The Effect of Chenodeoxycholic Acid (CDCA) in Mangosteen
(Garcinia mangostana) Pericarps Sensitizer for Dye-
Sensitized Solar Cell (DSSC)

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Abstract. Dye-sensitized solar cell (DSSC) is a third generation of solar cell, which has been pursued by numerous researcher to increase its efficiency, stability, and compatibility with our surrounding. One of advancement is a usage of a natural product or organic material to replace an artificial sensitizer such as ruthenium sensitizer, which is expensive, difficult to synthesize and has its own noxiousness. A natural product such as mangosteen (Garcinia mangostana) pericarps is easily obtained from eaten mangosteen fruits. Mangosteen fruits are mainly grown in Southeast Asia such as Malaysia and certain tropical areas around the globe. Mangosteen pericarps gave a promising performance in natural dye research however unable to compete with artificial due to low anchor groups such as carboxyl and hydroxyl. In this study, chenodeoxycholic acid (CDCA) was used to help increase the device performance. The concentration of CDCA in the sensitizer used in this study are 0.10 mM, 0.50 mM, 0.75 mM, 1.00 mM, 1.50 mM and 2.00 mM. There are several characteristics are studied such as UV-VIS spectrometer, cyclic voltammetry (CV), Fourier-transform infrared spectroscopy (FTIR) and current-voltage measurement (I-V). Mangosteen pericarps sensitizer itself applied on DSSC have efficiency of 0.36% with short-circuit current density ($J_{sc}$) = 1.00 mA/cm², open circuit voltage ($V_{oc}$) = 0.64 V and fill factor (FF) = 56.75%. The highest performance of DSSC with mangosteen sensitizer and CDCA are at 0.56% with short-circuit current density ($J_{sc}$) = 1.40 mA/cm², open circuit voltage ($V_{oc}$) = 0.65 V and fill factor (FF) = 62.03%. The increment of device performance shows that CDCA helps to increase mangosteen sensitizer performances by adding additional -O-H into the sensitizer which increases the ability to anchor onto the TiO$_2$ surface.

1. Introduction

From 1991, DSSC device has become an interest by numerous researchers when Gratzel and O'Regan were able to create an alternative device of silicon solar cells with an efficiency of 12% in a diffuse light [1]. A standard DSSC consist of photoanode, counter electrode, dye sensitizer, and electrolyte which each of them played a very critical role related to each other. As for this study, the sensitizer will be main focus, which it helps to harvest photons and producing photo-excited electron at the surface of photoanode [2]. A fully efficient sensitizer are needed to have several properties such as intense
absorption within visible light range (400–700 nm), absorbed or anchored robustly onto surface of photoanode thin film, high extinction coefficient, a stable oxidation form for regeneration phase, capable to have ~108 turnovers correspond to 20 years of cell operation and possess more negative lowest unoccupied molecular orbital (LUMO) level than conduction band (CB) of the semiconductor and also more positive highest occupied molecular orbital (HOMO) level than the redox potential of the electrolyte [3]. Throughout years there are several different types of photosensitizer was created and studied such as ruthenium (II) dye, porphyrin dye, coumarin and natural products sensitizer [4]. Natural photosensitizer was obtained from natural products such as fruits, leaves, seeds, and trees [5]. Natural sensitizer was selected based on its anthocyanin, chlorophyll, and carotenoids, which helps to give the colour to the products and consists carboxyl and hydroxyl groups [6]. Those groups help the sensitizer molecule to anchor on to the surface of a semiconductor. There are different types of natural products were studied to be able replacing the artificial sensitizer because of its rarity elements, poisonous, and expensive processes such as perilla and crocetin [7]. The natural photosensitizer is easy to be developed using cold extractions and the products easily found in our surrounding without damaging our planets. Mangosteen (Garcinia mangostana) fruit is easily found in a tropical place or Southeast Asia such as Malaysia and Indonesia. Mangosteen fruit itself has a structure which consists of aril and pericarps. Mangosteen pericarps were used in this study due to its infamous high performances due to the colour of purple provided by anthocyanin group. However, it has a staggering development such low efficiency of 1.17% at the active area of 0.2 cm² compare to artificial sensitizer due to lacking the amount the anchoring groups, dye aggregation and limited absorption light range [8]. There are several advancements were studied such as purifications, combining different types of dyes and adding a catalyst to boost performances [6]. CDCA was used as a catalyst to increase the amount of carboxyl and hydroxyl groups within mangosteen photosensitizer in order to improve the co-absorbance properties and chemical structure. In this study, it is also expected that the catalyst will reduce dark current, enhancing $V_{oc}$ and weakened dye aggregation.

2. Experimental

2.1. Materials

In this study, we obtained mangosteen dye extract from a dried pericarp of consumed mangosteen immersed in methanol 99.8% (JT. Baker) solvent. The extract was separated into six different dark glass bottles and added chenodeoxycholic acid (CDCA) powder (Solaronix) with concentrations of 0.10 mM, 0.50 mM, 0.75 mM, 1.00 mM, 1.50 mM and 2.00 mM respectively. DSSC fabrication consists of fluorine doped tin oxide (FTO) glass, titanium oxide (TiO₂) paste (Dyesol), platinum paste (Dyesol), iodine electrolyte (Solaronix).

2.2. Preparation of mangosteen dye sensitizer

Mangosteen pericarps are obtained from a consumed mangosteen fruits and cleaned thoroughly using tap water which to make sure no residue of mangosteen fruits. The pericarps were dried under sunlight for two to four days after cleaning process. The drying process was performed to make sure the pericarps does not contain any water or moist. The dried pericarps were turned into powder using pester and mortar, grinder, and blender. The processed pericarps powder was soaked in methanol solvent with a ratio of 1:10. This process was called as cold extraction. The first extraction of dye from the powder was taken durations of 24 hours [9]. After the extraction was filtered and separated from pericarps residue, the extractions were repeated two times in durations of three days. The repeating process of the extraction was conducted to make all the dye was fully extracted from the powder. The filtered extracted solutions were needed to have suitable dye colour, which is concentrated using rotary evaporator and able to be applied as a sensitizer for DSSC.

2.3. Fabrication of DSSC

A standard DSSC structure was used as a device to study the sensitizer with CDCA performance as catalyst. It consists of substrate glasses, photoanode, counter electrode, sensitizer, and electrolyte. In
In this study, one-sided FTO glasses was used as a substrate for both photoanode and counter electrode. The photoanode was using FTO glass with a resistivity of 15 Ω/square and counter electrode using FTO glass with a resistivity of 8 Ω/square. All FTO glasses in this study was cut into dimension of 3 cm x 2 cm using a diamond cutter and cleaned using ultrasonic bath using solvents of dilute acetone, dilute ethanol and DI water in sequence. The cleaning process was done in a duration of 10 minutes for each solvent then the substrates were dried using air dryer or nitrogen gas. For photoanode, initially, an area of 1 cm x 1 cm was created using a scotch tape and the first layer of TiO$_2$ (absorption layer) was deposited using a doctor-blade technique. The first layer of photoanode was annealed for 30 minutes at 450°C. Then by using the same technique and annealing process, on top of the annealed absorption layer, the second layer of TiO$_2$ (scattering layer) was deposited. A finished product of annealed photoanode was treated inside TiCl$_4$ solution for 10 minutes at 70°C then rinsed thoroughly with water. The photoanode was heated inside the furnace at 100°C then immediately immersed inside the mangosteen sensitizer dyes with CDCA for 24 hours. A different amount of CDCA powder was dissolve inside the dyes with each concentration of 0.10 mM, 0.50 mM, 0.75 mM, 1.00 mM, 1.50 mM and 2.00 mM. As for counter electrode, the substrate was deposited with platinum paste using doctor-blade technique and annealed at 450°C for 30 minutes. The annealed counter electrode and the dye-immersed photoanode was sandwiched together with adhesion (Surlyn) using heat press machine. Finally, iodine electrolyte was inserted inside the sandwiched device then sealed using a polymer glue.

2.4. Characteristics and device performances
The characteristics of mangosteen dye sensitizer with CDCA was studied using fourier transform infrared spectroscopy (FTIR), UV-Vis spectrometer, photoluminescence (PL) and cyclic voltammetry. FTIR spectra measured with Perkin Elmer Spectrum 400 FT-IR/FT-NIR & Spotlight 400 imaging systems on wavenumber 4000 to 650 cm$^{-1}$ [10]. Perkin Elmer UV-Vis spectrometer Lambda 35 was used to study the absorption strength at a certain wavelength range of 350 to 600 nm. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels can be studied and calculated from data collected in photoluminescence and cyclic voltammetry (CV). Equation (1) was used to calculate HOMO, LUMO and an energy gap ($E_g$), where $h$ is Planck's constant $(6.62607004 \times 10^{-34}$ m$^2$ kg s$^{-1}$), $c$ is the speed of light $(3.00 \times 10^8$ ms$^{-1}$) and the wavelength, $\lambda$ is the highest peak in PL. FLS920 Edinburgh Instrument was used to measured PL with excitation value of 400 nm [11]. From CV, the redox characteristic of the sensitizer with CDCA can be observed and investigated by using METROTHM AUTOLAB and NOVA software. An electrochemical cell was constructed for CV measurement consists glossy carbon as the working electrode (WE), Ag/AgCl immersed in 3 M NaCl as reference electrode (RE), platinum as the counter electrode (CE) and dye sensitizer consist of 0.1 M lithium perchlorate, 99+% from ACROS ORGANICS acted as an electrolyte. An empirical equation Bredas et al [2] was used to calculate the HOMO energy level, which is -4.4 eV is the value of ferrocene. The value of LUMO level can be calculated by inserting the value of HOMO level and $E_g$ in Equation (3).

$$E_g = \frac{hc}{\lambda}$$  \hspace{1cm} (1)

$$E (\text{HOMO}) = -e \left[ E_{\text{ox \ onset}} + 4.4 \right]$$  \hspace{1cm} (2)

$$E (\text{LUMO}) = E (\text{HOMO}) + E_g$$  \hspace{1cm} (3)

A DSSC device performances can be measured and study using current-voltage ($I$-$V$) characteristics. A Keithley 2400 source meter and solar simulator from SAN-EL ELECTRIC was used in the $I$-$V$ measurement. The luminosity of solar light is 1000 Watts/m$^2$ measured with the daystar meter. The
performance that can be observed from $I$-$V$ measurement is the efficiency of the cell, which can be calculated from the equation.

$$\eta = \frac{V_{oc} \times J_{sc} \times x \times FF}{Pin}$$

(4)

3. Results and discussions

3.1. Electrochemical properties

The properties of mangosteen sensitizer were changes when added CDCA as a catalyst. Numerous chemical compound count was increased as in FTIR studied. A strong and broad signal was identified at 3320 cm$^{-1}$ and 1026 cm$^{-1}$ in stretch vibrations manners, which represent O-H and C-O compound, respectively. There are increment amount of O-H and C-O from mangosteen sensitizer itself to added CDCA sensitizer. It shows the sensitizer helps to increase anchoring groups, hence improved the bonding process between TiO$_2$ and sensitizer. Photon spectra also studied using UV-Vis and PL measurements to determine the absorption spectra and $E_g$. The absorption spectra was observed within 400 to 600 nm with blue-shift behaviour. The highest peak, which is around 488 nm was observed from PL spectra. This value was substituted in the equation (1) to determine $E_g$, which is 2.54 eV, respectively. Both UV-Vis and PL measurements have increment intensity of peaks regards on the amount added catalyst but there are no additional peaks was found. CDCA helps broadening the wavelength spectra, where it changes the compound inside the mangosteen dye in methanol solvent. HOMO and LUMO levels were calculated from $E_{\text{oxidation onset}}$ obtained from extrapolated CV graph and $E_g$ from PL spectra using equation (1), (2), and (3). LUMO level played a role between CB of TiO$_2$ which it needed to be higher than -4 eV to -4.3 eV [12]. The redox potential is in the range of -4.6 to -5 eV which the HOMO level needed to be lower from the potential. Mangosteen itself has $E$(HOMO) and $E$(LUMO) at -4.81 eV and -2.27 eV respectively. $E$(HOMO) and $E$(LUMO) for photosensitizer with the catalyst amount of 2 mM CDCA is at -4.97 eV and -2.43 eV, respectively. The different gap between LUMO and CB of TiO$_2$ are needed to be more than 0.2 eV, which show the mangosteen capable to have high efficiency. However, large gap also can contribute with energy losses, then affect the performances. HOMO level for both mangosteen sensitizer and the sensitizer with CDCA however at the same level at the redox potential range, which explains low performances caused by poor dye regenerations [11].

3.2. Photovoltaic properties

The mangosteen dye with CDCA as a catalyst was applied as a photosensitizer for DSSC and its photovoltaic properties was observed and studied. One of the measurement was used is current-voltage measurement, which is able to obtain the whole device efficiency. Based on Figure 1 and Table 1, it shows that CDCA fully acted as a catalyst at the concentration of 1.00 mM, 1.50 mM, and 2.00 mM. The efficiency for concentration 0.10 mM, 0.50 mM, and 0.75 mM is at 0.34%, 0.37% and 0.36%, which are lower than the efficiency for mangosteen sensitizer by itself as DSSC sensitizer at 0.38%. This is due to the amount of CDCA was small and does not have enough amount of anchoring group to help increase the device performances. It also reduces the short circuit current density ($J_{sc}$), which is probably due to lack of anchoring group, which reduces the electrons diffusion from dye to TiO$_2$ surface. However, the concentration at 1.50 mM and 2.00 mM of CDCA have higher efficiency at 0.44% and 0.56%, respectively. Compared to mangosteen sensitizer, its own as DSSC photosensitizer. As the efficiency increases, the $J_{sc}$ also increase, which shows the higher amount of electron can transfer from the sensitizer to TiO$_2$ surface. All the concentrations do not have a significant change for open circuit voltage ($V_{oc}$), which shows the CDCA does not improve the recombination activity performance [13].
Table 1. Photoelectrochemical parameters for mangosteen sensitizer with CDCA.

| Sample | Sensitizer      | Voc (V) | Jsc (mA/cm²) | FF (%) | η (%) |
|--------|-----------------|---------|---------------|--------|-------|
| M      | Mangosteen      | 0.64    | 1.03          | 57.32  | 0.38  |
| M1     | Mangosteen + 0.10 mM CDCA | 0.64 | 0.93          | 56.75  | 0.34  |
| M2     | Mangosteen + 0.50 mM CDCA | 0.62 | 0.99          | 59.52  | 0.37  |
| M3     | Mangosteen + 0.75 mM CDCA | 0.62 | 0.95          | 64.28  | 0.36  |
| M4     | Mangosteen + 1.00 mM CDCA | 0.62 | 1.05          | 62.93  | 0.41  |
| M5     | Mangosteen + 1.50 mM CDCA | 0.63 | 1.14          | 63.32  | 0.44  |
| M6     | Mangosteen + 2.00 mM CDCA | 0.65 | 1.40          | 62.03  | 0.56  |

4. Summary
In this study, CDCA was used as a catalyst to increase DSSC performance by adding dye sensitizer. The CDCA helps to introduced more anchoring group inside dye molecule which increases electron transfer between the photosensitizer and TiO₂ surface. It also to reduce the dye aggregation occurs on the surface on TiO₂, which also affect the charge transfer performance. The highest efficiency is at 0.56% for CDCA concentration of 2.00 mM with Jsc = 1.40 mA/cm² compare to mangosteen sensitizer itself only have the efficiency of 0.38% with Jsc = 1.03 mA/cm². The catalyst for dye sensitizer shows improvement of the DSSC performance. However, the efficiency for the natural dye not capable to surpass the artificial sensitizer. Another advancement for dye sensitizer can be studied in future by increasing the amount of CDCA inside sensitizer, purification of natural dye sensitizer or add nobel metal to co-sensitized with the photosensitizer.
5. Appendices

| Equation Symbol | Definition |
|-----------------|------------|
| $h$             | Planck’s constant \((6.62607004 \times 10^{-34} \text{ m}^2 \text{ kg} \text{ s}^{-1})\) |
| $c$             | Speed of light \((3.00 \times 10^8 \text{ ms}^{-1})\) |
| $\lambda$       | The wavelength of the highest peak in PL |
| $E(\text{HOMO})$| Energy value at highest occupied molecular orbital |
| $E(\text{LUMO})$| Energy value at lowest unoccupied molecular orbital |
| $\eta$          | The efficiency of device performance |
| $V_{oc}$        | Open circuit voltage occurred at current = 0 A |
| $J_{sc}$        | Short circuit current density measured at voltage = 0 V |
| $FF$            | A measure of series resistance and junction quality of the cell |
| $P_{in}$        | The input power of incident light 1000 Watts/m² |

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