Anthocyanin as natural dye in DSSC fabrication: A review

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Abstract. Nowadays, solar cell technology that dominates the market is a silicon-based solar cell with efficiency of 15-20%. Unfortunately, this type of solar cell has some weaknesses such as complex production process, utilize hazardous compounds and expensive production price. Therefore, the researchers developed organic solar cell namely dye-sensitized solar cell (DSSC). Nevertheless, the efficiency of DSSC still lower than that of conventional solar cell. Several studies have been carried out to increase the efficiency of DSSC like the use of anthocyanin dye. Anthocyanin is a flavonoid compound that has a wide absorption range and has conjugated π bond to catch photons from sunlight. The use of anthocyanin in DSSC has been applied in several methods, such as the use of single anthocyanin dye, adding copigment, and mixing them with other dyes. The purposes are to increase stability and widen light absorption area due to result in better efficiency. This article reviews the development of anthocyanin utilization as a natural dye in DSSC fabrication as well as some modifications that have been done. The use of anthocyanin as a natural dye in DSSC fabrication is feasible to be developed in industrial scale.

1. Introduction

Sunlight is the renewable energy that doesn’t cause environmental pollution or noise. Solar energy can be used to substitute conventional fuels consumption such as petroleum. Solar energy can be utilized directly into electrical energy by using photovoltaic technology. Besides, everyone can utilize solar energy freely if compared to conventional energy prices in the past decades. So far some researches have been conducted to develop high-efficiency solar cells. Solar cell efficiency refers to a percentage of sunlight that converted into electrical energy [1]. Nowadays, a silicon-based solar cell dominates the market with efficiency of 15-20%. Unfortunately, silicon-based solar cells have some weaknesses due to complex production process, utilize hazardous compounds and expensive production price. Therefore, a new type of solar cells was developed namely dye-sensitized solar cells (DSSC). DSSC is a photochemical solar cell that use an electrolyte as a medium to convert sunlight into electrical energy. DSSC is easier to produce compared with conventional solar cells that are produced via slot die coating, screen printing or inkjet printing method [2-3].

One of the important components in DSSC is dye. Dye plays an essential role to absorb photon from sunlight and pass it to semiconductor layer such as TiO₂. Until now, synthetic dyes have been applied in DSSC fabrication. The highest DSSC power conversion efficiency was reported before used ruthenium complex dye (N719) ranged 11%-12%. Ruthenium complex is the most stable and effective dye, however it is toxic, expensive and difficult to produce. These reasons urge researchers to develop natural dyes [4]. Nowadays, various natural dyes have been developed like anthocyanin. Natural dyes can be extracted from plant, root, flower and fruit. Beside that, they are simply processed so decrease production cost. Natural dyes exist abundantly in nature, despite their efficiency and stability are lower than synthetic dyes [5]. Hence, researchers have performed various modifications to achieve better efficiency of DSSC. This article presents the research developments on anthocyanin dye as a sensitizer in DSSC fabrication. Anthocyanin dye is applied in three ways: as single anthocyanin dye, copigment on anthocyanin, and mixing anthocyanin with other dyes.
2. Dye-Sensitized Solar Cell (DSSC)

DSSC is a photoelectrochemical device which converts solar energy into electrical energy by receiving photons from sunlight. These photons will excite electrons from dye molecules and transfer them to mesoporous conductive band layer such as TiO\(_2\). A DSSC consists of some components as follow [3]:

1. A photoanode, which made from Transparent Conductive Glass (TCO) such as glass substrate which layered by semiconductors like TiO\(_2\) or ZnO with several methods viz doctor blade, screen printing or inkjet printing.
2. A layer of dye to absorbs photons from sunlight. The dyes are ruthenium complex-based synthetic dye or natural dyes such as chlorophyll [6-7], anthocyanin [6-7], curcumin [6] and betaxanthin [7].
3. An electrolyte liquid which contains redox mediator, solvent and additive. Redox mediator that have been used are I\(^{-}\)/I\(^{3-}\), SCN\(^{-}\)/SCN\(^{2-}\), SeCN\(^{-}\)/SeCN\(^{2-}\) or bipyridine cobalt (III/II). Several types of solvents are acetonitrile, ethylene carbonate, propylene carbonate, 3-methoxypropionitrile and N-metylpyridon. Meanwhile, an additive is utilized to enhance solar cell properties [8].
4. A counter electrode (cathode), consists of transparent conductive glass with catalyst layer such as Pt or carbon that receive electrons from the outer circuit and reduce I\(^{3-}\) ion to I\(^{-}\) by transfer electrons.

The sequence of the DSSC operational mechanism is as follows: photons that enter the photoanode are absorbed and excite an electron dye from low energy state to high energy state. The excited electron will be injected to mesoporous TiO\(_2\) layer, leaves dye molecule in oxidated ion state on TiO\(_2\)/dye interface. Next, the dye is regenerated by receiving an electron from I\(^{-}\) on electrolyte liquid redox couple, so that ion oxidated into I\(^{3-}\) and distribute it to DSSC’s counter electrode. Last, I\(^{3-}\) is regenerated on a counter electrode by receiving an electron that returns from the external load through the catalyst layer, viz Pt [3].

3. Anthocyanin as Natural Dye in DSSC

Anthocyanin is flavonoid compound and responsible for red and blue colours on most of plants and fruits. Anthocyanin can be found in leaves, seed coats, roots, stem and bulbils. Most of the anthocyanin was derived from six anthocyanidins that are pelargonidin, cyanidin, delphinidin, peonidin, petunidin and malvidin (Figure 1). Anthocyanin can be degraded rapidly or react with another compound during its synthesis. The high reactivity of anthocyanin depends on its structure and some factors such as pH, temperature, light, oxygen, and enzyme. pH is an important factor that influence the anthocyanin stability. Generally, anthocyanin is more stable under an acidic environment with pH < 7 [9-10].

Besides in the food field, anthocyanin is also used as a natural dye in DSSC fabrication. Several anthocyanin sources that have been investigated are jati leaf [11], mangosteen peel [12], Bougenville spectabilis petals [13], snake fruit [14] etc. Anthocyanin has a wide light absorption area ranged 450-600 nm. The advantage of anthocyanin as a natural dye in DSSC fabrication is the presence of carbonyl and hydroxyl groups in its molecule structure that help the attachment into TiO\(_2\) layer, resulting in better energy conversion efficiency. The darker the anthocyanin colour, the higher the energy conversion efficiency. The darker colour will enhance the light absorption [15]. Anthocyanin pigment has enough conjugated π bonds. These conjugated π bonds useful to catch photons from sunlight. The more conjugated π bonds, the more electron excited so that a higher efficiency is achieved [16].
3.1. The use of single anthocyanin

The selection of natural dye is based on the presence of hydroxyl (-OH) and carboxyl (-COOH) groups in the dye compound. These functional groups play a role in dye attachment process to TiO$_2$ through the metal complex that initiates transfer electron from dye molecule into TiO$_2$. Anthocyanin has carbonyl (-COO) and hydroxyl (-OH) group that will bond with TiO$_2$ so the transfer electron process can be carried out [17-18]. Generally, the researchers use single anthocyanin dye which is extracted from several sources in DSSC fabrication.

Table 1 shows the DSSC performance in term of open-circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$), fill factor (FF) and efficiency ($\eta$) when using single anthocyanin of plants origin. Besides, some treatments also have been performed to investigate their influence on DSSC efficiency such as varying the solution pH and soaking time of working electrode in dye solution. Baharuddin et al. [11] used anthocyanin from teak leaf methanol extract and followed by isolation using methanol : n-hexane solvent using vacuum liquid column chromatography method. The results showed solvent ratio 5:5 gave the highest efficiency. The adjustment of pH influenced the DSSC efficiency. The use of acidic dye (pH 6) provided the highest efficiency of 0.02898%; while of basic dye (pH 11) was 0.01188%.

Table 1. DSSC efficiency on the use of single anthocyanin as natural dye

| Anthocyanin Sources | $V_{oc}$ (mV) | $I_{sc}$ (mA) | FF | $\eta$ (%) | Ref. |
|---------------------|--------------|--------------|----|------------|-----|
| Teak leaf           | -            | -            | -  | 0.0512     | 7   |
| Mangosteen peel     | 293.1        | 2021.37      | -  | 0.592      | [12]|
| B. spectabilis petals | 448         | 0.00658      | -  | 0.0090     | [13]|
| Snake fruit         | 9160         | 6            | -  | 0.011      | [14]|
| Rose residue        | 300          | 0.291        | 0.426 | 0.04   | [20]|
| N. lappaceum leaf   | 290          | 0.0562       | -  | 0.0629     | [21]|

Generally, anthocyanin contains difference composition of N, C and H. The solubility and alkalinity of this nitrogenous compound will increase at lower pH/acidic condition so that the dye concentration will increase. Anthocyanin has a unique structure that depends on pH, where the pH adjustment will change the structure and colour of anthocyanin. In acidic condition, anthocyanin will be more stable and red in colour, while in the basic condition the colour will change into blue, yellow or colourless. This structural change has an impact on the anthocyanin ability to absorb sunlight so the number of electrons...
that can be excited also different. As a result, the pH adjustment also provides a different DSSC efficiency [18-19].

Besides pH, another factor that can increase the efficiency of DSSC is soaking time of working electrode in natural dye solution. Hardianti et al. [13] compared the soaking time of working electrode in anthocyanin extract dye of *I. balsamina L* and *B. spectabilis* for 48 hours and 66 hours. The best efficiency of DSSC was attained by soaking for 66 hours for these anthocyanin sources, i.e. 0.0090% for *I. balsamina L* extract; 0.0022% for *B. spectabilis* extract; and 0.0044% for mixture dye. The same result was achieved by Wendri et al. [14] who compared the soaking time of working electrode in snake fruit extract dye for 6, 12 and 24 hours. The longer the soaking time of working electrode in the dye, the more anthocyanin will attach on TiO$_2$ substrate thus increase the number of absorbed photons from sunlight. Therefore, the resulted current will be higher. Figure 2 shows the scheme of TiO$_2$ bond with anthocyanin molecule.

![Figure 2. Scheme of anthocyanin molecule attachment on TiO$_2$ [17]](image)

3.2. The use of copigment on anthocyanin

One of the ways to enhance the efficiency of DSSC is through anthocyanin copigmentation process. Anthocyanin copigmentation process is an anthocyanin interaction in form of flavillium cation with copigment compounds such as metal (Al$^{3+}$, Fe$^{3+}$, Sn$^{2+}$, Cu$^{2+}$) or organic compound. Copigmentation process will change the anthocyanin form into more complex compound with copigment through bathochromic effect. The formation of more stable and complex structure aims to increase photons absorption thus increase the efficiency of DSSC. In addition, copigmentation also aims to extend the lifetime degradation of anthocyanin. Copigmentation process is effective in low pH (<2), but less effective in pH range 2-5. At low pH, flavillium cation dominates anthocyanin pigment; while at pH range 2-5, the flavillium cation and quinoid are in equilibrium [9, 22-23]. Some of the copigments used are caffeine [24], malic acid [23], ascorbic acid [23], gallate acid [25], salicylic acid [22] and benzoic acid [26].

Junger et al. [24] used caffeine as copigment on anthocyanin that was extracted from Mayfair plant. Caffeine can increase the concentration of flavillium cation. The use of caffeine as copigment resulted in the DSSC efficiency of 0.08%. Hardeli et al. [25] used gallate acid as copigment on anthocyanin that was extracted from jengkol shell. Gallate acid is a low-cost phenolic compound, soluble in water, easy to crystallize, and stable in dry form. Copigmentation using gallate acid resulted in a DSSC efficiency of 1.40% after being soaked in dye solution for 48 hours. Hardeli et al. [22] also investigated the use of salicylic acid as copigment and generated a DSSC efficiency of 1.32%. The use of phenolic compound copigments such as gallate acid and salicylic acid included in intramolecular copigmentation, where the copigment are part of anthocyanin. The bond between anthocyanin and copigment is the acylation covalent bond so it is stronger than intermolecular copigmentation.
Table 2. DSSC efficiency on the use of copigment on anthocyanin

| Copigment          | \(V_{oc} \) (mV) | \(I_{sc} \) (mA) | FF | \(\eta \) (%) | Ref |
|-------------------|------------------|------------------|----|--------------|-----|
| Caffein           | -                | -                | -  | 0.08         | [24]|
| Malic acid        | -                | -                | -  | 0.303        | [23]|
| Ascorbic acid     | -                | -                | -  | 0.292        | [23]|
| Gallate acid      | -                | -                | -  | 1.40         | [25]|
| Salicylic acid    | 467              | 0.1057           | -  | 1.32         | [22]|
| Benzoic acid      | 364              | 0.0046           | 0.484 | 0.3709     | [26]|
| \(\text{Mg}^{2+} \) (\(\text{MgSO}_4\cdot7\text{H}_2\text{O}\)) | 0.530            | -0.18            | -  | 0.0924       | [27]|
| \(\text{Fe}^{3+} \) (\(\text{Fe}_2(\text{SO}_4)_3\)) | 0.640            | 0.00189          | 4.37x10^{-7} | 0.148     | [28]|

Besides organic compound, anthocyanin copigmentation also have been done using metal doped. Andayani et al. [27] used \(\text{Mg}^{2+} \) (\(\text{MgSO}_4\cdot7\text{H}_2\text{O}\)) on \textit{Hylocereus costaricensis} anthocyanin extract. The concentration of \(\text{MgSO}_4\cdot7\text{H}_2\text{O}\) was varied from 0 M, 0.005 M, 0.01 M, 0.05 M and 0.1 M. The highest efficiency was attained by adding \(\text{MgSO}_4\cdot7\text{H}_2\text{O} \) 0.01M that is 0.0924%. The use of \(\text{Mg}^{2+} \) doped causes the presence of S=O and \(\text{Mg}-\text{O} \) bonds on \(\text{TiO}_2\) paste. Besides, \(\text{Mg}^{2+} \) doping also change the dipole moment in the molecular structure of the dye so that it influences the transmittance value. A low transmittance value indicates the molecule is more polar and the absorbance of visible light is high. A polar bond is better at conducting electric current. Prasada et al. [28] used \(\text{Fe} \) doped on black glutinous rice anthocyanin extract. \(\text{Fe} \) was obtained from \(\text{Fe}_2(\text{SO}_4)_3\) by varying concentration of 0.1 M, 0.01 M and 0.001 M. The highest efficiency was achieved by using \(\text{Fe}_2(\text{SO}_4)_3 \) 0.1 M that was 0.148%. The \(\text{Fe} \) doping increased the dye conductivity through absorption spectrum expansion from 595 to 660 nm. This spectrum expansion was caused by intermolecular copigmentation through bathochromic effect. Copigmentation using metal will provide a pathway for electrons to flow faster to FTO (Flour-Doped Tin Oxide) substrate.

3.3. Utilization of mixture dye

The selection of dye in DSSC fabrication has an important role to acquire high efficiency. Dye roles to absorb solar energy so that generate excited electrons. One of the ways to enhance DSSC efficiency is by mixing dyes. The mixing of dyes intents to widen the visible light absorption range due to increase the electron excitation that transmitted to \(\text{TiO}_2\) for enhancing the current of DSSC. Table 3 encloses several studies about the use of mixture dye to increase the efficiency of DSSC. The mixing process can use a combination of some natural dyes or by adding synthetic dye into a natural dye.

Pratiwi et al. [30] used anthocyanin and ruthenium complex N719 mixture dye as a sensitizer that gave an efficiency of 0.054%. Puspitasari et al. [6] used a natural dye mixture consisting of anthocyanin, chlorophyll and curcumin and generated an efficiency of 0.0566%. This efficiency is higher than that of a single natural dye or a combination of two dyes. The use of three natural dyes mixture was also investigated by Sinha et al. [7] that used anthocyanin, chlorophyll and betaxanthine with DSSC efficiency was 0.602%. Shah et al. [29] compared the use of anthocyanin-chlorophyll and chlorophyll-anthocyanin mixture resulting in an efficiency of 0.81% and 0.56%, respectively. When \(\text{TiO}_2\) semiconductor is firstly soaked in anthocyanin, the electron that released by dye molecule will be injected efficiently to \(\text{TiO}_2\) semiconductor through anthocyanin carbonyl and hydroxyl groups. Deposition of dye liquid gradually is very useful to enhance the efficiency of DSSC.
Table 3. DSSC efficiency on the use of mixture dye

| Mixing Dye                              | $V_{oc}$ (mV) | $I_{sc}$ (mA) | FF | $\eta$ (%) | Ref |
|-----------------------------------------|---------------|---------------|----|------------|-----|
| Anthocyanin + chlorophyll               | 460           | 2.64          | 0.63 | 0.81       | [29]|
| Anthocyanin + ruthenium complex N719    | 430           | 0.49          | 0.51 | 0.054      | [30]|
| Anthocyanin + chlorophyll + curcumin   | 496           | 0.06          | 35.635 | 0.0566 | [6] |
| Anthocyanin + chlorophyll + beta xanthin| 530           | 1.65          | 0.68 | 0.602      | [7] |

4. Considerations for Scale-Up Process

Anthocyanin is the phenolic compound that abundantly available in nature. The phenolic compound is the polar compound, so it needs a polar solvent to extract anthocyanin from its sources. Polar solvents that can be used are water, ethanol and ethyl acetate. Besides, the extraction of anthocyanin is also recommended in acidic condition. The acidic condition will break down the vacuoles of plant cell which store anthocyanin, so that more anthocyanin will be yielded. Anthocyanin is more stable in acidic condition, because more flavylium will be formed and consequently will increase the sunlight absorption [31].

Based on Table 1-3, it can be concluded that the use of single anthocyanin dye is not recommended to produce DSSC in a larger scale. This is due to the use of single anthocyanin gives the poor efficiency of DSSC. Therefore, the use of anthocyanin as natural dye must be modified because it can increase its stability so that it can prolong the lifetime of DSSC. Modification are also conducted to widen the sunlight absorption spectrum so that better efficiency could be obtained. Stability enhancement can be achieved through anthocyanin copigmentation using phenolic compounds or metal. Based on Table 2, the use of gallate acid as anthocyanin copigment is very recommended to increase the DSSC efficiency. In terms of broadening absorption spectrum, the use of mixture dye is more recommended. Mixing dye method is also suggested through two-steps soaking, with anthocyanin dye is used in the first soaking step. This method aims to facilitate the electron transfer process so that it is generated better efficiency. Finally, it is necessary to investigate the influence of copigmentation using a phenolic compound such as gallate acid and two-step soaking on DSSC efficiency.

5. Conclusion

This article encloses various researches about the utilization of anthocyanin as a natural dye in DSSC fabrication. The use of single anthocyanin gives low efficiency so some improvements have been conducted such as the use of copigmentation and dye mixture. These methods successfully increase the efficiency of DSSC. Besides, other modifications have been done such as prolong the soaking time of working electrode in dye solution or adjust the pH of dye liquid into acidic. Although the resulting efficiency is still lower than that of synthetic dye, the use of natural dye like anthocyanin is suitable to further development. Anthocyanin dye is available in nature abundantly, easy to process and non-toxic so can substitute the use of ruthenium complex-based synthetic dye.

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