Charge Transfer Dynamics of Highly Efficient Cyanidin-3-O-Glucoside Sensitizer for Dye-Sensitized Solar Cells

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Abstract. This paper reports the novel efficiency achievement of black rice-based natural dye-sensitized solar cells. The higher dye concentration, the longer dye extraction as well as dye immersion onto a TiO₂ film, and the co-adsorption addition are key strategies for improved-cell performance compared to the highest previous achievement. The black rice dye containing 1.38 mM cyanidin-3-O-glucoside has been extracted without purification for 3 weeks at dark condition and room temperature. The anatase TiO₂ photoanode was dipped into dye solution within 4 days. Its electrode was firmly sealed to be a cell and was filled by I₂/I₃ electrolyte using vacuum technique. As a result, the overall solar-to-energy conversion efficiency was 1.49% at AM 1.5 illumination (100 mW.cm⁻²). The voltametric analysis has reported the interfacial electronic band edges of TiO₂-Dye-Electrolyte. Furthermore, electrochemical impedance spectroscopy has shown the kinetic of interfacial electron transfer dynamics among TiO₂-dye-electrolyte. The cell has the transfer resistance (Rₜ) of 12.5 Ω, the recombination resistance (Rᵣ) of 266.8 Ω, effective electron diffusion coefficients (Dₑ) of 1.4 x 10⁻³ cm²/s, Dye-TiO₂ effective electron transfer (τₑ) of 26.6 μs, effective diffusion length (Lₑ) of 33.78 μm, chemical capacitance (Cₑ) of 12.43 μF, and electron lifetime (τₑ) of 3.32 ms.

1. Introduction

Anthocyanin dye-sensitized solar cell (DSSC) is an attractive third generation solar cell based on the anthocyanin sensitization [1,2]. The dye plays the significant role to broaden the TiO₂ adsorption in the visible spectrum [3,4]. The black rice based anthocyanin dye containing 95% cyanidin-3-O-glucoside has a high molar extinction coefficient of 26,900 M⁻¹cm⁻¹. However, the highest efficiency of black rice dye still achieves 0.35% [5]. Therefore, the work will report the novel achievement of cell efficiency following the well-established previous optimization treatment conducted by Chien and co-worker [6]. Furthermore, the charge transfer dynamic of natural dye will be proposed following the previous electrochemical impedance spectroscopy method introduced by Bisquert [7-12]. Although the previous work reporting the highest efficiency of black rice dye due to the Cu metal intermediating the electron transfer, the improved dye attachment engineered by the dye concentration improvement and the co-adsorption addition can be proposed to enhance the efficiency of black rice-based dye-sensitized solar cell.
2. Materials and Methods

Black rice obtained from market is crushed to make powders. The black rice powder is then simply extracted at the high molarity by immersing 50 g powders with 100 ml ethanol and few drop of acetic acid as co-adsorption to form pH 1.0. Afterward, the solution is kept in dark place and temperature of 25°C. The solution is sentrifugated at 4500 rpm for 15 min after 3 weeks’ extraction. Subsequently, the solution is filtered through the Whatman’s filter paper. The unpurified anthocyanin dye is now ready to be used as photosensitizer with the 1.38 mM concentration analyzed by UV-Vis spectroscopy method.

The FTO glass substrate (2 cm x 2 cm) is cleaned using the isopropyl alcohol. Subsequently, the 0.75 cm² anatase TiO₂ paste (~13nm, ~120 m²g⁻¹ BET, Solaronix) is then deposited onto the FTO glass resulting ~7.3 µm film thickness. The film is preheated at 150°C for 15 min and subsequently calcined at 450°C for 1 h. After the film is cooling down to 80°C, the film is immersed in the dye solution. The dye-adsorbed TiO₂ is being kept for 4 days. Finally, cell is is produced by sandwiching the dye absorbed-TiO₂ film and the Pt-sputtered counter electrode sealed by 50 µm Dyesol surlyn ionomer. A drop of I /I⁻ electrolyte containing TBAI (0.5M)/Iodide (0.050 M), additives of ter-butylpyridine (70 mM), lithium, and pyridine in acetonitrile solution is then inserted through a hole of FTO glass.

The unpurified dye absorption spectrum is evaluated using Hewlett Packard 8453 Agilent Technologies UV-Vis Spectrophotometer. The dyes' direct energy gaps are predicted from UV-Vis spectra using Tauc Relation [13]. The anthocyanin concentration is measured using the Eq. (1) [14].

\[
\text{Anthocyanin concentration (mM)} = A \cdot \text{DF} \cdot 10^3 / c \cdot l
\]

where A is the absorbance, DF is the dilution factor, ε is the molar extinction coefficient, and l is the light-path length. A is the absorbance calculated using the Eq. (2).

\[
A = (A_{max} - A_{700})_{pH=1} - (A_{max} - A_{700})_{pH=4.5}
\]

According to the Bredas equations [15], the highest occupied molecular orbital (HOMO) of dye is obtained from the onset plot of voltammetry oxidation potential calculated using Eq. (3)

\[
E_{HOMO} = -e(E_{onset}^{ox} + 4.4)
\]

where the oxidation potential is measured using eDAQ potentiosstat equipped with e-coder 401; scan rate 50 mV/s; software Echem Ver. 2.1; initial direction is positive with the range of -1600 mV to +1600 mV. Three electrodes consisting of a platinum counter electrode, a glassy carbon electrode, and an Ag/AgCl reference electrode in 3 M NaCl solution are utilized in the measurement with 0.1 M KNO₃ addition as the supporting electrolyte [16].

The cell is illuminated under AM 1.5 100 mW.cm⁻² measured by Keithley 2400 source meter. The electrochemical impedance spectroscopy is evaluated under dark condition with the low frequency and 0 V forward bias potential measured by Agilent Precision LCR Meter E4980A in order to characterize the dye interfacial charge transfer dynamics [9-12]. The amplitude of alternative voltage is adjusted at 1.0 mV and the range of frequency is set from 20 Hz to 2 MHz. Finally, the equivalent circuits and impedance parameters are fitted by Z-View software (v3.3e, Scribner Associate Inc.).

Figure 1 shows the model of equivalent circuit elements showing diffusion-recombination transmission line under the reflected boundary conditions fitting a highly idealized photoanode schematic at various potentials in the dark. The data of a transport resistance between dye and TiO₂ (Rₜ), a recombination resistance when electrons are commonly recaptured by triiodide ion (Rₑ), and a chemical capacitance assessing the oxidized-dye regeneration will be evaluated to identify the charge transfer dynamics among TiO₂, dye and electrolyte [9-12].
3. Results and Discussion

Figure 2 shows the UV-Vis spectra from black rice in acidic condition. The absorbance peak at 532 nm indicates that black rice dye contains the main structure of cyanidin-3-O-glucoside compared to the standard absorption of anthocyanin dye [14,17]. In accordance to our previous theoretical work, this peak occurs due to the intramolecular electron transfer from bonding orbital (σ) to antibonding (σ*) of HOMO→LUMO transition [2]. The strong dye absorption around 380 to 600 nm has successfully broadened TiO$_2$ absorption in order to result in more harvested electrons. The hydroxyl group of anthocyanin dye strongly attaches onto TiO$_2$ surface. The conjugated single-double bonds of anthocyanin will also intermediate the electron transfer through the structure during dye excitation. The acetic acid addition as co-adsorption group possessing carboxyl moiety helps the dye adsorption ability during dye attachment onto the TiO$_2$ surface [1].

![Figure 2](image)

**Figure 2.** The absorption spectra of black rice dyes with 20 times dilution factor

Figure 3 shows that the oxidation onset potential is identified from voltamogram in order to measure the highest occupied molecular orbital of black rice dyes. The black rice onset oxidation potential is observed at 0.84 V. By using the Bredas equations, the HOMO is found at -5.24 eV. Its HOMO level provides the good dye regeneration process due to the lower potential from iodide level, which is observed at -4.8 eV. During the oxidation process, the electron from iodide ion (I$^-$) will be captured by the oxidized dye to refresh the photosensitization process. On the other hand, the undesired process of electron transfer to HOMO will also come from the TiO$_2$ conduction band edge or the excited state of dye as electron recombination. Therefore, the narrower band gap between HOMO and iodide potential is required to increase the cell efficiency [1,2].

![Figure 3](image)

**Figure 3.** Voltammetry of black rice dyes at a positive oxidation potential in the dark
Table 1 shows that the gap energy (Eg) of black rice dye is 1.98 eV. The narrower gap energy of black rice dye than Eg of TiO$_2$ indicates that the dye has successfully broadened the visible spectrum absorption as much as 600 nm. By summing the gap energy to the HOMO level, the LUMO is estimated at -3.26 eV. This level is good enough to inject the electron onto TiO$_2$. The competition between electron injection and electron recombination commonly captured by triiodide ion should be evaluated in order to comprehend the schematic reaction inside the cell system.

| Dye      | $\lambda_{max}$ (nm) | M (mM) | $E_{onset}^{ox}$ (eV) | Eg (eV) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) |
|----------|-----------------------|--------|-----------------------|--------|-----------------|-----------------|
| Black Rice | 532                  | 1.38   | 0.84                  | 1.98   | -5.24           | -3.26           |

Figure 4 reports the direct gap energy plotted from the graph calculated using Tauc equation. The direct band gap represents the vertical electron transition during the dye excitation without the change of its momentum converting phonon transfer. The band gap has been measured in order to estimate the dye LUMO level.

Figure 5 illustrates the schematic reaction of black rice dye during the photosensitization process. The electrochemical impedance spectroscopy method is employed to measure the transfer kinetics of dye excited state either the electrons injected to the TiO$_2$ or electrons recaptured by triiodide ion. The data of the effective electron transfer time ($\tau_d$) through TiO$_2$ nanoparticle compared to electron lifetime ($\tau_e$) confirms that the electron has transfer 125 times faster (26.6 $\mu$s) than its recombination (3.32 ms). The narrower band gap between LUMO and conduction band (CB) of TiO$_2$ will facilitate the faster electron transfer compared to the wider band gap between LUMO and tri-iodide potential ($I_3^-$).

Figure 4. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for direct transition of black rice dyes

Figure 5. The schematic reaction of black rice based DSSC
Table 2. The cell performance of black rice dyes compared to the highest previous efficiency achievement

| Dye                          | DSSC Structure                                      | M (mM) | $J_{sc}$ (mA cm$^{-2}$) | Voc (V) | FF (%) | $\eta$ (%) | Ref.          |
|------------------------------|------------------------------------------------------|--------|--------------------------|---------|--------|------------|--------------|
| Black Rice TiO$_2$-Dye       | (3 weeks extraction-4 days immersion) – Li/I-Pt     | 1.92   | 4.058                    | 0.51    | 0.73   | 1.49       | Our work     |
| Black Rice Cu:TiO$_2$-Dye    | (30 min extraction-24 h immersion) – Li/I-Pt        | ~0.38  | 0.125                    | 0.12    | 0.35   | 0.35       | [5]          |

Figure 6 shows the photochemical properties of black rice-based dye-sensitized solar cell. The photocurrent density, open circuit voltage, and overall cell efficiency are observed at 4.058 mA cm$^{-2}$, 0.51 V, and 1.49%, respectively. To best of our knowledge, this efficiency is the novel highest performance of black rice cell. Compared to the previous report, it can be analyzed that the higher dye concentration, the longer dye extraction time as well as immersion time are the key strategies for the improved performance of natural dye-sensitized solar cell. However, the dye aggregation during the attachment onto the semiconductor should be considered in decreasing cell performance. Therefore, the TiO$_2$ nanoparticles ($\sim$120 m$^2$ g$^{-1}$) with the higher porosity as well as the wider surface area have to be prepared to facilitate more attached-dyes. The data of cell performance is given in table 2.

![Figure 6. The I-V curve of black rice-based dye sensitized solar cell](image)

Figure 7 shows the device impedance characteristic using black rice dyes. A low frequency semicircle (A large arc) is assigned to the dye recombination resistance ($R_r$) coupled to $C_{\mu}$ representing the total electrolyte-solid interface capacitance. A high frequency semicircle (small arc) is assigned to the charge transport resistance ($R_t$) through TiO$_2$ nanoparticles. At low frequency and 0 V bias potential, a large arc are given by chemical capacitance of the back layer and the charge recombination dominates the impedance [11,12]. Therefore, the experiment is set as a diffusion-recombination transmission line under reflecting boundary conditions. In this condition, electrons, which are injected onto TiO$_2$ porous semiconductor diffuse through the outer edge of the film. The data of table 3 shows that the $R_t$ is shorter than $R_r$. The wider large semicircle resistance ($R_r$), the less electron recombination occurs. Inversely, the narrower small semicircle resistance ($R_t$), the faster electron injected to the TiO$_2$ surface [10-12].

Table 3. EIS parameters obtained by fitting the Nyquist plots for black rice based DSSC

| Dye                     | $R_t$ (Ω) | $R_r$ (Ω) | $C_{\mu}$ (µF) | $D_n$ (cm$^2$/s) | $L_n$ (µm) | $\tau_d$ (µs) | $\tau_n$ (ms) | $\eta$ (%) | Ref.          |
|-------------------------|-----------|-----------|----------------|------------------|-------------|---------------|---------------|------------|--------------|
| Black Rice              | 12.5      | 266.8     | 12.43          | 1.40 x $10^{-3}$ | 33.78       | 26.6          | 3.32          | 1.49       | Our work     |
| Cu-modified Black Rice  | 50.0      | 200.0     | -              | -                | -           | -             | -             | 0.35       | [5]          |
Therefore, the smaller R_t and higher R_r of our work indicate that the cell performance is better than previous report. The diffusion length of dye is 4.6 times longer (33.78 μm) than the TiO_2 film thickness (7.3 μm). The longer diffusion length, the more ways electrons moving through the TiO_2 nanoparticles.

4. Conclusions
The charge transfer dynamics of black rice based anthocyanin dye-sensitized solar cell (DSSC) have been successfully analyzed using the spectroscopy method. Several treatments supporting the improved performance of cell including dye extraction, dye immersion, and dye co-adsorption have been proposed in order to achieve the novel efficiency of black rice cell.

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