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The Sensitization of Xanthophylls-Chlorophyllin Mixtureson Titania Solar Cells

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Abstract *- Co-sensitization of natural dyes on $TiO_2$for dye-sensitized solar cell (DSSC) was proposed between chlorophyllin (C) and xanthophyll (X at various volume ratios of C/X. Chlorophyllin is chlorophyll derivative providing -COOH groups essential for binding to TiO_2. The chlorophyll was extracted from dried spinach (Amaranthusviridis) leaves in a mixture ofmethanol-acetone (70%:30%). Chlorophyll extract dye was obtained after partition of the crude extracts in diethyl ether solution. Then, it was hydrolyzed under alkaline condition to get chlorophyllin. Xanthophyll was extracted from fresh petal of chrysanthemum (Chrysanthemum indicum) flowers. Blending of chlorophyllin and xanthophyll was carried out at various volume ratios of C to X (1:0, 5:1, 1:1, 1:5, 0:1). Titania solar cells were constructed in sandwich system of conducting glass-titania/dyes as the photoanode and conducting glass-platinum as the photocathode. Electrolyte solution containing I^-/I_3^- was inserted between the electrodes by capillary action. All dye extracts and blending solutions were analyzed by UV-Vis spectrophotometer. It is shown that the absorption spectra of blending dyes are complimentary in the visible region resulted in a panchromatic response of the dyes. From the cyclic voltammogram of the dyes and blended-dyes, it is found that the energy level of xanthophyll is the lowest. TheI-V test at 100 mw/cm² irradiation confirmed that the energy conversion efficiency (η) of the blended dyes of xanthophyll and chlorophyllin-sensitized solar cell resulted in significant improvement than those of the single dye. Beneficially, the mixed dyes can be adsorbed from solution blend using single dipping step.*

Keywords—*Dye-sensitized solar cells,titania, natural dyes, chlorophyll*

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I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have become one of the most promising alternatives for solar cell devices as compared to the conventional p-n junction photovoltaic devices. The conversion of solar light into the electricity is based on sensitization of a wide band-gap semiconductor such as titania (TiO_2) by the charge-transfer dyes, usually Ruthenium complex (O'Regan and Gratzel, 1991). However, the ruthenium dyes are facing environmental issues and cost problem that will limit the large scale application of DSSC. Currently, development on solar cell system mostly focused in silicon-based solar cells. Instead, there have been plentiful natural dyes resources that have potential as dye sensitizer (Tennakone *et al.*, 1997;Dai and Rabani, 2002; Hao*et al.*, 2006; Kartini*et al.*, 2007; Kartini*et al.*, 2010). Research on the use of natural sensitizer for DSSCs has been slightly overlooked. Yet the efficiencies of DSSCs using natural sensitizers are also much lower than that of Ru-dye based solar cells, as well as their stability. Therefore, for further development of highly efficient and stable natural dye sensitizers, the dyes must be designed to absorb most of the sunlight radiation in visible and near-IR region and to have suitable electronic energy levels. The later requirement can be viewed to be suitable position of the HOMO-LUMO orbitals

matching the redox potential and the conduction band edge of TiO_2 and or suitable electronic energy levels to present synergism in capturing non-injected electron, thus suppressing recombination (Gratzel, 2001). Hence, this configuration will increase stability and cell performances.

One of strategies to fulfil those requirements is employing the co-sensitization approach for natural dyes (Kazuhiro *et al.*, 2003; Sayama*et al.*, 2003). The presence of high variability on molecular structure of available natural dyes enables them to be mixed synergistically by appropriate selection. Recent efforts have been focused on increasing efficiencyand lowering manufacturing costs by using Ru-free organic dyes.

Natural dyes as photosensitizer offer advantages, such as having large absorption coefficients, high light-harvesting efficiency,easily prepared, no resource limitations and no harm tothe environment, due to intramolecular π-π^* transitions and containing no noblemetals such as ruthenium (Sayama*et al.*, 2003).Sayama group (Sayama*et al.*, 2003) has studied the light capture efficiency of the cells by usingred, yellow and blue dyes for co-sensitizing solar cells; however,the increase in global efficiency was not remarkable compared with singledye sensitizing.

Naturally, in photosynthesis, excitation of pigments (chlorophylls and carotenoids) leads efficiently to a free-energy stabilizing charge separation (Peterman *et al.*, 1995). In the primary energy conversion process of photosynthesis, the quantum efficiency is nearly 100%. It is supposed that the process is co-performed by photosystem I (PSI) and photosystem II (PSII) which are linked like a 'Z' by middle electron transport. This model electron transport is called zig-zag chain (Liu *et al.*, 2008). Xanthophyll is one of carotenoids present naturally in thylakoid membrane. Xanthophylls are efficient quenchers of chlorophyll triplets that can originate on chlorophyll *a* molecules. This natural system provides interesting solution to the drawback of natural DSSC.

Chlorophyll obtained from spinach leaves are mixed and combined with natural xanthophyll to obtain sensitizer blending with antenna effect. Chlorophylls, the keymaterials for natural photosynthesis, are the most abundantcyclic-tetrapyrrole-based molecules on the Earth. It is now produced in large quantitiesfrom higher plants and seaweeds. Chlorophylls also have been used extensively in the food industry. However, chlorophyll is lack of binding sites to TiO_2. Thus, molecular engineering is necessary to open the phytil group of chlorophyll into the useful free carboxylic functional groups (Kay and Gratzel, 1993) resulted in chlorophyllin.

Another requirement for the ideal dye structure in DSSCs is the dyeshould haveseveral carbonyl or hydroxy groups capable of chelating tothe Ti^{IV} sites on the titanium dioxide surface (O'Regan and Gratzel, 1991).From an economic pointof view, the best choice proposed is to fabricate DSSCs with dye sensitizers that can be produced bysimple derivatization of natural chlorophyll molecules and apply co-sensitization. Therefore, this proposed work focused on fundamental studies on the natural sensitizers blending composition of such synergistic blending dyes sensitizers (chlorophyllin and xanthophyll). Electrochemical study was introduced to predict the HOM-LUMO energy level of the blended dyes system in DSSC.

II. Material and method

Materials used.

Diethyl ether, potassium hydroxide, petroleum ether, absolute ethanol, absolute methanol, acetone, nitric acid 65%, triton X-100, and ethylene glycol. They were purchased from the e-Merck Co., while potassium iodide and iodine were from Kimia Farma. The FTO glass (F-doped SnO2, 8 Ω/□) was provided by Hartford Glass Co. Titanium(IV) oxide (P25 TiO_2) were from Degussa. All chemicals were used as received without further purification. The spinach (*Amaranthusviridis*) leaves were obtained from local market in Yogyakarta. The yellow chrysanthemum flowers (*Chrysanthemum indicum*) were from local flower shop in Yogyakarta.

Dyes preparations. Chlorophyll was extracted from 30 g of dried spinach leaves soaked in 150 mL of mixed solvent of methanol to acetone of 70/30 v/v (Kusmita and Limantara, 2009). The filtrate of crude chlorophyll extract was then used for partition with diethyl ether solution. Derivatization of chlorophyll into chlorophyllin was carried out by adding 1 mL of KOH 7% in absolute methanol. The chlorophyllin obtained was then stored in the dark at cold place. Xanthophyll was extracted from the clean and fresh petals of yellow chrysanthemum. Five grams of the petals were ground in a mortar after 20 mL of mixed solvent (60% of absolute ethanol and 40% of petroleum ether) was added. The resulted solution was filtered and diluted into 20 mL using the same mixed solvent. The xanthophylls extract was then stored in the dark at cold place. The chlorophyllin and xanthophyll were each diluted with appropriate solvent and then blended at various volume ratio of chlorophyllin to xanthophyll (C:X) of 1:0, 5:1, 1:1, 1:5, and 0:1. The absorption spectra for each mixture were analyzed using UV-Vis spectrophotometer.

Dyes adsorption for sensitization study. The slurry paste of TiO_2 powder (P25) was made by adding nitric acid at pH 4 and one drop of triton X-100 until no lumps observed. The slurries were slip-casted on pre-cleaned fluorine doped tin oxide (FTO) glasses. The resulted films of TiO_2 were then sintered at 450 °C for 30 min. After sintering, the warm TiO_2 thin films were soaked in each dye solutions for 24 h. The absorption spectra of the dyed-TiO_2 films were recorded using UV-Vis spectrophotometer equipped with specular-reflectance accessories (Pharmaspec).

For estimation of oxidation potential of the dyes, cyclic voltammetry (CV) experiments were carried out in three electrodes consisting of an FTO-TiO_2/dyes working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode with scan rate 0.1V/s (VoltameterMetrohm μ-Autolab). The electrolyte used in this experiment were I^- and I_3^- from KI and I_2 with concentration 0.005 M : 0.0005 M respectively in ethylene glycol solution. While the band gap energy was measured from the absorption spectrum. The HOMO-LUMO determination of the resulted dyes composition was described separately (Dwitasari*et al.*, 2013).

Cell assembling and characterizations. The resulted dyed-TiO_2 films on FTO were used as photoanodes in DSSC. The photoanode was sandwiched with Pt-coated counter

electrodes obtained from Dyesol. The active area of the cell was 0.5 x 1.0 cm. The internal space of the cell was filled with liquid electrolyte (0.83 g KI and 0.13 g I_2) dissolved in 10 ml ethylene glycol by capillary action. The photocurrent-voltage (I-V) curves were measured under irradiation of Xenon lamp (100 mW/cm^2) using Keithley 1200 source measurement unit.

III. RESULTS AND DISCUSSIONS

Chlorophyll extract and chlorophyllin. Figure 1 shows the electronic absorption spectra of chlorophyll extract and its derivative (chlorophyllin). Dyes extract of chlorophyll *a* was identified by absorption peaks at 400-450 nm of the Soret 410 and 429 nm, as well as the Q_x absorption at 535, 575, and 615 nm and the Q_y absorption at 662 nm (Kay and Gratzel, 1993; Milenković*et al.*, 2012). The principal bands of chlorophyll a at 429 and 660 nm are shifted to 418 and 642 nm for chlorophyllin*a*. The shoulder of chlorophyll *a* centered at 410 nm is absent in the chlorophyllin*a*spectra. Similar observation on the disappearance of shoulder in the blue band has also been reported (Kay and Gratzel, 1993; Calogero et. al., 2014). It is presumably due to the loss of cyclopentanone ring as observed in the allomerized chlorophyll where the ring has been transformed (Oster et. al., 1964). Saponification of phytil ester groups by KOH resulted in the opening of cyclopentanone ring to form two additional carboxyl groups. The later groups are important for binding with TiO_2.

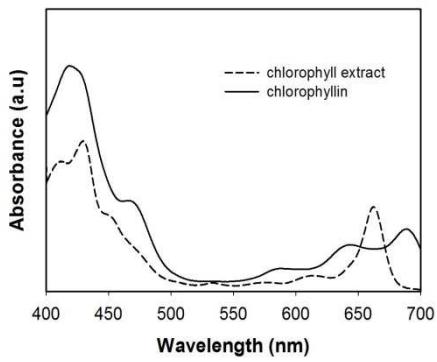

Figure 1.Absorption spectra of chlorophyll extract and its derivative (chlorophyllin)

The corresponding infrared spectra are illustrated in Fig. 2. They have in common broad bands at ~3400 cm^{-1} of enol form of cyclopentanone ring (Oster et. al., 1964). This band is observed only at porphyrin containing cyclopentanone ring (Falk and Willis, 1951 in Oster *et al*., 1964). The band at 1740 cm^{-1} present in chlorophyll extract can be ascribed to ester groups which is absent in chlorophyllin, while the formation of carboxylates for chlorophyllin were confirmed by peaks at 1566 and 1404 cm^{-1}.

Co-sensitizers absorption spectra. In order to mimic nature for photosynthesis in which chlorophyll and xanthophyll are synergized to obtain 100% quantum efficiency, here xanthophyll is coupled to co-sensitize chlorophyllin dye-sensitized titania solar cell. Figure 3 shows the absorption spectra of chlorophyllin (C) derived from chlorophyll extract, xanthophyll extract (X) and the mixtures (C:X) in volume fraction of those two natural dyes. Xanthophyll extract displayed absorption peaks in the blue band, since it has strong yellow color. Absorption peaks at 415, 435, and 465 nm are characteristics for xanthophyll extracted from fresh petals of yellow chrysanthemum flowers (Liu *et al.*, 2008). Spectra addition of those two dyes is clearly observed. The absorption peaks of chlorophyllin are prominent at where the amount of chlorophyllin is dominant (C:X=5:1), and vice versa. All absorption peaks of chlorophyllin and xanthophylls are still obvious at C to X ratio of 1:1. Similar observation has been reported for chlorophyll and xanthophyll blended dyes (Liu *et al.*, 2008). It is also confirmed that there is no new absorption peaks, neither is a peak shift. It is likely that the visible light absorption of the mixed dyes in solution is the linear superposition of the two single dyes.

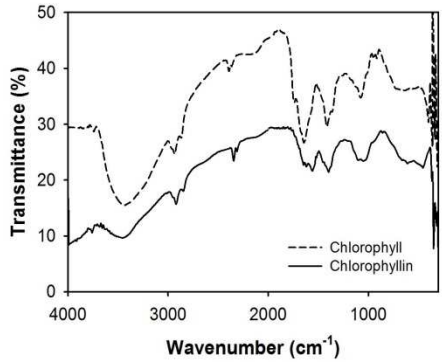

Figure 2.Infrared spectra of chlorophyll extract and its derivative (chlorophyllin)

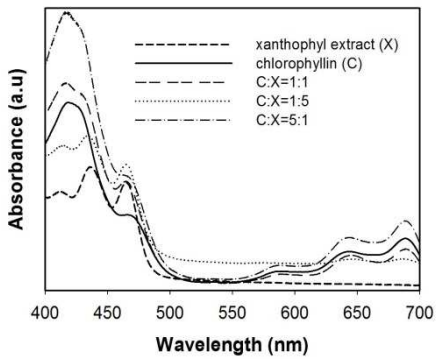

Figure 3.Absorption spectra of the single dyes extract and the mixed dyes

Sensitizationstudies. Figure 4 and 5 show the visible light absorption characteristics of chlorophyllin, xanthophyll and a mixture of chlorophyllin and xanthophyll on TiO_2 films. Spectra of the dyes in the solution are inserted for comparison. It can be seen that the spectra of the dyes on TiO_2 have different pattern from those in the solution. The absorption spectrum of the dyes has been extended in the visible region. The curves are also much smoother than those in the solution. No clear absorption peaks are observed. Secondly, on TiO_2, the absorption spectra of the dyes are obviously stronger than those in the solution. These phenomena may be attributed to the strong interactions between TiO_2 and the dyes molecules (Sayama *et al.*, 2003; Wu *et al.*, 2010). The interactions are likely formed utilizing the carboxylate and hydroxyl groups of chlorophyllin and xanthophyll, respectively.

The strong interaction between TiO_2 and the dyes molecules may induce the dye aggregation (Kamat, 1993). It can be determined by examining the peak maxima shifting on the spectra of the dyes solution to the corresponding spectra of the dyes on TiO_2. The peak maxima and the peak shifting are identified in Table 1.

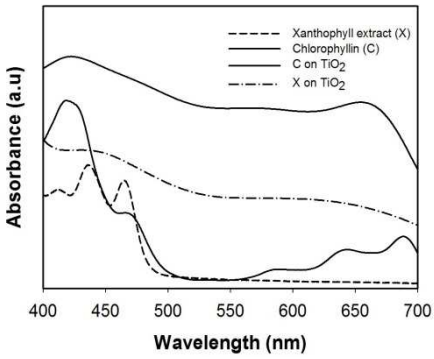

Figure 4.Absorption spectra of single dyes extract and the adsorbed dyes on TiO_2 films

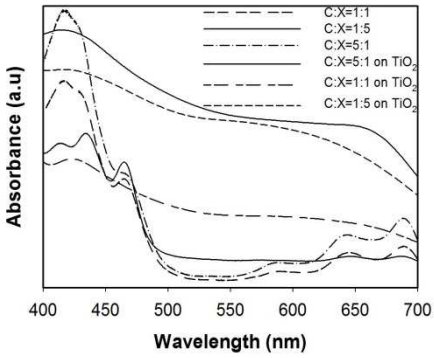

Figure 5.Absorption spectra of mixed dyes extract and the adsorbed dyes on TiO_2 films

Table 1.Peak maxima of the dyes in solution and on the surface of TiO_2

Dyes	λ_{max} (nm)		Shifting (nm)*
	in solution	on TiO_2 surface	
Chlorophyllin	418	423	5
Xanthophyll	436	431	-5
C:X = 5:1	418	415	-3
C:X = 1:1	416	423	7
C:X = 1:5	435	416	-19

*The negative sign indicates a blue shifting

It is envisaged that the adsorbed chlorophyllin and C:X (1:1) dye solution on TiO_2 resulted in red-shift, indicating the formation of *J*-type dye aggregates, while the others gave blue-shift, suggesting the formation of *H*–type dye aggregates (Kamat, 1993; Sayama*et al.*, 2003). No dyes adsorbed as monomeric molecule on TiO_2. Aggregate type interaction is beneficial for sensitization since the dyes are linked to the semiconductor by chemical bonding. It is believed that such bonding facilitates the electron transfer, thus increasing the photon to current conversion efficiency (Sayama*et al.*, 2003; Kartini*et al.*, 2010; Kartini*et al.*, 2014). Then, the photoelectrochemical behavior of the dyes was studied in sandwich cell of titania-based solar cell. The titania used was commercial TiO_2 (P25) which has typically 80% of anatase and 20% rutile polymorphs. It is believed that anatase domain is preferred for the solar cell due to its higher surface area compared to rutile, ensuring high amount of the monolayer loading dyes on the surface. Dyes will act as the light harvesting materials, so the higher the monolayer adsorbed dyes, the higher the photon converted into current, thus generating more electricity.

Table 2.Photoelectrochemical properties of chlorophyllin-xanthophyll dyes on titania solar cell

Dyes	V_{OC} (V)	I_{SC} (mA)	J_{SC} (mA/cm^2)	Fill Factor, *FF* (%)	Efficiency, η (%)
Chlorophyllin	0.27	0.032	0.036	23	2.23 x 10^{-3}
Xanthophyll	0.31	0.080	0.091	26	7.30 x 10^{-3}
C:X = 1:5	0.36	0.068	0.077	38	10.50 x 10^{-3}

Table 2 shows the parameters of the photoelectrochemical solar cell using chlorophyllin, xanthophyll, and the mixture as the sensitizer. The *J-V* curves of the corresponding cells are displayed in Figure 6. The light driven electrochemical process in the dye-sensitized solar cells (DSSC) is regenerative and the working voltage produced by the device is the difference between chemical potential of TiO_2 and the redox potential of the mediator (I^-/I_3^-). We used the same TiO_2 (P25) films for all tested cells, therefore the open-circuit voltage (V_{OC}) of the cells were almost the same of about 300 mV. This value is somewhat lower than those reported for nanotube TiO_2 (Kartini*et al.*, 2014). Then, differences on the tested cell construction should only arise from different dyes used as the sensitizers. From Table 2, it is clearly observed that xanthophyll-sensitized solar cell resulted in the highest current densiy (J_{SC}), indicating efficient electron transfer from the dye into conduction band of titania. In contrast, the highest overall efficiency is generated from the C:X=1:5 sensitized solar cell. This may be ascribed due to the work of xanthophyll dyes which has large blue-shift in visible region. In general, the constructed titania solar cells generated too low overall cell efficiency.

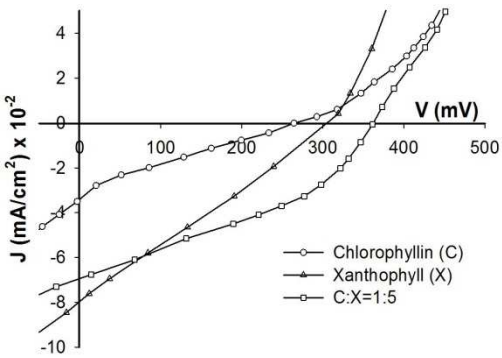

Figure 6.The I-V curves of titania solar cells with single and mixed dyes

To get an efficient charge separation, the dyes used on titania solar cell must conform to the thermodynamic requirements: theHOMOlevel of the dye has to be sufficiently positive in

the redox potentialfor efficient regeneration of the oxidized dye by the holetransportmaterial, and the LUMO of the dye has to be sufficientlymore negative than the conduction band edge of the TiO_2 (Ecb). Figure 7 exhibits energy level diagram of chlorophyllin-xanthophyll dyes extract sensitized solar cells. Based on cyclic voltammogram of the dyes, the HOMO values were determined. The calculation of HOMO-LUMO was presented elsewhere (Dwitasari*et al.*, 2013).

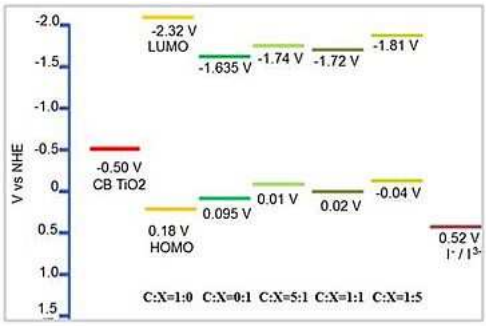

Figure 7.The predicted energy level of nDSSC sensitized with chlorophyllin, xanthophyll, and the mixed dyes

Figure 7 provides possible reasons of the low solar cell efficiency of the tested cells. All the dyes show more negative LUMO than the conduction band of titania, and more negative HOMO than the redox electrolyte potentials. The later position resulted in difficulties to the dye sensitizer to regenerate by accepting electrons from the redox couple, leading to lowering photon to current conversion, thus decreasing the global efficiency (η) of the solar cell. It is noteworthy that the xanthophyll- and C-X (1:5)-sensitized solar cells generated almost similar current density, as predicted thermodynamically by their LUMO position relative to the conduction band of TiO_2. But, xanthophyll cell has lower efficiency compared to the mixed dyes cell. It is presumably due to the stronger interaction of the dyes and TiO_2 through the formation of *H*-type aggregates as indicated by larger blue-shift than that of the xanthophyll-sensitized cell (Table 2). While, the chlorophyllin-sensitized solar cell showed low sensitization efficiency, even the distance of the LUMO to the conduction band of TiO_2 is shorter than those firstly described dyes. This probably due to the formation of *J*-type aggregates. It has been reported that the *J*-like aggregates showed hardly sensitization efficiency, therefore, it is suggested that the suppression of formation of the *J*-like aggregates is attributed to the promotion of the solar cell efficiency (Sayama*et al.*, 2003).

IV. CONCLUSIONS

It is concluded that the absorption spectra of the sensitizers could be expanded by the multi-dyes system. However, the J_{sc} and η were not always improved by this method. It was shown that the mixed sensitizers generated higher photon conversion to current. It is probably that the adsorption pattern of the dyes on TiO_2 surface has great influence to the current conversion efficiency. Blue-shifted sensitization has resulted higher current conversion compared to the red-shifted sensitization. Apart from the approaches to reach high efficient natural dye sensitized solar cell, the present study is expected to contribute in developing a colorful solar cell for stained-glass window or fancy goods such as clock and toys. The light intensity is weak for the indoor applications, thus problems such as sealing, heat and stability can be avoided.can be concluded that by-product of palm oil plantation and mill had good nutritional value. Therefore, this feedstuff can be used to formulate complete feed for sheep. It also proved that this effort successfully increased the nutrient digestibility.

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