

Natural dye sensitizer from cassava (*Manihot utilissima*) leaves extract and its adsorption onto TiO₂ photo-anode

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Abstract. Interaction between TiO₂ and dyes sensitizer have been studied. The chlorophyll presents in the crude leave extract (CLE-dye) from cassava (*Manihot utilissima*) was immobilized on to the photo-anode, consists of TiO₂ supported by fluor doped Tin oxide (SnO₂-F) Glass. The TiO₂ was prepared by Rapid Breakdown Anodization (RBA) method then immobilized on to glass coated by SnO₂-F using doctor blade technique, to give CLE-dye/TiO₂/SnO₂-F/Glass photo-anode. The prepared photo-anode was characterized by UV-Vis-DRS, FTIR, XRD, SEM, electrochemical and spectro-electrochemical systems. In this study, the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy level of the CLE-dye were empirically determined by cyclic voltammetry method, while spectro-electro-chemistry method was used to determine the coefficient of degradation and formation of the dyes, and diffusion coefficient of the hole recombination as well. Good anchoring between TiO₂ with dye extracts (CLE-dye) can be seen from value of dye LUMO energy level (-4.26 eV), which is approaching the conduction band of TiO₂ (-4.3 eV). The coefficient of degradation and formation of the CLE-dye showed a quasi reversible and diffusion coefficient hole recombination values were small, indicated that it is quite suitable as a sensitizer in a dyes sensitized solar cell.

Keywords: TiO₂, chlorophyll dyes, crude leave extract, cassava leaves, spectroelectrochemistry

1. Introduction

In addition to various types of solar cells, a solar cell based on dyes sensitized TiO₂ photo anode has been successfully developed by Gratzel [1]. This dyes sensitized solar cell (DSSC) is a type of solar cell that utilizes dye or pigment as harvesting photons from sun rays [1]. This type of solar cell is generally made up from various components such as photo anode support (metal oxide semiconductor coated on to a conductive oxide glass), photo sensitizer (dye), electrolyte and counter electrode. Optimization and compatibility of each components, especially the spectral response of photo anode and proper interaction between semiconductors and dyes [2] are very important in the dyes sensitized solar cell systems.

The dyes served for harvesting photons to provide an excited electron in the LUMO (lowest unoccupied molecular orbital) and positive hole in the HOMO (highest occupied molecular orbital) levels of the dyes. The excited electron will be transferred to the semiconductor and further transported to the counter electrode, *via* external circuit, then involved in redox couple reaction of the electrolyte before refilled the positive hole of the dyes. Among various dyes, the natural dyes are the interesting candidate to construct the DSSC, due to the availability of abundant resources of natural dyes, non-toxic



property, environmentally friendly and readily available and affordable. In addition to these reasons, the selection of natural dyes also takes advantage of the natural behavior of the natural pigments, such as chlorophyll that can do a photochemistry naturally.

There are a lot of reports on the utilizing natural dyes as a sensitizer in the DSSC, such as chlorophyll, anthocyanin, flavonoid and carotenoids which are derived from leaves, flowers, fruits, seeds, etc. [3]. According to the reports, so far, the highest efficiency value was achieved by betanin pigment (3%), while the chlorophyll extracted from papaya leaves only give 0.28% efficiency. Compared to synthetic dyes, in which nearly 20% efficiency can be obtained, the natural dyes have much lower efficiency value. This might be due to a weak bond between the natural dyes with the metal oxide (TiO_2) and low charge transfer spectrum of natural dyes on the boundary solar ray spectra [4]. The lack of available bonding site between the dyes and TiO_2 molecules may hinder the electrons flow from the excited dye molecules to the TiO_2 films [5]. In addition, the timely imbalance in the refilling of electron in the HOMO level of the natural dyes may cause the degradation of the dyes, resulting a short life time of the sensitizer [6].

Based on the above conditions, the present work was designed to study the interaction between TiO_2 semiconductor with the sensitizer (natural dyes). The natural dye used in the present study was chlorophyll crude extract derived from cassava leave (*Manihot utilissima*). The TiO_2 was coated on to Fluor doped Tin Oxide (FTO) by Doctor Blade Method, in which it was immersed in the chlorophyll crude extract to obtain the sensitized TiO_2 photo anode. The photo anode was then subjected to a spectro-electro-chemical study to gain the insight of the energy level values (LUMO level position) and the stability feature of the dyes.

2. Materials and methods

2.1 Fabrication and characterizations of TiO_2

TiO_2 was synthesized by using rapid breakdown anodization (RBA) method. Ti foil (4 x 1 cm) was washed using acetone, ethanol and aquadest for 30 min by ultrasonication, respectively. Ti foil served as anode and Pt foil as cathode. Perchloric acid (0.15 M) was used as electrolyte and 15 V bias potential was applied during anodization. Anodization process was conducted until all Ti foil was submerged in the electrolyte decays perfectly. The obtained TiO_2 precipitate was then centrifuged and dried in oven over night, then calcinated for 3 h at 450°C. The prepared TiO_2 was characterized by UV-Vis Reflectance (UV-DRS), XRD and SEM-EDX, to get information on its band gap value, crystallinity, and morphology feature, respectively.

2.2 Extraction of natural dye

The cassava leaves (*Manihot utilissima*) were obtained from Cipeucang village, Pandeglang, Banten. The leaves were washed and dried under sun light. The dried leaves was then crushed to obtain the intended fine powder. Approximately 20 gram of the obtained fine powder of cassava leaves was macerated in the 200 mL ethanol for 3 hours with the aid of sonication then it was kept for another 3 hours, and followed by filtration with a filter paper (Whatman no.1). The aqueous filtrate was further extracted using hexane, to obtain two fractions, which are ethanol and hexane fractions, respectively. These two fractions were concentrated using rotary evaporator (40°C for 4 hours). The concentrated extract fractions were stored in dark bottle, ready to be used for the next step of the research. The obtained extracts was then characterized by FTIR to get an insight of the available functional groups and UV-Visible spectrometer to determine absorption spectra in visible light.

2.3 Preparation of photo-anode

FTO (fluorine-doped tin oxide, $\text{SnO}_2\text{-F}$) film was prepared on a glass slide (50x75x1 mm). Before coating, the glass plate was first cleaned in a detergent solution in an ultrasonic bath for 15 minutes,

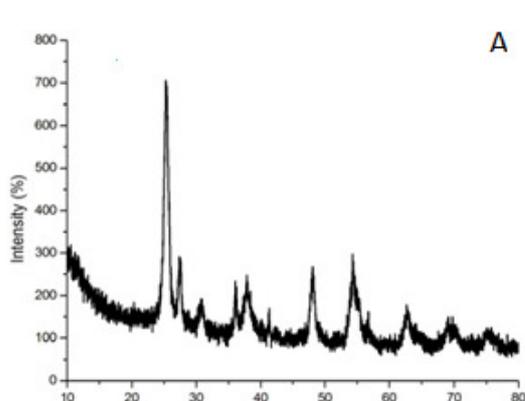


Figure 1a. XRD pattern of prepared TiO₂ by the RBA method.

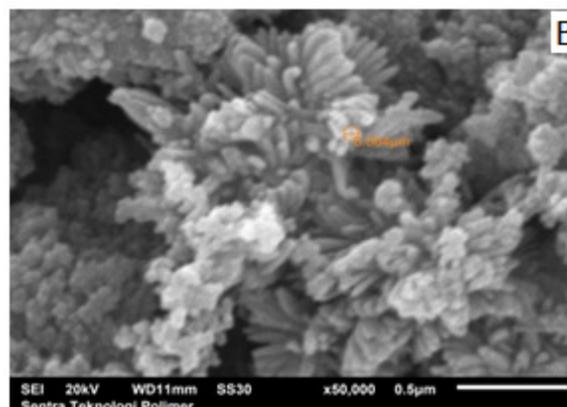


Figure 1b. SEM image of prepared TiO₂ by the RBA method.

rinsed with mix of ethanol and acetone, followed by water, and then dried. The SnO₂-F precursor solution was homogenously sprayed on to the glass surface, followed by heat treatment, according to Supriyono *et al.* method [7], to obtain the proper FTO (good transparency and good conductivity). The self prepared TiO₂ was then deposited on the FTO conductive glass by doctor-blade technique in order to obtain a TiO₂ thin film. The TiO₂ film was preheated at 200°C for 10 min and then sintered at 450°C for 45 min. After cooling to 80°C, the TiO₂ electrode was immersed in a natural dye solution for 24 h. The fresh prepared photo-anode was then characterized by UV-Vis, UV-Vis-DRS, FTIR, spectro-electrochemical measurement to determine HOMO-LUMO energy level, degradation and formation coefficient and diffusion hole percolation coefficient.

3. Results and discussion

3.1. Fabrication and characterization of TiO₂

The self prepared TiO₂ by a Rapid Break-down Anodization (RBA) method was characterized by using XRD and SEM to see the phase of crystallite and morphology of TiO₂, respectively. Figure 1a shows XRD pattern of the prepared TiO₂, in which the characteristic observed the peaks of 2θ at 25°, 38°, 48°, and 54° indicated the existence of anatase crystalline phase. Further elaboration by using Scherer equation revealed the existence of particle with crystallite size of approximately 5.23 nm [8, 9]. While figure 1b shows morphology feature (SEM image) that indicated a nanotubular structure of the as-grown powder with a nanotube diameter of approximately 64 nm.

3.2. Characterization of cassava leave extract UV-Vis spectra

The fresh cassava leave extract (CLE) dye, TiO₂/SnO₂-F/Glass, and CLE-dye/TiO₂/SnO₂-F/Glass were characterized by UV-Vis spectrometry. Figure 2a shows the absorption spectra of CLE dye solution in the wavelength range of 350-800 nm. The CLE dye mainly consists of chlorophyll mixture, thus unsurprisingly have absorption peaks at wavelength of 410 and 665 nm. The observed absorption peaks are well matched with the absorption data characteristic of chlorophyll dye [10]. Chlorophyll absorbs strongly in the blue and red region but poorly in green region of light spectrum [11]. The excitation energy value corresponds to 410 nm absorption is equal to 3.03 eV photon energy, according to equation as follow,

$$E = \frac{h \cdot c}{\lambda}$$

where the Planck constant, h , (6.63×10^{-34} Js), light velocity, c , (3×10^8 m/s), and 1J equal to $6.24150934 \times 10^{18}$ eV). While figure 2b shows spectra pattern of CLE) dye, TiO₂/SnO₂-F/Glass, and

CLE-dye/TiO₂/SnO₂-F/Glass. It can be observed that almost no absorption peak of TiO₂/SnO₂-F/Glass is in the visible region. On the other hand, a typical chlorophyll absorption peaks are clearly observed in the CLE-dye/TiO₂/SnO₂-F/Glass and CLE dye. Furthermore an existence of red shift in absorption peak of pure dyes and TiO₂/Dyes was observed, that is from 665 nm of pure dyes to 670 nm of TiO₂/Dyes respectively. The red shift can be attributed to the characteristic of chlorophyll bonded on to TiO₂ surface [6].

3.3. Fourier transform infrared characterization

Fourier Transform Infra Red spectrometry was conducted, in order to get an insight on the functional group information of the fresh cassava leave extract (CLE), TiO₂/SnO₂-F/Glass, and CLE-dye/TiO₂/SnO₂-F/Glass. Figure 3a shows a wide range of absorption peaks appear, e.g. typical peak at wavenumber range of 3300–3500 cm⁻¹ due to the O–H stretching vibration of the fresh CLE, a sharp peak at 2900–3000 cm⁻¹ which corresponds to the C–H stretching vibration of chlorophyll. Other sharp peak at wave number 1640 cm⁻¹ indicating the existence of -C=O group. While peak at 1040-1100 cm⁻¹ and 1380 cm⁻¹ are assigned as a C-C and C-N of a ring of chlorophyll domain. Figure 3b shows FTIR

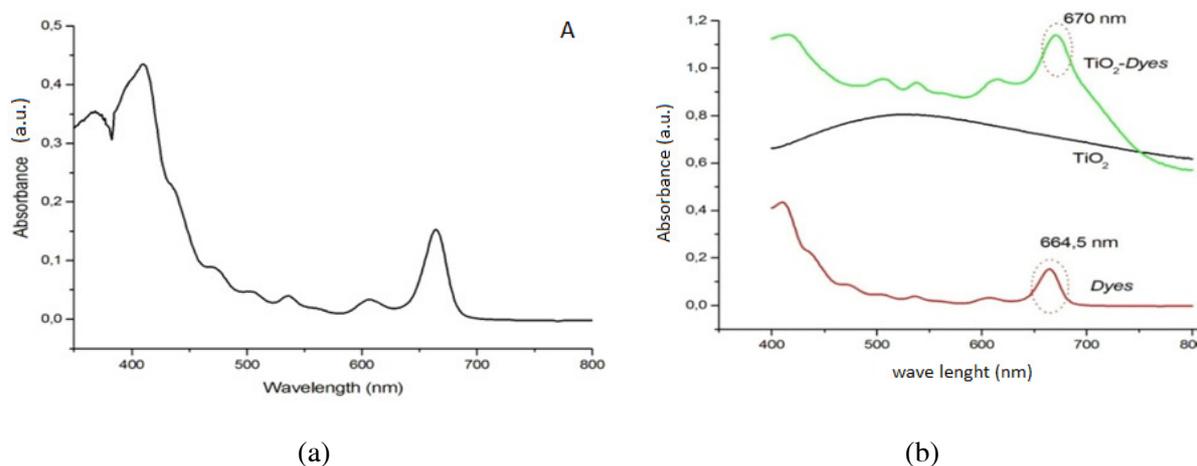


Figure 2. Visible spectra of (a) the fresh cassava leaf extract (CLE) dye, (b) CLE-dye, TiO₂/SnO₂-F/Glass, and CLE-dye/TiO₂/SnO₂-F/Glass.

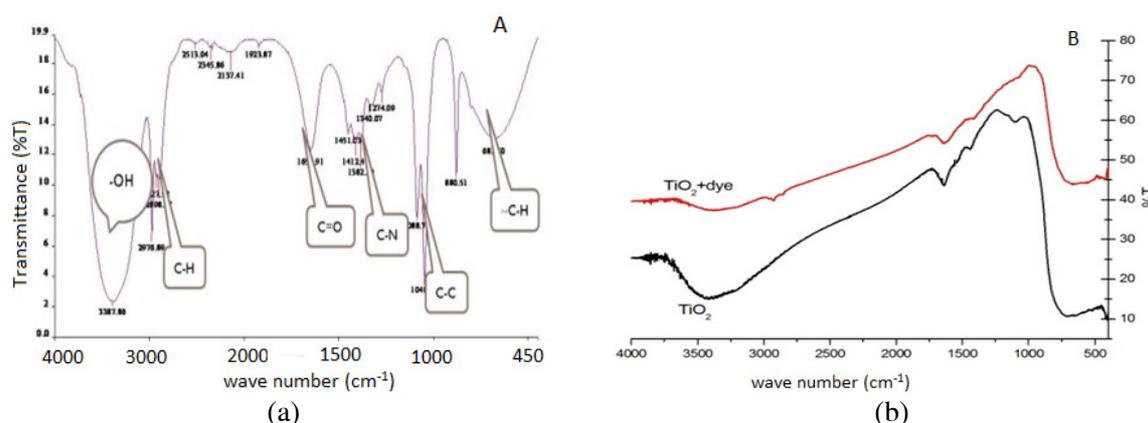
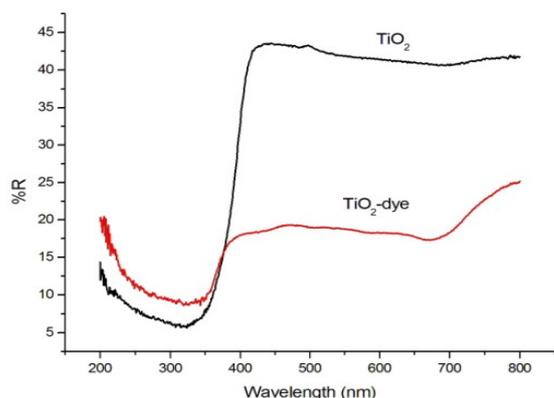
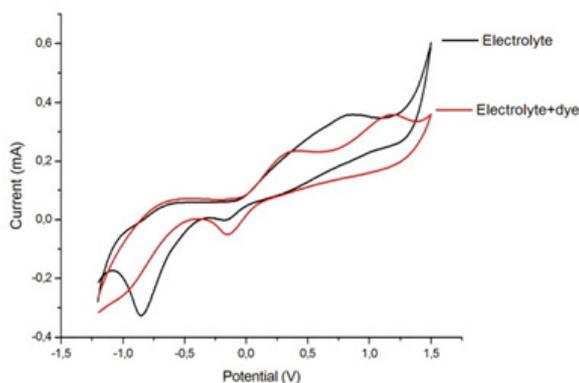


Figure 3. FTIR spectra of (a) the fresh cassava leaf extract (CLE) and (b) TiO₂/SnO₂-F/Glass (below), CLE-dye/TiO₂/SnO₂-F/Glass (above).



(a)

Figure 4. UV-Vis DRS spectra before and after dye loading.

(b)

Figure 5. Cyclic voltamogram of TiO₂/SnO₂-F/Glass working electrode under electrolyte and electrolyte containing dyes.

spectra of TiO₂/SnO₂-F/Glass and CLE-dye/TiO₂/SnO₂-F/Glass, where a typical peak at 500-700 cm⁻¹ due to -Ti-O-Ti- bound were observed in both samples. The disappearance of typical -OH bonding at 3300-3500 cm⁻¹ in CLE-dye/TiO₂/SnO₂-F/Glass may suggest the -T-O-dye interaction, thus eliminate the -OH from titanyl (-Ti-OH) and hydroxyl (R-OH).

3.4 UV-Vis diffuse reflectant spectrometry characterization

The UV-Vis-DRS spectra provide information of the band gap value of TiO₂ and the visible response of the CLE-dye/TiO₂/SnO₂-F/Glass. It is clear that the typical UV-Vis-DRS spectra due to the first transition absorption corresponds to wavelength of about 398-410 nm were observed in both samples (figure 4), which indicates the energy gap value of 3.0-3.2 eV. Importantly, the spectrum of CLE-dye/TiO₂/SnO₂-F/Glass shows a significant absorption (inverse of reflectance) in the visible region. It is inferred the presence of CLE-dye on TiO₂ surface.

3.5 Cyclic voltametry (CV) investigation

The CV investigations were conducted in an electrochemical cell comprise of TiO₂/SnO₂-F/Glass working electrode, Pt as counter electrode, and Ag/AgCl as reference electrode. The supporting electrolyte was solution of tetra butyl ammonium perchlorate (0.5 M) and ferrocene (0.002 M Fc/Fc⁻) in acetonitrile. The solution of CLE-dye in acetonitrile was used to investigate CLE-dye/TiO₂/SnO₂-F/Glass. The investigation results are shown in figure 5, where definitive oxidation peaks are observed in the supporting electrolyte and in the electrolyte containing dye. Cyclic voltamogram of the system containing supporting electrolyte only shows an oxidation peak at (+) 0.75 V and two reduction peaks at (-) 0.176 V and (-) 0.83 V which are corresponded to the oxidation and reduction peak of ferrocene.

There are new peaks of oxidation and reduction after the CLE-dye was being added. These are oxidation peaks at (+) 1.17 V and reduction peak (-) 0.144 V, which can be attributed to the oxidation and reduction the CLE-dye. The bias potential values of oxidation and reduction peak of the CLE-dye can be correlated to HOMO and LUMO energy level of the dyes. Where the oxidation peak is corresponded to the HOMO and reduction peak is corresponded to the LUMO. The HOMO level acts as the ground state which is the highest energy molecular orbital (MO) containing at least one electron. Correspondingly, the LUMO is the lowest orbital energy level where electrons will excite. Referring to the energy diagram which is presented in figure 6, the energy level of the HOMO and LUMO of CLE-

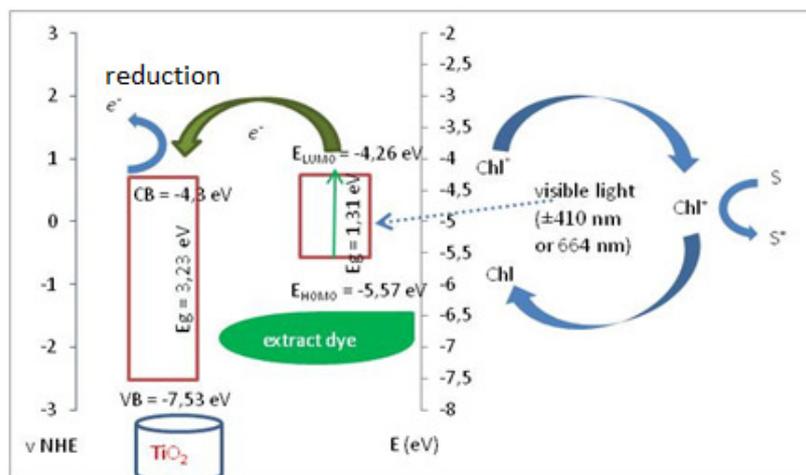


Figure 6. Illustration mechanism of chlorophyll-TiO₂ system by sunlight illumination (modified from Budhee *et al.* 2014 [2]).

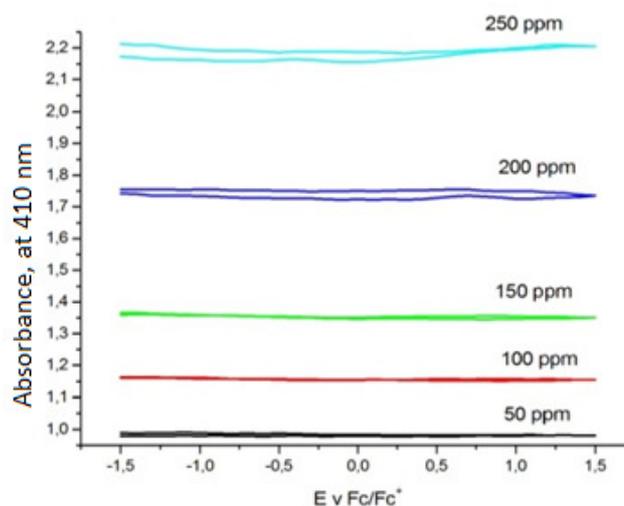


Figure 7. Absorbance at 410 nm values as a bias potential function at various CLE-dyes concentrations.

dye are -5.57 and -4.26 eV, respectively [12]. Thus, the CLE-dye LUMO level (-4.26 eV) is higher than the conduction band energy level of TiO₂, which may facilitates electron transfer to the conduction band.

3.6 Spectro-electro-chemical

To get an insight on the ratio of oxidation rate (degradation) and reduction rate (formation or regeneration) of the CLE-dyes and the hole percolation coefficient, a spectro-electrochemical investigation was conducted. The cyclic volta-absorptometry (CVA) which combines the electrochemical and UV-Visible spectrometer was applied in this study. CVA was measured at the highest absorbance value (410 nm, see figure 2a). The same wavelength was also used to investigate the changing of absorbance as bias potential function. The bias potential was given in the range from -1.5 V to +1.5 V, while the concentrations of CLE-dye were 50, 100, 150, 200, and 250 ppm.

Figure 7 shows the absorbance changes due to potential. When the bias potential shifted to the more positive voltage, the absorbance tends to be lower, while with the more negative voltage, the absorbance tends to be higher. This observed phenomena occurred because when the electrode was given a positive bias potential, energy level of electron from electrode became lower and at some point the electron from

solute in electrolyte is transferred to electrode. Electron leaping from solution to electrode can be attributed to the oxidation of CLE-dye to CLE-dyes⁺. On the contrary, when the electrode was given a negative bias potential, energy level of electron became higher and at some point electron from electrode is transferred to solute in electrolyte which causes leaping electron. That leaping electron is reduction process, where CLE-dyes⁺ (degradation) return back to CLE-dyes (formation). By that, we can determine $k_{degradation}$ and $k_{formation}$ of CLE-dyes from the change of absorbance versus time, which electrochemically a first order reaction.

$$\frac{-d[A]}{dt} = k[A] \quad (2)$$

$$\ln[A] = -kt + \ln[A]_0 \quad (3)$$

$\ln [A]$ is the concentration of CLE-dyes as y axis and time (t) as x axis. Slope value from that linear equation is the coefficient degradation and formation of the dye, as shown in figure 8.

Generally, it was observed that the degradation rate is smaller compared to the formation rate, as shown in table 1. It indicated that the recovery of the hole on HOMO level is fast enough to recover the oxidized dyes during operation. The reaction of CLE-dyes \leftrightarrow CLE-dyes⁺ + e⁻ is quasi reversible, so the investigated CLE-dyes is suitable as a sensitizer.

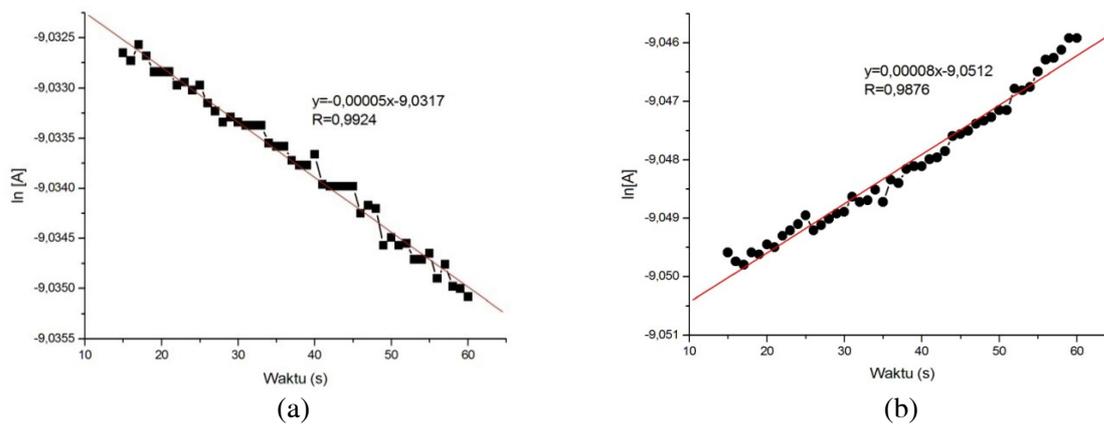


Figure 8. (a) degradation and (b) formation coefficient value of dye.

Table 1. $k_{degradation}$ and $k_{formation}$ values at various CLE-dyes concentration

ppm (mg/L)	M (10^{-4})	$k_{degradation}$ (s^{-1})	$k_{formation}$ (s^{-1})
100	1.12	-0.00001	0.00003
150	1.69	-0.00005	0.00008
200	2.23	-0.00005	0.00008

Table 2. Hole diffusion coefficient of CLE-dye

ppm (mg/L)	M (10^{-4})	D_{app} (cm^2/s)
100	1.12	2.56×10^{-11}
150	1.69	1.21×10^{-10}
200	2.23	4.6×10^{-10}

3.7 Diffusion hole coefficient

In this study, the dynamics of hole percolation (CLE-dyes⁺) was investigated in a CLE-dye/TiO₂/SnO₂-F/Glass. The absorbance versus time data on the chronoabsorptometry mode of the reduction stage was used to determine the coefficient of hole percolation through the following equation [13],

$$D_{app} = \frac{\Delta OD^2 \times \pi \times d^2}{t \times 2 \Delta OD_f^2} \quad (4)$$

where D_{app} : hole diffusion coefficient; ΔOD_f : change in absorbance; t : time; d : thick of the film (660 nm in this case). The resulting data of diffusion hole coefficient of dye is shown in table 2, where the value of hole diffusion coefficient is quite small, which means, the possibility of recombination is also small. Thus, the investigated CLE-dye has a potential for the sensitizer in a DSSC, since it will have a long life time.

4. Conclusions

The cassava leave extract dye (CLE-dye) coated on the TiO₂ layer resulted a good visible light response. Spectro-electrochemical study indicated that the LUMO energy level (-4.26 eV) of CLE-dye slight above the conduction of TiO₂ (-4.3 eV), makes it suitable for the sensitizer in the DSSC system. In addition, the CLE-dye has a $K_{formation}$ value higher than its $K_{degradatio}$ and has a quite low hole diffusion coefficient (4.6×10^{-10} - 2.56×10^{-11} cm²/s), which indicated a long life time, makes it suitable for a sensitizer in a DSSC.

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