Photoelectric Characteristics of Natural Pigments Self-Assembly Fabricated on TiO₂/FTO Substrate

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Natural pigment can act as an inexpensive and biologically-friendly dye, which is fabricated on a TiO₂/FTO substrate. Natural pigments promote the efficiency of the photoelectric conversion in water-based DSSC with the aqueous electrolyte of the Ce⁴⁺/³⁻ system. The open-circuit voltage (Vₜ) of natural pigment in water-based DSSC is 0.640 V. The short-circuit current (Iₛ) of natural pigment in water-based DSSC is 0.658 mA/cm². The efficiency of the photoelectric conversion in water-based DSSC of natural pigment is up to 0.131%. The natural pigments in DSSC are potentially applicable to turning solar energy into environmentally-friendly energy.

Keywords: Natural Pigment, Water-Based DSSC, Chlorophyll.

1. INTRODUCTION

Many studies have focused on sensitizer pigment, since pigment plays a key role in harvesting sunlight and transforming solar energy into electric energy.¹ The complex has an intense charge-transfer absorption in the whole visible range, a long excitation lifetime, and highly efficient metal-to-ligand charge transfer.

Among several kinds of dye-sensitized solar cells (DSSC), the water-based dye-sensitized solar cell (DSSC) is a good candidate for use in nontoxic and biologically-friendly solar energy devices. The development of an environmentally-friendly method for preparation of advanced DSSC is thus desirable. Except for the early experiments of Grätzel et al.,² little research has been conducted on the construction of water-based DSSCs because aqueous electrolytes generally yield very low conversion efficiencies (<1%) compared with organic electrolytes. Takahashi et al.³ yielded high conversion efficiency for water-based DSSC with water or ethanol as an electrolyte when using N719 as a dye. When light absorption takes place, electron injection from the excited pigment to the conduction band of the semiconductor may occur on an ultrafast time scale. The development of natural pigments on the electrode is one cost-effective way to fabricate water-based DSSC, but most work on this has reported low efficiency.

In this study, natural pigments loaded on the TiO₂ photoelectrode of a water-based DSSC were fabricated. The efficiency of photoelectric conversion was measured, with chlorophyll acting as an inexpensive and biologically-friendly photosensitizer. The present work further extends our investigations involving natural pigments as cost-free photosensitizers and reports the successful use of extracts of Bontainvillea brasiliensis Rauh., Garciaria suaveolenta, Ficus Reusa Lian., and Rheo spathacea (Sw.) Stennes, in water-based DSSC. These four natural pigments are all widely disseminated over the tropic region. The aqueous electrolyte of the Ce⁴⁺/³⁻ system was also first reported in a green water-based DSSC, which has a lower potential than the I₃⁻/I⁻ system⁴ to improve the photoelectric conversion efficiency. Due to the simple preparation technique, wide availability, and low cost, natural pigments are promising alternative sensitzers for water-based DSSC, potentially applicable for use in environmentally-friendly solar energy devices.

2. EXPERIMENTAL DETAILS

2.1. Preparation of the Photoelectrodes of Water-Based DSSC

12 g of P-25 TiO₂ (Degussa, Japan) powders in 15 ml of DI-water mixed with 0.2 ml of Triton-X 100 (Sigma Chemical Co., USA) and 0.4 ml of Acetylated (99.5%, Fluka, Germany) was vibrated ultrasonically for 3 days.
Then, 0.5 ml of TiO$_2$ solution was spin-coated on a fluorine-doped tin oxide (FTO glass, 8 Ω/cm$^2$, made by Solaronix Sa, Swiss) substrate (2 × 2 cm$^2$) as the anodic photoelectrode of the water-based DSSC with 1000 rad/sec for 20 seconds, and then sintered at 500 °C for 10 h. The cathodic photoelectrode of the water-based DSSC was prepared by sputtering silver on the indium-doped tin oxide (ITO) glass substrate.

2.2. Preparation of Pigment Sensitizers and Adsorption of Pigments on the Photoelectrode of a Water-Based DSSC

A variety of natural pigment sensitizers were adopted in this study. The dye in this investigation was chlorophyll (Tokyo Chemical Industry Co., Japan) mixed in alcohol solution (17.5 μM). The natural pigment sensitizers were also prepared in alcohol. The alcohol extracts of Bongainvillea brasiliensis Raesch., Garcinia subelliptica., Ficus Reusa Linn., and Rhodeo spathacea (Sw.) Stearn. were obtained according to the following steps: The clean fresh samples of Bongainvillea brasiliensis Raesch., Garcinia subelliptica., Ficus Reusa Linn., Rhodeo spathacea (Sw.) Stearn. and kelp were dried at 40 °C in a vacuum drying oven; after crushed into a fraction let, the raw materials of 0.5 g/100 ml were put into a 95 wt% ethanol solution and kept in ambient temperature without exposure to direct sunlight for several weeks to adequately extract natural pigment in the solution; solid residues were then filtrated out and the natural pigment solutions were concentrated to one quarter with a rotatory evaporator at 40 °C; After that, the natural pigment sensitizer alcoholic solutions (17.5 μM) were prepared.

2.3. Assembly of Water-Based DSSC

The anodic photoelectrode of the water-based DSSC loaded with an Au NPs layer was immersed in various pigment sensitizer alcohol solutions for two days. The electrolyte was a water-based solution (35% ethanol and 65% water), including 0.1 M Ce(NO$_3$)$_3$/0.05 M Ce(NO$_3$)$_4$ (99%, ICN Biomedicals, Inc., USA). The assembly of water-based DSSC is schematically depicted in Figure 1.

2.4. Instruments and Measurements

The absorption spectra of pigments were determined using the UV-VIS spectrum (Hitachi U-2001 spectrophotometer, Japan). The samples were directly injected into a quartz tube for UV-vis analysis. The photoluminescence (PL) spectra of the samples were analyzed by a Fluorescence Spectrophotometer (Hitachi F-4500 FL Spectrophotometer, Japan). The photo-current conversion efficiency was measured in the dark and under simulated solar irradiation of 1 sun intensity (AM 1.5G). The fill factor was calculated at 100 mW/cm$^2$ by dividing the maximum product of current and voltage from the illumination.

3. RESULTS AND DISCUSSION

3.1. Absorption Spectra of Various Kinds of Natural Pigment in the Water-Based DSSC

During the stage of spectroscopic research, the absorption spectra of pigments were always monitored. They provided information on the probability of the absorption transition between the pigment ground and excited states and the energy range of solar energy absorbed by the pigment species. Figure 2 shows the UV-VIS absorption spectra of chlorophyll and natural pigments, (Bongainvillea brasiliensis Raesch., Garcinia subelliptica., Ficus Reusa Linn., and Rhodeo spathacea (Sw.) Stearn.), with kelp extracts in alcohol. Chlorophyll absorbs most strongly in the blue and red but poorly in the green portions of the absorption spectrum, hence the green color of chlorophyll-containing tissues, such as plant leaves. The absorption peaks of chlorophyll α are at 665 nm and 430 nm. The shift of the absorption bands is usually due to the delocalization of π electrons in the conjugated molecular system and/or to the aggregation of pigments. This can also be explained by assuming the energy-transfer process where excitation energy is produced through the near-field dipole–dipole interaction (Förster transfer process).
The absorption spectra directly reflect the optical transition probability.

Figure 2 shows the absorption spectra of *Bongainvillea brasiliensis* Rauesch., *Garcinia subelliptica*, *Ficus Reusa Linn.*, and *Rhoeo spathacea* (Sw.) Stearn. It can be seen that they have the same absorbent peak, except for *Bongainvillea brasiliensis* Rauesch., with a small variation of absorbance. The other three pigments also have the characteristic peaks of chlorophyll and non-chlorophyll. The absorption peaks of chlorophyll and the natural pigments are centered at the wavelengths of about 665 and 670 nm, respectively. The absorption peak of chlorophyll exhibits a red shift (i.e., bathochromic shift) compared with that of the natural pigment. Chlorophyll is a well-known compound for photosynthesis, whose molecule has a porphyrin skeleton similar to heme, incorporating Mg$^{2+}$ with a closed shell. The chlorophyll molecules tend to aggregate in polar solvents, and upon aggregation, both absorption and PL spectra exhibit bathochromic shift.

### 3.2. Photoelectron Emission of Various Kinds of the Commercial and Natural Pigment in a Water-Based DSSC

Photoluminescence is a process in which a chemical compound absorbs a photon (electromagnetic radiation), thus transitioning to a higher electronic energy state, then radiating a photon back out, and returning to a lower energy state. Ultimately, available chemical energy states and allowed transitions between states (and therefore wavelengths of light preferentially absorbed and emitted) are determined by the rules of quantum mechanics. In this respect, there may be a correlation between the phenomenon of photoelectron emission and the photoelectric property in a water-based DSSC system.

Figure 3 shows the emission intensity of chlorophyll and four kinds of natural pigments (*Bongainvillea brasiliensis* Rauesch., *Garcinia subelliptica*, *Ficus Reusa Linn.*, and *Rhoeo spathacea* (Sw.) Stearn.), with kelp extracts in alcohol. Although chlorophyll has bright fluorescence at 673 nm, it is not easily observed compared with the emission intensity of the natural pigment in Figure 3.

Figure 3 shows the emission intensity of *Bongainvillea brasiliensis* Rauesch., *Garcinia subelliptica*, *Ficus Reusa Linn.*, and *Rhoeo spathacea* (Sw.) Stearn. The same trend of emission intensity centered at 450 and 670 nm occurs. The emission intensity of chlorophyll exhibits a little red shift and a smaller photoluminescence compared with those of the natural pigments. The chlorophyll molecules may tend to aggregate in polar solvents. Upon aggregation, both absorption and PL spectra exhibit bathochromic shift.

### 3.3. Photoelectric Property in Water-Based DSSC Sensitized by Various Kinds of Commercial and Natural Pigment

In DSSC, the current–voltage curve of a solar cell yields important operational parameters, among which are the short-circuit current $I_{sc}$, the open-circuit voltage $V_{oc}$, the current, $I_{mp}$, and voltage, $V_{mp}$, at the maximum power point, $P_{max}$. The fill factor (ff) is calculated as

$$ff = \frac{P_{max}}{V_{oc}I_{mp}} = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}}$$

(1)

The solar conversion efficiency ($\eta$) is given by

$$\eta = \frac{P_{max}}{P_{i}} = \frac{ff \cdot V_{oc} \cdot J_{sc}}{P_{i}}$$

(2)

where $P_{i}$ is the input solar irradiance (e.g., 100 mW/cm$^2$).

The current–voltage curves obtained with the water-based DSSC sensitized by chlorophyll and natural pigments (*Bongainvillea brasiliensis* Rauesch., *Garcinia subelliptica*, *Ficus Reusa Linn.*, and *Rhoeo spathacea* (Sw.) Stearn.) are shown in Table I. Photoelectric conversion efficiencies of *Bongainvillea brasiliensis* Rauesch., *Garcinia subelliptica*, *Ficus Reusa Linn.*, and *Rhoeo spathacea* (Sw.) Stearn. were 0.0626%, 0.0602%, 0.0787%, and 0.131%, respectively. Photoelectric conversion efficiency of *Rhoeo spathacea* (Sw.) Stearn. is the highest. The results show that the natural pigments, adsorbed onto the TiO$_2$ photoelectrode, absorb visible light and promote electron transfer across the pigment/semiconductor interface. Conversion of visible light into electricity by sensitization of TiO$_2$ with readily obtained natural pigments is an encouraging alternative to be further developed. Since the carbonyl and hydroxyl groups were present on anthocyanin molecules, they can be bound with the surface of TiO$_2$ film, which is capable of chelating to the Ti(III) sites of the TiO$_2$ surface and thus favor the photoelectric conversion effect.

The other reason for the decrease in the photocurrent sensitized by the pigments is the high thermal relationship of these pigments when they are aggregated or mixed.
Table I. Photoelectrochemical data obtained with the water-based DSSC sensitized by chlorophyll and natural dyes in Ce$^{3+}$/Ce$^{4+}$ system irradiating 100 mW/cm$^2$.

<table>
<thead>
<tr>
<th>J–V curve</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>f.f. (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorophyll</td>
<td>0.520</td>
<td>0.918</td>
<td>25.10</td>
<td>0.1200</td>
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<tr>
<td>[Diagram]</td>
<td></td>
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<tr>
<td>Garcinia subelliptica.</td>
<td>0.498</td>
<td>0.253</td>
<td>47.83</td>
<td>0.0602</td>
</tr>
<tr>
<td>[Diagram]</td>
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</tr>
<tr>
<td>Rhoeo spathacea (Sw.) Steam.</td>
<td>0.640</td>
<td>0.658</td>
<td>33.04</td>
<td>0.1310</td>
</tr>
<tr>
<td>[Diagram]</td>
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<tr>
<td>Bongainvillea brasiliensis Rausch.</td>
<td>0.371</td>
<td>0.494</td>
<td>50.90</td>
<td>0.0626</td>
</tr>
<tr>
<td>[Diagram]</td>
<td></td>
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<tr>
<td>Ficus Reusa Linn.</td>
<td>0.313</td>
<td>0.764</td>
<td>32.89</td>
<td>0.0787</td>
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<td>[Diagram]</td>
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together. Creation of aggregated pigment species leads to a decrease in the photoconversion process, since in aggregated pigments, absorbed energy is mostly changed into heat, and thus lost in the thermal process rather than used for charge separation.

4. CONCLUSIONS

Natural pigments in water-based DSSC with the aqueous electrolyte of Ce$^{4+/3}$ system can act as low-cost and environmental-friendly natural pigments, which present good light harvesting and good photoelectric properties on a TiO$_2$ photoelectrode. The four natural sensitizers applied in water-based DSSC are thus suitable for the improvement of efficiency in environmentally-friendly energy devices.

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References and Notes


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