.58% to 2.03%. When fabricating a cell by pre-dyeing method using EosinY dye, improvement of cell performance was seen performing hot pressing treatment, but the cell performance was still considerably lower than that of the traditional method.

In the preparation of pre-dyeing ZnO (pd-ZnO), the amount of pigment is expected to be small relative to the amount of ZnO. Therefore, through increasing the dye concentration, hit the purpose of raising the amount of dye. When the dye concentration is 1.25 mM (dye amount 5.0×10^{-5}mol/g-ZnO), Jsc 4.57 mA/cm^2, conversion efficiency 1.97% was achieved. Performance improved by using D149 dye

with a wider absorption wavelength range instead of EosinY dye. Even in the D 149 dye, as with the Eosin Y dye, the dye adsorption can be increased by increasing the amount of dye relative to the amount of ZnO, and at the dye concentration of 1.25mM, Jsc 9.4mA/cm^2 and Conversion efficiency of 4.24% are achieved.

Absorption of photon in wide wavelength region is an important requirement for the enhancement of photo-conversion efficiency of dye sensitized solar cell. The mixture of two kinds of pigment which has different wavelength absorption show the better performance to dye sensitized solar cell, by the increase of dye coverage density and more wide absorbing wavelength range. Three kinds of dyes D131, D358 and EosinY show yellow, purple and pink color, respectively. By adopting mixed pigment, it was able to increase the absorption wavelength range. In the mixed dye sensitization system, a dye-adsorbing porous ZnO electrode was prepared by the following four methods. 1) The ZnO electrode prepared by the traditional method was sequentially immersed in two kinds of dye solutions to adsorb dye. 2) A ZnO electrode prepared by a traditional method is immersed in a mixed solution of two kinds of dyes to adsorb a dye. 3) A method in which a paste is prepared by mixing a pre-dyeing ZnO powder to which two kinds of dyes are separately adsorbed, and the coating is applied (single layer). 4) A method of sequentially applying a pre-dyeing ZnO paste in which two types of dyes are individually adsorbed (double layer). Dye combination to broaden the absorption of light. The Jsc is improved by combining with the D131 dye having the maximum absorption wavelength on the shorter wavelength side, and the conversion efficiency is improved in any case. Since mixed pd-ZnO powder is the unique method for pre-dyeing method, a variety of mixed dye systems were compared with a single dye to observe changes in the absorption spectra for DSSCs using multiple dyes. Efficiency improvements are observed in three kinds of DSSC made of pd-ZnO mixed film. In our successive investigation for various dye combination, the best results was obtained by purple D149 and D131 combination. The photovoltaic parameters of the best DSSC were Jsc = 9.73 mA cm^{-2}, Voc = 0.71 V, FF = 0.68 and η =4.56%. It is notable that not only Jsc improvement but also higher Voc contribute the improvement of efficiency. Although the traditional method and pre-dyeing method have achieved almost the same efficiency, the pre-dyeing process is simpler and more suitable for roll-to-roll process. Overall, compared with traditional method, the pre-dyeing method has small variance and good stability. The maximum efficiency is 4.61% (traditional method). We achieved a 4.57% efficiency using a double layer electrode by pre-dyeing method. Employing either the traditional method

or the pre-dyeing method, the DSSCs based on mixed pigments could result in improved efficiency. How to increase the conversion efficiency at low cost is important, and the mixed dye adsorption method can increase the light absorption capacity and absorption the band while keeping the structure close to the current solar cell structure.

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.

List of Publication

International Journals

1) L. Zhang, A. Konno (2018) Development of Flexible Dye-sensitized Solar Cell Based on Zinc Oxide Nanoparticle Adsorbed Dye Mixture, *Int. J. Electrochem. Sci.*, **13**, 344-352.

2）L. Zhang, A. Konno, Production of dye-sensitized solar cells by pre-dyed ZnO multiple layers, submitted to Japanese Journal of Applied Physics.

Conference and proceedings

1）発表年月：2013.7
開催場所：岐阜大学
会議名：第 24 回　東海地区光電気化学研究会
題目：先染め酸化亜鉛電極を用いる複合色素増感型太陽電池
著者名：張亮、昆野昭則

2）発表年月：2014.12
開催場所：静岡大学
会議名：第 4 回教育フォーラム
題目：Development of flexible dye-sensitized solar cell based on zinc oxide nanoparticle adsorbed dye mixture
著者名：張亮、昆野昭則

3）発表年月：2015.11
開催場所：三重大学
会議名：中部化学関係学協会支部連合秋季大会
題目：複合色素を用いる先染め色素増感型太陽電池の開発
著者名：張亮、磯和樹, 昆野昭則

4）発表年月：2016.2
開催場所：静岡大学
会議名：国際シンポジウム若手ワークショップ
題目：Development of pre-dyeing dye-sensitized solar cells using double pigments
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