UTILIZATION OF NATURAL PIGMENTS IN DYE-SENSITIZED SOLAR CELLS

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Abstract

To minimize the environmental pollution effect in the production of electrical energy, researchers have been constantly searching for new sources of electrical energy that have no negative impact on the environment. A possible solution is utilization of dye-sensitized solar cells (DSSC) with natural colors. One of the advantages is that they do not use harmful chemicals for dye synthesis, but instead utilize colors found in various natural products such as fruits and vegetables, resulting in low-cost natural dyes. On the other hand, one of the primary challenges of these cells is how to improve their efficiency and the low stability of natural pigments. By using the extract from red beetroot (Beta vulgaris rubra) achieved solar cells efficiency is 3.5%, while by using the ethanol extract of the Hibiscus surattensis achieved efficiency is 1.14%. In comparison to the efficiency of solar cells produced from monocrystalline or polycrystalline silicon, which can reach values around 26%, the efficiency of these DSSCs is much lower. Further research is necessary to optimize the application of natural pigments and potentially increase their efficiency. This paper describes the working principle of DSSCs and provides an overview of studies on the use of natural colors in their production.

Keywords: dye-sensitized solar cells (DSSC), efficiency, natural pigments

INTRODUCTION

The sources of energy on which the world largely depends today are mainly classified as non-renewable sources, which often have a harmful effect on the environment, in terms of emitting pollutants that contribute to the greenhouse effect and many others. One potential solution to this issue is the utilization of renewable energy, such as solar energy, which can be converted into electrical power. Silicon-based solar cells are currently used worldwide for generating electrical energy. However, one of the primary challenges in their use is the high production cost, so it is essential to find solar cells with lower production costs, and one of the possible solutions are dye-sensitized solar cells (DSSC) [1,2]. The basic components and the operating principle of DSSC are illustrated in Figure 1. Fluorine-doped tin oxide (FTO) glass is used as the anode, onto which a thin film of TiO_2 is deposited, followed by dye molecules that attach to the TiO_2 surface. The cathode consists of FTO glass coated with a layer of graphite. To complete the circuit, an electrolyte solution is used, with one of the most commonly used solutions being a mixture of iodine and iodide ions.

The dye absorbs incident light, causing electrons to transition from the ground state to an excited state of molecule. Electrons from the excited state of the dye then move into the conduction band of the semiconductor TiO_2, resulting in the oxidized form of the dye. Electrons from the conduction band of TiO_2 move through the conductive glass and an electrical conductor toward the cathode. The oxidized form of the dye reacts with the present electrolyte, undergoing reduction and returning to its original state, while the electrolyte is regenerated through a reaction with electrons from the cathode [1,3].

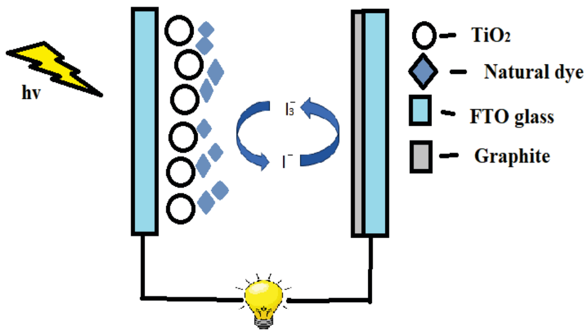

Fig. 1. *Working principle of DSSC*

In commercially available DSSCs, ruthenium complexes are commonly used as dyes. However, the high cost, limited availability, and complex synthesis of these complexes have led to the need for the use of new dyes, such as synthetic and natural organic dyes. Organic dyes have demonstrated impressive efficiency levels, reaching as high as 9.8%. Nevertheless, these dyes have encountered challenges, such as complicated synthesis processes and limited yields. In contrast, natural dyes present in various parts of plants, such as flowers, leaves, and fruits, can be easily extracted through straightforward methods and subsequently utilized in DSSCs [4]. Main advantages of using natural dyes in DSSC are [4]:

- Easy availability
- Nontoxicity
- Complete biodegradability

Since natural dyes are candidates for sensitizers in DSSCs, the exposition part of the paper reviews the use of natural dyes in DSSCs.

ANTHOCYANINE DYES AS PHOTOSENZITIZERS IN DSSC

Anthocyanins, which are a type of flavonoid, serve primarily as natural coloring agents. The levels and types of anthocyanin pigments present in fruits and vegetables are affected by genetic and environmental factors and these pigments are primarily responsible for the various colors observed in different parts of plants and fruits, such as bright orange, pink, red, violet, and blue. The presence of carbonyl and hydroxyl functional groups in anthocyanin molecules enables effective binding of the dye to the surface of TiO_2, which is one of the crucial requirements for enhancing the efficiency of DSSC [1,5].

Ghann et al., 2017 [6], used anthocyanins extracted from pomegranate and berry fruits for the production of DSSC. Fresh pomegranates and berries were first peeled, and their juices were obtained from the pulp coats using a commercial fruit juice extractor. Subsequently, a series of steps including filtration, centrifugation, and decantation were employed to eliminate any solid particles in the initial extract. The working electrode was created by applying a thin layer of TiO_2 onto the conductive side of a FTO glass using a spin coater and then heating it at 380°C for 2 hours. Afterward, the TiO_2-coated FTO glass was immersed in a $TiCl_4$ solution for an hour and annealed for 30 minutes. Then electrode was submerged in concentrated pomegranate juice. Cathode was prepared either by applying carbon soot onto an FTO glass slide or by coating it with colloidal graphite. Finally, the pomegranate dye-sensitized electrode and the carbon electrode were assembled to create a solar cell, with a iodine/iodide electrolyte solution in between. After optimization of the photo-anode and counter electrode, a photoelectric conversion efficiency (η) of 2%, an open-circuit voltage (Voc) of 0.39 mV were achieved.

The comparison of DSSC efficiency obtained using anthocyanin extracts from different fruits is depicted graphically in Figure 2.

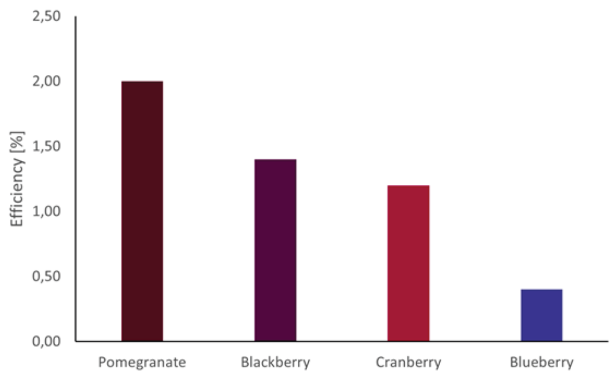

Fig. 2. *Efficiency of different DSSC [6]*

As observed in Figure 2, the most efficient DSSC is cell in which a pomegranate extract is used as the photosensitizer, while the cell with the lowest efficiency is the one which used a blueberry extract as the natural dye.

The highest open-circuit voltage was achieved by the cell utilizing a blackberry extract as the photosensitizer (0.47 V), while the lowest was recorded for the DSSC with a pomegranate extract (0.39 V) (Figure 3).

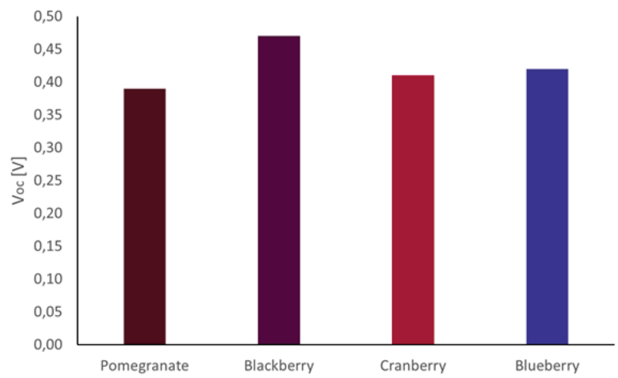

Fig. 3. *Open-circuit voltage of different DSSC [6]*

Fernando et al., 2008 [7], extracted anthocyanins from several plants, including *Rhododendron arboretum zeylanicum, Sesbania grandiflora, Hibiscus rosasinensis, Hibiscus surattensis, Nerium oleander, and Ixora macrothyrsa*. They used 96% ethanol as a solvent, and the obtained extracts were allowed to stand overnight before use. Prior to usage, the extracts were filtered, washed with hexane, and acidified with a few drops of HCl. They employed FTO glass coated with TiO_2 as the photoanode. These prepared electrodes were immersed in the dye extract for 12 hours. The electrolyte used was a solution of tetrabutylammonium iodide and iodine in a mixture of acetonitrile and ethylene carbonate (6:4 v/v). Platinum-coated FTO glass was used as the cathode. The cell utilizing the *Hibiscus surattensis* extract exhibited the highest efficiency (1.14%) with an open-circuit voltage of 0.392 V, outperforming the other tested cells.

BETALAIN DYES AS PHOTOSENZITIZERS IN DSSC

Betalains are water-soluble pigments that can be either yellow (betaxanthins) or purple (betacyanins). The primary pigment in red beet, betanin, is the most well-known member of this group. Betalains possess advantageous light absorption properties and feature a carboxylic (COOH) functional group, enabling them to bond with TiO_2. These pigments demonstrate robust absorption within the 400–600 nm range [1,3]. In red beet, there are multiple types of betanines, and it is precisely betacyanin is one responsible for the dark purple color of this plant. Betacyanine is used in different studies as sensitizer in DSSC.

Upadhyay et al., 2014 [8], extracted betacyanin from red beet (Beta vulgaris). The underground part of the beet, after drying and grinding, was extracted with absolute ethanol and then concentrated using a rotary vacuum evaporator. The resulting extract was subsequently purified through column chromatography, separating betaxanthins from betacyanins. In contrast to many studies that used TiO_2, these authors utilized a TiO_2-CeO_2 mixture synthesized via the sol-gel method. They employed a solution of 0.5 mol/dm^3 LiI and 0.05 mol/dm^3 I_2 in acetonitrile as the electrolyte, while platinum-coated conductive glass was used as the cathode. This resulted in an effective energy conversion efficiency of 3.5%.

Isah et al., 2015 [9], utilized pigments from Bougainvillea glabra and investigated the influence of the extract's pH on the characteristics of the obtained cells. They obtained the color extracts by grinding 20 g of flowers and adding 50 ml of water. After filtration, the pH of the resulting extract was 5.7, and it was divided into three parts, with the pH of two parts adjusted using HCl to 3 and 1.23, respectively. Conductive glass coated with TiO_2 paste, followed by heating and immersion in a $TiCl_4$ solution, was used as the photoanode. Dye-sensitized solar cells with an extract at pH 3 exhibited the highest photocurrent density (Jsc) of 3.72 mA/cm^2 and a fill factor (FF) of 0.59. In contrast, DSSCs using dye sensitizers at pH values of 1.23 and 5.7 had fill factors of 0.43 and 0.61, respectively. The maximum power outputs for these DSSCs were 0.50 mW/cm^2, 1.64 mW/cm^2, and 0.94 mW/cm^2, corresponding to dye sensitizers at pH values of 1.2, 3.0, and 5.7, respectively. The authors explained the low photocurrent density values at pH 1.27 by noting that strong acid conditions lead to pigment degradation, while lower values at pH 5.7 compared to 3 are attributed to weaker binding of dye molecules to the TiO_2 surface. Figure 4. illustrates the impact of Bougainvillea glabra extract pH on DSSC efficiency, showing that the highest efficiency occurs at pH 3, while the lowest is observed at pH 1.27.

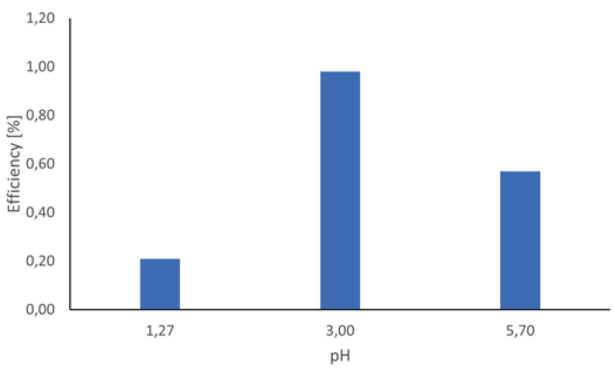

Fig. 4. *Effect of pH extract on DSSC efficiency [9]*

Ramamoorthy et al., 2016 [10], utilized betalain pigments and anthocyanins, as well as a mixture of extracts, to construct dye-sensitized solar cells. Betalain pigments were extracted from the fruits of the *Opuntia dillenii* plant using methanol as the solvent, while anthocyanins were extracted from *Tamarindus indica*. They used conductive glass coated with TiO_2 paste as the photoanode and conductive glass with a platinum layer as the cathode. The highest conversion efficiency was 0.47% for betalain dyes, followed by 0.14% for anthocyanin dye-sensitized solar cells. When a combination of these dyes (in a 1:1 mixture) was absorbed onto TiO_2, the efficiency reached 0.20%. The authors compared the efficiency of these cells with DSSCs using the N719 standard dye ((Bu4N)2[Ru(4-carboxy,40 -carboxylato-2,20 -bipyridine)2(NCS)2]). The efficiency of DSSCs with N719 was 7.19%, significantly higher than DSSCs using natural dyes. However, despite this difference, Ramamoorthy et al., 2016, conclude that natural dyes represent a sustainable and environmentally friendly option, offering a green and renewable energy source for creating dye-sensitized solar cells.

CHLOROPHYLL AS PHOTOSENZITIZERS IN DSSC

Chlorophyll is a green pigment found in plants, primarily in their leaves, and plays a crucial role in the process of photosynthesis. Chlorophyll a, however, does not readily adhere to the TiO_2 film, resulting in significantly low cell efficiency, despite often achieving high Jsc values [11]. Chlorophyll is frequently studied as a sensitizer in DSSCs [1].

Chang et al., 2010 [12], employed natural dyes for dye-sensitized solar cells (DSSCs), which were derived from spinach extract, ipomoea leaf extract, and a combination of both. Initially, they immersed spinach and ipomoea leaves separately in ethanol to extract chlorophyll, which served as the natural dyes for the DSSCs. The authors deposited TiO2 nanoparticles onto the indium tin oxide (ITO) conductive glass, creating a TiO_2 thin film with a thickness of

11.61 micrometers. This thin film was sintered at 450°C to enhance its compactness. Subsequently, the sintered TiO2 thin film was immersed in natural dye solutions extracted from both spinach and ipomoea leaves, completing the production of the DSSC anode. The authors investigated the influence of extraction temperature on the ultimate efficiency of the obtained DSSCs. The highest efficiency of 0.278 with an open-circuit voltage of 540 mV was achieved when using ipomoea leaves at a temperature of 50°C. To further optimize the efficiency, the authors adjusted the pH value of the extract obtained at 50°C, and they achieved the best efficiency of 0.318 at a pH of 1.

Syafinar et al., 2015 [13], extracted chlorophyll from spinach using two solvents - water and ethanol. They finely ground 5 grams of spinach and poured 10 ml of either ethanol or water over it, then performed extraction in an ultrasonic bath. Afterward, they separated the spinach leaves from the solution through centrifugation. As the photoanode, the authors utilized conductive ITO glass with a layer of TiO_2, while as the cathode, they used conductive glass with a graphite layer. When ethanol was used for extraction, an open-circuit voltage was 384 mV and a short circuit current was 0.32 mA. Conversely, when water was employed as the extraction solvent, an open-circuit voltage was 440 mV and a short circuit current was 0.35 mA.

CONCLUSION

Dye-sensitized solar cells with natural dyes represent environmentally friendly solar cells used for converting solar energy into electricity. Natural dyes are readily available, cost-effective, and biodegradable, unlike ruthenium-based sensitizers that are expensive, giving them an advantage in terms of cost. The primary drawback of natural dyes for DSSCs is their relatively low efficiency. The most commonly used natural dyes in DSSCs include anthocyanin dyes, betalains, and chlorophyll. Natural dyes can be used in undergraduate courses to illustrate the working principles of DSSCs. However, further research and optimization of the extraction process (temperature, pH), modification of the TiO2 layer, and potentially using a mixture of different natural pigments are necessary to enhance the efficiency of such DSSCs and their broader applications.

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