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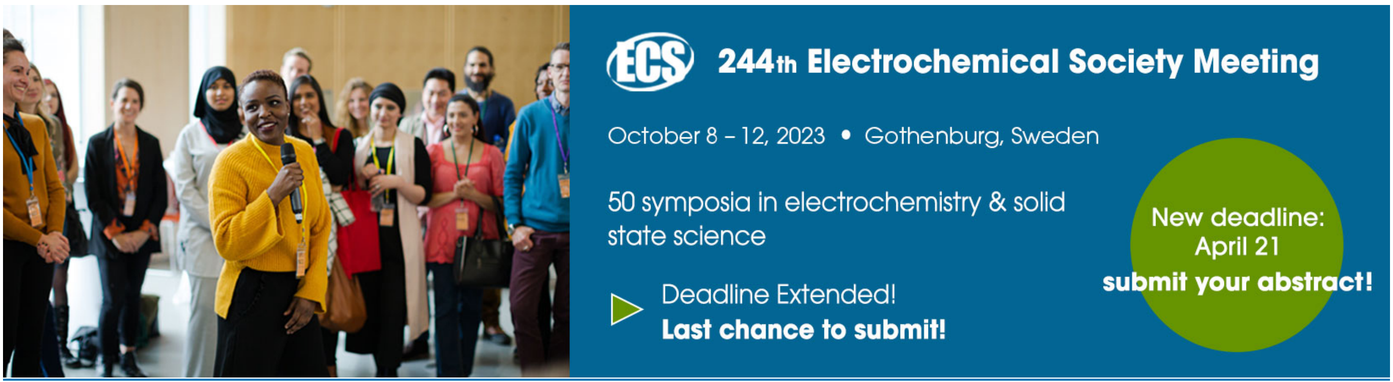

Performance of primrose willow (*Ludwigia peruviana*) as a photosensitizer in dye-sensitized solar cell (DSSC)

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Abstract. Natural dyes have been extracted from leaves (green) and flowers (yellow) of primrose willow (*Ludwigia peruviana*) and were used as a photosensitizer of dye-sensitized solar cell (DSSC). The result of this research showed that absorption peaks of leaf extract were located at 420nm and 665nm. Open-circuit voltage, short-circuit current, and power conversion efficiency of natural green materials were obtained at 580mV, 0.0067mA, and 0.52%, respectively. Bandgap, absorbance coefficient and field factor values were around 2.96eV and 1.87eV, 2.58k.m-1 and 1.63k.m-1 and 0.2196, respectively. However, absorption peak of flower extract was located at 450nm. Open-circuit voltage, short-circuit current, and power conversion efficiency of flowers were obtained at 466mV, 0.0089mA, and 0.488%, respectively. Bandgap, absorbance coefficient, and field factor values were discovered at 2.76eV, 2.41 k.m-1, 0.1722 respectively. To sum up, primrose willow has a potential as a source of DSSC photosensitizer. Its rapid growth will become a prospective source of natural dye.

1. Introduction

Primrose willow (*Ludwigia peruviana*) is usually found in wetlands and swamps, native to Mexico, Central America, the Caribbean, and South America, also naturalized overseas in the coastal districts of central New South Wales, Australia, south-eastern India, Sri Lanka, Indonesia, south-eastern USA and French Polynesia [1]. Peruvian primrose is easily found in South Sumatra, supported by the province's swamp's land (about 72.3% of the land mass). Primrose willow is regarded as an environmental weed; its tall, dense growth can reduce local biodiversity, cause more wide-ranging ecological damage, through increasing sedimentation and accumulation of organic materials.

Dye Sensitized Solar Cell (DSSC) is a semiconductor solar cell that can convert solar radiation into electricity using photo-electrochemical principle [2,3]. DSSC is composed of a transparent conductive oxide (TCO) glass substrate, a mesoporous semiconductor layer, a sensitizer, an electrolyte with a redox couple, and counter electrode [4]. Sensitizer harvests incident light, converts photons into excited electrons and injects them into semiconductor, and regenerated by redox couple in electrolyte [5]. The kind of dye used as sensitizer could affect DSSC performance [6]. Absorption spectrum and binding of the dye to the surface of TiO_2 are main parameters determining the efficiency of the cell [7].

DSSC sensitizers might be developed from metal complex, synthetic organic materials, and/or natural dyes. The use of natural dyes in DSSC is rapidly growing due to several factors, namely a large number of natural dye resources, low cost, environmental friendly, non-toxic, and ease in fabrication process [6,7]. Natural dye is obtained from extracting plant parts such as roots, leaves, flowers, fruits, trunk, seeds, and rind [8]. Sources of plant's molecule pigment used as natural dyes consist of chlorophyll, anthocyanin, carotene, flavonoid, and tannin [9].

Extracted components from leaves and flowers are potentially exploited as photosensitizer because they can facilitate current flow in DSSC system due to excited electron movement. Previous reports indicated that efficiencies of DSSC conversion prepared by chlorophyll dyes ipomoea, pomegranate, dried spinach, and shiso leaf extracts were 0.318% [10], 0.59% [11], 0.29% [12], and 0.59% [13] respectively. So far, previous studies utilizing primrose willow plant were severely limited. Because of its potential overflow, this study explored Primrose willow leaves and flowers as a source of photosensitizer in DSSC system.

2. Methodology

In this study, willow samples were collected from Ogan Ilir District wetlands, South Sumatera Province, Indonesia. Nano powder TiO_2 (Merck), ethanol PA and ITO conductive were employed during the development. Equipment included muffle furnace, digital pH meter, digital multi-meter (*Fluke, Heles UX-369C*), oven, analytical balance, transfer pipette (micropipette) *Acura* 825, and potentiometer.

Leaves and flowers were washed with distilled water, then dried in room temperature. Afterward, they were cut in small pieces and dried at 45ºC for 24 hours, before blended to obtain granular materials. Then, dried leaves and flowers were immersed in an absolute ethanol solution at ratio of 1:3 for 7 days at room temperature in a dark room. By using a vacuum filter, the solution was subsequently filtered in order to remove solid fragments, and then kept in dark bottle to avoid sunlight. Dye solution was obtained and used as a dye photosensitizer. In order to obtain its absorption spectra, we employed a Ray Leigh UV-9200 spectrophotometer at the wavelength of 400 nm – 700 nm.

Titanium dioxide powder of 0.5 g was dissolved in 2 ml ethanol and stirred until evenly mixed using a magnetic stirrer for 15 minutes. Capacitive touch screen glass substrate with dimension 2.5 cm × 2.5 cm was used as a working electrode and placed in a conductive position upward. It was glued with tape by the number of layers according to specified thickness. We glued with following specifications: 0.5 cm at right and left sides; 0.3 cm at bottom side as offset gap. Then, TiO_2 paste was deposited at working electrode by using doctor blade method followed by calcination for one hour at 450ºC temperature. After cooling to room temperature, it was then soaked in natural dye solution for 24 hours and stored in a dark place [10,14]. Subsequently, working electrode was cleaned with ethanol followed by drying. For counter electrode, glass conductive side was directed to candle fire soot until a clear carbon layer was formed; which was characterized by solid black glass [15]. Adherent carbon was removed using a cotton bud with size of 0.15 cm on right and left sides. Upper side carbon of counter electrode was also removed with a magnitude of 0.3 cm resulting in carbon area of 2.2 cm x 2.2 cm.

DSSC encapsulation comprised of a photoelectrode (a transparent conducting oxide glass which contains indium doped tin oxide/ITO, mesoporous metal oxide layer/TiO2 nanoparticles, and sensitizer/natural dye molecules), and counter electrode (a TCO glass coated with candle carbon) which were stacked up as sandwich-like cell. Both electrodes were clamped on both sides prior to dripping with electrolyte solution (I-/I3). Subsequently, double-sided offset electrodes were connected to a jumper cable and electrical performance was measured.

Natural dye band-gap which was absorbed by TiO_2 surface was calculated using equation (1) [16] where h is Planck constants, v is frequency $\left(v = \frac{c}{\lambda}\right)$, λ is wavelength and c is velocity. Numerical values of h = 6.63 x 10^{-34} Js, c = 3.0 x 10^{8} m.s^{-1}, 1 eV = 1.60 x 10^{-19} J were used to calculate photon energy E.

$$E = hv = \frac{hc}{\lambda} \quad \text{.....(1)}$$

Absorption coefficient determines how far the light can penetrate into materials at a specific wavelength before it is absorbed. The coefficient observed from each wavelength was obtained by division of absorbance by the wavelength as shown in equation (2) using Boltzmann constants K [16].

$$\alpha = \frac{4\pi k}{\lambda} \quad \text{.....(2)}$$

The power produced by DSSC was calculated using equation (3) as follows [17]:

$$P_{out} = V_{oc}.I_{sc}.FF \quad \text{.....(3)}$$

where: P_{out} is power produced by DSSC (mW), V_{oc} is open circuit voltage (mV), I_{sc} is short circuit current (mA) and FF is filled factor.

Fill factor (FF) is a ratio of voltage and current at maximum condition under open voltage and short circuit current such as shown in equation (4):

$$FF = \frac{V_{maks} \cdot I_{maks}}{V_{oc} \cdot I_{sc}} \quad \text{.....(4)}$$

The efficiency of DSSC (η) is determined by power percentage magnitude produced by DSSC against the power that reaches its surface (equation 5):

$$\eta = \left(\frac{P_{out}}{P_{in}}\right) x100\% \quad \text{.....(5)}$$

3. Results and discussion

Analysis of FTIR for chlorophyll dye, presented in Figure 1, showed some functional groups vibration as follows [18]: weak stretching vibration of –OH group from ethanol occurred at 3322.41cm^{-1}; strain vibration with a very wide ribbon of carboxylic acid-COOH occurred at a range of 3000cm^{-1}-3700cm^{-1}; symmetrical and asymmetrical strain vibration of CH_3 from alkyl alkanes happened at 2972.91cm^{-1} and 2883.34cm^{-1} which is reinforced by presence of C-H group strain vibration at 1379.63cm^{-1}, sharp stretching vibration of C=N indicating chlorophyll pigments occurred at 2359,88 cm^{-1}, strain vibration of C-O-C from ester occurred at 1087.16cm^{-1}, sharp stretching vibration of C-O from primary alcohol was visible at 1045.00cm^{-1}.

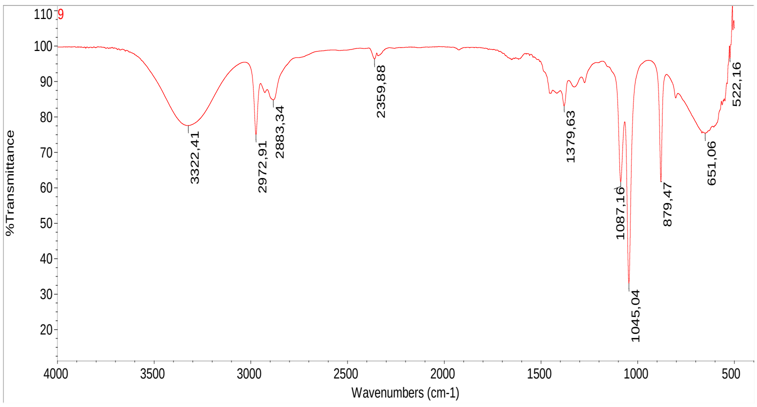
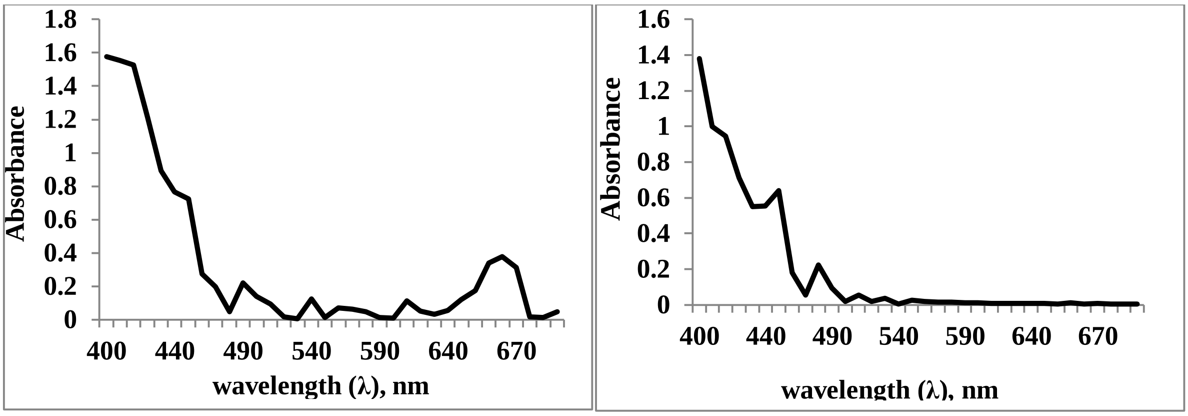


Figure 1. FTIR spectrum of chlorophyll dye from Peruvian primrose leaves.

Figure 2A depicts that peak absorbance from Primrose leaves natural dye (b-chlorophyll) was at 400nm wavelength with absorbance value 1.576, while a-chlorophyll was at 665 nm wavelength with absorbance value 0.379 [19–21]. In Figure 2B, peak absorbance from Primrose flowers natural dye (carotenoid pigment) was found at 450nm wavelength with absorbance value 0.642 nm.

The energy difference between conduction ribbon and valence ribbon is known as band gap energy, which is used to analyze DSSC performance related to solar energy absorption. Table 1 shows band-gap energy (equation 1) and absorption coefficient (α) (equation 2) of leaves and flowers natural dyes. Willow leaves had band-gap energy 1.87eV-3.11eV and absorption coefficient (α) 1.07 k.m^{-1}-1.78

$k.m^{-1}$, for peak absorbance 665 nm and 400 nm, respectively. Willow flowers yielded 2.76eV and 2.41 $k.m^{-1}$ for band-gap and absorption coefficient (α), respectively. It was found that band-gap energy was affected by the absorbed wavelength and would decrease with increasing absorbed wavelength [22].



A B

Figure 2. Absorbance of dye extract from willow leaves (A) and flowers (B).

Table 1. Band gap energy and absorption coefficient (α) of willow leaves and flowers natural dye.

Natural Dyes	Peak Absorbance (nm)	Absorption range (nm)	Band gap (eV)	Absorption coefficient (α), $k.m^{-1}$
Primrose willow leaves	400	400-700	3,11	1,78
Primrose willow leaves	665	400-700	1,87	1,07
Primrose willow flower	450	400-500	2.76	2.41

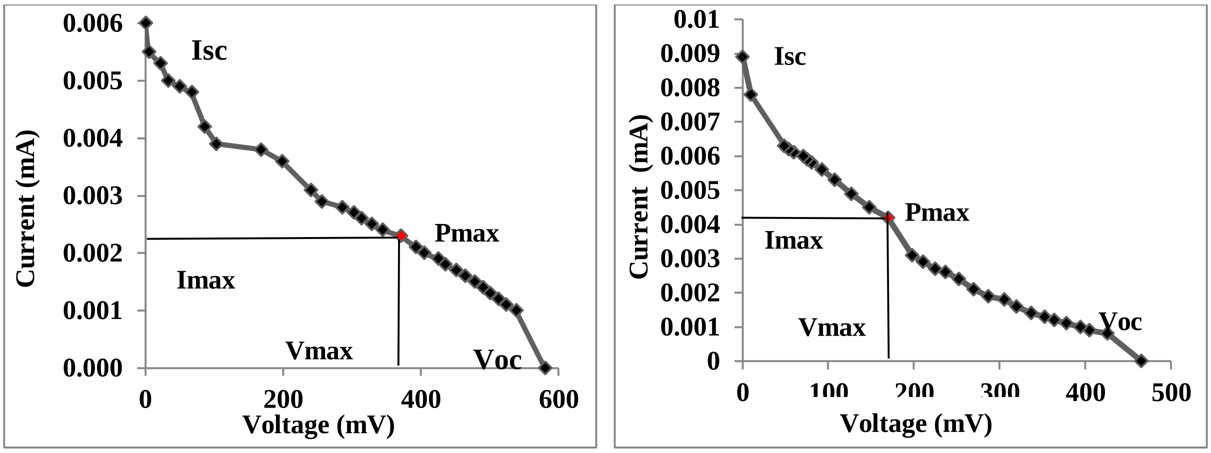
Measurement of DSSC performance for natural dyes is presented in Table 2. This research found that for willow leaves, open circuit voltage (V_{oc}), short circuit current (I_{sc}), maximum voltage (V_{max}), and maximum current (I_{max}) were 580 mV, 0.0067 mA, 371 mV and 0.0023 mA, respectively. Meanwhile, willow flowers yielded open circuit voltage, short circuit current, maximum voltage, and maximum current about 466 mV, 0.0089 mA, 170 mV and 0.0042 mA, respectively. Calculation using equation (4) showed that fill factors (FF) produced by DSSC of leaves and flowers were 0.2196 and 0.1722, respectively. Measuring DSSC efficiency using equation 5 obtained 0.5233% and 0.488% for leaves and flowers, respectively.

Table 2. Power (P_{in}), Voltage (V), current (I), fill factor (FF), and DSSC efficiency (Eff) of natural dye.

Dye sources	P_{in} (nW)	V_{oc} (mV)	I_{sc} (mA)	I_{max} (mA)	V_{max} (mV)	FF	Eff (%)
Primrose willow leaves	163,0465	580	0.0067	0.0023	371	0.2196	0.5233
Primrose willow flowers	146.3238	466	0.0089	0.0042	170	0.1722	0.4880

Efficiency is the ratio of output power (P_{out}) to input power (P_{in}) that exists in DSSC system. Because input power has a stable value, then DSSC efficiency is highly determined by output power produced by DSSC system itself. Values of output power (P_{out}), field factor (FF) and efficiency (E_f) are determined by open voltage, short circuit current, maximum voltage and maximum current which are affected by DSSC constituent factors, such as wave spectrum area of dye, dye molecular bonds at semiconductor surface [19,23], thickness of TiO_2 semiconductor layer [24], surface area of TiO_2

semiconductor layer [25], solvent, electrolyte, co-absorber, and catalyst, as well as cell active area [26].



A B

Figure 3. Characteristic curve (I-V) of DSSC from Primrose willow leaves (A) and flower (B).

Relationship between voltage (V) and current (I) from DSSC measurement in form of I-V curve is presented in Figure 3. Curvature of this relationship is affected by fill factor.

4. Conclusion

Primrose willow leaves and flowers can serve as a natural dye for DSSC system. Absorption peaks of willow leaf extract were observed at 400 nm and 665 nm, while observed flower extract absorption peaks were at 450 nm. Based on its performance, this natural dye can be used as a photosensitizer, so that rapid growth of primrose willow would become a potential source of natural dye.

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