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Research Article

Characterization of Natural Dye Extracted from Wormwood and Purple Cabbage for Dye-Sensitized Solar Cells

Ho Chang,[1] Mu-Jung Kao,[2] Tien-Li Chen,[3] Chih-Hao Chen,[4,5] Kun-Ching Cho,[6] and Xuan-Rong Lai[1]

[1] *Graduate Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 10608, Taiwan*
[2] *Department of Vehicle Engineering, National Taipei University of Technology, Taipei 10608, Taiwan*
[3] *Department of Industrial Design, National Taipei University of Technology, Taipei 10608, Taiwan*
[4] *Graduate Institute of Mechanical and Electrical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan*
[5] *Department of Thoracic Surgery, Mackay Memorial Hospital, Taipei 10449, Taiwan*
[6] *Department of Civil Engineering, Texas A & M University, College Station, TX 77843-3136, USA*

Correspondence should be addressed to Ho Chang; f10381@ntut.edu.tw

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This study used natural dyes as sensitizers of dye-sensitized solar cells (DSSCs) to replace expensive chemical synthetic dyes. We prepared two natural dyes, chlorophyll dye and anthocyanin dye, by extracting them from wormwood and purple cabbage, respectively. Moreover, we mixed the prepared chlorophyll dye and anthocyanin dye at 5 different volume ratios to form cocktail dyes. For preparation of photoelectrode, P25 TiO_2 nanoparticles were used to prepare paste, which was coated on fluorine-doped tin oxide (FTO) conductive glass by the spin coating method at different spin coating speeds in order to form TiO_2 thin films with different thicknesses. The DSSC prepared by the cocktail dye achieves photoelectric conversion efficiency (η) of 1.95%, open-circuit voltage (V_{OC}) of 0.765 V, and short-circuit current density (J_{SC}) of 5.83 mA/cm^2. Moreover, the prepared DSSC sensitized solely by chlorophyll extract of wormwood achieved a photoelectric conversion efficiency (η) of 0.9%, whereas the DSSC sensitized solely by anthocyanin extract of purple cabbage achieved a photoelectric conversion efficiency of 1.47%, achieving the longest lifetime of electrons amongst these three dyes.

1. Introduction

In 1954, Bell Laboratories introduced a crystalline silicon solar cell with efficiency reaching 4.5%, bringing about the development of solar cells in the subsequent decades [1]. However, crystalline silicon solar cells have a disadvantage; that is, the process of making a single crystal silicon is very expensive. Therefore, the development of highly efficient and low-cost solar cells became a necessary trend. In the early 1990s, O'Regan and Grätzel developed the dye-sensitized solar cell (DSSC). This kind of solar cell can be prepared in a general environment, and the preparation cost is tremendously reduced [2]. On the other hand, compared to the crystalline silicon solar cell, DSSCs use a solid-liquid interface, which is produced from a solid-state semiconductor and an electrolyte as the driving force. Since the interface can be formed easily, the preparation process of DSSCs is simpler. Therefore, the photosensitive dye or TiO_2 thin film electrode has aroused extensive study in academic circles. Many studies have investigated the application of nano-TiO_2-made photoelectrode thin film to DSSCs.

In current studies of DSSCs, DSSCs are mostly sensitized by chemical synthetic dyes because their photoelectric conversion efficiency can reach 11-12% [3, 4]. However, these kinds of synthetic dyes, such as N3 and N719, have high production costs and easily create environmental pollution. In comparison, fruits and vegetables are indispensable. Moreover, they are organic, easily obtainable, and inexpensive. Thus, fruits and vegetables can reduce the cost of DSSCs and achieve more economical and environmental protection effects. Since ruthenium dyes are very rare and expensive, there is considerable interest in recent times toward the use of natural organic dyes extracted from various plants, fruits, flowers, and leaves as molecular sensitizers in DSSCs [5]. Several natural pigments such as anthocyanin, chlorophyll, tannin, and carotene have been successfully used as sensitizers in DSSCs [6–11]. Hao et al. took extracts of black rice, capsicum, erythrina variegata flower, rosa xanthine, and kelp as natural dyes. His research results showed that the DSSC sensitized by black rice had the greatest photoelectric conversion efficiency at 0.327% [12]. Sirimanne et al. used anthocyanin in pomegranate as dye, and the photoelectric conversion efficiency of the prepared DSSC was 0.6% [13]. Calogero and Marco took the red Sicilian orange and purple eggplant as photosensitizers. The DSSC sensitized by red Sicilian orange achieved higher photoelectric conversion efficiency at 0.66% maximum [14]. Jin et al. took wormwood as a natural dye, and the photoelectric conversion efficiency of the prepared DSSC was 0.9% [15]. Calogero et al. used carrot and fruit of the overlord tree as natural dyes, and the photoelectric conversion efficiencies of the prepared DSSCs were 1.7% and 1.26%, respectively [16]. Zhou et al. took 20 different kinds of natural dyes to conduct analysis and found that the DSSC prepared by mangosteen pericarp had the highest photoelectric conversion efficiency at 1.17% [17]. Zhu et al. extracted a photosensitizer from frozen blackberries and purified single-wall nanotubes as the counterelectrodes to prepare a DSSC. The photoelectric efficiency of the prepared DSSC was 1.46% [18].

In DSSCs, dye plays an important role. It is better for a dye to possess wider light absorption features. Taking N3 and N719 as an example, they have an absorption band at a nearly full wavelength. However, most of the natural dyes have narrower light absorption wavelength ranges, so that the photoelectric conversion efficiency of the prepared DSSC cannot be increased. However, cocktail pigments make use of the light absorption complementary features of different pigments to increase the photoelectric conversion efficiency of DSSCs. Kumara extracted shisonin and chlorophyll from shiso leaves and then mixed them to form cocktail dye. The photoelectric conversion efficiencies of the prepared DSSC was as high as 1.3% [19]. Chang extracted chlorophyll from pomegranate and anthocyanin from mulberry, and the photoelectric conversion efficiency of the prepared DSSCs were 0.597% and 0.548%, respectively. After mixing the extracted chlorophyll and anthocyanin in a volume ratio of 1 : 1, the photoelectric conversion efficiency of the prepared DSSC was increased to 0.722% [20]. This study extracted chlorophyll dye from wormwood and anthocyanin dye from purple cabbage and mixed the extracted chlorophyll dye and anthocyanin dye at 5 different ratios to blend a cocktail dye so as to increase the photoelectric conversion efficiency of DSSCs. As to the part of photoelectrode, we employed the spin coating method at three different speeds, 500, 1000, and 1500 rpm, to acquire photoelectrode thin films of three different thicknesses, and explored the effects of different thin film thicknesses on the photoelectric properties of the prepared DSSCs. Furthermore, this study also compared the effects of the DSSCs prepared by different natural dyes on voltage decay, lifetime of electrons, and incident photon to current efficiency (IPCE).

2. Experimental Details

The anthocyanin dye and chlorophyll dye used by this study were extracted from purple cabbage and wormwood, respectively. First of all, 40 g of purple cabbage was added to 80 mL of absolute ethanol. They were heated at 50°C by double-container boiling and stirred by a magnet for 30 minutes. Finally, impurities were filtered out by filter paper with pores at 0.1 μm, and then anthocyanin was prepared. Next, 2.632 g of wormwood was added to 50 g of absolute ethanol. The same extraction procedure was carried out again for anthocyanin, and then the chlorophyll dye was prepared. In addition, we prepared a cocktail dye by mixing the prepared anthocyanin dye and chlorophyll dye at five different volume ratios, 1 : 1, 1 : 2, 2 : 1, 1 : 3, and 3 : 1. As for the preparation procedure of TiO_2 paste, 25 g of P25 TiO_2 powder was added to 40 ml of nitric acid solution at 0.1 M and then added to 0.8 g of polyethylene glycol (PEG) (M.W. = 8000) and 2 ml of Triton X-100. The blended solution was stirred well until all substances inside were completely dissolved. After that, the solution underwent ultrasonic oscillation for 2 hours, and TiO_2 paste was prepared. For the process of making the photoelectrode, fluorine-doped tin oxide (FTO) conductive glass was firstly cut to the size of 2.5 cm∗2 cm. The conductive glass was sequentially placed in acetone, deionized water, and ethyl alcohol and then underwent ultrasonic oscillation for 20 minutes. The washed and cleaned conductive glass was placed in an oven at 60°C to be baked dry. After the surface became dry, a 3 M tape was stuck onto the conductive side of the conductive glass. Finally, spin coating was carried out at three preset spin coating speeds: 500, 1000, and 1500 rpm. The prepared paste was evenly coated on the conductive glass to prepare TiO_2 thin films with three different thicknesses [21]. After that, having completed spin coating process, the conductive glass was placed at room temperature to be dried for 30 minutes. Then the conductive glass was placed in a sintering furnace to be heated with the temperature rising 10°C/min until it reached 450°C. After being heated continuously for one hour, the conductive glass was placed at room temperature again. Then the preparation of photoelectrode thin film was completed.

After the sintered TiO_2 photoelectrode had been soaked in dye at a suitable temperature for 24 hours, the photoelectrode thin film could completely adsorb the dye molecules. This study blended 0.1 M of LiI, 0.05 M of I_2, and 0.5 M of 4-tert-butylpyridine and acetonitrile (ACN) to form an electrolyte. This study used tert-butylpyridine as an additive of electrolyte to increase the V_{oc} value. However, the presence of pyridine derivative like TBP will decrease the J_{sc} value and result in a decrease in the overall efficiency of the prepared DSSC [22]. In order to solve this problem, this study used spin coating method at different spin speeds to acquire an even TiO_2 thin film with optima thickness. A dropper was used to drop a certain amount of electrolyte on the counterelectrode, which was then covered by a photoelectrode. For the counterelectrode, a layer of platinum (Pt) thin film with a thickness 20 nm was sputtered on fluorine-doped tin oxide (FTO) conductive glass, and sandwich assembling was finally conducted. The two sides were fixed by clamps, and simple packaging of DSSC was completed.

This study used a UV/visible spectrophotometer to measure the absorption spectra of different natural dyes so as to understand the feature peak positions and light absorption ranges of different dyes. The photoelectric conversion efficiencies were measured with a potentiostat under illumination by a Xe lamp as the light source and an *I-V* Curve Analyzer (Keithley 2400). The light intensity corresponding to AM 1.5 was calibrated using a standard silicon solar cell. The intensity of the light was 100 mW/cm^2. The measured results formed an *I-V* curve. Through the *I-V* curve, the open-circuit voltage V_{OC} (V), short-circuit current density J_{SC} (mA/cm^2), fill factor (FF), lifetime of electrons, and open-circuit voltage decay can be acquired. Additionally, a Fourier transform infrared (FTIR) spectrophotometer was used to test the functional groups in the dye molecules. Field emission scanning electron microscopy (FE-SEM) was used to observe the surface and cross-section form of the TiO_2 thin film. Furthermore, we used this measurement system to measure the incident photon to current efficiency (IPCE) of the prepared solar cell.

3. Results and Discussion

In the experiment, P25 TiO_2 nanoparticles were used to prepare a paste. After using the spin coating method to coat the paste on FTO conductive glass, thermal treatment was carried out, and a layer of thin film was obtained. As shown in Figure 1, it can be observed from the FE-SEM image that the diameter of the TiO_2 particle is around 25 nm. It is also observed that there is no crack or gap on the thin film surface, and the particles are evenly distributed. After spin coating of TiO_2 paste at 3 spin coating speeds, 500, 1000, and 1500 rpm, 3 thin films with 3 different thicknesses were prepared. Thin film thickness is related to spin coating speed and the viscosity of paste. The advantage of using the spin coating method is that the acquired thin film can achieve even thickness. As shown in the cross-section image of TiO_2 thin film in Figures 2(a)~2(c), under the conditions of spin coating speeds at 500, 1000, and 1500 rpm, the thicknesses of 3 thin films are around 35, 24, and 18 μm, respectively.

Figure 3 shows the UV/visible absorption spectra of wormwood, purple cabbage, and cocktail dyes. As seen in the figure, these three dyes have better absorption features in the UV light zone. In the visible light zone, the absorption peaks of chlorophyll dye extracted from wormwood are at 410 nm and 660 nm, and the main absorption ranges are 400–450 nm and 650–700 nm. However, the absorption peak of anthocyanin dye extracted from purple cabbage is at 550 nm, and the main absorption range is 450–650 nm. It can be seen that within the range of 400–450 nm, the light absorption abilities of chlorophyll, anthocyanin, and cocktail dyes appear to be decreasing. This study made use of the varied absorption features of chlorophyll and anthocyanin in the light visible zone and mixed chlorophyll dye with anthocyanin dye at a fixed volume ratio to form the cocktail dye. As seen in Figure 3, the cocktail dye also possesses the absorption peaks of both chlorophyll and anthocyanin and has an increased visible light absorption range, thus achieving the enhancement effect. Therefore, more electrons in excited state were transmitted to TiO_2 to enhance the photocurrent strength of the solar cell.

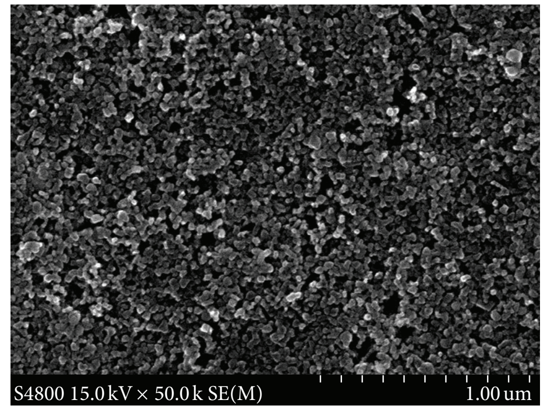
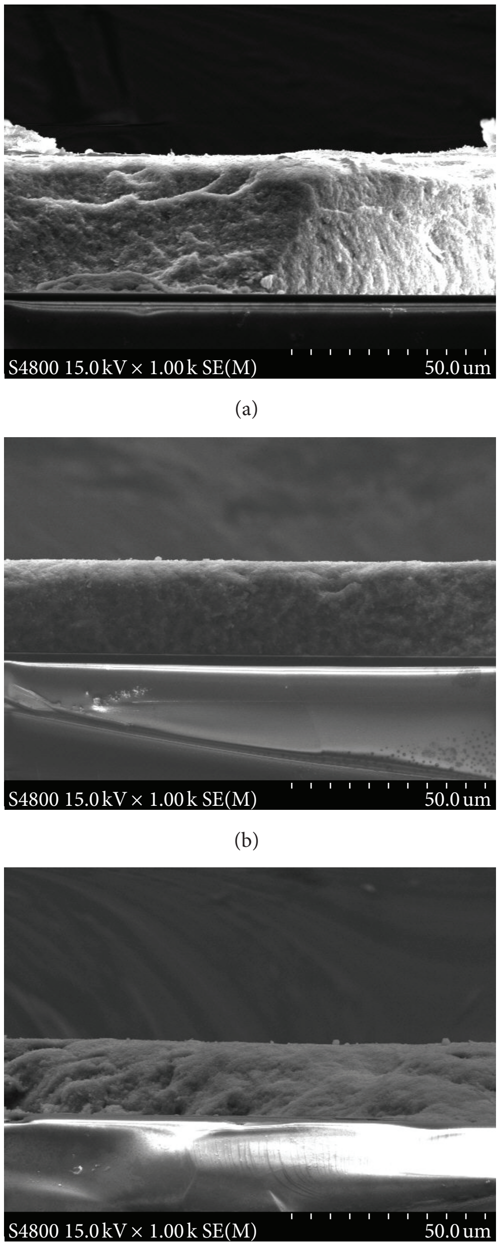


Figure 1: FE-SEM image of TiO_2 thin film.

The DSSC of this study took TiO_2 thin film as photoelectrode thin film. Dyes need to have specific functional groups for them to be effectively adsorbed onto TiO_2 thin film. As mentioned in a previous study [23], in the functional groups of chlorophyll dye and anthocyanin dye, esters, hydroxyl groups (–OH), and carbonyl groups (–CO) bound with TiO_2. Figure 4 shows the FTIR spectra of the spectral range within the wave band of 4000~400 cm^{-1}. As observed from the functional groups of chlorophyll dye extracted from wormwood in Figure 4(a), CH_3 vibration and C–H_2 vibration are observed at 2930 cm^{-1} and 2817 cm^{-1}, respectively. Moreover, C=O vibration at 1721 cm^{-1}, C–O vibration at 1045 cm^{-1}, and C–N vibration of porphyrins at 1644 cm^{-1} are also observed. As observed from the functional groups of anthocyanin dye extracted from purple cabbage in Figure 4(b), H-bond among molecules at 3418 cm^{-1}, C=O stretching vibration at 1639 cm^{-1}, and stretching vibration of C–O–C esters at 1053 cm^{-1} are found.

This study mixed chlorophyll dye with anthocyanin dye to form a cocktail dye in order to achieve the complementary effect of light absorption. This act was advantageous to the photoelectric conversion efficiency of DSSC. As for the process of making the photoelectrode, the spin coating method was used to carry out spin coating at the spin coating speed of 500 rpm for 5 seconds, and then a layer of TiO_2 thin film with a thickness 35 μm was prepared. As known from the experimental results shown in Table 1 and Figure 5, the DSSC sensitized by chlorophyll dye can achieve a photoelectric conversion efficiency of 0.538%; the DSSC sensitized by anthocyanin dye can achieve a photoelectric conversion efficiency of 0.75%. After chlorophyll dye and anthocyanin dye were mixed at a volume ratio of 1 : 1 to form the cocktail dye, it can be seen in the figure that the DSSC sensitized by the cocktail dye has the best photoelectric conversion efficiency at 1.29%, short-current density at 3.16 mA/cm^2, and open-circuit voltage at 0.66 V. Therefore, it can be proved that using



(a)

(b)

(c)

Figure 2: FE-SEM image of thin film thicknesses at (a) 35.66 μm, (b) 24.40 μm, and (c) 18.58 μm.

Table 1: Photoelectrical parameters of DSSCs sensitized by chlorophyll, anthocyanin, and cocktail dye.

Dye	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
Wormwood	0.585	1.96	47	0.538
Purple cabbage	0.66	2.08	53	0.75
Cocktail dye	0.66	3.16	62	1.29

a cocktail dye as the sensitizer of a solar cell can enhance the performance of pure chlorophyll dye or pure anthocyanin dye.

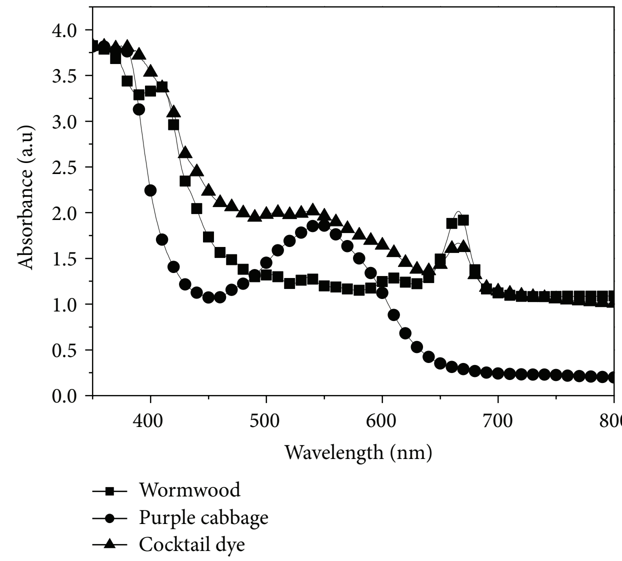


Figure 3: Absorption spectra of chlorophyll dye, anthocyanin dye, and cocktail dye.

Table 2: Photoelectrical parameters of DSSCs sensitized by cocktail dyes at different volume ratios.

Wormwood : Purple cabbage	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
(1 : 1)	0.66	3.16	62	1.29
(2 : 1)	0.675	2.55	67	1.15
(1 : 2)	0.635	1.98	52	0.652
(3 : 1)	0.605	2.82	53	0.896
(1 : 3)	0.585	2.01	52	0.612

This study not only blended a cocktail dye at a volume ratio of 1 : 1 but also additionally blended 4 cocktail dyes at 4 different ratios. As for the process of making the photoelectrode, the spin coating method was used to carry out spin coating at a speed of 500 rpm for 5 seconds, and then a layer of TiO_2 thin film with a thickness of 35 μm was prepared. As known from the experimental results shown in Figure 6 and Table 2, the prepared DSSC sensitized by the cocktail dye mixing two dyes at a ratio of 1 : 1 can achieve better photoelectric conversion efficiency at 1.29%. However, for the DSSCs prepared by cocktail dyes mixed in ratios of 2 : 1 and 1 : 2, the photoelectric conversion efficiencies obviously fall to 1.15% and 0.652%, respectively. Moreover, for the DSSCs prepared by cocktail dyes mixed at ratios of 3 : 1 and 1 : 3, the photoelectric conversion efficiencies are also poor, at only 0.896% and 0.615%, respectively. Therefore, for the mixing ratio of the cocktail dyes, the DSSC sensitized by a cocktail dye with chlorophyll and anthocyanin dyes mixed at a ratio of 1 : 1 can achieve better photoelectric conversion efficiency. The reason for this was that the cocktail dye mixed at volume ratio of 1 : 1 had better light absorption and had less absorption competition and interference between dyes. As a result, better photoelectric conversion efficiency was obtained.

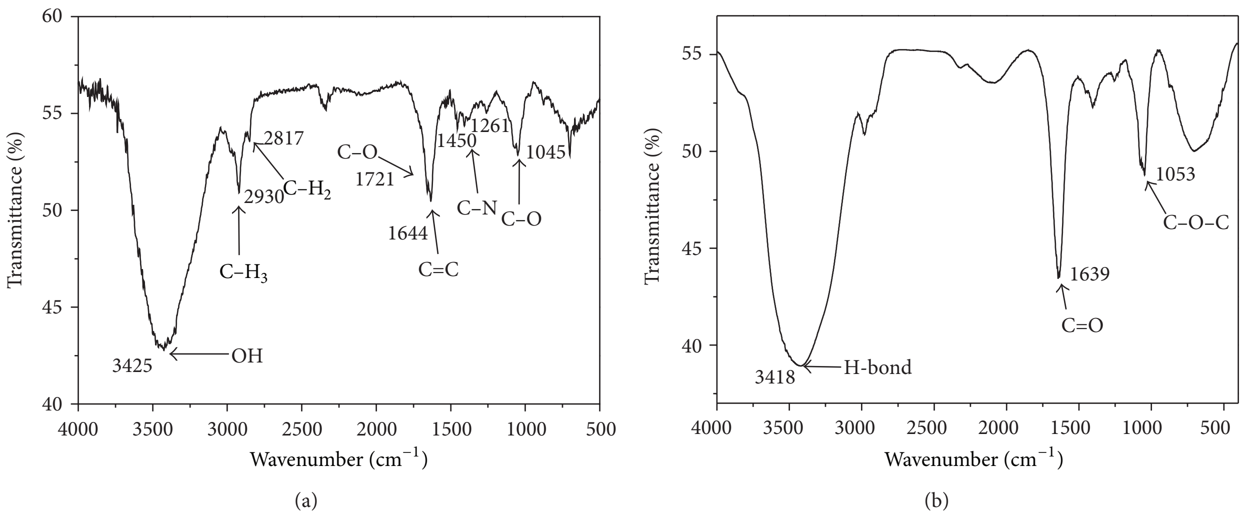


Figure 4: FTIR spectra of (a) chlorophyll dye, (b) anthocyanin dye.

Table 3: Photoelectrical parameters of DSSCs sensitized by cocktail dyes with different thicknesses of TiO_2.

Rotational speed (rpm)	Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
500	35.66	0.66	3.16	62	1.29
1000	24.40	0.765	5.83	48	1.95
1500	18.58	0.675	4.6	51	1.58

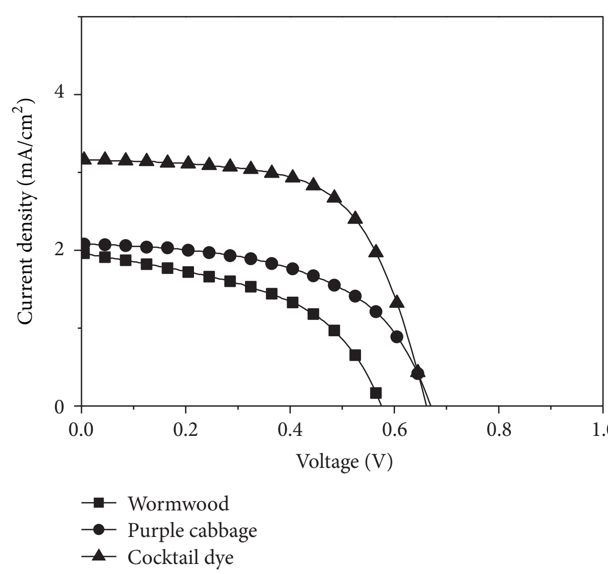


Figure 5: *J-V* curve of DSSCs sensitized by chlorophyll, anthocyanin, and cocktail dye.

Figure 7 shows the photoelectric conversion efficiency of DSSCs prepared with three different thin film thicknesses. As shown in the results in Figure 7 and Table 3, when the photoelectrode thin film thickness is 24.40 μm, the DSSC prepared has the best photoelectric conversion efficiency at 1.95%. However for the DSSC prepared by a photoelectrode with a thin film thickness at 35.66 μm, the photoelectric conversion efficiency falls to 1.29%. The reason is that, with the increase of photoelectrode thin film thickness, incident light could not effectively penetrate the bottom most layer of the thin film, restricting the transmission of the excited dye molecules to the photoelectrode. Furthermore, with a photoelectrode thin film thickness of 18.58 μm, the photoelectric conversion efficiency of the DSSC falls slightly to 1.58%. The reason is that, with the gradual decrease of photoelectrode thin film thickness, the amount of dye adsorption on TiO_2 thin film was decreased, so that its photoelectric conversion efficiency was relatively low. As proved in the experiments, under the condition where the photoelectrode thin film thickness is at 24.40 μm, the photoelectric conversion efficiency of the DSSC sensitized by chlorophyll dye reached 0.9%, and the photoelectric conversion efficiency of the DSSC sensitized by anthocyanin dye reached 1.47%.

Figure 8 shows the voltage decay feature of the DSSCs sensitized by the three natural dyes. This experimental test was conducted for 60 seconds. After DSSCs were continuously irradiated by light for 5 seconds, the light was turned off. As seen in the results shown in Figure 8, under illuminating condition, the V_{oc} of these 3 dyes appears to be at constant values. After the light was removed, the voltage decay time of the anthocyanin dye was the longest. After 60 seconds, it still had around 0.1 V_{oc}. The voltage value of chlorophyll dye fell rapidly to zero after 20 seconds, but the voltage value of the cocktail dye was the only one close to zero after 30 seconds. After conversion of the results acquired in Figure 8 by the equation, the lifetime of electrons can be acquired, as shown in Figure 9. As seen in Figure 9, the DSSC sensitized by anthocyanin dye had longer lifetime of electrons. In contrast, the DSSC sensitized by chlorophyll dye had the shortest lifetime of electrons. The reason was that when the light was turned off, the extent of electrolyte oxidization of the chlorophyll dye molecules in the excited state was stronger, and the electrons in the TiO_2 thin film could be easily

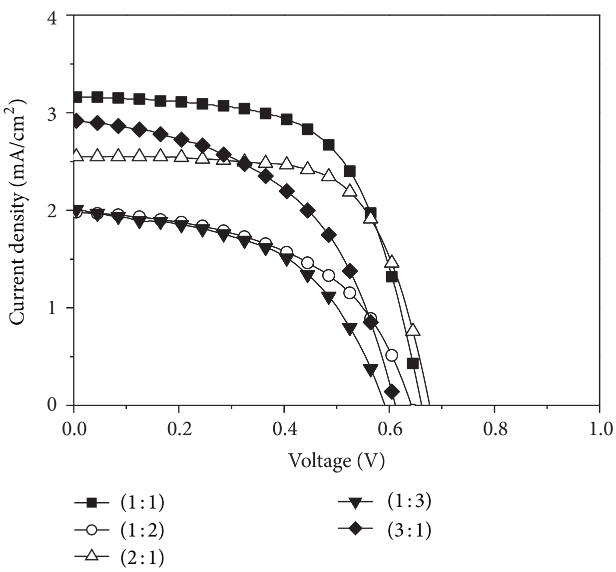


Figure 6: *J-V* curves of DSSCs sensitized by cocktail dyes at different volume ratios.

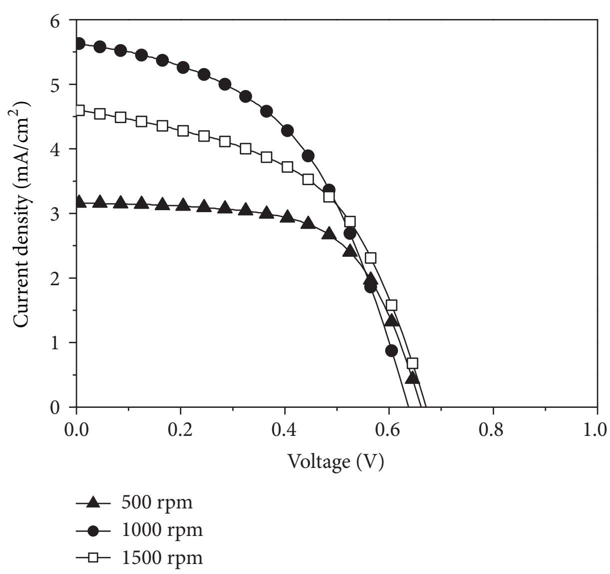


Figure 7: *J-V* curves of DSSCs sensitized by cocktail dyes with different thicknesses of TiO_2.

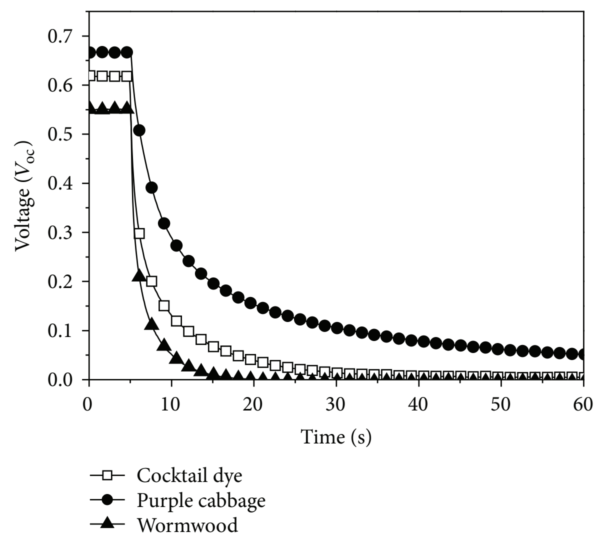


Figure 8: Open-circuit voltage decay of DSSCs sensitized by chlorophyll, anthocyanin, and cocktail dye.

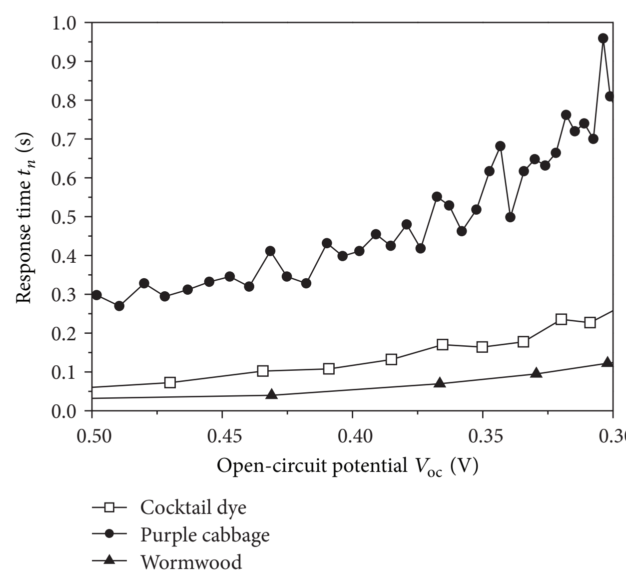


Figure 9: Lifetime of electrons of DSSCs sensitized by chlorophyll, anthocyanin, and cocktail dye.

captured by I_3 ions in the electrolyte. Therefore, the lifetime of electrons of the DSSC with chlorophyll dye was relatively short.

For the raw pigment extracts prepared by the paper and yielding higher quantum and energy conversion efficiencies, the mechanisms involved are (1) dye has functions of broadening the spectral response due to presence of many chromophore molecules and forestering type energy transfer between different chromophore molecules. Besides, pigment molecules contain radical group that can easily combine with the surface of nanosemiconductor. For example, –COOH or –CO on pigment would combine with –OH on TiO_2 to form esters, thus increasing the electronic coupling of 3d orbital of TiO_2 conduction band and π orbital of pigment and making electronic transition easier. In addition, suppression of concentration quenching is due to presence of effective nonchromophore molecules. (2) The oxidation state (D^*) and excited state (D^*) of dye has higher stability and activity, and the life of dye in excited state has longer life and higher electric charge transmission efficiency. Besides, pigment has sufficient oxidation-reduction potential in excited state in order to ensure that the excited electrons can inject on TiO_2 conduction band. In addition, relatively low potential energy exists in oxidation-reduction process (ground state and excited state) so as to suffer less loss of free energy in the process of first and secondary electron transfer.

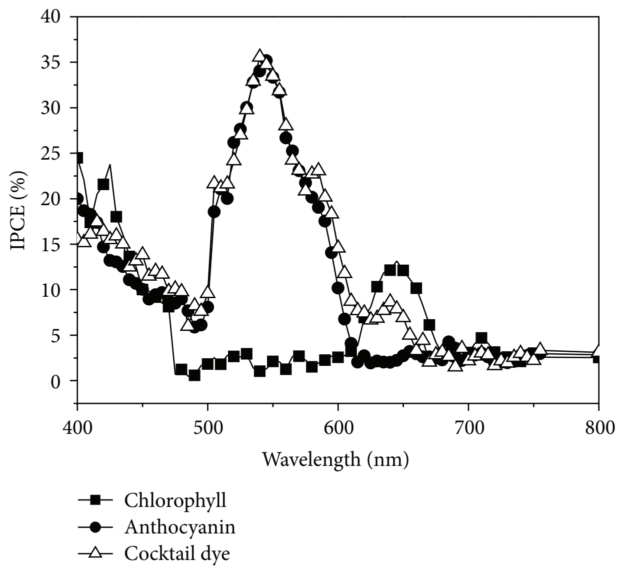


Figure 10: IPCE curves of DSSCs sensitized by chlorophyll, anthocyanin, and cocktail dye.

Figure 10 shows the IPCE of the prepared DSSCs sensitized by chlorophyll, anthocyanin, and cocktail dye. As shown in the figure, when the incident light wavelength is at 420 nm, the DSSC prepared by chlorophyll dye has the greatest IPCE value at around 24%; when the incident light wavelength is at 550 nm, the DSSC prepared by anthocyanin dye has the greatest IPCE value at around 37%. After chlorophyll and anthocyanin dyes were mixed to form cocktail dye, it can be seen in the figure that, within the wavelength range of 510–580 nm in the light visible zone, the situation is similar to that of anthocyanin dye in that they have higher IPCE values. Therefore, within the light visible range, the DSSC sensitized by the cocktail dye has better ability to transform light energy into electricity energy than do the other two DSSCs. Moreover, comparing the UV-VIS curve with the IPCE curve, it can be proved that the cocktail dye has similar absorption features in relation to the visible light range and IPCE.

4. Conclusions

This study used natural dyes as sensitizers for DSSCs. We extracted chlorophyll and anthocyanin from wormwood and purple cabbage, respectively, to serve as natural dyes. Additionally, this study mixed chlorophyll dye and anthocyanin dye at different volume ratios to form cocktail dyes. As known from the experimental results shown in the UV/VIS and IPCE curves, the cocktail dye possesses light absorption range and IPCE features of both dyes. Moreover, the DSSC sensitized by cocktail dye significantly enhanced the photoelectric conversion efficiencies of the two single dyes before mixing, 0.538% and 0.75%, to 1.29% after mixing. In addition, as shown in the experimental result of the effects of different TiO_2 thin film thicknesses on photoelectric conversion efficiency, the DSSC prepared with a photoelectrode thin film thickness at around 24 μm has the highest photoelectric conversion efficiency of 1.95%.

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