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Synthesis and Characterization of *Allium Cepa* L. as Photosensitizer of Dye-Sensitized Solar Cell

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Abstract. The synthesis and characterization of *Allium cepa* L. used as natural pigment for natural dye sensitizer of solar cell has successfully done and anthocyanin is extracted. Anthocyanin is color pigment of plant which has characteristic absorption spectrum of photon and excites electrons up to pigment molecules. As the anthocyanin absorbed light increases the excited electrons increase as well. The generated current also increases and it leads to the efficiency increase. The energy conversion efficiency of the cells sensitized with dye of *Allium cepa* L. was $3,045 \times 10^{-4}\%$. A simple technique was taken to fabricate dye sensitizer solar cell is spincoating.

INTRODUCTION

Dye-sensitized solar cells (DSSCs) as low-priced photovoltaic device have been catching the researcher attentions due to their's capabilities in converting sunlight into electric energy [1]. These devices consist of photosensitizer, transparent conductive glass, TiO₂ film and electrolyte those have been elaborated using organic pigments [2]. The organic pigments are very desirable because of the easy and low cost processing, non-poisonous, the easy disposal and the more ecofriendly than synthetic metal complexes [3]. In comparison with silicon-based conventional solar cell, DSSC has some benefits such as having a colorful and transparent look, excellent portability [4], easily available, profusion and safety of the source [5], simple to extract, no require further purification, green [6], color diversity [7], low energy payback time [3], reasonable worthy efficiency, the aptitude for cheap production cost including nonvacuum processing at room temperature, supple light weight products, and an access to new markets [4,8,9].

To design very efficient sensitizer, it is necessitated three conditions as follows: wide spectral range of photosensitizer have similarities with the solar emission spectrum, electron allows inject fastly into the conduction band of the semiconductor, and the injected electron recombines slowly with the sibling dye cation [5].

There are three main groups of plant pigments namely anthocyanins, betalains and chlorophylls. The color spectrum for orange-to-blue are generated of anthocyanins existance, while both yellow-to-red spectrum and green spectrum are generated by carotenoids and betalains, repectively. Flowers, leaves and fruits consist of anthocyanins which can be extracted for photosentizers [10].

Recently, the studies are focused on the development of natural color pigments of plants as photosentizers. This selection is taken by considering on large absorption coefficient, high solar energy conversion, low production cost, easy storage and ecofriendly. Some natural color pigments which are extracted of various plants such as jaboticaba

(*Myrtus cauliflora* Mart) and calafate (*Berberies buxifolia* Lam) [11], shiso leave [12], black rice, capsicum, *erythrina variegata* flower, *rosa xanthina*, and kelp [1], *rosella (Hibiscus sabdariffa L.)* and blue pea (*Clitoria Ternatea*) flowers [13], mulberry (*Morus alba* Lam), blueberry (*Vaccinium myrtillus* Lam), and jacobin's skin (*Mirtus cauliflora* Mart) [8], red sicilian orange and purple eggplant fruits [14], *Canna indica* L., *Salvia splendens*, cowberry and *Solanum nigrum* L. [15], leaves and mulberry fruit [16], Monascus Yellow [17], rhododendron, herba *artemisiae scopariae*, mangosteen pericarp, and coffee [18], *Delonix regia* [6], *Hibiscus*, chlorophyll [19], walnuts, rhubarb, and pomegranate [20], *punica granatum*, rose [21], *Ixora* flower (*Ixora* sp. (Rubiaceae) and the outer dark purple skin of 'Kembayau' (*Canarium odontophyllum*) fruit [12], *Oryza nivara*, *Brassica oleracea* L. [22], *Canarium odontophyllum* [10], *Vitis vinifera*, red cabbage (*Brassica oleracea* var. *capitata* f. *rubra*) [2], Welch grape juice [23], gardenia yellow (*Gardenia jasminoides*) and cochineal (*Dactylopius coccus*) [7], spinach (*Spinacia oleracea*), red radish (*Raphanus sativus* L), winter jasmine (*Jasminum nudiflorum*), and black rice (*Oryza sativa* L. *indica*) [24], have been used as sensitizers in DSSCs. Anthocyanins, natural pigments for colors of red, violet and blue, were used as sensitizers. The advantage of usage of anthocyanin is carbonyl and hydroxyl group binding on pored TiO₂ film surfaces so that the electron transfer from anthocyanin molecules to TiO₂ conduction bands occur [25]. In this reasearch *Allium cepa* L. was extracted and characterized to determine their light absorbances and expectedly, it is available to fabricate dye sensitizer of organic solar cell. The fabricated DSSC is characterized to determine it's efficiency and performance.

MATERIALS AND METHOD

Materials used in this research include *Allium cepa* L. extract, PEDOT:PSS, polyethylene glycol (PEG), ITO substrate, 96% ethanol, DI-water, acetate acid, pyroxylic spirit, and object glass. The research equipments consist of beaker glass, measuring cylinder, filter paper, blender, distillator, bunsen burner, glass cutter, magnetic stirrer, spincoater, Vis-Nir, UV-Vis spectrophotometer, I-V meter and CCD Camera (MS 804).

The cut *Allium cepa* L. is mixed with solution of DI-water, ethanol and acetate acid in composition of 20, 100 and 4 gram, respectively. The extracted *Allium cepa* L. is made into five different mass fractions (0,2; 0,3; 0,4; 0,5 and 0,6) of samples with contents of *Allium cepa* L. are 31, 62, 83, 124 and 186 gram, respectively.

TABLE 1. Mass fractions of *Allium cepa* L. extraction.

| Sample codes | Mass fractions [x] | Allium cepa L. [g] | Solution [g] |
|--------------|--------------------|--------------------|--------------|
| A | 0,2 | 31 | 124 |
| B | 0,3 | 62 | 124 |
| C | 0,4 | 83 | 124 |
| D | 0,5 | 124 | 124 |
| E | 0,6 | 186 | 124 |

A mixture of *Allium cepa* L. and solvent for each fraction was blended for 2 minutes, allowed to stand for a moment, and then filtered. The solution volume of each mass fraction was measured by using cylinder measuring glass and the it is casted into distillator tube to be heated up on bunsen burner. During distilation process, the initial heating time, a moment when vapour trickled in glass beaker and time when vapour trickling stoped are observed.

The residue solution in the distillator tube was re-casted into cylinder measuring glass to determine a volume change occurs and casted to be stirred in heated condition at rotation speed of 500 rpm up to it coagulated. The *Allium cepa* L. extract was bottled. Before used as substrate, the object glasses were cleaned using ethanol 96%. The *Allium cepa* L. extract is spincoated on to object glasses in the dimension of 1 cmx1,25 cm for 30 seconds, dried and heated at 150°C for 10 minutes in oven. The resulted thin films were characterized using IV-meter, Vis Nir

spectrophotometer and CCD microscope MS-804 to investigate electrical properties, light absorbances, and surface characteristics of each fraction of *Allium cepa* L. extract.

The fabricated structure of device can be seen as seen in Figure 1 which consists of four layers deposited on the ITO substrate and a contact pad of aluminium as anode. The layers in a serie from ITO substrate to anode include PEDOT:PSS, PEG, PEG + *Allium cepa* L. anthocyanin, and *Allium cepa* L. anthocyanin. The organic layer, PEDOT:PSS, is spincoated on the ITO substrate at 500 rpm for 30 seconds and then dried using oven at 150°C for 60 seconds. The second layer is PEG thin film, coated at 500 rpm for 100°C and dried at 220°C. Next, PEG and *Allium cepa* L. anthocyanin were mixed, coated on the second layer at 2500rpm and dried at 200°C. The photoactive layer of *Allium cepa* L. extract was coated on the third thin film layer before aluminium metallization. The aluminium foil was evaporated to make contact layer (anode).

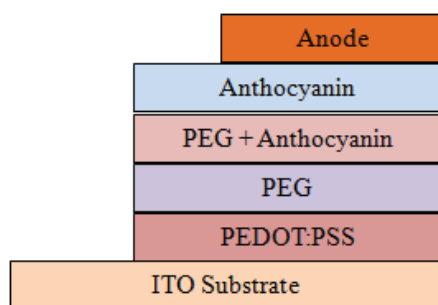


FIGURE 1. Device structure of solar cell.

RESULTS AND DISCUSSION

During distillation process, *Allium cepa* L. extracts were separated from their solutions, the volatile compounds were separated from un-volatile part. The vapours condensed and flowed into cup container.

The microstructures of *Allium cepa* L. extract thin films with different compositions are presented in Figure 2, homogeneity of thin film surfaces seem different. Sample A seems more homogeneous than others and sample B shows large voids which are suspected caused by prebake process. Sample B is relatively more homogeneous than sample D. Nevertheless, microstructures of thin films tend to more homogeneous with *Allium cepa* L. extract content increasing.

Absorbances of all samples were characterized using Ocean Optic Vis-Nir USB4000 spectrophotometer which are slightly different. These show that the *Allium cepa* L. extract content affected thin film properties.

As shown in Figure 3, sample D has highest absorbance of light than others. The light absorbance of sample C is lower than that of D. The light absorbance of sample B nearly equals to that of E, and the lowest one is that of A. It is known that as the mass fraction of *Allium cepa* L. extract content increases the light absorbance increases as well. As we know that the high absorbance material is better for application of solar cell.

The resulted data of sample characterization using FTIR is shown Figure 4. They have reatively same chemical bonding structures. Based on the analysis of chemical bonding structure which are done by Kim (2013), spectrum of sample A has wavenumber of 3395,45 cm^{-1} which informs a vibration of collection of free hydroxyls on phenol fenol (Ar-OH) with transmittance of 4,05%. To identify a chemical bond structure using FTIR is necessitated at least three peaks of transmittances which correspond to each wavenumber. In the characterization of sample A, four strong spectrum peaks on the wavenumbers and transmittances: 922,81 cm^{-1} (14,67%), 867,34 cm^{-1} (14,73%), 818,16 cm^{-1} (13,64%), dan 779,70 cm^{-1} (13,13%) show that a vibration of C-H bond of alkene bond (RCH=CH2). Another peak of 1637,66 cm^{-1} (9,86%) shows an absorbance of infrared by C=C bond. The wavenumber and transmittance of spectrum sample B are 3405,34 cm^{-1} and 3,73% respectively which show a vibration of free

hydroxyl collection on phenol (Ar-OH). Wavenumbers and transmittances of four peaks of sample B spectrum consist of 921,96 cm⁻¹ (16,44%), 867,58 cm⁻¹ (16,56%), 818,46 cm⁻¹ (15,10%), dan 779,51 cm⁻¹ (14,60%) which show a vibration of C-H bond of RCH=CH₂) bond. Another peak of wavenumber and transmittance of 1633,09 cm⁻¹ and 10,41% respectively informs infrared absorbance by C=C bond. Based on the spectrum produced of sample C characterization, a peak with wave number of 3400,51 cm⁻¹ and transmittance of 4,31% indicates a vibration of free hydroxyl on phenol (Ar-OH). Except it, four peaks also are identified with wavenumbers and transmittances: 921,33 cm⁻¹ (17,92%), 818,48 cm⁻¹ (16,19%), 779,49 cm⁻¹ (15,42%), and 671,61 cm⁻¹ (15,62%) which show vibration of C-H bond of alkene bond (RCH=CH₂). Another peak is for wavenumber of 1633,64 cm⁻¹ and transmittance of 11,57% which shows an absorbance of infrared by C=C bond. Sample D generates spectrum which includes a peak with wavenumber of 3399,96 cm⁻¹ and transmittance of 1,45%, an indicator for existing vibration of free hydroxyl collection on the phenol (Ar-OH). Other four peaks are founded on the wavenumbers and transmittances as the followings: 921,10 cm⁻¹ (12,41%), 866,10 cm⁻¹ (12,03%), 818,39 cm⁻¹ (11,49%), and 779,82 cm⁻¹ (10,96%) those show existing vibration of C-H bond of alkene bond (RCH=CH₂). Next one peak existed with wave number of 1625,59 cm⁻¹ and transmittance of 6,75% confirms infrared absorbance by C=C bond. Four peaks identified of spectrum of sample E consist of wavenumbers and transmittances: 921,91 cm⁻¹ (16,60%), 865,57 cm⁻¹ (16,07%), 818,73 cm⁻¹ (12,61%), and 779,58 cm⁻¹ (11,09%), reveal a vibration existing of C-H bond of alkene bond (RCH=CH₂). Two other peaks are with wavenumbers and transmittances of 3400,52 cm⁻¹ (0,84%) in that order, exhibit vibration be present of free hydroxyl collection of phenol (Ar-OH) and with wavenumber and transmittance of 1637 cm⁻¹ (6,55%) in that order, shows infrared absorbance existing of C=C bond. Based on the active layer characterization results, the *Allium cepa* L. extract with mass fraction of 0,5 is selected as active layer in the device fabrication. Sample D has peak with highest absorbance namely 2,201 and Ar-OH bond of sample D represents electron charge has also highest transmittance.

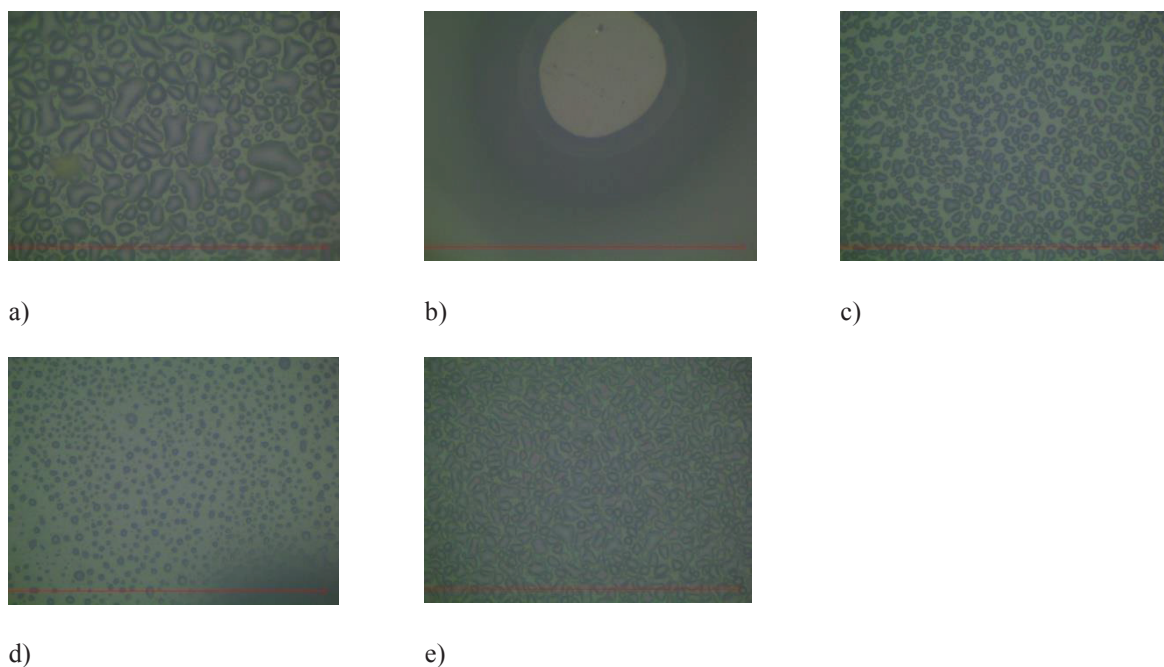


FIGURE 2. The structures of *Allium cepa* L. extract thin films with mass fractions each of: a) 0,2; b) 0,3; c) 0,4; d) 0,5 and e) 0,6.

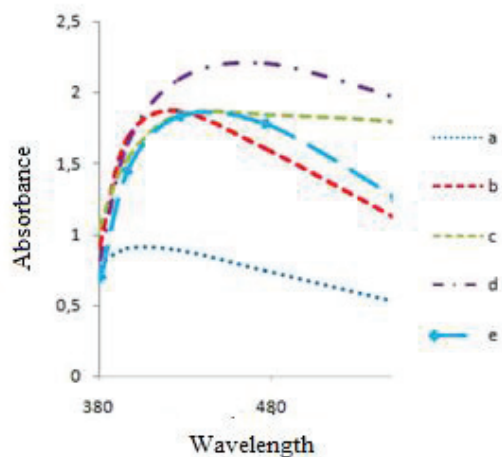


FIGURE 3. The absorbances of *Allium cepa* L. extract of samples A, B, C, D and E in the range of 380-550 nm.

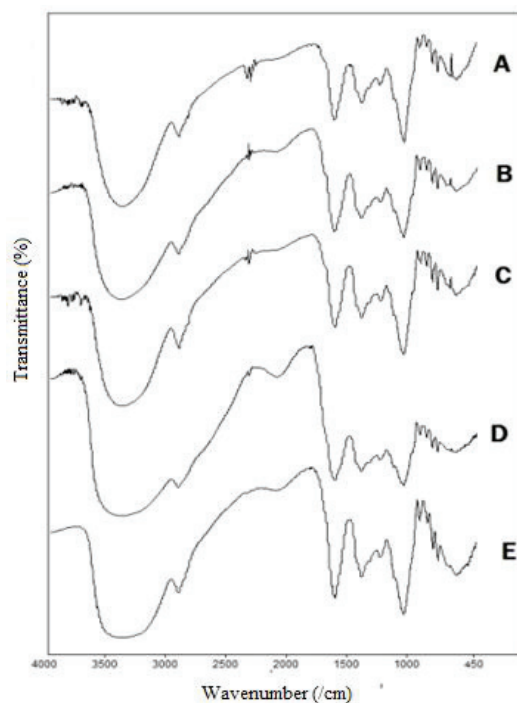


FIGURE 4. FTIR spectrum of thin film of *Allium cepa* L. anthocyanin extract.

The electrical properties of chlorophyll solution are shown in Figure 4. This graph is used to determine film conductivity of *Allium cepa* L. extract. The difference of light absorbances of *Allium cepa* L. extract affects the electron mobility which is proven by I-V characteristics of solutions. Sample D with highest absorbance of light shows highest electrical conductivity. In Fig. 5, a comparison of conductivities of all samples is exhibited. Seriesly electrical conductivities (σ) of samples from the highest down to lowest one are σ_B , σ_C , and σ_E .

The fabricated DSSC generates current for short circuit (J_{sc}) $5,52 \times 10^{-7}$ A and open circuit (V_{oc}) 0,5000346 V. Based on the calculation, Fill Factor (FF) and achieved efficiency of DSSC are 1,103 and $3,045 \times 10^{-4}\%$, respectively. Different responses of device under light illumination and dark condition can be seen in Fig. 6. This shows device can work well although the achieved efficiency has been relatively low.

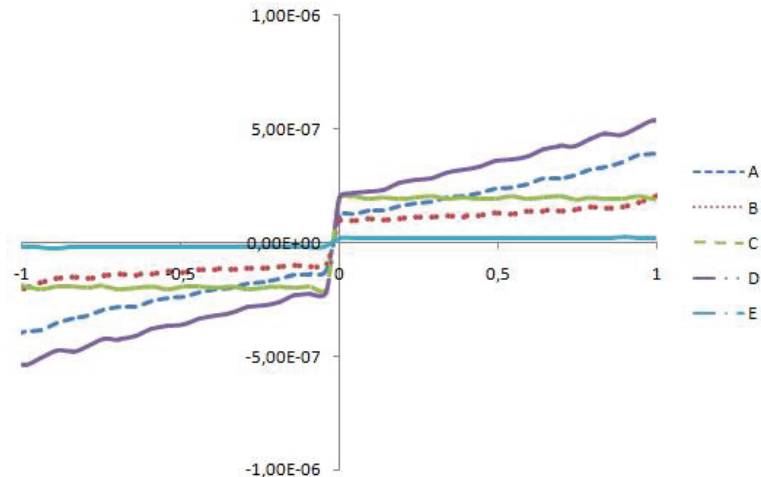


FIGURE 5. IV-Curve of *Allium cepa* L. extract.

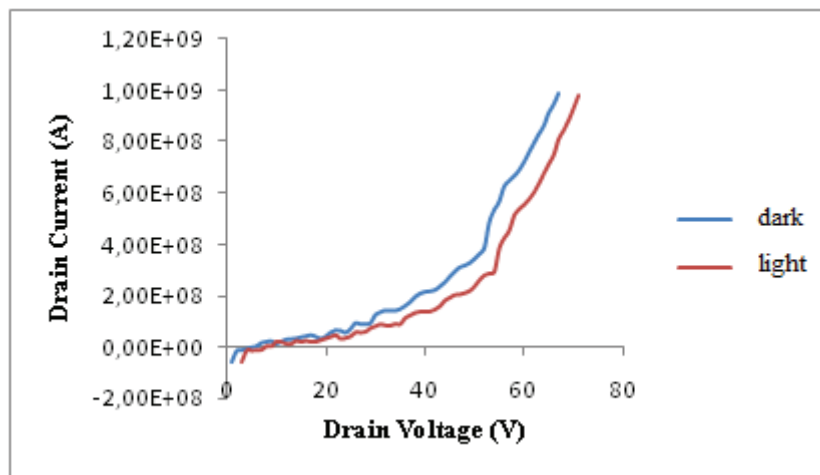


FIGURE 6. Generated drain currents of *Allium cepa* L. anthocyanin-based DSSC on dark and under light illumination.

CONCLUSION

Allium cepa L. is organic compound containing anthocyanin namely a color pigment which is giving purplish red color in its morphology structure. In this research, anthocyanin films with different amount give different responses to incident light which are indicated by different light absorbances. *Allium cepa* L. extract is very potential for solar cell active material. Red *Allium cepa* L. extract layer in thin film with mass fraction of 0,5 has highest electrical conductivity and light absorbance than others. Except it, electrical conductivities and light absorbances are affected by distillation and spincoating process. The efficiency of resulted DSSC is $3,045 \times 10^{-4}\%$.

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