

Dye-sensitized solar cells using 20 natural dyes as sensitizers

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Twenty natural dyes, extracted from natural materials such as flowers, leaves, fruits, traditional Chinese medicines, and beverages, were used as sensitizers to fabricate dye-sensitized solar cells (DSCs). The photoelectrochemical performance of the DSCs based on these dyes showed that the open circuit voltages (V_{oc}) varied from 0.337 to 0.689 V, and the short circuit photocurrent densities (J_{sc}) ranged from 0.14 to 2.69 mA cm⁻². Specifically, a high V_{oc} of 0.686 V was obtained from the dye extracted from mangosteen pericarp sensitizer. The photo-to-electric conversion efficiency of the DSC sensitized by the ethanol extract of mangosteen pericarp without purification reached 1.17%. Moreover, various components of the ethanol extract were extracted using different organic solvents. The photoelectrochemical performance of these extracts demonstrated that rutin was the most effectual component of the sensitizer for DSC.

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~~1. Introduction~~

Since Grätzel et al. developed dye-sensitized solar cells (DSCs), a new type of solar cells, in 1991 [1], these have attracted considerable attention due to their environmental friendliness and low cost of production. A DSC is composed of a nanocrystalline porous semiconductor electrode-absorbed dye, a counter electrode, and an electrolyte containing iodide and triiodide ions. In DSCs, the dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electric energy. Numerous metal complexes and organic dyes have been synthesized and utilized as sensitizers. By far, the highest efficiency of DSCs sensitized by Ru-containing compounds absorbed on nanocrystalline TiO₂ reached 11–12% [2,3]. Although such DSCs have provided a relatively high efficiency, there are several disadvantages of using noble metals in them: noble metals are considered as resources that are limited in amount, hence their costly production. On the other hand, organic dyes are not only cheaper but have also been reported to reach an efficiency as high as 9.8% [4]. However, organic dyes have often presented problems as well, such as complicated synthetic routes and low yields. Nonetheless, the natural dyes found in flowers, leaves, and fruits can be extracted by simple procedures. Due to their cost efficiency, non-toxicity, and complete biodegradation, natural dyes have been a popular subject of research. Thus far, several natural dyes have been utilized as sensitizers in DSCs, such as cyanin [5–17],

carotene [18,19], tannin [20], and chlorophyll [21]. Calogero and Marco reported that a conversion efficiency of 0.66% was obtained using red Sicilian orange juice dye as sensitizer [13]. Wongcharee et al. employed rosella as sensitizer in their DSC, which achieved a conversion efficiency of 0.70% [8]. Roy et al. indicated that when using Rose Bengal dye as sensitizer, the J_{sc} and V_{oc} of their DSC reached 3.22 mA cm⁻² and 0.89 V, respectively, resulting in a 2.09% conversion efficiency [11]. Furthermore, Wang et al. carried out structural modification of coumarin and used the coumarin derivative as sensitizer in their DSC, which provided an efficiency of 7.6% [22–25]. Thus, optimization of the structure of natural dyes to improve efficiency is promising.

In this paper, 20 types of natural dyes were extracted from flowers, fruits, traditional Chinese medicines, and beverages, such as rhododendron, herba artemisiae scopariae, mangosteen pericarp, and coffee. To the best of our best knowledge, most of these natural dyes, especially traditional Chinese medicines, are reported as sensitizers of DSCs for the first time. These extracted dyes were characterized by UV–vis absorption spectra. The photoelectrochemical properties of the DSCs using these extracts as sensitizers were investigated. Additionally, stepwise purification of the extract obtained from mangosteen pericarp was performed. The photovoltaic properties of DSCs sensitized by the purified products were studied.

~~2. Experiment~~

~~2.1. Preparation of natural dye sensitizers~~

All dyes, except for rose, lily, coffee, and leaves of Chinese holly for which water was used as the extraction solvent, were extracted

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with ethanol. The dyes extracted with ethanol were obtained by the following steps: fresh plants, fruits, Chinese medicines, and beverages were washed with water and vacuum dried at 60 °C. After crushing into fine powder using a mortar, these materials were immersed in absolute ethanol at room temperature in the dark for one week. Then the solids were filtrated out, and the filtrates were concentrated at 40 °C for use as sensitizers. The dyes obtained from rose, lily, coffee, and leaves of Chinese holly were extracted by the following steps: the materials were immersed in boiling water for 2–3 h, and the solids were filtrated out. The resulting filtrates were used as sensitizers.

2.2. Preparation of dye-sensitized solar cells

FTO conductive glass sheets (Asahi Glass, fluorine-doped SnO₂, sheet resistance: 15 Ω/sq), were first cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol, and then dried. Ti-nanoxide-D pastes (Solaronix, Co. Ltd.) were deposited on the FTO conductive glass by doctor-blading technique in order to obtain a TiO₂ film with a thickness of 9 μm and an area of 0.2 cm². The TiO₂ film was preheated at 200 °C for 10 min and then sintered at 500 °C for 30 min. Subsequently, the TiO₂ film was treated in 40 mM TiCl₄ solution at 70 °C for 30 min and then at 500 °C for 30 min. After cooling to 80 °C, the TiO₂ electrode was immersed in an ethanol solution containing a natural dye for 10–12 h [26].

The dye-sensitized TiO₂ electrode and a sputtered-Pt counter electrode were assembled to form a solar cell by sandwiching a redox (I⁻/I₃⁻) electrolyte solution. The electrolyte solution was composed of 0.03 M I₂, 0.06 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodine, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine in acetonitrile [19].

2.3. Measurements

The UV–vis transmission and reflectance spectra of the dyes absorbed in the TiO₂ films were taken on a UV-550 using an integrating sphere setup. The solution spectra were referenced against the appropriate solvent by a HP 8453 UV–vis spectrophotometer. The electrochemical impedance spectra (EIS) experiment was carried out at -0.78 V bias in the dark with an electrochemical workstation (Zenium Zahner, Zahner). The measured frequency range was from 100 mHz to 1 MHz, and the AC amplitude was set at 10 mV. The current–voltage curves of the DSCs were obtained by applying an external bias to the cell and measuring the generated photocurrent under white light irradiation with a Keithley digital source meter (Keithley 2601, USA). The intensity of the incident light was 100 mW cm⁻², and the instrument was equipped with a 300 W solar simulator (Solar Light Co., Inc., USA) that served as the light source. The photon flux was determined by a power meter (Nova, Ophir optronics Ltd.) and a calibration cell (BS-520, s/n 019, Bunkoh-Keiki Co., Ltd.).

3. Results and discussion

3.1. Absorption of natural dyes

We attempted to use 20 kinds of colorful natural dyes as sensitizers for DSCs. Table 1 lists the UV–vis absorption data of the dyes extracted with ethanol or water from flowers, leaves, fruits, traditional Chinese medicine, and beverages. Fig. 1 shows the representative UV–vis absorption spectra for the ethanol extracts of flowery knotweed, Begonia, and Perilla. As shown in Table 1, the ethanol extracts of begonia and rhododendron, as well as the 0.1 M HCl ethanol extract of violet, exhibit an absorption peak of ca. 540 nm. This absorption ascribes to their identical components,

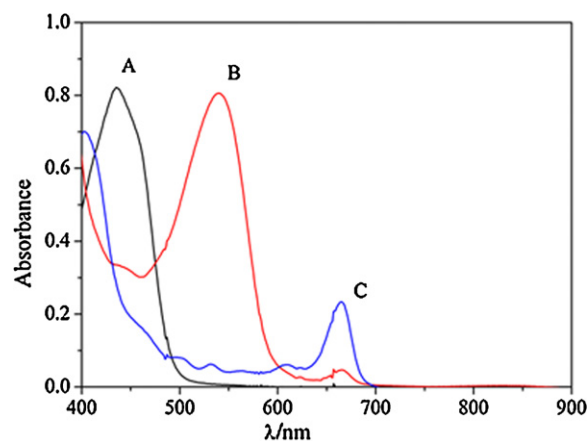


Fig. 1. UV–vis absorption spectra of (A) flowery knotweed, (B) begonia, and (C) perilla in ethanol solution.

namely, anthocyanins, a group of natural phenolic compounds. The chemical adsorption of these dyes is generally accepted to occur because of the condensation of alcoholic-bound protons with the hydroxyl groups on the surface of nanostructured TiO₂ [27].





















Table 1 also demonstrates that the ethanol extracts of petunia, perilla, China loropetal, and China redbud, whose colors are green, reach a maximum absorption peak of 665 nm. The main component of these five extracts is chlorophyll. Furthermore, the absorption peaks for the ethanol extracts of yellow rose, tangerine peel, *Fructus lycii*, marigold, and flowery knotweed in the 400–500 nm visible range may be attributed to xanthophyll, flavone, carotene, xanthophyll, and rhein, respectively. The ethanol extracts of rose and lily were found colorless; thus, water was used as the extraction solvent for rose and lily. The water extracts of rose, lily, coffee, and leaves of Chinese holly, as well as the ethanol extract of mangosteen pericarp, showed various colors, whereas no obvious maximum absorption peak in the visible light region was observed. This result can be attributed to the superposition of absorption peaks.

3.2. Photoelectrochemical properties of DSCs sensitized with natural dyes

Photovoltaic tests of DSCs using these natural dyes as sensitizers were performed by measuring the current–voltage (*I*–*V*) curves under irradiation with white light (100 mW cm⁻²) from a 300 W solar simulator. The performance of natural dyes as sensitizers in DSCs was evaluated by short circuit current (*J*_{sc}), open circuit voltage (*V*_{oc}), fill factor (*FF*), and energy conversion efficiency (*η*). The photoelectrochemical parameters of the DSCs sensitized with natural dyes are listed in Table 1. The typical *I*–*V* curves of the DSCs using the sensitizers extracted from mangosteen pericarp, rhododendron, perilla, leaves of Chinese holly, and herbal *artemisiae scopariae* are shown in Fig. 2.

As displayed in Table 1 and Fig. 2, the fill factors of these DSCs are mostly higher than 60%. The *V*_{oc} varies from 0.337 to 0.689 V, and the *J*_{sc} changes from 0.14 to 2.69 mA cm⁻². Specifically, a high *V*_{oc} (0.686 V) and *J*_{sc} (2.69 mA cm⁻²) were obtained from the DSC sensitized by the mangosteen pericarp extract; the efficiency of the DSC reached 1.17%. These data are significantly higher than those of the DSCs sensitized by other natural dyes in this work. Moreover, as shown in Table 1, the *V*_{oc} of the DSC using the mangosteen pericarp extract as sensitizer is comparable to that of the DSC sensitized by a Ru complex *cis*-RuL₂(SCN)₂ (*L* = 2,2'-bipyridyl-4,4'-dicarboxylic acid) (N-719), which is widely used in DSCs. This result regarding the mangosteen pericarp extract will be further discussed in Section 3.3. Chlorophyll plays an important role in plant photosyn-

Table 1
Photoelectrochemical parameters of the DSCs sensitized by natural dyes extracted with (a) ethanol, (b) water, and (c) 0.1 M HCl–ethanol. N719 was extracted with the mixture of (d) acetonitrile and *tert*-butyl alcohol; (e) λ_{max} in the visible light range is shown.

Natural dye		λ_{max}^e (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	η (%)
Begonia ^a		540	0.63	0.537	72.2	0.24
Tangerine peel ^a		446	0.74	0.592	63.1	0.28
Rhododendron ^a		540	1.61	0.585	60.9	0.57
Fructus lycii ^a		447, 425	0.53	0.689	46.6	0.17
Marigold ^a		487	0.51	0.542	83.1	0.23
Perilla ^a		665	1.36	0.522	69.6	0.50
Herba artemisiae scopariae ^a		669	1.03	0.484	68.2	0.34
China loropetal ^a		665	0.84	0.518	62.6	0.27
Yellow rose ^a		487	0.74	0.609	57.1	0.26
Flowery knotweed ^a		435	0.60	0.554	62.7	0.21
Bauhinia tree ^a		665	0.96	0.572	66.0	0.36
Petunia ^a		665	0.85	0.616	60.5	0.32
Lithospermum ^a		520	0.14	0.337	58.5	0.03
Violet ^c		546	1.02	0.498	64.5	0.33
Chinese rose ^c		516	0.90	0.483	61.9	0.27
Mangosteen pericarp ^a		/	2.69	0.686	63.3	1.17
Rose ^b		/	0.97	0.595	65.9	0.38
Lily ^b		/	0.51	0.498	66.7	0.17
Coffee ^b		/	0.85	0.559	68.7	0.33
Broadleaf holly leaf ^b		/	1.19	0.607	65.4	0.47
N-719 ^d	/	515	13.74	0.773	57.6	6.11

thesis; the DSCs using chlorophyll derivatives as sensitizers also obtained a relatively high conversion efficiency [28,29]. However, the DSCs sensitized by natural dyes mainly composed of chlorophyll in this work, such as China loropetal and China redbud, did not offer high conversion efficiencies. This is because there are

no available bonds between the dye and TiO₂ molecules through which electrons can transport from the excited dye molecules to the TiO₂ film [6]. This result indicates that the interaction between the sensitizer and the TiO₂ film is significant in enhancing the energy conversion efficiency of DSCs.

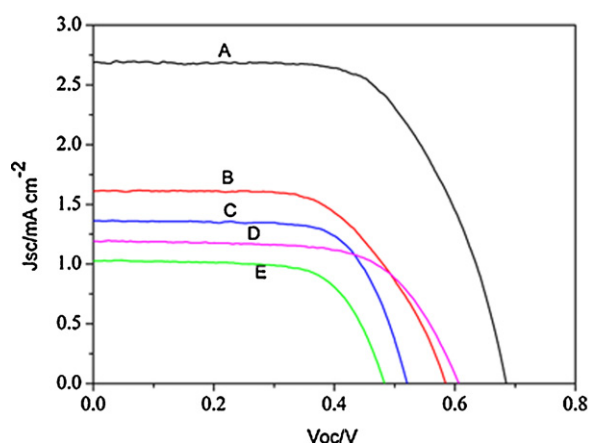


Fig. 2. Current–voltage curves for the DSCs sensitized by five kinds of plant extracts: (A) mangosteen pericarp, (B) rhododendron, (C) perilla, (D) broadleaf holly leaf, and (E) herba artemisiae scopariae.

3.3. Purification and characterization of extracts from mangosteen pericarp

As mentioned previously, the conversion efficiency of the DSC sensitized by mangosteen pericarp extract was the highest among the 20 dyes. To further clarify the reasons for its high efficiency, stepwise purification of the extract obtained from mangosteen pericarp was carried out [30–32]. Fig. 3 presents the whole purification process of the extract from mangosteen pericarp. As shown in Flowchart I, two kinds of extracts were obtained from mangosteen pericarp, denoted as solution A and solution B, respectively. Solution B was further purified, as displayed in Flowchart II; five kinds of extracts were obtained from solution B using five solvents, corresponding to petroleum ether (I), chloroform (II), ethyl acetate (III), *n*-butanol (IV), and water (V), respectively. Among the five extracts, petroleum ether extract (I) was colorless, while the other four extracts had colors.

As shown in Fig. 4, the main components of the extracts of mangosteen pericarp with chloroform, ethyl acetate, and *n*-butanol are mangostin, rutin, and mangosteen trihamnosid, respectively [30–32]. The UV–vis absorption spectra of the four extracts II–V, displayed in Fig. 5, were investigated; the extracts with different solvents exhibit different absorption peaks, and the absorption of solution B is the superposition of all four extracts. The major anthocyanins found in the pericarp were cyanidin-3-sophoroside and cyanidin-3-glucoside, which agree with the findings of Du and Palapol [33,34].

Fig. 6 shows the UV–vis spectra of rutin and mangosteen pericarp extracts adsorbed on TiO₂ film. A similar shape of the absorption spectra was observed between the rutin and mangosteen pericarp; this result indicates that rutin is the major component of mangosteen pericarp. The absorption spectra which mangosteen pericarp extract adsorbed on TiO₂ is obviously wider and red-shift compared with that in ethanol solution (Fig. 6). When the dyes were adsorbed on the TiO₂ film, a red shift in the peak was observed. The average value of the shift is 10 nm, which means that the interaction between the dyes and the cationic TiO₂ surface was observed. The interaction was formed through a chemical bond, the C–O–Ti bond, as discussed in the literature [6].

Fig. 7 shows the action spectra of the monochromatic incident-to-current conversion efficiency (IPCE) for the DSC sensitized with solution B. The IPCE for the DSC reached ca. 18% at 420 nm. The shape of the action spectra was also observed to be similar to that of the UV–vis absorption spectrum of solution B.

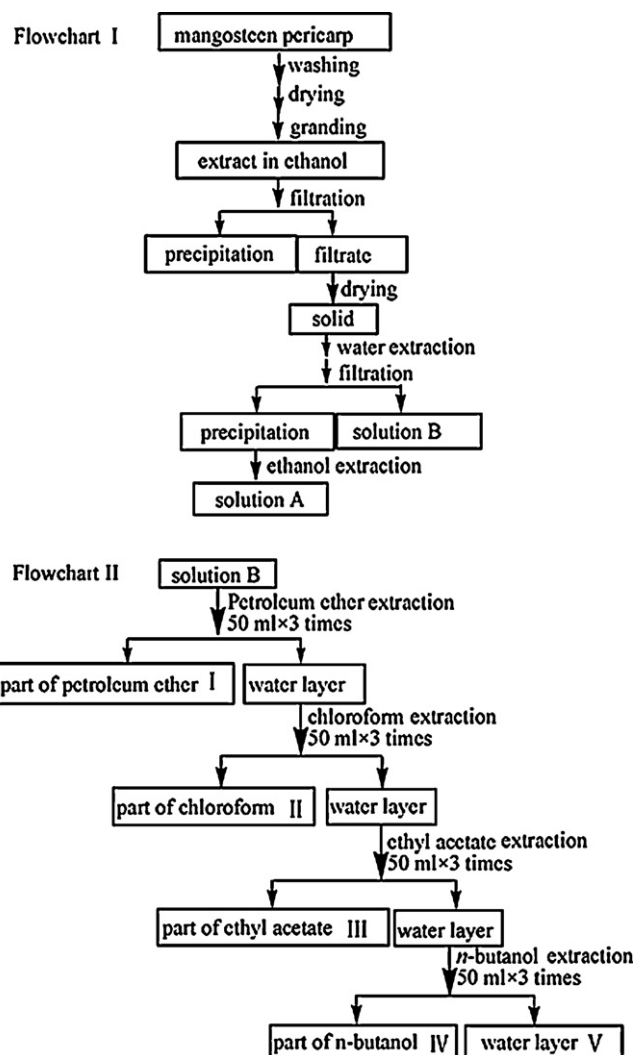


Fig. 3. Flow chart for the purification process of the extract obtained from mangosteen pericarp.

The photovoltaic properties of the DSCs sensitized by the dyes extracted from mangosteen pericarp with various solvents were studied by measuring *I*–*V* curves, and the corresponding photoelectrochemical parameters are listed in Table 2. As observed, the efficiencies of the DSCs using solution A and B as sensitizers are 0.43% and 1.17%, respectively. The efficiencies of Extracts II, III, IV, and V obtained from Solution B are 0.92, 1.12, 0.33, and 0.30%, respectively. Table 2 shows that the Voc, Jsc, and η of the extracts with chloroform (II) and ethyl acetate (III) are higher than those of the extracts with *n*-butanol (IV) and water (V), possibly due to the chemical bonding between the alcoholic-bound protons in extracts II–III and the OH groups of TiO₂ [27]. Among extracts II–V, the efficiency of extract III mainly composed of rutin was the highest. Thus,

Table 2
Photoelectrochemical parameters of the DSCs using the extracts of mangosteen pericarp with various solvents as sensitizers.

Natural dye	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	η (%)
Solution A	0.698	0.92	66.3	0.43
Solution B	0.686	2.69	63.3	1.17
Part II	0.621	2.55	58.0	0.92
Part III	0.611	2.92	62.6	1.12
Part IV	0.562	0.96	61.7	0.33
Part V	0.562	0.83	64.8	0.30

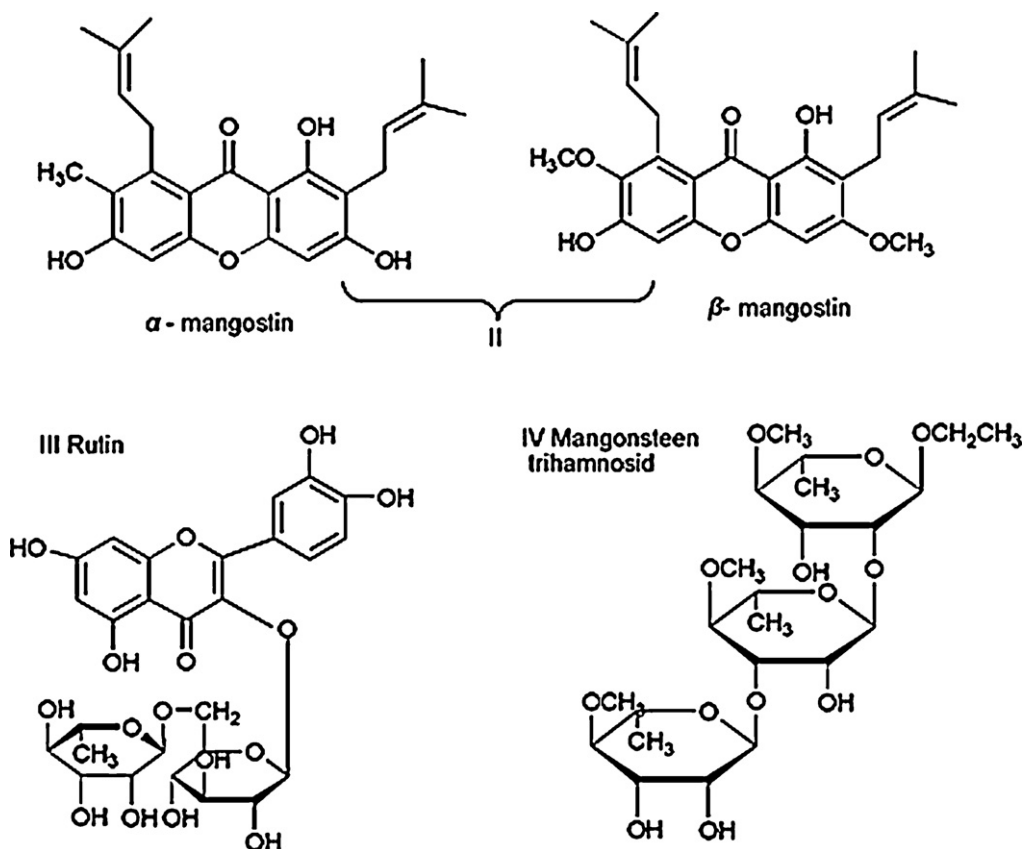


Fig. 4. Basic molecular structures for the main components of the extracts of mangosteen pericarp with various solvents: (II) chloroform, (III) ethyl acetate, and (IV) *n*-butanol.

we carried out the photovoltaic test of rutin with a content of 98%. The efficiency of rutin was 1.00%, which is consistent with that of extract III. Therefore, the main effectual component of the mangosteen pericarp extract as a sensitizer for DSC is speculated to be rutin, extracted with ethyl acetate. The efficiency of DSC using solution B as sensitizer is also much lower than the sum of the efficiencies of the DSCs sensitized with extracts II, III, IV, and V. This result indicates that the mixed extract adsorbed on TiO_2 does not show synergistic photosensitization compared with individual extracts, which is in accordance with the results reported by Wongcharee et al. [8]. However, Kumara and co-workers reported that the efficiency of the DSC sensitized with the extract containing shisonin

and chlorophyll is 1.31%, which is almost the sum of the efficiencies of the DSCs sensitized with shisonin (1.01%) and chlorophyll (0.58%). This is due to synergistic sensitization by the dye mixture extracted from a single natural resource [9]. We hypothesize two possible reasons for this phenomenon in which the mixed extract of mangosteen pericarp did not show synergistic photosensitization. First, although the DSC sensitized with the mixed extract of mangosteen pericarp utilizes the light of several spectral regions, the coadsorption suppresses electron injection possibly due to the increase in concentration quenching. Second, the strong steric hindrance of mangostin, rutin, and mangosteen trihamnosid prevents the dye molecules from effectively arraying on the TiO_2 film.

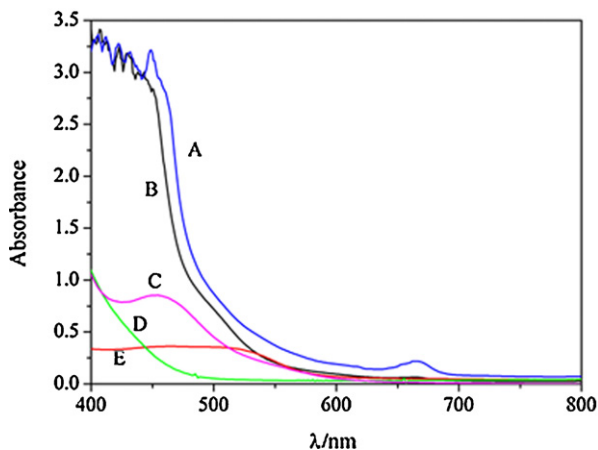


Fig. 5. UV-vis absorption spectra of the extracts with different solvents from mangosteen pericarp: (A) solution B, (B) part of ethyl acetate, (C) part of *n*-butanol, (D) part of chloroform, and (E) water layer.

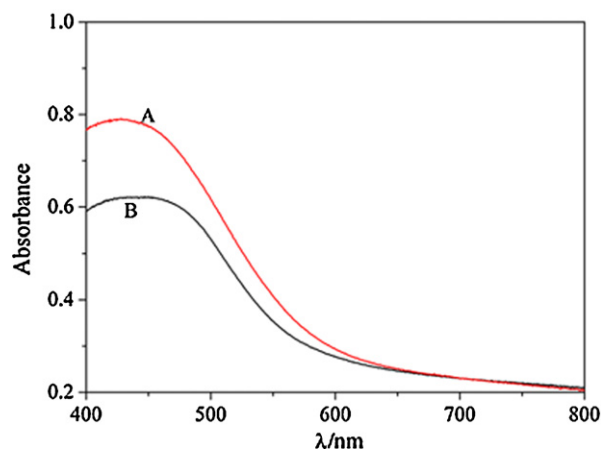


Fig. 6. Light absorption spectra of dyes adsorbed on TiO_2 : (A) rutin, (B) mangosteen pericarp extracts.

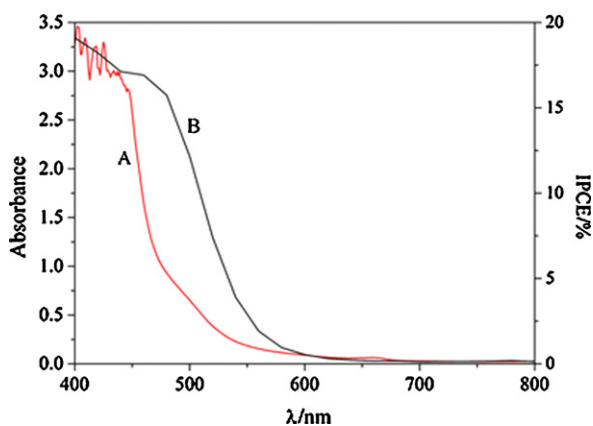


Fig. 7. Absorption spectra of the extract of mangosteen pericarp (A) and photocurrent action spectrum of a solar cell sensitized by the extract of mangosteen pericarp (B).

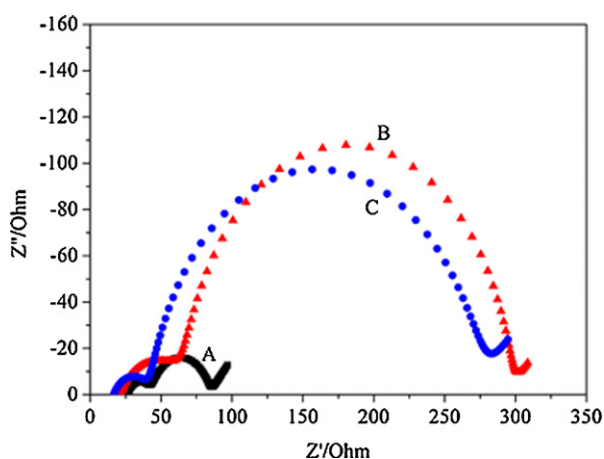


Fig. 8. Electrochemical impedance spectra of DSCs: (A) N719, (B) rutin, and (C) mangosteen pericarp extracts.

3.4. Electrochemical impedance spectroscopy (EIS) studies

To investigate the internal resistance of the DSCs based on natural dyes, EIS was measured. The fitting results of EIS obtained are shown in Fig. 8, and the analyzed data are summarized in Table 3. In general, the EIS of DSCs exhibits three semicircles, as shown in Fig. 8; the high-frequency (>100 MHz) interception on the real axis can be attributed to series resistance (R_s). The two semi-circles in the high-frequency (100 MHz–10 KHz) and middle-frequency (10 KHz–100 Hz) regions correspond to the resistance capacitance (RC) networks of the Pt/electrolyte and $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interfaces, including the charge transfer resistance (R_{ct}) and the constant phase element (CPE), respectively. The big semi-circles at low frequency (<100 Hz) are assigned to Warburg resistance, the diffusion properties of the redox couple (I_3^-/I^-) in the electrolyte.

The charge transfer resistances (R_{ct1}) are 17.33, 47.30, and 25.44 Ω , and the charge transfer in the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface resistance (R_{ct2}) is 40.68, 227.7, and 231.1 Ω corresponding to

Table 3

Results of the impedance analysis for DSCs using four kinds of natural dyes as sensitizers.

	R_s (Ω)	R_{ct1} (Ω)	R_{ct2} (Ω)
N719	26.04	17.33	40.68
Rutin	20.75	47.3	227.7
Mangosteen pericarp extracts	16.69	25.44	231.1

the DSCs based on N719, rutin, and mangosteen pericarp extracts, respectively, as shown in Table 3. The R_{ct1} and R_{ct2} of the DSCs with three dyes are different, which is caused by the binding between the dye molecules and the TiO_2 film. This is because the dyes of mangosteen pericarp extract aggregated on the TiO_2 films, which led to a weaker binding and greater resistance. Moreover, the high R_{ct2} can lead to a decrease in J_{sc} , which is why the efficiency is low for the DSC sensitized using mangosteen pericarp extract. Therefore, introducing a functional group, such as $-\text{COOH}$, and optimizing the structure of the natural dye are necessary in order to improve the efficiency of DSCs.

4. Conclusions

Twenty dyes obtained from nature, including flowers, leaves of plants, fruits, traditional Chinese medicines, and beverages, were used as sensitizers in DSCs. The dyes extracted from these materials contained cyanine, carotene, chlorophyll, etc. The photoelectrochemical performance of the DSCs based on these dyes showed that the V_{oc} ranged from 0.337–0.689 V, and J_{sc} was in the range of 0.14–2.69 mA cm^{-2} . The DSC sensitized by mangosteen pericarp extract offered the highest conversion efficiency of 1.17% among the 20 extracts. Specifically, the V_{oc} of mangosteen pericarp extract is comparable to that of the DSC sensitized by a Ru complex N719. Furthermore, the extract obtained from mangosteen pericarp was purified stepwise. The photoelectrochemical performance for the extracts of mangosteen pericarp with different solvents indicated that the main effectual component was rutin. The conversion efficiency is expected to be further improved by introducing functional groups, such as the carboxyl group. Overall, natural dyes as sensitizers of DSCs are promising because of their environmental friendliness, low-cost production, and designable polychrome modules.

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References

- [1] B. O'Regan, M. Grätzel, A low cost, high efficiency solar cell based on dye sensitized colloidal TiO_2 films, *Nature* 353 (1991) 737–740.
- [2] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L.Y. Han, Dye sensitized solar cells with conversion efficiency of 11.1%, *Jpn. J. Appl. Phys.* 45 (2006) L628–L640.
- [3] R. Buscaino, C. Baiocchi, C. Barolo, C. Medana, M. Grätzel, Md.K. Nazeeruddin, G. Viscardi, A mass spectrometric analysis of sensitizer solution used for dye sensitized solar cell, *Inorg. Chim. Acta* 361 (2008) 798–805.
- [4] G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, High efficiency and stable dye sensitized solar cells with an organic chromophore featuring a binary π -conjugated spacer, *Chem. Commun.* (2009) 2198–2200.
- [5] P.M. Sirimanne, M.K.I. Senevirathna, E.V.A. Premalal, P.K.D.D.P. Pitigala, V. Sivakumar, K. Tennakone, Utilization of natural pigment extracted from pomegranate fruits as sensitizer in solid state solar cells, *J. Photochem. Photobiol. A* 177 (2006) 324–327.
- [6] S. Hao, J. Wu, Y. Huang, J. Lin, Natural dyes as photosensitizers for dye sensitized solar cell, *Sol. Energy* 80 (2006) 209–214.
- [7] A.S. Polo, N.Y. Murakami Iha, Blue sensitizers for solar cells: natural dyes from Calafate and Jaboticaba, *Sol. Energy Mat. Sol. Cell* 90 (2006) 1936–1944.
- [8] K. Wongcharee, V. Meeyoo, S. Chavadej, Dye sensitized solar cell using natural dyes extracted from rosella and blue pea flowers, *Sol. Energy Mat. Sol. C* 91 (2007) 566–571.
- [9] K. Tennakone, A.R. Kumarasinghe, G.R.R.A. Kumara, K.G.U. Wijayantha, P.M. Sirimanne, Nanoporous TiO_2 photoanode sensitized with the flower pigment cyaniding, *J. Photochem. Photobiol. A* 108 (1997) 193–195.
- [10] D. Zhang, S.M. Lanier, J.A. Downing, J.L. Avent, J. Lumc, J.L. McHale, Betalain pigments for dye sensitized solar cells, *J. Photochem. Photobiol. A* 195 (2008) 72–80.

- [11] M.S. Roy, P. Balraju, M. Kumar, G.D. Sharma, Dye-sensitized solar cell based on Rose Bengal dye and nanocrystalline TiO_2 , *Sol. Energ. Mat. Sol. C* 92 (2008) 909–912.
- [12] J.M.R.C. Fernando, G.K.R. Senadeera, Natural anthocyanins as photosensitizers for dye-sensitized solar devices, *Curr. Sci.* 95 (2008) 663–666.
- [13] G. Calogero, G.Di. Marco, Red Sicilian orange and purple eggplant fruits as natural sensitizers for dye-sensitized solar cells, *Sol. Energ. Mat. Sol. C* 92 (2008) 1241–1246.
- [14] Q. Dai, J. Rabani, Photosensitization of nanocrystalline TiO_2 films by anthocyanin dyes, *J. Photochem. Photobiol. A* 148 (2002) 17–24.
- [15] N.J. Cherepy, G.P. Smestad, M. Grätzel, J.Z. Zhang, Ultrafast electron injection: implications for a photoelectrochemical cell utilizing an anthocyanin dye-sensitized TiO_2 nanocrystalline electrode, *J. Phys. Chem. B* 101 (1997) 9342–9351.
- [16] P. Luo, H. Niu, G. Zheng, X. Bai, M. Zhang, W. Wang, From salmon pink to blue natural sensitizers for solar cells: *Canna-indica* L., *Salvia splendens*, cowberry and *Solanum nigrum* L., *Spectrochim. Acta Part A* 74 (2009) 936–942.
- [17] S. Furukawa, H. Iino, T. Iwamoto, K. Kukita, S. Yamauchi, Characteristics of dye-sensitized solar cells using natural dye, *Thin Solid Films* 518 (2009) 526–529.
- [18] N.M. Gómez-Ortiz, I.A. Vázquez-Maldonado, A.R. Pérez-Espadas, G.J. Mena-Rejón, J.A. Azamar-Barrios, G. Oskam, Dye-sensitized solar cells with natural dyes extracted from achioté seeds, *Sol. Energ. Mat. Sol. C* 94 (2010) 40–44.
- [19] E. Yamazaki, M. Murayama, N. Nishikawa, N. Hashimoto, M. Shoyama, O. Kurita, Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells, *Sol. Energy* 81 (2007) 512–516.
- [20] R. Espinosa, I. Zumeta, J.L. Santana, F. Martí'nez-Luzardo, B. González, S. Docteur, E. Vigil, Nanocrystalline TiO_2 photosensitized with natural polymers with enhanced efficiency from 400 to 600 nm, *Sol. Energ. Mat. Sol. C* 85 (2005) 359–369.
- [21] G.R.A. Kumara, S. Kaneko, M. Okuya, B. Onwona-Agyeman, A. Konno, K. Tenakone, Shiso-leaf pigments for dye-sensitized solid-state solar cell, *Sol. Energ. Mat. Sol. C* 90 (2006) 1220–1226.
- [22] Z. S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, Photophysical and (photo)electrochemical properties of a coumarin dye, *J. Phys. Chem. B* 109 (2005) 2907–2914.
- [23] Z. S. Wang, Y. Cui, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, A high-light-harvesting efficiency coumarin dye for stable dye-sensitized solar cells, *Adv. Mater.* 19 (2007) 1138–1141.
- [24] Z. S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, Thiophene-functionalized coumarin dye for efficient dye-sensitized solar cells: electron lifetime improved by coadsorption of deoxycholic acid, *J. Phys. Chem. C* 111 (2007) 7224–7230.
- [25] Z. S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, Molecular design of coumarin dyes for stable and efficient organic dye-sensitized solar cells, *J. Phys. Chem. C* 112 (2008) 17011–17017.
- [26] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Grätzel, M.K. Nazeeruddin, M. Grätzel, Fabrication of thin film dye-sensitized solar cells with solar-to electric power conversion efficiency over 10%, *Thin Solid Films* 516 (2008) 4613–4619.
- [27] S. Meng, J. Ren, E. Kaxiras, Natural dyes adsorbed on TiO_2 nanowire for photovoltaic applications: enhanced light absorption and ultrafast electron injection, *Nano Lett.* 8 (2008) 3266–3272.
- [28] A. Kay, R. Humphry-Baker, M. Grätzel, Artificial photosynthesis. 2. Investigations on the mechanism of photosensitization of nanocrystalline TiO_2 solar cells by chlorophyll derivatives, *J. Phys. Chem.* 98 (1994) 952–959.
- [29] K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier, M. Grätzel, Sensitization of TiO_2 in the visible light region using zinc porphyrins, *J. Phys. Chem.* 91 (1987) 2342–2347.
- [30] J. M. Hu, J. J. Chen, Y. X. Zhao, R. R. Wang, Y. T. Zheng, J. Zhou, Chemical constituents from fruit hulls of *Garcinia mangostana* (Cuttiferace), *Acta Botanica Yunnanica* 28 (2006) 319–322.
- [31] W. Mahabusarakam, P. Wiriyaichitra, W.C. Taylor, Chemical constituents of *Garcinia mangostana*, *J. Nat. Prod.* 50 (1987) 474–478.
- [32] Y. Zhao, C. Y. Wang, P. Y. Li, Chemical Constituents from the Pericarp of *Garcinia mangostana* L, *Spec. Wild-Econ. Anim. Plant Res.* 3 (2007) 39–42.
- [33] C.T. Du, F.J. Francis, Anthocyanin of mangosteen (*Garcinia mangostana* L.), *J. Food Sci.* 42 (1997) 1667–1668.
- [34] Y. Palapol, S. Ketsa, D. Stevenson, J.M. Cooney, A.C. Allan, I.B. Ferguson, Colour development and quality of mangosteen (*Garcinia mangostana* L.) fruit during ripening and after harvest, *Postharvest. Biol. Technol.* 51 (2009) 349–353.