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The Effect of Alum as Additive in Mix Dye for Dye Sensitized Solar Cell (DSSC)

Mohd Shahrul Ashraf Bustam, Mohamad Hafiz Mamat and Mohd Hanapiah Abdullah*

***Abstract*— Dye-sensitized solar cell (DSSC) is the third-generation solar cell that first co-invented by Michael Gratzel and Brian O'Regan. In this study, TiO_2 photoelectrode are sensitized with natural blackberry dye and spinach is used as co-sensitizer (mix dye). The aluminium sulphate, $Al_2(SO_4)_3$ (alum) is used as the additives to treat the dye. FESEM and EDXs techniques are used to characterise the photoelectrodes, while UV-Vis and FTIR were used to examine the dye characteristics. Finally, I-V characteristic measurements were used to evaluate the performance of DSSCs. Based on the result, since of the inclusion of chlorophyll (spinach) in sensitizer, blackberry/spinach/alum performs somewhat worse than blackberry/alum because the findings on Uv Vis spectra indicates that peak of anthocyanin (blackberry) has decreased with the addition of chlorophyll (spinach). The highest efficiency (0.782%) is attained for devices that use a Blackberry/Alum sensitizer, based on device electrical parameters.**

Keywords*— *Co-sensitizer, Additive, Alum, DSSC, Blackberry

I. Introduction

NON renewable energy sources, such as coal, are difficult to replace in a timely manner. As a result, renewable energy sources like solar cells are one of the finest alternatives to non-renewable energy. Michael Gratzel and Brian O'Regan were the first to discover the dye sensitised solar cell (DSSC), which is a third-generation solar cell [1]. Due to their relatively high conversion efficiency [2] and simple production techniques [3], DSSC have proven to be a promising low-cost and sustainable alternative energy source. The critical components that can affect device performance are TiO_2 and dye. To achieve sufficient and efficient contact between the dye molecules and the TiO_2 electrode, the TiO_2 photoelectrode is routinely immersed in a dye bath solution for many hours (typically 8–24 h) at room temperature [4]–[9]. Natural dye is readily available and occurs naturally, making it simple to locate and extract from leaves, woods, fruits, or flowers [5]. Furthermore, in comparison to other complex dyes, the technique for extracting the natural dye is easy [10], [11] allowing the DSSC device to be easily sensitised with natural plant material.

Co-sensitization (mix dye) and additives are the methods that frequently used by DSSC researchers in order to increase performance and improved efficiency. Due to the additive that adds extra -O-H to the sensitizer, the dye's ability to anchor onto the TiO_2 surface improves [12], [13]. After mixing nickel with dye, D.D. Pratiwi et al [14] discovered that the efficiency of the dye was increased by 135% when compared to pure dye. As the concentration of Ni was increased, the conductivity increased as well. Furthermore, due to a lower rate of electron and hole recombination, mixed-dye DSSCs outperform conventional solar cells sensitised with single dyes [15]. Based on Lung Nhat Dang Quang et al [16], 8% of efficiency was obtained in DSSC with dye co-sensitization (mixing) than its single dye (6.9% for N719 and 6.5% for D35). Based on these studies, its proven that additives and mix dye help improve performance and increase device efficiency.

Alum is most commonly used and reported in the wastewater environment as a coagulant-flocculant additive that neutralises charge and clumps particles into larger flocs so that they may be removed from the water more easily [17]–[20]. Vito L. Punzi et al. [21] used alum to solve the water purification problem and reported that alum is effective in reducing the use of chemicals for water purification. Radha Kashyap et al. [22] and Rattanaphol Mongkholrattansit et al. [23] used alum as a mordant in their study and reported that alum improved the absorption of dyes into fabrics. In another study, Davood Jalil Naghan et al. [24] reported the use of alum to remove dyes from fabrics. It has been found that alum can remove up to 68% of the colorant from the crude solution under optimal conditions that increase the purity of the colorant solution. Also, Arash Dalvant et al. [25] reported that alum was effective in removing red dye from fabrics under optimal conditions, reaching 98.2% of the maximum efficiency. Finally, the effect of alum in dye removal is supported by M.Z.B Mukhlish et al. [26] and Nilgun Balkaya et al. [27], who used alum to remove synthetic reactive dyes. It can therefore be concluded that alum not only helps neutralize the charge, but also improves the dye purification process (by removing the dye), thereby improving the adsorption of the dye. These properties have proven useful in terms of natural dye sensitizers for DSSCs. The more dye adsorbed to the TiO_2 surface, the higher the efficiency of the DSSC device [28]–[33].

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Despite the fact that Alum has been shown to improve dye adsorption in the water treatment process, however, there has been no research on Alum as a dye additive, particularly for mix dye in DSSCs. Therefore, the aim of this research is to investigate the effect of Alum in mix dye for DSSCs. Blackberry are used as the main dye, while spinach is used as the co-sensitizer, that mix with blackberry. The samples are treated with alum as additive in order to improve the performance. The structure and optical properties of isolated dyes was confirmed using FTIR and UV-Vis spectroscopy (UV-Vis). Meanwhile, the morphology and TiO_2 composition of dyes were identified using SEM and EDX, respectively. Finally, the performance of the fabricated DSSCs were investigated for photocurrent conversion efficiency, I-V.

II. METHODOLOGY

A. Material used

Biotain Crystal provided the ITO conductive glasses (resistivity 7 ohm/sq., transparency 78.8 percent). Sigma Aldrich provided the TiO_2 (nano-powder), whereas OEM Brand Manufacturing provided the aluminium sulphate powder (alum) used in this study. Frozen blackberry (R. fruticosis) from Tesco Store (Malaysia) was utilised as a natural dye. All of the other chemicals were laboratory analytical quality and utilized without being purified.

B. Preparation of ITO

The ITO conductive side were identified using multi-meter. Next, the glass substrates were then washed with detergent, rinsed with deionized water and isopropanol, and dried with a hot air blower.

C. Preparation of TiO_2 paste

2 grams of TiO_2 powder were mixed with 1 mL acetic acid, 1 mL detergent, and 5 mL deionized water to make TiO_2 nanoparticle paste, which was then stirred constantly with a magnetic stirrer until ingrained. For future usage, the combination was placed in a small portable bottle.

D. Preparation of Dye sensitizer

30g of blackberry were crushed into a well-mixed solution using a mortar, and the solid residues were filtered into containers using filter paper (NICE,12.5 cm, 102 Qualitative) for untreated dye preparation. The dye was then mixed with 5 mL of methanol, which was then utilized as the research's solvent. For the untreated dye was used as prepared without any purification made. Meanwhile, for the treated dye, 0.5g of aluminium sulphate, $Al_2(SO_4)_3$, were added into another separate containers and the mixture were stirred for 2 minutes using glass rod. After that, spinach was used as co-sensitizer in this study. 30 grams of spinach were blended and mixed with 5 mL methanol then filtered for dye extraction. The treated and untreated blackberry dye were mix with the extracted spinach dye. All the samples were stored in 4 different containers.

E. Preparation of electrolyte

0.05 M Iodine (I2), 0.5 M Tetrabutylammonium Iodide (TBAI), and 10 mL acetonitrile were used to make the electrolyte. The prepared electrolyte was filled into small bottle and stir using magnetic stirrer.

F. Preparation of counter electrode

The 8B pencil lead (Faber Castell) was used to make the graphite-coated counter electrode. The graphite was evenly distributed on the conductive side of the ITO surface by rubbing it with the pencil lead. There was no heat treatment applied to the counter electrode.

G. Fabrication of DSSCs

First, by using the doctor blade procedure, cleaned ITO conductive glass surfaces were coated with prepared TiO_2 paste. Second, the ITO/TiO_2 was annealed in a tube furnace (Nabertherm Universal Tube Furnace, B180) at 450°C for 30 minutes before cooling to ambient temperature. The estimated TiO_2 thickness on the photoelectrode was $15um$. Third, the sintered sample were immersed into the treated, untreated and co-sensitized prepared dye containers. After 24 hours of immersion time, the immersed samples were rinsed with methanol to remove the excess dye molecule before being dried at room temperature. The electrolyte was then applied to the sensitizers' surface. Finally, samples were clamped securely against the conducting surface of counter electrodes to create a sandwich-type structure for photovoltaic measurement.

H. Characterization

The surface shape and elemental content of TiO_2 nanoparticles were investigated using a Field Emission Scanning Electron Microscope (FESEM - NOVA NANOSEM 450) and Energy Dispersive X-Ray spectroscopy (EDX). Here, the crystal structure TiO_2 electrodes were analysed by X-ray diffraction (XRD) with Cu-Kα radiation (Rigaku-X'pert PRO, ($\lambda = 1.5405A^{\circ}$)). The functional groups of treated and untreated dyes were then detected using FTIR (Thermo Scientific Nicolet 6700; software: OMNIC 8) and dye adsorption spectra were analyzed using UV-Vis (UV Vis Spectrophotometer, Lambda 25, Perkin Elmer). In order to analyse the photo conversion efficiency of DSSCs, photovoltaic I-V measurements of DSSCs were conducted using Keithley 4200 SCS under LED light source.

III. RESULT AND DISCUSSION

A. FESEM and EDX

Fig. 1 shows the TiO_2 surface morphology that examined using Field Emission Scanning Electron Microscopy (FESEM). Based on the image, the morphological of TiO_2 appears to have a sponge-like structure. Furthermore, there were small gaps between the particle structure, that enable more dye to be trapped and easily absorbed by the TiO_2 layers during the dye soaking procedure. The device's conversion efficiency improves as the amount of dye adsorbed on the TiO layer increases [28]–[33]. This small spaces occur due to the TiO_2 nanoparticles sparse arrangement. According to Gaiven Varshney et al. [34], coating TiO_2 paste with a doctor blade is highly recommended and can be done at speeds of several metres per minute. Fig. 2 depicts a particle investigation utilising energy dispersive X-ray spectroscopy (EDX). In the EDX analysis, the presence of titanium (Ti) and oxygen (O) peaks indicates the presence of TiO_2 nanoparticles.

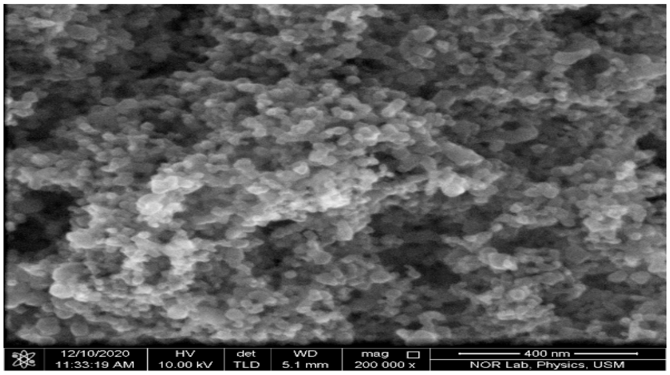

Fig. 1. TiO_2 surface morphology

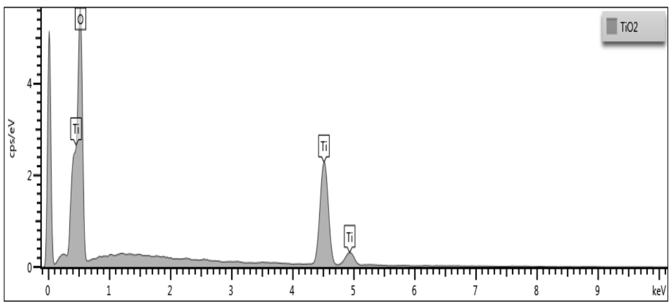

Fig. 2. Energy dispersive X-ray spectrometry (EDX) of TiO_2 nanoparticle.

The components found in TiO_2 photoelectrodes are listed in Table I. O has an atomic percentage of 68.28 percent, while Ti has an atomic percentage of 31.722 percent, according to the table. The weight (wt percent) of O and Ti, respectively, is 41.83 and 58.17. This suggests that no other elements in the photoelectrode could be detected, leaving only TiO_2.

TABLE I
UNITS FOR MAGNETIC PROPERTIES

Element	Atomic%	Weight%	Weight% Sigma
Oxygen, O	68.28	41.83	0.8
Titanium, Ti	31.72	58.17	0.8
Total	100	100	

B. FTIR and pH Measurement

The FTIR spectra of alum-treated and untreated sensitizer dye are shown in Fig. 3 These pattern were visible because of the infrared radiation emitted by the dye's functional groups [35]. The O-H stretching band of the alcohol/phenol hydroxyl group is indicated by the dye transmittance peak at 3301 cm^{-1}. The C=O stretching group of the carboxyl compound can be observed at a peak of 1637 cm^{-1}, whereas the ester group of the C-O-C stretching band can be seen at a peak of 1014 cm^{-1}. Most investigations on extracted anthocyanin dyes indicated that the hydroxyl (O-H) group, carboxyl (C=O) group, and C-O-C ester were reflecting the primary peak of anthocyanin functional group, and this pattern was identical [4], [35], [36]. Furthermore, the presence of a carbonyl group (C=O) and a hydroxyl group (O-H) in anthocyanin can boost the dye-sensitized solar cell's conversion efficiency [36]. Because of the dye molecules that contain both hydroxyl and carboxyl functional groups, the dye can be absorbed on the TiO_2 surface. So, it can be seen that the alum does not affecting the samples functional group, however, it manages to regulate the pH level of the dye solution.

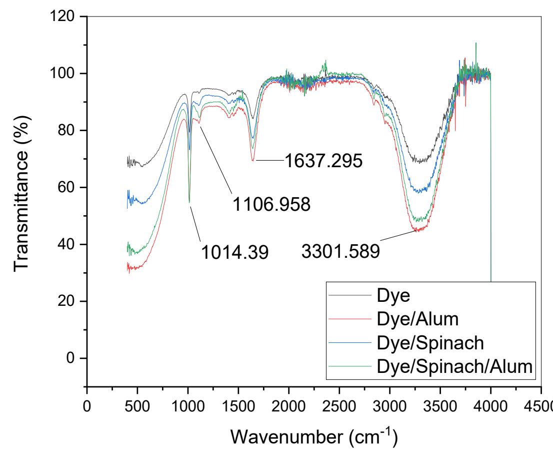

Fig. 3. FTIR spectra for the alum-treated and untreated sensitizer

Fig. 4 shows the chemical structure of anthocyanin dye at two distinct acidity levels, with the pH of each dye solution determined with an E-Digital Model 8424. Based on the pH meter, Dye/Spinach/Alum is more acidic (pH 1.7) compared to Dye/Spinach (pH 4), meanwhile Dye/Alum and Dye have pH value of 1.5 and 4.2 respectively. This situation is directly linked to the existence of excess hydrogen ions resulting from the breakdown of alum in water, as shown by the chemical reaction in (1) and (2).

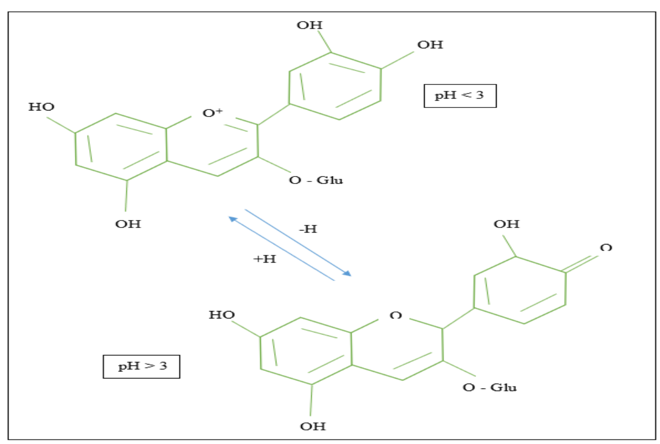

Fig. 4. Structure of anthocyanin in acidic form

When the alum is combined with the dye, the free positive hydrogen ion is produced, according to Jack Lin et al. [37]. Reactions (1) - (2) below are examples of this condition.

$$Al_2(SO_4)_3 + H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} \quad (1)$$

$$2Al^{3+} + 3H_2O \rightarrow Al(OH) + 3H^{+} \quad (2)$$

Based on earlier FTIR observations, the hydroxyl group (OH) and carboxyl group (C=O) allow the dyes to immobilise in the surface of TiO_2. As a result, the co-sensitization device that has been treated will outperform the dye device that has not been treated. Although alum does not modify the functional group, it can raise the OH of the sample, allowing more dye to bind to the TiO_2 surface.

C. UV-Visible

Fig. 5 (pictures (a), (b), (c) and (d)) shows the dye solution comparison images for untreated and Alum-treated samples. Figure (a) (starting from left) shows the sensitizer solution for Dye, Dye/alum, Dye/spinach, and Dye/Spinach/Alum before being filtered using filter paper, while figure (b) shows the sensitizer sample after being filtered. Based on figure (b), the Dye/alum appears to have a darker (dark purple) colour compared to Dye. The dark colour can also be noticed on Dye/spinach and Dye/spinach/alum. To demonstrate this point, figure (c) displays the colour change after each dye solution was diluted in 10 ml methanol. The colour of Dye was pink at first, but with additional of alum (Dye/alum), it turned into a reddish colour. Besides, the figure also shows the colour changes on Dye/spinach (pink) and Dye/spinach/alum (lighter pink) after dilution. Next, image (d) shows the dried remnant (floc/flake) that appear from flocculation-coagulation process that occur after alum is added in the Dye. In colloidal chemistry, flocculation occurs when tiny particles cluster together to create a floc that can either float to the top of the liquid, resulting in dry flake, or settle to the bottom, resulting in sediment. This flake could be caused by impurities in the crude blackberry natural dye, such as soluble sugars, lipids, proteins, and other polyphenolic substances [38], [39].

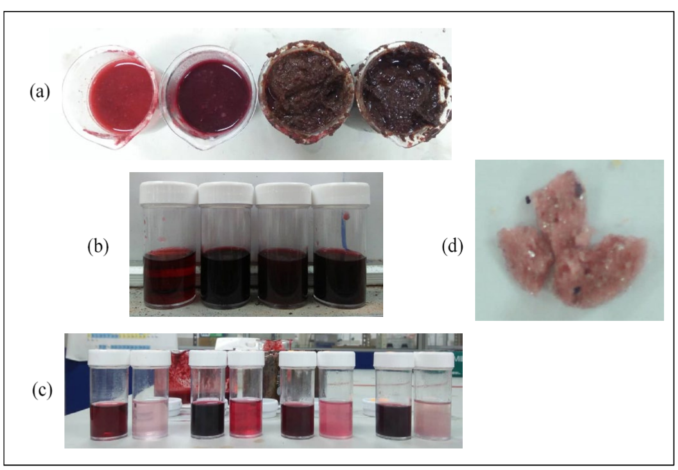

Fig. 5. Alum-treated and untreated sensitizer

Fig. 6 shows the Uv Vis spectra for alum-treated and untreated sensitizer in the visible wavelength spectrum. The spectra demonstrate that the Dye/Alum has a larger overall absorption spectrum than Dye, notably because the absorbance peak running from 400 nm to 600 nm has a significant quench. The peak between 400nm and 600nm has shrunk after mixing spinach with blackberries, and new peaks have emerged, especially at wavelengths 300-400 and 650-700. This shows that the pigment chlorophyll derived from Spinach is present. The addition of alum to Blackberry/Spinach results in a considerable increase in peak adsorbance at wavelengths between 300 and 400 nm. As a result of these findings, it can be stated that as compared to Blackberry alone, Blackberry/Spinach possesses both anthocyanin and chlorophyll adsorbance peaks, and the presence of both peaks has been found to help improve device performance, according to some studies [40]–[44]. The dye solution's pH dependence, which is highly related to the measured pH value, can be explained to the strong quench in the UV-Vis spectra. This is in line with the findings of Favaro et al [35] and C.L Luchese et al [45]. The positive charge is neutralised by the hydrated inner ring, and the anthocyanin loses its pigment at higher pH values [35], all visible light wavelengths are passed equally to the eye, and the dye is colourless. Therefore, it can be seen that alum changes the dye acidity. The dye with a lower pH value (acidic) has a larger peak absorption than the dye with a higher pH value (alkaline) [45]. Because of their structure, dye molecules are protonated at increased acidity; in other words, the dye's pH value lowers when there are free positive hydrogen ions [46].

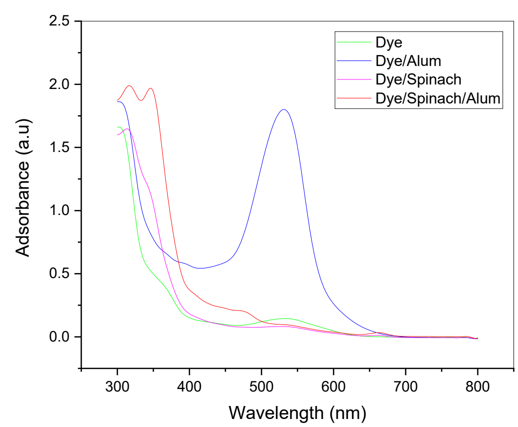

Fig. 6. Uv-Vis Spectra of the alum-treated and untreated sensitizer

After alum is added into the diluted sensitizer, the colour changes on blackberry/spinach is slightly different compared to blackberry alone. The presence of chlorophyll in blackberry/Spinach accounts for the differential. Spinach is one of the sensitizers with chlorophyll pigment, according to natural dye researchers [47]–[49]. After adding alum to blackberry/Spinach, the senitizer's colour diminishes. This is attributed to the chlorophyll dye dominating the sensitizer, as indicated by the uv-vis data, where the peak anthocyanin (blackberry) has dropped after chlorophyll was added (spinach). Based on study conducted by Anting Wulandari et al. [46], if the acidity of the sensitizer increases, the colour of the chlorophyll will remain on the original pigment. According to the study, increasing acidity raises the absorbance peak. This corresponded to the findings of the UV-Vis results.

The quantity dosage, which is applied by DSSC researchers [50]–[53] to maximize efficiency on natural DSSC devices, is another aspect that influences Dye absorption. According to a study conducted by researchers [54], [55], the dosage amount affects the dye concentration, and overdosing causes the device's performance to degrade. Since alum is applied as an additive in this research, the amount of alum used is expected to alter the device efficiency. This is supported by vikash kumar et al. [13] that study the effect on additive in dye. Apart from enhancing the natural performance of DSSC, the concept of alum as an additive can also be applied to the dyeing sector, particularly for those that use anthocyanin as the primary dye. The coloration of the dye can be changed simply by adding alum, depending on personal preference. Last but not the least, Alum also aids particle adsorption in water treatment according to various research [56], [57]. Therefore, the uses of alum as an additive can boost dye absorption in DSSC, hence improving the device's performance [28]–[33].

D. Photovoltaic Characterization

Fig. 7 shows the electrical characteristics of the DSSCs for Dye, Dye/Spinach, Dye/Alum and Dye/Spinach/Alum. It is clear from the graph that alum-treated sensitizer cells outperform untreated dye cells, and their photovoltaic properties are reported in Table II. Mixing the Dye with Spinach and/or alum had proven to increase the efficiency of the device. This can conclude that mixing Dye can improve the performance [40]–[42], [58]. Studies have shown a significant increase in efficiency after mixing the dye. In addition, the efficiency of the mixed dye can be further increased by adding alum to the sensitizer. In terms of efficiency, dye/spinach/alum showed higher efficiency compared to dye/spinach, 0.723% and 0.672%, respectively. In water purification [56], [57] alum is used as an additive to increase the adsorption capacity. Furthermore, dye treatment researchers agree that alum has a good ability to increase adsorption on dye removal [25], [27]. That's why, with the addition of alum, DSSC efficiency can improve. Alum was used as an additive in this study to boost the dye absorption on the TiO_2 surface, and the more the dye is absorbed, the better the device's performance [28]–[33]. Based on Table II, the highest efficiency is achieved for devices using Blackberry/Alum(0.782%). Blackberry/spinach/alum (0.723%) is the second, followed by blackberry/spinach (0.672%) and blackberry (0.594%). Due to the presence of chlorophyll in the sensitizer, blackberry/spinach/alum performs slightly lower than blackberry/alum. Chlorophyll has dominated the sensitizer, as explained in prior Uv-Vis results, forcing existing anthocyanin to compete with chlorophyll. The competition between anthocyanins and chlorophyll causes reduced performance. This is supported by [59], stating that competition between sensitizers and additives might limit the quantity of dye placed on the TiO_2 surface, lowering performance. When compared to devices that used chlorophyll as a sensitizer, devices that use anthocyanin shows better performance [60].

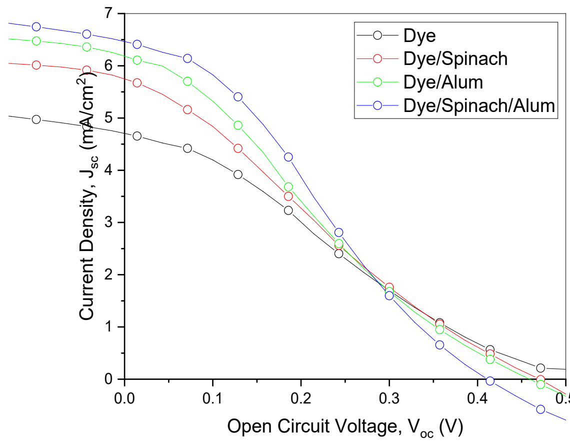

Fig. 7. Electrical characteristics of the DSSCs

The device's efficiency can be considerably boosted if the two sensitizers are paired with the correct dose. But since alum is used as an additive in this study, it is highly recommended to continue this study by studying the effect of alum dosage in mixed sensitizers. This is because based on Surajit Ghosh et al [61], two critical criteria impacting DSSC performance are dye concentration and dye loading time. Overdosing the dosage of alum in the dye can increase the concentration and reduce the effectiveness of absorption of dye into the surface of TiO_2, thus decrease the device efficiency [5].

TABLE II
PHOTOVOLTAIC PROPERTIES OF THE DSSCS

	Jsc (mA/cm^2)	Voc (mV)	FF (%)	Efficiency (%)
Blackberry	4.77	471.47	26.41	0.594
Blackberry/Alum	5.47	472.42	24.74	0.672
Blackbery/Spinach	6.44	471.41	25.47	0.782
Blackberry/Spinach/ Alum	6.60	414.26	26.43	0.723

IV. CONCLUSION

In this study, dye-sensitized based on mixed dye was successfully fabricated using TiO_2 photoelectrode. Blackberry are used as main dye, spinach is used as co-sensitizer and the treated dye was prepared by adding alum as the dye additive to enhanced the overall performance. FESEM was used to examine the surface morphological pictures of TiO2, which revealed that the nano-porous TiO2 structure covered the whole surface of the TiO2 photoelectrode. The porous structure of the photoelectrode was beneficial because it facilitates dye adsorption to the TiO2 layers. The functional group of in all samples was identical, the addition of Alum has no effect on their functional group. So far, it's been determined that the existence of O-H and C=O bonding in the treated dye assists in improving device performance. Meanwhile, based on the UV-Vis spectra, it can be deduced that the greater absorbance spectra were attributed to the dye's pH dependence. Therefore, the interaction between the dyes and the alum can affect the absorption on the surface of TiO_2. However, due to the presence of chlorophyll in the sensitizer, blackberry/spinach/alum performs slightly lower than blackberry/alum because the Uv-vis adsorption peak of anthocyanin (blackberry) has dropped after chlorophyll was added (spinach). Based on device electrical properties, the highest efficiency is achieved for devices using Blackberry/Alum sensitizer (0.782%).

V. ACKNOWLEDGMENT

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