Optoelectronic Properties of Combinations of Anthocyanin, Betalain, and Chlorophyll doped with Ag Metal as the Photosensitizers in Dye-Sensitized Solar Cell

Nurosyid, Fahru
Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret (UNS)

Riyadi, Untung
Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret (UNS)

Widiyandari, Hendri
Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret (UNS)

Iriani, Yofentina
Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret (UNS)

他

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Optoelectronic Properties of Combinations of Anthocyanin, Betalain, and Chlorophyll doped with Ag Metal as the Photosensitizers in Dye-Sensitized Solar Cell

Fahru Nurosyid*, Untung Riyadi, Hendri Widiyandari, Yofentina Iriani, Khairuddin Khairuddin, Risa Suryana

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret (UNS), Jl Ir. Sutami 36A Surakarta 57126, Indonesia

*Author to whom correspondence should be addressed:
E-mail: fahrunurosyid@staff.uns.ac.id

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Abstract. This article discussed the performance of the combinations of chlorophyll, anthocyanin, and betalain dyes and their mixture doped with Ag metal to broaden the light absorption spectrum and enhance the efficiency of Dye-Sensitized Solar Cell (DSSC). The anthocyanin (A), betalain (B), and chlorophyll (C) dyes were extracted from natural sources of dragon fruit peel, bougainvillea glabra flowers, and cassava leaves, respectively. The dye solutions in the manufactured DSSCs were modified by mixing two and three dyes, including AB, AC, BC, and ABC, and doping Ag metal in ABC dye (ABC/Ag). The ABC/Ag dye revealed the highest conductivity of 0.534 Ω^{-1} m^{-1}. The bandgap energy of the TiO_2 photoanode immersed in ABC/Ag was reduced by 3.0 eV. The efficiency values of the DSSCs manufactured with dyes of A, B, C, AB, AC, BC, and ABC were 0.263%, 0.24%, 0.125%, 0.435%, 0.387%, 0.299%, and 0.602%, respectively. It revealed that the mixtures of two and three dyes provided more light absorption, enhancing the efficiency. Meanwhile, the value for the DSSC with ABC/Ag exhibited the highest conversion efficiency of 0.742%. It denoted that the conductive nature of Ag metal added in the dye mixture played a role in improving the DSSC efficiency.

Keywords: anthocyanin; betalain; chlorophyll; Ag metal doping; dye absorption; bandgap energy; DSSC performance

1. Introduction

Sunlight is an abundant and environmentally friendly renewable alternative energy source that can be converted to electrical energy by means of a solar cell device[1]. Dye-sensitized solar cells (DSSCs) attract researchers' attention due to their promising potential, accompanied by easy and low-cost fabrication. Besides, they are flexible, transparent, environmentally friendly, and sensitive to low light levels, so they are expected to dominate the photovoltaic cell market[2-5]. The DSSC sandwich structure comprises two transparent conductive oxide (TCO) glasses, a semiconductor material as a photoanode (usually TiO_2), a dye known as a photosensitizer, and an electrolyte. The dye is the crucial element directly affecting the formation of photoelectrons, electron transfer, and light absorption[6].

In the current DSSC study, synthetic dyes, such as N3 and N719, could achieve an 11-12% conversion efficiency because they can maintain stability during the metal-ligand charge-transfer transition (MCLT) and absorb charge transfer in low light. Unfortunately, the dyes may be poisonous and contain heavy metals that can pollute the environment[7,8]. Additionally, synthetic dyes are expensive and challenging to synthesize. Natural dyes possess the potential to be photosensitizers in DSSC. They are plentiful, inexpensive, biodegradable, non-poisonous, and easily synthesized[7]. Plant components such as leaves, flowers, fruit stems, roots, seeds, and fruit skins used to extract those containing anthocyanin, betalain, and chlorophyll pigments can all be utilized to make dyes.

For the excited electrons to jump, the energy location of the excited state dye must be higher than the TiO_2 conduction band. Electrons in metal complexes and dyes can be excited by light at low to high energies. Some of the strongest photovoltaic reactions can be produced by the two pigments of betalain and anthocyanin[9,10].

Dye mixing plays a role in broadening light absorption, improving the conversion efficiency of the DSSCs[11]. Richhariya et al., 2018 have mixed hibiscus dye and eosin Y, demonstrating a DSSC efficiency of 2.02% in the wavelength absorption region of 440-560 nm. The results also reported that the mixture of the two dyes produced a higher photocurrent than the single dyes[12)]. Kumar et al., 2016 extracted betacyanin from cactus and chlorophyll from Bermuda grass and reported the DSSC efficiencies with the respective single dyes were 0.674 % and 0.113%. Meanwhile, the efficiency increased to 1.1% due to improved charge transfer ability when the mixture of the two dyes was employed[13)]. Another study also exposed that mixing three dyes of betalain, chlorophyll, and curcumin reduced the bandgap energy of the TiO_2 photoanode to 2.66 eV and demonstrated an efficiency of 0.867%[14)]. Based on previous research, anthocyanins showed a strong light absorption at visible wavelengths (300-400 nm and 500-600 nm), while chlorophyll dye ranged from 400-500 nm and 600-700 nm, and betalain dye was about 530-550 nm[15)].

In particular, metal doping can enhance electron transport and result in a narrow bandgap energy that will ease the electrons to be excited. Prasada et al. have conducted a study on natural dyes doped with Fe metal and reported enhanced efficiency nine times compared to pure dyes[16)]. Meanwhile, another research reported that Cu metal doping in the dye sensitizer increased the efficiency from 0.0027% to 0.0055%, and the insertion of Ni metal improved the efficiency to 0.0769%, equal to 135% times the efficiency with a single dye [17)].

This study aimed to modify dyes as photosensitizers in DSSCs by mixing two and three natural dyes (anthocyanin, betalain, and chlorophyll). Further, the modification was also conducted by doping the mixture of three dyes with Ag metal. Doping natural dyes with Ag metal was preferred in this study because Ag has good corrosion resistance and high conductivity, which can enhance the performance of the DSSC. Additionally, it can inhibit the rutile phase of TiO_2, thereby increasing charge transfer and charge pair efficiency[18)]. Hence, this justification suggests that, to improve DSSC efficiency, dye mixtures consisting of two or three different dyes and Ag doping in the mixtures should be investigated.

2. Experimental Method

This study employed the combinations of anthocyanin (A), betalain (B), and chlorophyll (C) dyes extracted from natural sources as the photosensitizers in the DSSC sandwiches. Anthocyanin (A) was extracted from dragon fruit peels. The process was done by dissolving the dragon fruit peels in methanol, acetic acid, and distilled water in a ratio of 25:4:21 (v/v). It was left for 24 hours and then filtered to obtain anthocyanin extract. Betalain (B) was extracted from bougainvillea glabra flowers. The flowers were immersed in distilled water and acetone in a ratio of 2:1 (v/v). It was left for 24 hours and then filtered to get betalain extract. Meanwhile, chlorophyll was extracted from cassava leaves. The leaves were soaked in acetone and ethanol in a ratio of 1:5 (v/v). It was left for 24 hours and filtered to obtain chlorophyll extract. Dye modifications were done by mixing two and three dyes in 1:1 and 1:1:1 (v/v) ratios, respectively. The mixing of two dyes included anthocyanin and betalain (so-called AB), anthocyanin and chlorophyll (AC), and betalain and chlorophyll (BC). In comparison, the combination of three dyes was a mixture of anthocyanin, betalain, and chlorophyll (ABC). Further, the dye modification was also conducted by doping Ag metal in ABC dye (so-called ABC/Ag). It was finished by adding $AgNO_3$ solution to the ABC dye in a ratio of 1:10 (v/v) while stirred on a hotplate at 300 rpm and 40ºC for 4 hours.

$$\sigma = \frac{1}{R}\frac{l}{(A)} \quad (1)$$

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \quad (2)$$

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{I} \times 100\% \quad (3)$$

The photoanodes were made by depositing TiO_2 paste on FTO substrates with an active area of 0.5 x 0.5 cm using a spin coating method. They were then annealed in a furnace at 450ºC for 30 min. They were then immersed in the single and mixed dyes for 24 hours to absorb the dye molecules into the TiO_2. The counter electrodes used platinum paste coated on a glass substrate with the spin coating method and annealed at 450°C for 10 min. The electrolyte solution was a mixture of potassium iodide (KI) and polyethylene glycol (PEG) with a ratio of 0.8:10 (v/v) added with 1.2 grams of Iodine (I_2).

The optical properties of the single and mixed natural dyes were observed via a Hitachi UV-Vis Spectrophotometer. The I-V meter (Keithley 2602A) with a two-probe method was performed to analyze the conductivity properties of the dyes, calculated using Equation (1). Further, the instrument was also employed to investigate electrical parameters of the manufactured DSSCs, including fill factor (FF), current density (J_{sc}), short circuit current (I_{sc}), open-circuit voltage (V_{oc}), and efficiency (η), estimated using Equations 2 and 3.

3. Results and discussion

3.1 Optical properties of the single and mixed dyes

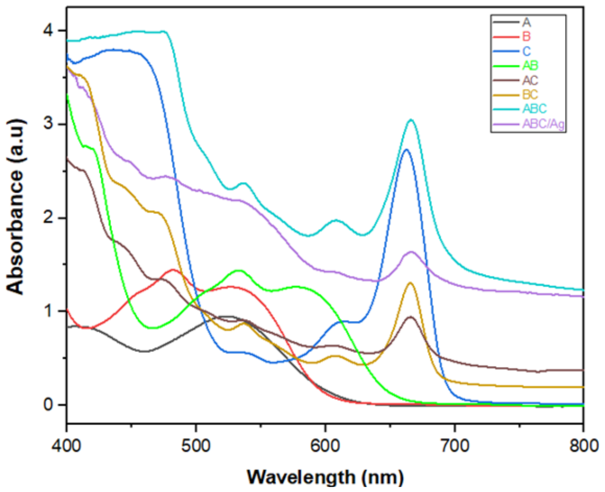

Fig. 1: UV-Vis spectra of the single and mixed natural dye solutions

Figure 1 shows the UV-Vis absorption spectra of anthocyanin, betalain, and chlorophyll, mixtures of two and three dyes (AB, AC, BC, and ABC), and Ag-doped ABC dye (ABC/Ag). It can be seen that the maximum absorption of anthocyanin dye (A) extracted from dragon fruit peel was in the wavelength range of 450-580 nm. This result differed from previous research, denoting that the absorption of the anthocyanin dye from the same source was in 450-650 nm[20]. This difference was due to the solvents used, whereas the previous research used methanol and distilled water. Further, the spectrum of the betalain dye (B) extracted from bougainvillea glabra exhibited two absorption peaks at around 481 and 540 nm. The peaks could be attributed to indicaxathin and the presence of betanin, respectively[21]. Additionally, the spectrum of the chlorophyll dye (C) from cassava leaves had absorption peaks at 413 and 663 nm, which is characteristic of chlorophyll. The prior research also reported that the absorption of chlorophyll dye ranged between 400-490 nm and 630-700 nm[22].

Based on Fig. 1, the mixed dye solutions show the absorption spectrum reflecting the optical transition probability between the ground and excited state[19]. The spectrum of the AB dye exhibits an absorption region of about 420-630 nm with two absorption peaks at 532.5 nm and 576.5 nm. Similarly, the spectrum of the AC dye revealed a broadened absorption region from 400 to 700 nm. This indicates that adding anthocyanins broadened the absorption spectrum in the 450 to 580 nm range, depending on the plant or solvent used[23]. The absorption peaks shown by the spectrum of the BC dye were 410, 481, and 520 nm. The redshift at the characteristic peaks of B and C in the BC dye spectrum revealed the higher absorption intensity due to the dominant behavior of betalain dye. The spectrum of the ABC dye demonstrated absorptions in the wavelength range of 410-700 nm. The absorption intensity of the ABC dye was the highest among all single and mixed dyes, with absorption peaks at 453, 536.5, 608.5, and 666 nm. Nevertheless, at the spectrum of the ABC/Ag dye, giving the $AgNO_3$ solution could lower the absorbance intensity in the 500–600 nm range [20]. The absorption peaks at the ABC/Ag dye were 408, 470.5, 536, and 666 nm, in the 400-700 nm absorption range.

3.2 Optical properties of the photoanodes immersed in the mixed dyes

Figure 2a presents the transmittance spectra of the pure TiO_2 photoanode and those immersed in the mixed dyes. It can be seen that the transmittance peak of the pure TiO_2 photoanode was 67.4%. After immersion in the ABC dye solution, the transmittance peak decreased to 61.97%. Then, immersing the photoanode with ABC/Ag reduced the transmittance peak significantly by 45.17%. It is considered because there is Ag diffusion when it binds to TiO_2, allowing light to pass through a higher wavelength, thereby reducing the transmittance[24].

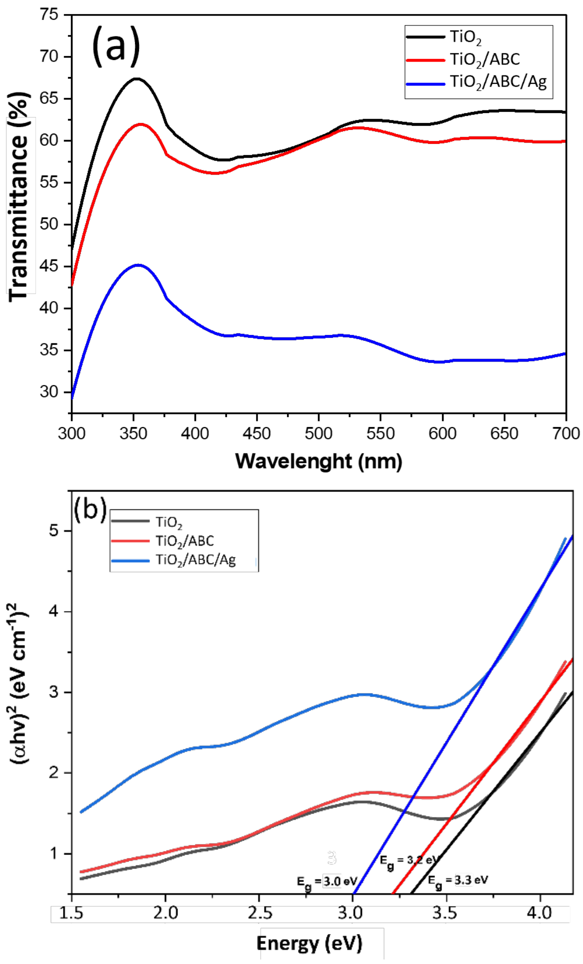

Fig. 2: (a) The transmittance spectra of pure TiO_2 photoanode and those immersed in ABC (TiO_2/ABC) and ABC/Ag (TiO_2/ABC/Ag) dyes (b) Tauc plot of indirect transition to determine bandgap energy

Furthermore, the Tauc plots shown in Fig. 2b demonstrate that the bandgap energy of the pure TiO_2 was 3.3 eV. After immersing with ABC and ABC/Ag dye solutions, the bandgap energy values were reduced by 3.2 eV and 3.0 eV, respectively. The dye has an amorphous structure, and Ag has good conductive properties, resulting in a reduced bandgap in TiO_2[25].

3.3 Conductivity properties

The conductivity values of the single and mixed dyes are listed in Table 1. The conductivity values of A, B, C, AB, AC, BC, ABC, and ABC/Ag dyes were 0.2128, 0.186, 0.0134, 0.2138, 0.1993, 0.2435, 0.2385, and 0.534 Ω^{-1} m^{-1}, respectively. It indicates that the dye solutions can conduct an electric current properly. Further, the values denote an increment after mixing two or three dyes. The higher conductivity represents the faster electron donor ability. A decrease in conductivity is influenced by the higher pH, indicating the abundance of ions in the solution[26].

Table 1. Conductivity values (σ) of the single and mixed dyes in this study

Dyes	σ dark ($\Omega^{-1}m^{-1}$)	σ bright ($\Omega^{-1}m^{-1}$)	Δ σ ($\Omega^{-1}m^{-1}$)
A	0.3711	0.5839	0.2128
B	0.4132	0.5992	0.186
C	0.0081	0.0215	0.0134
AB	0.4678	0.6816	0.2138
AC	0.5256	0.7249	0.1993
BC	0.4449	0.6884	0.2435
ABC	0.5421	0.7806	0.2385
ABC/Ag	0.5503	1.0843	0.534

Furthermore, Table 1 demonstrates that Ag metal doping in the ABC dye significantly enhanced conductivity. This is because the metal-doped dye mixture could produce an excellent electric current, causing it to be more conductive when absorbing light[27]. The concentration, chemical bond, types of dye, and ion mobility in the solution affect conductivity[6,28]. When the dye molecules are exposed to light, the photon energy will cause the electrons in the HOMO (Highest Occupied Molecular Orbital) to be excited to the LUMO (Lowest Occupied Molecular Orbital), increasing the conductivity value. The dye possesses the potency to be exploited as a DSSC photosensitizer since it responds to light exposure.

3.4 Current density-voltage (J-V) analysis and DSSC characterization

The J-V characteristics of the DSSC sandwiches manufactured in this study were tested with IV-Meter (Keithley 2602A) under a light source with a power of 1000 W/m^2. Figure 3 demonstrates the J-V curves of the manufactured DSSCs with the single and mixed natural dyes. Table 2 presents the current density, voltage, fill factor, and efficiency values of the manufactured DSSCs with different dyes.

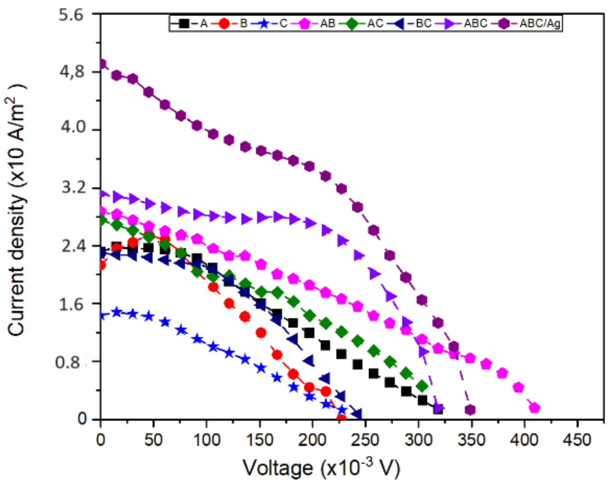

Fig. 3: J-V curves of the manufactured DSSCs with the single and mixed dyes

According to Fig. 3 and Table 2, the single dye A had the potential to provide better efficiency (0.263%) compared to dye B (0.24%) and dye C (0.125%). Dye anthocyanins (A) and betalain (B) interact with carbonyl and hydroxyl groups with the TiO_2 film, resulting in stronger electron coupling carriers in fast forward and reverse electron transfer reactions, resulting in higher photocurrents[29]. Meanwhile, the low efficiency of the DSSC with the single chlorophyll dye is considered due to the presence of -OH and -O ligands, causing poor bonding. Thus, it is insufficient to delocalize the excited electrons from the dye to the photoanode[30].

The efficiency values of the mixtures of the two dyes were 0.435%, 0.387%, and 0.299% for AB, AC, and BC, respectively. The values increased substantially compared to those with single dyes, and the highest was achieved by AB dye. This is thought to be caused by the binding of dyes A and B to TiO_2 as a result of extended conjugation. The performance of the anthocyanin-betalain (AB) dye mixture in the manufactured DSSC has increased J_{sc} value. The AB dye mixture effectively transfers energy synergistically to the TiO_2 semiconductor, improving the efficiency. Thus, mixing anthocyanin-betalain (AB) dye with a ratio of 1:1 was more effective because it had better light absorption, better light harvesting, and less interference between dyes, resulting in better efficiency.

Nevertheless, adding betalain to chlorophyll (BC) can also improve electron transport. Chlorophyll has a vital role in converting photons to electrons, and the presence of longer R groups in betalain dye pigments causes better binding to the TiO_2 surface. Overall, mixed dyes perform better due to the broad band of light energy absorbance that facilitates photoelectron injection due to energy levels between electrons in adjacent dye molecules.

Table 2. Electrical characteristics of the manufactured DSSCs with the single and mixed dyes

Dyes in DSSCs	V_{oc} (V)	J_{sc} $(x10\ Am^{-2})$	FF	$\eta(\%)$ x10-1
A	0.318	2.28	2.63	2.63
B	0.227	2.02	2.40	2.40
C	0.227	1.40	1.25	1.25
AB	0.409	2.70	4.35	4.35
AC	0.303	2.60	3.87	3.87
BC	0.242	2.29	2.99	2.99
ABC	0.318	3.12	6.02	6.02
ABC/Ag	0.348	4.89	7.42	7.42

The ABC dye gave a higher DSSC efficiency of 0.602% compared to the single and mixtures of two dyes. Fill factor (FF) is the proportion of maximum passable power to the sum of short circuit current and open circuit voltage. By photon absorption and the presence of various anchoring groups, dye is crucial in determining the DSSC efficiency. A mixture of three dyes has a broad absorption band of light energy with the existence of all individual binding groups. FF is determined by the degree of electron recombination between the dye molecules and the electrolyte. Low recombination will produce a minimum dark current and maximum photoelectron lifetime, resulting in a high FF value.

Mixing the three dyes increases the J_{sc}, representing the bond between the dye molecules and TiO_2 particles, while a higher V_{oc} is associated with the proper conduction band. The combination of three different dyes (ABC) showed enhanced dye interactions due to increased binding sites and the elongation of the conjugate length. Therefore, the mixed dye experiences improved electron injection and charge transfer to the TiO_2 conduction band.

The conversion of solar energy into electrical energy occurs through a series of processes, starting with the excitation of electrons from the dye in the valence band, which is then injected into the semiconductor's conduction band. To excite electrons from the valence band to the conduction band, a certain amount of energy is needed. The minimum energy required for the transition of an electron from the valence band to the conduction band is called the energy of the bandgap. The dye can reduce the bandgap energy of the semiconductor layer because the chromophore causes electrons to move from the outer orbitals to higher orbitals by absorbing energy in the void area. The chromophore contains π bonds, which can move and conduct electricity because they resonate, causing the movement of electrons[31)].

It can be observed in Table 2 that the addition of Ag metal into ABC dye induced the DSSC to have the highest efficiency value of 0.742%. From the data presented, the current density increased with the addition of Ag ions, causing the dye to be more conductive. The more conductive nature of dyes can improve their ability to conduct electric current to reduce the bandgap energy[18)]. This reduction will optimize the absorption of sunlight because electrons can migrate from HOMO to LUMO by taking an optimal path to produce optimal efficiency. The higher efficiency leads to the higher DSSC performance in converting light into electrical energy.

4. Conclusion

In this study, anthocyanin (A), betalain (B), and chlorophyll (C) dyes extracted from dragon fruit peel, bougainvillea glabra flower, and cassava leaves had light absorption in three different wavelength regions. The mixtures of two dyes could widen the absorption in the 400-700 nm wavelength range. Meanwhile, mixing the three dyes (ABC) could increase the absorption intensity and widen the absorption area. Further, Ag doping in the ABC dye mixture reduced the absorbance intensity, which could be possible because of the conductive nature of Ag. The transmittance value of the TiO_2 photoanode immersed in ABC/Ag was 45.17%, whereas the pure TiO_2 layer had the highest transmittance value. The Tauc plot method revealed a decreased bandgap energy in the TiO_2/ABC/Ag photoanode by 3.0 eV. The Ag doping in the ABC dye caused it to have the highest conductivity value, making it potentially applicable in the DSSC. The mixture of three dyes (ABC) had a reasonably good DSSC performance compared to mixtures of two dyes and single dyes, with a DSSC efficiency of 0.602%. Then, doping Ag metal could significantly improve the efficiency by 0.742 %.

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Nomenclature

σ	Conductivity ($ohm^{-1}\ m^{-1}$)
R	Resistance (ohm)
l	Distance between two electrodes (m)
A	Area (m^2)

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