Enhancing the Conversion Efficiency of Dye-Sensitized Solar Cells based on Betalain Natural Dye as The Potential Photosensitizer: A Review

Christyowati Primi Sagita¹,²,*

¹ Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung, Malang, 65151, Indonesia
² Department of Industrial Chemistry, Pukyong National University, Busan, 48513, South Korea

*Corresponding Author: christyowati.primi@machung.ac.id (Tel. +62-341-550171; Fax +62-341-550175)

Abstract
Natural dyes have gained much attentions as the cheap photosensitizer for dye-sensitized solar cells because of their abundant availability in nature. One of natural dyes having potential as the photosensitizer is betalain dye. Betalain dye mostly can be found in the family plant of Caryophyllales. This dye has carboxyl groups and can absorb light until wavelength of 600 nm since betalain dye exists in red-purple color. However, betalain dye is still reported to give a lower efficiency in dye-sensitized solar cells device because of its natural properties as compared to the synthetic dyes. This encourages many researchers to investigate the method for developing betalain ability in purpose to enhance the cell device efficiency. To date, there are two methods having been reported for their positive results in increasing the efficiency of cell device based on betalain dye, i.e., combining the betalain dye with other natural dyes, and selecting the suitable solvent and pH in betalain dye extraction. Therefore, in this review, the summary about the potential application of betalain dye as photosensitizer and what properties of this dye have as the photosensitizer would be described. The summary of methods for optimizing betalain dye in improving the conversion efficiency of dye-sensitized solar cell also will be presented for better understanding the potential of this dye.

Keywords: betalain dye, carboxyl groups, photosensitizer, natural dye, dye-sensitized solar cells

INTRODUCTION
Solar cell is one of the technologies that gain much attraction from recent researchers to further develop as it has promising potential in the practice of renewable energy sources. Among the various solar cell technologies classified in the third-generation cells, the dye-sensitized solar cells (DSSCs) have been widely suggested as the low-cost solar cell because a low-cost material can be used as the photosensitizer in this system [1]. Besides, the DSSC also use a simple technique in the process of device fabrication to produce a semi-flexible and semi-transparent solar cell that allows being used in various system [2]. These features make DSSCs even more popular perspective in cost-benefit, despite their conversion efficiencies still lower than other generation cells, i.e., silicon solar cells and thin-film solar cells. The DSSCs device commonly needs a transparent and conductive substrate, semiconductor photoelectrode (working electrode) with coated-photosensitizer, electrolyte, and a counter electrode that can be seen in Figure 1 with TiO₂ as the mostly used semiconductor photoelectrode [3,4]. On the DSSCs device, each component surely has a notable role in the mechanism of converting photons from sunlight to electric current electrochemically. However, most efforts have been delivered to the selection or modification of photosensitizer for optimizing the conversion efficiency of the DSSC. This because what still be the major challenge of DSSCs device is the instability of photosensitizer whereas...
this component will act as the source of photoelectrons that will be transferred into the conduction band of semiconductor, and transported to the counter electrode continuously. Therefore, many research reports were publishing their results in the last decades about up-to-date photosensitizer materials for sustainable DSSCs [5,6].

According to the history of photosensitizer usage in DSSCs devices, the first photosensitizer used in the DSSCs device firstly discovered in the early 1970s was chlorophyll [3]. At that moment, the photon was able converted into electricity through electron transfer from excited photosensitizer molecule to the conduction band of ZnO as the semiconductor electrode. However, the adsorption ability of dye molecules over the semiconductor was still poor, thus it resulted in the low efficiency of the first-period DSSCs devices. The porphyrin and derivatives, and other dyes such as phthalocyanines then were reported to have better adsorption ability onto the surface of semiconductor throughout the 1980s because they have carboxyl groups in their molecules as compared to chlorophylls [3,7]. But those dyes also still showed adsorption instability, notably when the pH condition change. Afterward, in 1991, Grätzel group reported 7.12% efficiency of DSSCs device-based on trime- tric ruthenium (Ru) complex dye and nanoporous TiO$_2$ electrodes [8]. The remarkable efficiency in that period then promoted many efforts to modify the first Ru complexes to have broader light absorption up to the red of visible spectrum and NIR region, and also enhanced the molar extinction coefficient. Therefore, various Ru complex synthetic dyes such as N3, N749 (black dye), N719, N945, Z910, K19, K8, K9, Z907, N621, and others were introduced with various device efficiencies up to above 11% [3,9,10]. However, the Ru complex dyes still face limitation for large commercialization as the ruthenium is expensive, less abundant and not environmentally friendly, so the attentions started to move towards developing the cheaper organic-dyes. The organic dyes mostly have construction based on donor-acceptor (D-A) structure as like with the organic material structure for polymer solar cells [3,11,12]. Their low cost of preparation process still carries a promising future for making commercial DSSCs devices, even though the efficiencies of DSSCs device-based organic dyes in most cases are lower than those of Ru complex dyes. Besides, they also have a higher light absorption coefficient compared to the Ru complex dyes, bringing a benefit to the photoelectron generation [12,13]. The recent highest efficiency of DSSCs device-based on organic dye was 13% achieved by using modified porphyrin sensitizers [14]. The organic dyes can be divided into synthetic dyes and natural dyes. The indoles, coumarin, porphyrins, triarylamine, phenothiazine, and carbazole are known as synthetic organic dyes [12], while well-known natural dyes are anthocyanin, chlorophyll, flavonoid and carotenoid [15].

Betalain dye is one of natural dye that also have potential to be photosensitizer in DSSCs device. It has carboxyl group for making good anchor with semiconductor, as compared to other natural dye such as anthocyanin and chlorophyll [11,16]. Unfortunately, the utilization of betalain dye as the sensitizer for DSSCs device is still less popular than those dyes. Based on previous reported researches, the betalain dyes also still provide lower DSSCs device efficiency as like other natural dyes if compared to the synthetic organic dyes [11,16–19]. Despite of that, many researchers still try to develop betalain dyes ability for enhancing the efficiency of DSSCs device-based on natural dye because of the abundant availability of natural dye for low-cost fabrication. However, the published review article about optimization of betalain dye as photosensitizer for increasing the cell device efficiency is still few. Therefore, this review will summarize the potential of betalain dye as a photosensitizer in DSSCs device and the methods for optimizing the ability of betalain dye in enhancing the conversion efficiency of the DSSCs device.

**Figure 1.** The device structure of dye-sensitized solar cells.

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**BETALAIN DYE AND ITS UTILIZATION IN DYE-SENSITIZED SOLAR CELLS (DSSCs)**

**Betalain Dye**

Betalain dye is a natural pigment that has nitrogen and three carboxyl groups in its chemical structure [16,20]. The betalain structure is actually the result of betalamic acid condensation with cyclo-DOPA and/or amino acids so, it is also recognized as the natural pigment with a nitrogenous core structure. The condensation with those two different compounds causes betalain to have two major classes i.e., betacyanins (formed from condensation with cyclo-DOPA) that give the red-purple color and betaxanthins (formed from condensation with amino acids) that give the yellow-orange color [11,16,21]. Those structures are displayed in Figure 2. The colors usually appear on flower petals, leaves, fruits, stems, and also roots of Caryophyllales plants. The Caryophyllales plants widely known as the betalain dye sources are bougainvillea, amaranths, beetroot, and cactus family, such as prickly pear [11,16,22]. Betalain dye also can be found in the red dragon fruit or pitahaya (belongs to genus *Hylocereus*) and pitaya (belongs to genus *Selenocereus*)[20]. For practical application, betalain dye has been extensively used as the natural color for food [20,23,24]. It is widely known to have a water-soluble property like anthocyanin even their structures are different from each other [23]. This property supports betalain dye to be identified as the one of important bioactive molecules.
As the bioactive molecules, betalain dye has been widely reported to have antioxidant, anti-diabetic, anti-cancer, anti-lipidemic, and antimicrobial activities [23–25]. Slimen’s group has summarized the antioxidant activities of some betalains that were measured using DPPH radical scavenging activity method [23]. They noted that betacyanins have inhibition percentage of up to 50% while betaxanthins were up to 60%. The good antioxidant activities of betalains then can bring benefit in inhibiting lipid oxidation to prevent cardiovascular diseases [21,25]. Furthermore, the ability of betalain from beetroot extract in inhibiting hexokinases enzyme for controlling blood sugar level has been reported by Kabir’s group, confirming its potential as an anti-diabetic compound [26,27]. Moreover, the investigation of betalain from beetroot as an anti-cancer compound through in vitro studies showed favorable inhibition to various cancer cells in breast, colon, stomach, and lung [20,25]. The betalains also have been reported to have an ability in chelation of inner cations that the parasites need [20]. Therefore, it will inhibit the microbial growth in the living cells.

**Betalain Dye as Photosensitizer in Dye-Sensitized Solar Cells (DSSCs)**

According to its important role, the photosensitizer has been known as the molecule that can absorb ultraviolet up to visible light region of solar spectrum, then utilize the chemical effects of light to convert a molecule into other or new molecule chemically [3,4]. It is the reason why the photosensitizers have specific colors that would emit the light absorbed by their colors. This characteristic is identified as the luminescent properties. Since the betalain dye has two different specific colors depending on the compound structure, this dye has potential to be used as the photosensitizer. The photosensitizer or dye needs to fulfill two important requirements that will affect the efficiency of dye-sensitized solar cell device i.e., having intense light absorption in visible region, and robust anchorage to the surface of semiconductor [3,4,6]. Based on the UV-vis spectra analysis, the red-purple betacyanin showed absorptivity maximum at 535 nm (betanin), and at 542 nm (betanidin). Meanwhile, the yellow-orange betaxanthin showed absorptivity maximum at 482 nm (indicaxanthins) [11,16]. This confirms that the betalain dye is able to absorb light up to 600 nm. However, the intense of light absorption of betalain dye still depends on the pH condition and the solvent used in dye extraction process. Regarding the anchorage to surface of semiconductor, betalain dye has three carboxyl groups that can form strong binding with hydroxyl group in TiO₂. The carboxyl group in betalain dye has been reported to have good anchor with TiO₂ compared to hydroxyl group in anthocyanin [28]. This become the reason why betalain dye has higher efficiency than dye-sensitized solar cell based on anthocyanin as has been informed in previous natural sensitizer reports [28–31]. The reported conversion efficiency of DSSCs device based on betalain dyes are summarized in Table 1 below.

For having possible electron injection thermodynamically between dye and semiconductor (for example is TiO₂), the dye must have lower excited state redox potential energy than TiO₂’s. In other words, the LUMO energy level of dye should be higher than TiO₂ conduction band [3]. This parameter becomes crucial point for dye to be a favorable sensitizer for solar cell device. For betalain dye, Butera’s group [32] reported that betanin and indicaxanthin have a reduction potential of 0.62 V and 0.83 V, respectively, referring to the normal hydrogen electrode (NHE) at pH neutral (around pH 7.4). Then, to know the excited state redox potential energy, the reduction potential was subtracted by the E₀ of 0-0 excitation energies from ground state [16]. The value of E₀ was roughly estimated as 1.9 eV based on the visible absorption band onset at 650 nm, which has been mentioned in previous review report. Therefore, the excited state redox potential energy of betanin and indicaxanthin at pH neutral (in water) are estimated to be -1.28 V and -1.07 V, respectively. Those values are lower than the excited state redox potential energy of TiO₂ at pH 7 (which is around -0.6 V) [16] thus, confirming that betalain dye is favorable to undertake the electron injection onto TiO₂.

In the fabrication of device, the binding of functional groups between dye and TiO₂ occurred through soaking process [3]. In this process, the TiO₂ is in the form of a film layer that was deposited onto a transparent-conductive substrate such as FTO or TCO. Interestingly, in the case of betalain dye, the yellow-betaxanthin compound showed strong adsorption with TiO₂ film compare to betacyanin [16,33]. Same previous report clarified that betanin indeed has weakly adsorption onto the surface of TiO₂ film, and it will well-adsorbed on TiO₂ film surface after adding the acid treatment to the solution [16]. The better adsorption of betaxanthin onto TiO₂ surface has been reported in giving higher short-circuit photocurrent and energy conversion efficiency than betacyanin. This gives insight that the high absorbance in visible region which observed on betanin in the raw extract is not only parameter to result in high device efficiency. It should be considered that how strong the binding between dye and TiO₂ also can determine the energy conversion of solar cell device, as the anchorage will affect the electron injection process. However, it does not mean only betaxanthin that can bring high efficiency of device based on betalain dye. The combination of betaxanthin and betacyanin in proper composition has been clarified in enhancing the total number of visible photons (Nₐ) in previous report [33]. The pink bougainvillea (BG) had Nₐ of 53.2% which contained 57.3% of betaxanthins and 42.7% of betanins. The Nₐ value was higher compared to yellow BG that
contained 93.8% of betaxanthins and purple BG that contained 52.7% of betanins. Once more, this result also showed that higher betaxanthin composition gave significant result in device efficiency and to achieve higher efficiency of device based on betalain dye, the favorable composition is importantly needed. Furthermore, the absorption spectra of betalain dye-TiO$_2$ film (both betaxanthin and betanin) were also reported to have red-shift absorption compare to the absorption of dye in solution state [16,28,31]. This red-shift implied the existence of strong electronic coupling between betalain dye and TiO$_2$ film [16], carrying the possibility to achieve higher DSSCs device efficiency in comparison with other natural dyes.

Table 1. The photovoltaic parameters of reported dye-sensitized solar cells device-based on betalain dyes.

| Plant source                | Preparation method and parameters | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $\eta/FF$ (%) | Reference |
|-----------------------------|----------------------------------|-----------------------|--------------|---------------|-----------|
| Red Turnip                  | Acidified juice                  | 9.5 (B)               | 0.425 (B)    | 1.70/0.37 (B) | [34]      |
| Wild Sicilian Prickly pear  | (pH: 1-2)                        | 7.32 (A)              | 0.40 (A)     | 1.21/0.41 (A) |           |
| Sicilian Indian Fig         | A: without blocking layer        | 8.20 (B)              | 0.375 (B)    | 1.19/0.38 (B) |           |
| Bougainvillea               | B: with blocking layer           | 2.7 (A)               | 0.375 (A)    | 0.5/0.54 (A)  |           |
|                             |                                  | 2.1 (A)               | 0.3 (A)      | 0.36/0.57 (A) |           |
| Beetroot                    | Acidified juice (pH 6, with buffer solution) | 10.55 (A)            | 0.35 (A)     | 2.04/0.57 (A) | [35]      |
|                             | A: without blocking layer        |                       |              |               |           |
|                             | B: with blocking layer           | 13.91 (B)             | 0.36 (B)     | 2.71/0.56 (B) |           |
|                             | Electrolyte solvent: ACN         |                       |              |               |           |
| Bougainvillea glabra        | Acidified juice (pH 5.7, with HCl 1 M) | 1.86 (V)             | 0.23 (V)     | 0.31/0.71 (V) | [36]      |
| Bougainvillea spectabilis   | V for violet color, R for red color | 2.34 (R)             | 0.26 (R)     | 0.45/0.74 (R) |           |
| Sicilian prickly pear       | Immersed in ethanol, added HCl 0.1 M (pH 5.5) | 7.85                 | 0.382        | 1.87/0.62 | [29]      |
| Beta vulgaris               | Acidified juice (pH 3.5, with HCl 1 M) | 2.71                 | 0.576        | 0.89/0.572 | [37]      |
|                             | (*) with TEOS as stabilizer      | 2.08*                 | 0.609*       | 0.68/0.537* |           |
| Pastinaca sativa            | Extracted in ethanol (E)         | 7.0 (E)               | 0.42 (E)     | -0.05 (E)    | [38]      |
| Beta vulgaris               | Extracted in water (W)           | 7.2 (W)               | 0.42 (W)     | -0.90 (W)    |           |
|                             | Addtion of HCl 1 M               | 3.45 (E)              | 0.46 (E)     | -0.90 (E)    |           |
| Red bougainvillea glabra    | Extracted in water               | 1.13 (a)              | 0.44 (a)     | 0.21/0.43 (a) | [39]      |
|                             | Variation of pH (a)1.2; (b)3.0; (c)5.7 | 3.72 (b)              | 0.44 (b)     | 0.98/0.59 (b) |           |
|                             |                                  | 2.27 (c)              | 0.41 (c)     | 0.57/0.61 (c) |           |
| Beetroot                    | Extracted in ethanol             | 0.75                  | 0.453        | 0.197/0.58  | [40]      |
| Opuntia ficus indica        | Extracted in ethanol             | 3.42                  | 0.507        | 0.674/38.81 | [30]      |
| Bougainvillea glabra        | Extracted in mixture of ethanol and water with ratio variation (30; 50; 70; 90 %) | 1.22 (30%)           | 0.34 (30%)   | 0.24/0.50 (30%) | [41] |
|                             |                                  | 0.58 (50%)            | 0.39 (50%)   | 0.13/0.515 (50%) |           |
|                             |                                  | 0.65 (70%)            | 0.34 (70%)   | 0.127/0.52 (70%) |           |
|                             |                                  | 0.55 (90%)            | 0.34 (90%)   | 0.11/0.52 (90%) |           |
| Opuntia dilleniid           | Extracted in mixture of methanol and HCl | 1.09                 | 0.521        | 0.47/0.69  | [28]      |
| Red spinach (Amaranthus dubius) | Extracted in water              | 0.882                 | 0.338        | 0.134/0.449 | [42]      |
| Bougainvillea               | Extracted in solution variation: (a) acetone/water (32:68) | 0.25/0.595 (P, a)    | 0.215/0.45 (O, a) |           |
|                             |                                  | 0.185/0.45 (Y, a)     |              |               | [33]      |
| Beetroot                    | (b) ethanol/HCl 0.1 M             | No data               | No data      |               |           |
|                             | (c) water/HCl 0.1 M               | 0.467/0.469 (a)       | 0.112/0.414 (b) |           |
|                             |                                  | 0.229/0.392 (c)       |              |               |           |
| Beetroot                    | Extracted in isopropanol         | 12.7                  | 0.578        | 1.29/0.66   | [31]      |
BETALAIN DYE OPTIMIZATION METHODS FOR ENHANCING THE CONVERSION EFFICIENCY OF DSSCs

The abilities of betalain dye in absorbing light up to the visible region and effective anchoring the semiconductor surface through its carboxyl groups are the prominent keys of betalain dye potential as the photosensitizer for DSSCs device. However, as summarized in Table 1, betalain dye still shows low conversion efficiency to the DSSCs device. Hence, the betalain dye needs optimization to enhance the efficiency of the DSSCs device. The methods for optimizing betalain dye are described in the sub-sections below.

Combining the Betalain Dye with Other Natural Dyes (Co-sensitization)

The anchorage of dye to the semiconductor surface has become one of crucial concern in affecting the conversion efficiency of DSSCs device. Although the anchorage of betalain dye using the carboxyl group is better than other natural dyes, this fact is not enough making betalain dye to have high device efficiency. Thus, the researchers start to think about the optimization method of the betalain dye based on the binding site point of view. One of the methods have been reported is combining the betalain dye with other natural dyes. This combination term is actually similar with mixing definition. The main consideration supporting this method is combining the different dyes could increase the number of binding sites between natural dye and semiconductor [31]. If the number of binding sites rises, then it would lead to strong interaction with semiconductor and result in the increasing of electron injected.

The combining method has been reported widely as two-mixed natural dyes. The mixing could be between either same natural dyes or different dyes. However, mixing the same dyes that still belong to same family has been investigated in giving not good enough result even the dyes are from different sources. For example, the mixing of betalain dyes from beetroot and yellow bougainvillea leaves gave an average cell efficiency of 0.269%, which was laid between the average cell efficiency of those dyes individually [33]. The average cell efficiency of betalain dye from beetroot in the report was 0.32% while from yellow bougainvillea was 0.19%. The possible reason is the dyes from different family could become competitors to bind with the semiconductor as they have similar functional groups to anchor. Interestingly, the cell efficiency of mixing two betalain dyes from different sources is still better than the efficiency of mixing two anthocyanin dyes in the same condition [33]. From the reported result, it also needs to be noticed that betalain dyes from different sources could gave different cell efficiency because each source definitely contains different mixture components which could affect the composition of dye extracted. Bearing to the unsatisfactory result from mixing two similar dyes, the combination method using different dyes become more desirable. This method is also known as the co-sensitization with purpose of extending the light absorption efficiency and suppressing the recombination kinetics [43].

The betalain dyes have been studied extensively concerning their combination with different natural dyes, thus far with chlorophyll or anthocyanin dyes [28–30,40,43]. Sengupta groups reported their propitious result in combining betalain dye from beetroot and chlorophyll from spinach leaves as the photosensitizer with using ZnO as the photoanode [40]. Based on their investigation, when these two dyes were combined, both betalain and chlorophyll showed a synergistic effect. On one side, the chlorophyll help betalain to extend its light absorption spectrum since chlorophyll can harvest light until wavelength of 700 nm. The combined dye then showed a broader range of light absorption as compared to betalain dye individually. The light absorption area of the combined dye covered almost the entire wavelength of visible light spectra. Besides, the light absorption spectra of combined dye also showed the absorption characteristic of individual betalain (peaks at 482 nm and 530-550 nm) and chlorophyll (peaks at 434 nm and 668 nm), indicating the two dyes were well-mixed. The change in light absorption area could be occurred because the dye combination would extend the π-conjugation length of dyes so, it made the combined dyes can absorb the light in wider wavelength area [30]. Then, the broad light absorption caused an increase in the extinction coefficient (ε) and leads to an increase in Jsc value.

On the other side, betalain dye can support chlorophyll limitation in binding with ZnO surface because of having carboxyl groups. In chlorophyll dye, the dye would form a binding interaction with semiconductor surface through carboxyl (C=O) and -O ligands [30,31,40,43]. These two ligands tended to form poor binding site with photoanode (in this case is ZnO) surface because they would compete to get fixed to the ZnO surface. This condition would give inadequate delocalization of photo-excited electron then leading to low Voc. Meanwhile, betalain dye only use the carboxyl group to bind with semiconductor surface. The binding site produced ester bond that favorable for rapid electron transfer. If the electron injection process become rapid, it would increase the electron injection lifetime thus, reduce the charge recombination. In this point, the carboxyl group in the betalain dye structure holds an important role in increasing the Jsc and Voc of DSSCs device. So, the co-sensitization between betalain and chlorophyll could promote a formation of intermediate excited levels that contribute to reducing charge recombination. As the result, the combined dye showed the highest value of Jsc i.e., 1.244 mA/cm², and efficiency achieved 0.294% [40]. The efficiency was higher than both betalain and chlorophyll dye individually. This result confirming the co-sensitization has successfully enhanced the efficiency of DSSCs device.

Other previous reports regarding co-sensitization between betalain and chlorophyll dye was also presented by Kumar’s group [30]. In their research, they investigated the effect of co-sensitization of various dyes using TiO₂ as the photosensitizer, in reducing the charge recombination. The dyes used were anthocyanin from Jambolana, chlorophyll from Bermuda grass, curcumin-carotenoid from Curcumin, and betalain (betacyanin) from Cactus-Opuntia. Since this group focused in recombination reduction, they used both recombination and charge transfer resistance parameters to elucidate the character of each dye as the photosensitizer. A cell device is supposed to have high efficiency if having high recombination resistance and low charge transfer resistance. The results showed that the recombination resistance (Ron) of betalain dye was 104.26 Ω, which was the highest value of Ron compared to the other dyes individually. Meanwhile, the charge transfer resistance (Rct) of betalain dye was the lowest from the other dyes i.e., 29.74 Ω. This become a confirmation to the betalain dye ability in reducing charge recombination due to the presence of carboxyl group (-COOH) as have been explained above. Hence, the combination between betalain and other dyes (i.e., anthocyanin, curcumin, and chlorophyll, respectively) gave the higher value of recombination resistance appealed with individual dye. The betalain-anthocyanin gave the Rct of 169.92 Ω, betalain-curcumin gave 620.52 Ω, and betalain-chlorophyll gave 694.34 Ω. Among those combined dyes, betalain-chlorophyll outplayed the other dyes with Jsc of 4.97 mA/cm², Voc of 0.495 V, FF of 46.26%, and efficiency of 1.139%. The efficiency of betalain-chlorophyll was better than efficiency of DSSCs device using mono-sensitization of betalain i.e., 0.674%. The other result of betalain-chlorophyll co-sensitization was also reported by Patni’s group research [31]. They used the source of betalain from B. vulgaris, and the chlorophyll was from S. oleracea. The combination between betalain and chlorophyll in their research showed Voc of 0.893 V, short-circuit current (Isc) of 15.5 mA, FF of 65%, and efficiency of 2.41%. As well as the other reports,
the combined dye elevated the efficiency of cell device compared to using betalain (η of 1.29%) and chlorophyll (η of 0.95 %) individually. This research group [31] also investigate co-sensitization of betalain-anthocyanin and the combination gave higher efficiency of 3.09% than individual of anthocyanin (η of 1.47%).

Regarding on the combination of betalain with anthocyanin, Ramamoorthy’s group gave confirmation that betalain dye extracted from cactus fruits (O. dilleni) could help elevating the efficiency of cell device-based anthocyanin (η of 0.14%) to be 0.20% [28]. The anthocyanin dye was from T. indica. Since the anthocyanin use two -OH group to bind with TiO\textsubscript{2} surface, the carboxyl group (-COOH) in betalain structure become favorable to have strong binding with TiO\textsubscript{2} which then affect the charge transfer between dye and TiO\textsubscript{2}. As mentioned in previous explanation, the carboxyl group would lead to fast electron transfer to TiO\textsubscript{2} surface thus extend the electron lifetime (τ) of combined dye i.e., 7.3×10\textsuperscript{-4} s. The electron lifetime of betalain-anthocyanin had higher value than anthocyanin itself (τ of 8.1×10\textsuperscript{-4} s). However, in their research, the combination just improved the anthocyanin dye as photosensitizer. It might be because of the aggregation occurred when TiO\textsubscript{2} was soaked into anthocyanin first so, this condition would limit the adsorption of betalain in next turn. The aggregation could be affected by the solvent used in extracting the dyes, so the solvent selection become crucial. In case of Ramamoorthy’s group result, the dye aggregation could occur because of using mixture of methanol and HCl as the solvent. The utilization of different organic solvent for dye extraction also become the reason why the efficiency of similar dye in the various research groups become different. As for example, Patni’s group [31] used isopropanol for extracting each dye (anthocyanin, chlorophyll, and betalain) which may be better for anthocyanin thus, the efficiency of device-based anthocyanin dye in Patni’s group was higher than Ramamoorthy’s group [28]. The method of selecting solvent and pH for extracting dye, especially for betalain dye, will be more discussed in the next section. Apart from chlorophyll and anthocyanin, the combination between betalain and curcumin has ever been reported by Kabir’s group [42]. The curcumin dye was from Turmeric, and the betalain dye was from red spinach. Because the betalain dye was dominant in red color, so it was betacyanin. Since the curcumin has light-harvesting area until 500 nm, betalain helped to extend the light absorption up to 600 nm. This combination also gave positive impact to betalain as the absorption coefficient of betalain increased from 2.11 to 2.52 (combined dye) because of extension conjugation length from curcumin. The efficiency of combined dye was 1.079% which was 8 times higher from betacyanin (0.134%) and 2.85 times higher from curcumin (0.378%) individually.

The combination of two different dye between betalain and other dyes has received positive attention according to their better results from the individual dye. The increase of binding site when two different dye combined become the crucial point to optimize the betalain dye. Hence, Patni’s group also tried to investigate the combination of three different dye i.e., anthocyanin, chlorophyll, and betalain [31]. After three dyes were combined, the interaction of anthocyanin (A)-betalain (B)-chlorophyll (C) dye was increased due to the increase of number binding site and the extended conjugation length. The proposed structure of three combined dye interacting with TiO\textsubscript{2} surface is shown in Figure 3. This state led the combined dye to have improved electron injection and charge transfer to the TiO\textsubscript{2} conduction band. Therefore, the efficiency of three combined dyes achieved 3.73% with J\textsubscript{sc} of 23 mA, FF of 69% (similar with N3 as the reference in their research), and V\textsubscript{oc} of 0.883 V. The efficiency of ABC dye was the highest as compared to the two-combined dyes and each individual dye. This confirms that combination of three dyes can give positive result to optimize betalain dye in enhancing the efficiency of DSCCs device.

**Figure 3.** The proposed structure of three combined dye interacting with TiO\textsubscript{2} surface.

Furthermore, the combination of betalain with other dyes not only improve the light-harvesting ability of betalain and raising the number of binding sites with semiconductor surface, but also can improve betalain stability which certainly in the combined form. Since betalain dye is less stable than other dyes such as anthocyanin and chlorophyll [33,40], this co-sensitization method become a valuable chance for betalain to have longer lifetime. The betalain-chlorophyll combined form in Sengupta’s group showed light absorption characteristic with better temperature stability when the temperature was elevated gradually compared to betalain dye individually [40]. The absorbance of only betalain dye decreased up to 36% when the temperature was raised from room temperature to 70°C meanwhile the absorbance of betalain-chlorophyll combined dye had maximum decreasing only up to 4.9%. Patni’s group also reported the three combination of anthocyanin-betalain-chlorophyll dye gave better efficiency stability for 50 hours which was higher than each individual dye stability [31]. The cell
device efficiency based on three combined dye has decreased as much as 40% against the N3 synthetic dye as the reference dye whereas the device efficiency based on each individual dye has dropped up to 80%. The decreasing efficiency stability pattern of three combined dye for 50 hours (around 22%) also resembled with N3 synthetic dye (21%) in the same range of time. Therefore, the combination or co-sensitization method is promising for enhancing betalain dye ability in enhancing the cell device efficiency.

Selecting Suitable Solvent and pH in Extracting Betalain Dye

The other method that can be proposed to prepare betalain dye for enhancing the DSSCs device efficiency is selection the solvent and pH in extracting the dye. The solvent and pH generally hold important role in providing the betalain dye in aqueous form with beneficial properties that the cell efficiency would depend on. Since betalain dye has its own unique structure, not all organic solvent could be suitable for betalain extraction and because betalain dye sources are vegetables or plants, the selection of suitable solvent become important to get high composition and purity of betalain than other components containing in the natural sources. We also should notice that organic solvent would affect the adsorption process of dye to the semiconductor surface since in the DSSCs device fabrication, the semiconductor film coated on the transparent glass as the photoanode will be dipped in natural dyes. Therefore, in this section, the author has summarized various reports regarding the solvent selection for betalain dye extraction that resulting in improved efficiency of DSSCs device-based betalain dye.

The common solvents have been extensively reported are ethanol and water [29,30,37,40]. Besides, other organic solvents having been used in betalain dye extraction are methanol [28], isopropanol [31], and acetone [33]. The organic solvent definitely will affect the pH change of betalain dye when the dye is extracted. Betalain has known to have good stability in neutral pH and easy to convert into another compound as the pH increase or decrease [16,33]. Betanin would be converted to betanidin as the pH increase (in acid condition) [33], and when the pH increase to be base condition, it would be converted to betalamic acid [16]. Hence, some previous reports have investigated betalain dye to have decreased absorbance in pH below 3 and over 10 [40]. Garcia-Salinas’s group reported that betalain dye extracted from beetroot by using H₂O/HCl (0.1 M) had a lower efficiency (η = 0.229%) than betalain extracted by using acetone/H₂O (32/68 %vol) [33]. The pH of betalain dye extracted using H₂O/HCl (0.1 M) was 1.3-1.4 meanwhile, the pH of betalain dye extracted using acetone/H₂O (32/68 %vol) was 5-6. This confirms the pH of betalain dye could significantly affect the efficiency of cell device. This research group also tried to extracted betalain dye from beetroot by using ethanol as the solvent with addition of HCl 0.1 M, resulting in pH 1.6-1.7. The absorbance of this betalain extract was the lowest compare to betalain dye extracted in acetone/H₂O and in H₂O/HCl (0.1 M), resulting in the lowest efficiency of device-based betalain dye in this study (η = 0.112%). This might be due to the combination between alcohol solvent such as methanol or ethanol with acid solution would lead to formation of aggregation [28] thus, limiting the dye ability to absorb the light and injected the electron to the semiconductor surface.

The comparison of solvent used in betalain dye extraction also reported by Hemmatzadeh and Mohammadi [38]. They investigated how to improve the optical absorptivity of betalain dyes that were extracted from Pastinaca sativa and Beta vulgaris (beetroot). The solvents used were ethanol and water, respectively, with addition of HCl solution in concentration variation (0.1 M and 1 M). The addition of acid solution was reported to be able enhanced. The dye extracted in ethanol solvent also gave higher absorbance intensity compared to in water solvent. However, the dye extracted in water showed better cell device performance than in ethanol, with Jsc of 7.2 mA/cm² (with HCl 1N), Voc of 0.42 V, and FF of 0.9. The effect of acid treatment in enhanced device performance could be attributed to improved adsorption of betacyanin to the semiconductor surface. As have been explained in previous section, betacyanin tends to have good adsorption with TiO₂ if having acid treatment. Despite of that, the acid treatment should be in control as the lower pH would lead to low efficiency of cell device. Meanwhile, for betalain dye from Beta vulgaris, they reported the extracted in ethanol solvent with acid treatment in concentration of 1 M gave higher performance of cell device, i.e., Jsc of 3.45 mA/cm², Voc of 0.46, and FF of 0.9 than the acid concentration of 0.1 M [38]. In case of acid treatment, this research group did not give pH data in detail, so the explanation of effect of acid treatment is not deep enough. Moreover, the investigation of acid treatment in betalain extraction using acetone solvent need to be studied more in future research because acetone showed favorable potential in betalain dye extraction as reported by Garcia-Salinas’s group. For using the isopropanol solvent [31], betalain dye has reported having efficiency of 1.29% and the device efficiency based on betalain dye that extracted in mixed of methanol and HCl was 0.47% [28].

CONCLUSION

Betalain dye is one of natural dye that has potential as the natural photosensitizer for dye-sensitized solar cells. Betalain consists of two main compounds i.e., betaxanthins that give yellow-orange color, and betacyanin that give red-purple color. The range of that color make this dye has ability to absorb light until wavelength of 600 nm. Unfortunately, because natural dyes commonly still have lower DSSCs device efficiency and especially betalain dye has lower stability than other natural dyes, this dye is less popular as the sensitizer for DSSCs device than anthocyanin and chlorophyll dyes. Therefore, in order to optimize the ability of this dye as the photosensitizer in enhancing the cell device efficiency, there are two methods are presented: a) combining the betalain dye with other natural dyes, and b) selecting suitable solvent and pH in extracting the betalain dye. The combination of betalain and other natural dyes such as chlorophyll, anthocyanin, and curcumin give positive results in enhancing the efficiency of DSSCs device. This because betalain dye has favorable properties such as good anchoring with semiconductor surface owing to its carboxyl group, so this makes a synergistic effect with other natural dye. Meanwhile, the other natural dyes would extend the light absorption area of betalain so, it leads to enhance the electron generation and injection to the semiconductor surface. The selection suitable solvent and adjusting the pH in betalain dye extraction also can help betalain to optimize its ability in absorbing the light and transferring the electron to the semiconductor. As the result, the proper solvent and good pH condition can result in better performance of DSSC’s device. Various organic solvents that widely used are ethanol and water. In addition, acetone solvent also gives positive result in enhancing the device efficiency. The acid treatment has been investigated to give higher absorptivity of betalain, however, the addition of acid should be in control to prevent lower pH condition. For future research, the combination of betalain and other natural dye that extracted in acetone solvent with acid treatment could be studied more for widening our insight about betalain dye potential as the photosensitizer in enhancing the DSSCs device efficiency.

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