

## Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells

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Received 10 April 2006; received in revised form 27 July 2006; accepted 2 August 2006

Available online 26 September 2006

Communicated by: Associate Editor Sam-Shajing Sun

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### Abstract

The dye-sensitized solar cells (DSCs) were assembled by using natural carotenoids, crocetin (8,8'-diapocarotenedioic acid) and crocin (crocetin-di-gentiobioside), as sensitizers and their photoelectrochemical properties were investigated taking a presence or absence of carboxylic group in the dye molecule into consideration. In these carotenoids, crocetin that has carboxylic groups in the molecule can attach effectively to the surface of TiO<sub>2</sub> film so that it performed the best photosensitized effect resulting in the short-circuit photocurrent with 2.84 mA under irradiation of 1.0 cm<sup>2</sup>. On the other hand, crocin that has no carboxylic group in the molecule showed lower photoelectrochemical performance because of its lower affinity to the surface of TiO<sub>2</sub> film. These results indicate that it is possible to apply carotenoid as sensitizers for DSCs at the presence of effective function groups.

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*Keywords:* Dye-sensitized solar cells; Natural dyes; Carotenoid

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### 1. Introduction

Dye-sensitized solar cells (DSCs) are unique and attractive devices for the conversion of solar energy into electricity based on sensitization of wide bandgap semiconductors. In DSCs, nanoporous semiconductor films have a large surface area that adsorbs large amount of dyes (O'Regan and Grätzel, 1991). The adsorbed dye absorbs visible light and injects electrons into the TiO<sub>2</sub> conduction band. Since dye plays an important role in absorbing visible light and transferring photon energy into electricity, much attention has been paid to survey the effective sensitizer dyes. It is necessary for sensitizer dyes to have enough energy levels to transfer electrons and anchor group(s) to have affinity for semiconductors. One of the most efficient sensitizers are synthetic dyes, such as ruthenium(II) polypyridyl com-

plexes with carboxylated ligands, since these compounds present intense and wide-range absorption of visible light as well as suitable ground- and excited-state energy levels with respect to TiO<sub>2</sub> conduction band energy and to the redox potential of electron donor I<sup>-</sup> (Nazeeruddin et al., 1993; Pechy et al., 1995; Nazeeruddin et al., 2001).

On the other hand, many studies have also concentrated on exploration into natural dyes, such as cyanin (Sirimanne et al., 2006), anthocyanin (Hao et al., 2006; Kumara et al., 2006), tannin (Espinosa et al., 2005), chlorophyll (Hao et al., 2006; Kumara et al., 2006) and so on (Garcia et al., 2003) for sensitizers. Although these natural dyes often work poorly in DSCs, these are expected as low cost and prepared easily comparing to ruthenium(II) polypyridyl complexes.

Gardenia fruit is widely used in Asian countries as a natural colorant in food industries. It is known that gardenia's yellow derives from yellow of two carotenoids, such as crocetin and crocin. Carotenoids are usually responsible for petal colors in yellow-to-orange (Kishimoto et al.,

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## Nomenclature

$\eta$	energy conversion efficiency	FF	fill factor
$I_{SC}$	short-circuit photocurrent (A/cm <sup>2</sup> )	AM	air mass
$I$	current (A)	M	mole concentration (mol/l)
$V_{OC}$	open-circuit voltage (V)	$\epsilon$	molar extinction coefficient (M <sup>-1</sup> cm <sup>-1</sup> )
$V$	voltage (V)		

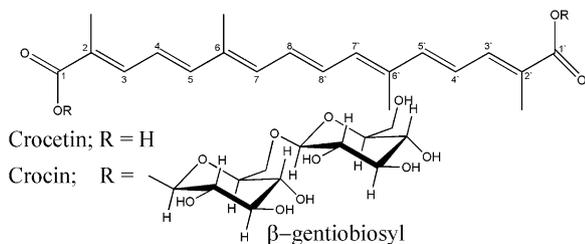


Fig. 1. The molecular structures of crocetin and crocin.

2005). Crocetin and crocin are similar with the same carotenoid frame, but these are different in structure with or without free carboxylic groups (Fig. 1). In this study, crocetin and crocin were employed as natural sensitizers in DSCs and the photoelectrochemical performances of these cells were investigated.

## 2. Experimental

### 2.1. Materials and chemicals

Crocin, crocetin-di-gentiobioside, from gardenia fruit was bought from Tokyo Kasei Industry. Unless otherwise indicated, all chemical reagents were the guaranteed reagent grade.

### 2.2. Preparation crocetin

Crocetin, 8,8'-diapocarotenedioic acid, was prepared by hydrolyzing crocin with HCl. Four grams of crocin were hydrolyzed with 1 M HCl for 3 h at 95 °C. The solution was cooled down to room temperature and centrifuged at 5000×g for 10 min. To remove the gentiobiose and unreacted crocin, the supernatant was separated and the precipitate was washed by water thoroughly. Finally, the precipitate was suspended with water and lyophilized. Crocetin (0.5 g) was obtained as a brick red powder. The purity of this crocetin was confirmed by comparing it with standard crocetin (Wako Pure Chemical Industry) by using a HPLC (Waters 2697 Alliance) equipped with a semi-micro column (Inertsil C18, 1.5 mm i.d. × 150 mm, GL Science), a 996-photodiode array detector (Waters). The flow rate was 0.1 ml/min and the elution was first with water for

5 min and second with a linear gradient ranging to 100% methanol for 20 min.

### 2.3. Preparation of TiO<sub>2</sub> electrode

TiO<sub>2</sub> porous film electrode was manufactured by the modified method of Murayama and Mori (2006). As the precursor paste, 4.0 g TiO<sub>2</sub> nano-powder (size 25 nm, p25, Degussa AG) were mixed with 0.45 ml of nitric acid and 10 ml of water, and then the mixture was ground for 200 min. Finally, several drops of Triton X-100 (Wako Pure Chemical Industry) were added to ease adhesion of TiO<sub>2</sub> particles to an F:SnO<sub>2</sub> conductive glass substrate layer (FTO, sheet resistance 12 Ω/sq., Asahi Glass Co.). Area ≈1.0 cm<sup>2</sup> of TiO<sub>2</sub> paste was spread on a FTO by using a glass rod and then calcinated at 450 °C for 30 min. When cooled to 130 °C, the TiO<sub>2</sub> film was immersed in the 3.0 mM dye-pyridine solution for 12 h at room temperature with gently shaking. After this immersion, the TiO<sub>2</sub> film was washed with pyridine and allowed to air-dry. As a counter electrode, Pt sputtered ITO conductive glass was employed. Between the electrodes, a 50 μm space was retained using a pair of PTFE film spacer and electrolyte was injected into the space. The electrolyte composition was 0.03 M I<sub>2</sub> and 0.5 M KI in ethylene carbonate/acetonitrile (80:20, v/v).

### 2.4. Optical and electrical measurements

Absorption spectra of dyes in pyridine and on TiO<sub>2</sub> films were measured by using a V-580 System spectrophotometer (Jasco) and a MPC-3100 UV/vis spectrophotometer (Shimadzu Co.), respectively.

The current–voltage ( $I$ – $V$ ) curve was obtained using a source measure unit (Model 2400, Keithley Instruments) under irradiation (0.1 W/cm<sup>2</sup>:AM 1.5) by a solar simulator (Module X, Ushio). The  $I$ – $V$  curve was used to calculate the short-circuit photocurrent ( $I_{SC}$ ), the open-circuit voltage ( $V_{OC}$ ), the fill factor (FF), and the energy conversion efficiency ( $\eta$ ) of DSCs.

### 2.5. Adsorption amount of dye on TiO<sub>2</sub>

The adsorption amount of dye on TiO<sub>2</sub> film was evaluated from the concentration of dye in 0.1 M KOH

desorbed solution using a V-580 System spectrophotometer (Jasco).

### 3. Results and discussion

#### 3.1. UV/vis absorption spectra of crocetin and crocin

Fig. 2 shows the UV/vis absorption spectra of crocetin (a) and crocin (b) in pyridine. Spectral figures for crocetin and crocin are similar with having three absorption peaks based on the same carotenoid frame. The absorption peaks were 414, 436, and 463 nm for crocetin, and 421, 442, and 471 nm for crocin, and then crocetin displays strong absorption in the visible region with high molar extinction coefficient ( $\epsilon$ ) up to  $3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 436 nm while that of crocin was low with  $6.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 442 nm. These absorption peaks of crocetin are slightly blue-shifted compared to those of crocin. Binding of gentiobiosides to crocetin molecule would be enhanced red-shift in visible region. On the other hand, crocetin is easily dissolved in pyridine although the solubility of crocin is rather low. So the effect can be explained by interactions between the dye molecule and the solvent to stabilize the ground states. Comparing to crocin, the ground state of ionic crocetin have much more polar character than that of the excited states, so the alkalinity of pyridine is beneficial to lower the energy of the ground states relative to the excited states of the dye molecules (Zhao et al., 1999).

Fig. 3 shows the absorption spectra of crocetin (A) and crocin (B) in pyridine (a) and onto  $\text{TiO}_2$  film (b). Each of three absorption peaks of crocetin and crocin seen in pyridine (Fig. 3A-a and B-a) were expanded and integrated, and gave one single large-broad peak (Fig. 3A-b and B-b). Further, the absorption range for crocetin on  $\text{TiO}_2$  film is obviously expanding toward the red comparing to that of in pyridine (Fig. 3A), which is in favor of photoelectric conversion effect (Ma et al., 2002). Although there are

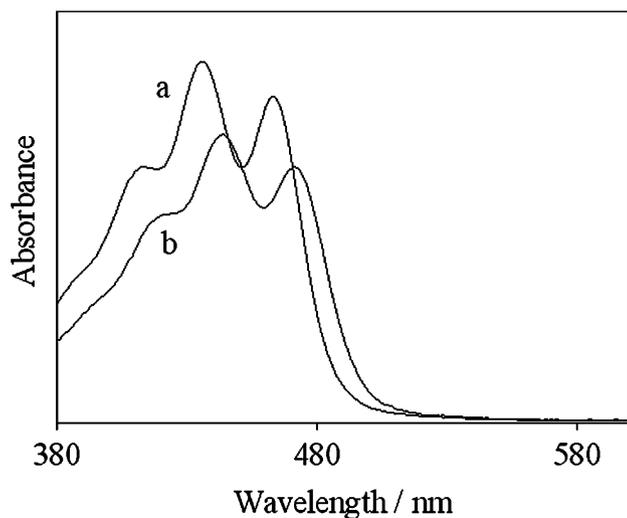


Fig. 2. The absorption spectra of crocetin (a) and crocin (b) in pyridine solution.

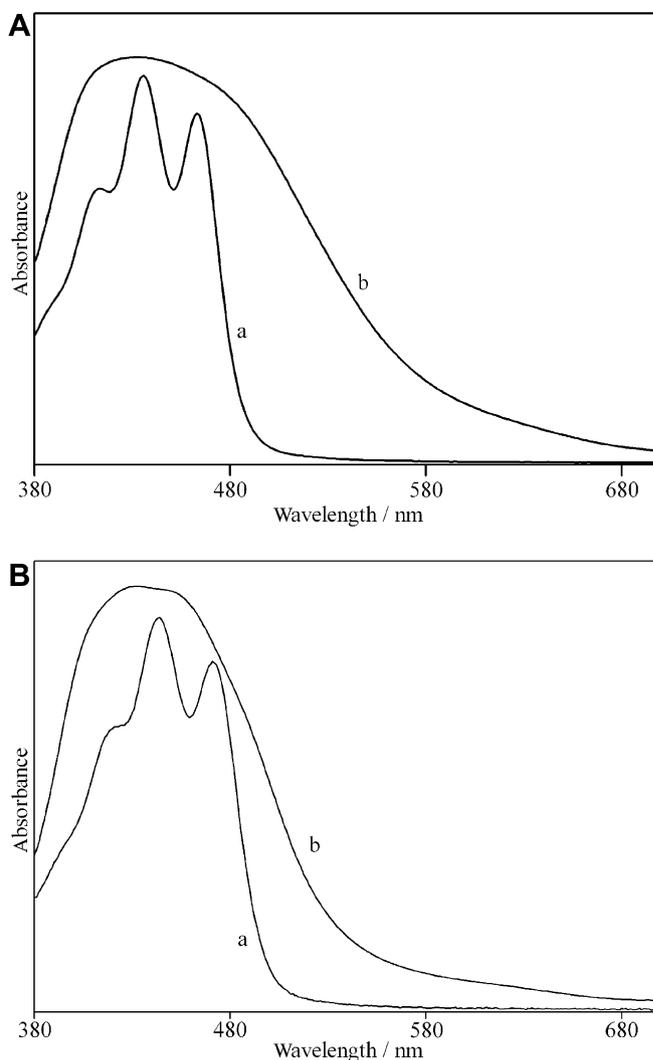


Fig. 3. (A) The absorption spectra for crocetin in pyridine (a) and coated on  $\text{TiO}_2$  film (b). (B) The absorption spectra for crocin in pyridine (a) and coated on  $\text{TiO}_2$  (b).

slightly-blue-shifted vibronic absorptions (West and Geddes, 1964) in the spectra of two carotenoids (Fig. 3A-b and B-b), any distinct blue-shifted peaks which attribute to the aggregate formation of dyes and/or the disarranging of dyes on the surface of  $\text{TiO}_2$  film (Ehret et al., 2000) are not detected. The large broadening of the spectrum of crocetin onto  $\text{TiO}_2$  film (Fig. 3A-b) is implying that a strong interaction has occurred between crocetin and the surface of  $\text{TiO}_2$  film and the delocalized  $\pi^*$  state of the crocetin injects effectively into the  $\text{TiO}_2$  conduction band (Ma et al., 2002), in the same manner as the ruthenium(II) complex (Nazeeruddin et al., 1993). These also imply that terminal carboxylic groups of crocetin can achieve a formation of covalent bond with metallic site in solid  $\text{TiO}_2$  (Fig. 4). On the other hand, a rather small broadening spectrum data was observed for crocin on  $\text{TiO}_2$  film (Fig. 3B-b), which indicates the occurrence of a weak interaction between crocin and the surface of  $\text{TiO}_2$  film, dependent on an electrostatic force of attraction.

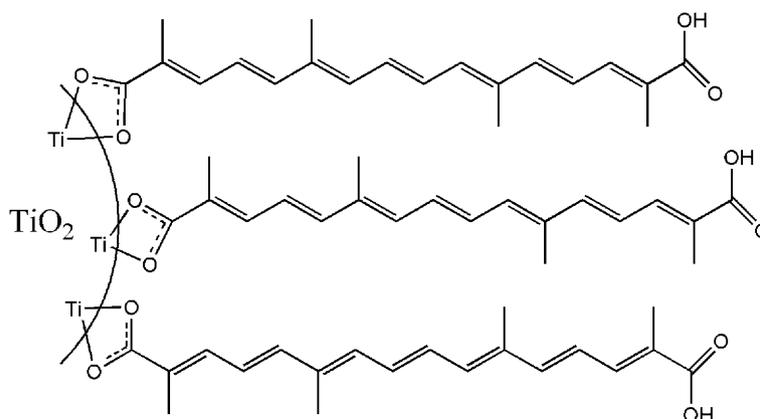


Fig. 4. Possible mechanism of the binding between crocetin and  $\text{TiO}_2$  surface.

### 3.2. Photoelectrochemical properties of DSCs sensitized with crocetin and crocin

The photovoltaic tests of DSCs using crocetin and crocin as sensitizers were performed by measuring the  $I$ - $V$  character curve under irradiation of  $1.0 \text{ cm}^2$  dye-sensitized solar cells. Fig. 5 shows typical results of the  $I$ - $V$  curves of DSCs sensitized with crocetin (a) and crocin (b). The photoelectrochemical parameters evaluated from five independent experiments are summarized in Table 1. A high  $I_{\text{SC}}$  (2.84 mA) was obtained from the DSCs sensitized with crocetin, which was more than six times high comparing

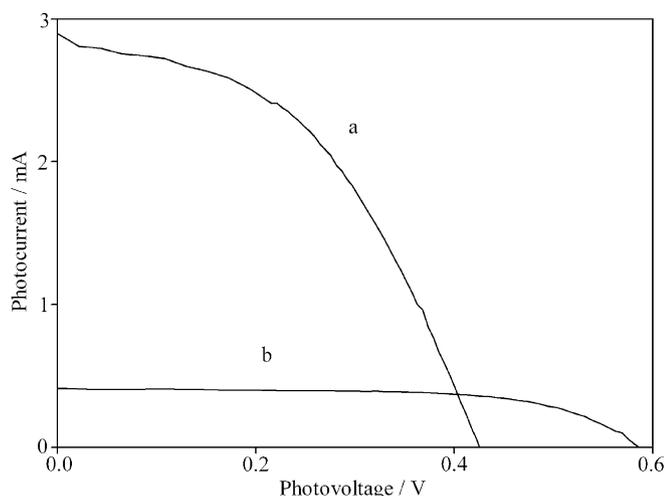


Fig. 5.  $I$ - $V$  characteristics of DSCs sensitized with crocetin (a) and crocin (b).

Table 1  
Photoelectrochemical parameters of DSCs sensitized with crocetin and crocin at the working area of  $1.0 \text{ cm}^2$

Dye	$I_{\text{SC}}$ (mA/cm <sup>2</sup> )	$V_{\text{OC}}$ (V)	FF	$\eta$ (%)
Crocetin	2.84	0.43	0.46	0.56
Crocin	0.45	0.58	0.60	0.16

to that of crocin (0.45 mA). To the surface of  $\text{TiO}_2$  porous films, the  $I_{\text{SC}}$  greatly depends on the binding affinity. The amounts of crocetin and crocin molecules adsorbed on the surface of  $\text{TiO}_2$  films were determined by spectroscopic measurement of the dyes desorbed from the surface of  $\text{TiO}_2$  film in a KOH (0.1 M) resulting in  $20.0 \times 10^{-8} \text{ mol/cm}^2$  for crocetin and  $9.2 \times 10^{-8} \text{ mol/cm}^2$  for crocin, respectively. These results indicate that the amounts of adsorbed dyes are remarkably different, although the same thickness of the  $\text{TiO}_2$  film and the same concentration of the dye for immersing were used. These differences are considered to be the difference in the adsorption state of the dyes on the  $\text{TiO}_2$  film, i.e., chemical adsorption and physical adsorption. Thus, this low amount of adsorbed crocin ascribes to weakly bond between their dye molecule and the surface of  $\text{TiO}_2$  film.

A low  $V_{\text{OC}}$  was observed from the DSCs sensitized with crocetin, which was 0.43 V and was  $\approx 74\%$  as high as that of crocin. By binding with di-gentiobioside, higher conduction band would be appeared in crocin molecule and it favored higher open-circuit voltage as observed.

It can be seen from the data presented from in Table 1, crocetin exhibits the best photoelectrochemical performance among two carotenoids; the photoelectric conversion efficiency ( $\eta$ ) of DSCs sensitized with crocetin (0.56%) is three times or more as high as that of crocin (0.16%). The high photoelectric conversion data for crocetin are equivalent or superior to those obtained with natural dyes (Sirimanne et al., 2006; Hao et al., 2006; Garcia et al., 2003), which indicates that crocetin possesses the excellent photoconductivity exceeding many known dye-stuff obtained from natural resources.

Up to now, carotenoids have been not paid attention as sensitizers for the DSCs for two reasons. First, most carotenoid species do not have effective functional group to bond with  $-\text{OH}$  of  $\text{TiO}_2$ . Secondly, strong steric hindrance of long chain alkane of carotenoid species prevents the dye molecules from arraying on  $\text{TiO}_2$  film efficiently. Due to the two reasons, carotenoid species are not nearly adsorbed on  $\text{TiO}_2$  film and sensitizing effect on  $\text{TiO}_2$  film tends to be

low. However, crocetin, that is, a carotenoid with carboxylic groups in the molecule was exhibited a high binding ability to the surface of TiO<sub>2</sub> semiconductor film and its photoelectrochemical performance was superior to crocin. In this study, a potential of carotenoid species as a sensitizer for DSCs was demonstrated by using crocetin. This evidence is expanding the interest in both photochemistry and carotenoid chemistry; it will change the negative view of carotenoids and promote it to a potential new sensitizer.

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