Research Article

TiO₂/Chitosan-NH₄I(+I₂)-BMII-Based Dye-Sensitized Solar Cells with Anthocyanin Dyes Extracted from Black Rice and Red Cabbage

M. H. Buraidah,¹ L. P. Teo,¹ S. N. F. Yusuf,¹ M. M. Noor,^{1,2} M. Z. Kufian,¹ M. A. Careem,³
S. R. Majid,¹ R. M. Taha,⁴ and A. K. Arof¹

¹ Centre for Ionics University Malaya, Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia

² Centre for Foundation Studies, International Islamic University Malaysia, Jalan Universiti, 46350 Petaling Jaya, Selangor, Malaysia

³ Department of Physics, University of Peradeniya, 20400 Peradeniya, Sri Lanka

⁴ Institute of Biological Sciences, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence should be addressed to A. K. Arof, akarof@um.edu.my

Received 8 July 2011; Revised 26 August 2011; Accepted 2 September 2011

Academic Editor: Gaetano Di Marco

Copyright © 2011 M. H. Buraidah et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Dye sensitized solar cells (DSSCs) were fabricated using anthocyanin dye and polymer electrolyte with ammonium iodide (NH₄I) salt. The study was designed to focus on increasing the efficiency of the DSSC. DSSC using 26.9 wt. % chitosan-22 wt. % NH₄I(+2.2 wt. % I₂)-48.9 wt. % IL solid electrolyte, black rice anthocyanin with Pt counter electrode showed J_{sc} of 172 $\mu\text{A cm}^{-2}$ and V_{oc} of 195 mV. The performance of the cell with Pt electrode was further improved by coating a blocking layer on the indium tin oxide (ITO) substrate. The black rice DSSC using 11 wt. % (chitosan:PEO, wt. ratio 30:70)-9 wt. % NH₄I-80 wt. % BMII gel electrolyte exhibited J_{sc} of 1213 $\mu\text{A cm}^{-2}$, V_{oc} of 400 mV, FF of 0.47, and η of 0.23%. The red cabbage anthocyanin DSSC containing (phthaloyl chitosan-PEO)-NH₄I-BMII gel electrolyte using tartaric acid to adjust the pH of anthocyanin solution showed the best performance with the fill factor of 0.39, J_{sc} of 3503 $\mu\text{A cm}^{-2}$, V_{oc} of 340 mV, and an overall conversion efficiency of 0.46%.

1. Introduction

Dye-sensitized solar cells (DSSCs) have gained much interest as energy converters since they are inexpensive compared to conventional silicon solar cells, easy to fabricate, and can achieve high solar energy conversion efficiency [1]. Dye-sensitized solar cell (DSSC) which is a type of photoelectrochemical cell utilizing electrolyte as a medium for charge transport comprises a transparent conducting oxide (TCO) glass, semiconductor as photoelectrode, dye-sensitized agent, electrolyte containing redox mediator, and counter electrode. Titanium dioxide (TiO₂) is most commonly used as photoanode in DSSC application since it is nontoxic, inert, and has a large energy bandgap (E_g of ~ 3 eV) as well as good optical and electrical properties and, thus, can be efficiently sensitized by a dye [2].

Other than photoelectrode, counter electrode is also one of the main constituents in DSSC which makes it worthy

of investigation. The function of counter electrode is to transfer electrons received from the external circuit into the electrolyte and enable the reduction of the oxidized charge mediator. The selection of material as counter electrode requires the material to possess low charge-transfer resistance, good chemical and electrochemical stability in the electrolyte/electrode interface, and capability to catalyze the reduction of redox mediator [3]. Platinum (Pt) and carbon-based materials are two most popular choices to serve as counter electrode. Others include conducting polymers, that is, poly(3,4-ethylenedioxythiophene) (PEDOT) [4], polypyrrole (PPy) [5], and polyaniline (PANI) [6]. Some examples of carbon-based materials include graphite [7], activated carbon [8], carbon black [9], and carbon nanotube [10, 11]. However, Pt is more suitable to serve as counter electrode than carbon-based materials due to its excellent catalytic activity and low charge-transfer resistance [12]. Pt exhibits excellent catalyst behaviour, high electrical conductivity, low

charge-transfer resistance, and light reflecting properties [3, 13]. Hence, Pt was employed as counter electrode in the present study. Herein, Pt was deposited on indium tin oxide (ITO) glass substrate via thermal decomposition method which is an easy and cheaper way of preparation compared to sputtering technique.

The function of dye is to absorb light, inject electrons into the TiO_2 conduction band, and then accept electrons from the redox mediator in the electrolyte. Although the ruthenium (II) polypyridyl complexes are the most popular synthetic dye-sensitizing agent [14–17], it has several disadvantages including high cost, long-term unavailability, and complex process of synthesis and is environmentally unfriendly due to the heavy metal it contains [18]. As an alternative, natural dye can be used as sensitizer for DSSC. Natural dye is readily available and cheap, thus, making it environmental friendly and can reduce the cost of DSSC devices.

Anthocyanins are natural compounds commonly found in flowers, fruits, and leaves of plants such as the canary bird flower (*Rosa xanthina*) [19], blue pea (*Clitoria ternatea*) flowers [20], strawberries [21], blackberries [22], pomegranate fruits [23, 24], and maple leaves [25]. Anthocyanin used in this study was extracted from black rice (*Oryza sativa*) and red cabbage (*Brassica oleracea*) both of which have been reported to exhibit antioxidant property [26–28]. Black rice was chosen as it shows the best sensitization as reported by Hao and coworkers [19]. Anthocyanin from red cabbage is used mainly in food coloring and beverage industries as well as in making sweets and chewing gum [29, 30]. The utilization of red cabbage as sensitizer is worthwhile investigating since up to now only Zhang's [31] and Furukawa's groups [32] employed anthocyanin dye from red cabbage as sensitizer in DSSC.

Polymer electrolytes (PEs) that offer many advantages such as fast ion transport, electrochemical stability, and good mechanical properties [33] have replaced the use of liquid electrolytes in semiconductor/electrolyte junction solar cells [34, 35]. Intensive efforts have been geared towards increasing the conductivity of the polymer electrolytes in order to improve the performance of the solar cells. These efforts include blending of polymers [36–38], adding plasticizers [39–41] and ionic liquid (IL) [42–44] into the polymer electrolyte. Ionic liquids (IL) are nonvolatile and nonflammable materials. They have high thermal stability, high ionic conductivity, and wide potential windows [45–47]. Gel polymer electrolytes exhibit both the cohesive property of a solid and also diffusive nature of a liquid which results in high ionic conductivity, long-term stability, and superior interfacial contact between electrodes and electrolyte [48].

In our earlier work [49], 50 wt. % ionic liquid 1-butyl-3-methylimidazolium iodide (BMII) was added into a chitosan ammonium iodide (NH_4I) polymer electrolyte. A TiO_2 DSSC was fabricated with ITO as counter electrode using anthocyanin extracted from black rice and betacyanin from the callus of *Celosia plumosa*, respectively, as sensitizer. In this work, DSSC is fabricated from a combination of relatively cheap materials containing TiO_2 photoelectrode, natural dye, polymer electrolyte containing I^-/I_3^- redox mediator, and

TABLE 1: Various electrolyte composition.

Chitosan (wt. %)	Phthaloyl chitosan (wt. %)	PEO (wt. %)	NH_4I (wt. %)	BMII (wt. %)
27.5	—	—	22.5	50
11	—	—	9	80
3.3	—	7.7	9	80
—	11	—	9	80
—	3.3	7.7	9	80

counter electrode. In this study, chitosan- NH_4I electrolytes containing different amounts of IL were prepared in solid and gel forms, and the relationship between conductivity of the polymer electrolytes and DSSC performance (short-circuit current density) was examined. To the best of the authors' knowledge, all the natural dye DSSCs reported in the literature are using liquid electrolyte.

2. Experimental

2.1. Preparation and Characterization of the Electrolyte. The composition of the electrolytes is shown in Table 1. The electrolyte film consisting of chitosan- NH_4I -BMII and (chitosan-PEO)- NH_4I -BMII were prepared by the solution cast technique. The appropriate amounts of chitosan, PEO, NH_4I , and BMII were dissolved in 50 mL 1% acetic acid solution at room temperature. The solutions were then cast in different petri dishes, and the solvent was allowed to evaporate to form films. Gel polymer electrolytes for that composition were prepared by reducing the solvent to 20 mL.

For the preparation of electrolyte containing phthaloyl chitosan- NH_4I -BMII and phthaloyl chitosan-PEO- NH_4I -BMII, 10 mL dimethylformamide (DMF) was used as solvent. 0.04 g of iodine (I_2) crystals was added into the electrolytes in order to provide I^-/I_3^- redox couple for DSSC applications. Impedance of the electrolytes was measured by the complex impedance technique using the HIOKI 3531-01 LCR Hi-Tester in the frequency range from 50 Hz to 1 MHz.

2.2. Preparation of Anthocyanin Extracts. The natural colorant-containing anthocyanin was extracted from black rice and red cabbage, respectively. 100 g black rice was immersed in 80 mL ethanol solution (95%) and kept at room temperature without exposing to light. 100 g red cabbage was soaked in 120 mL ethanol, and the red cabbage was replaced after 5 hours in order to obtain concentrated solution. The residues were removed by filtration, and the pH of the dye was adjusted by adding hydrochloric acid (HCl) or tartaric acid. The absorption characteristics of the anthocyanin containing natural colorant at different pHs in the range 400 to 700 nm were determined using a Shimadzu PC3101 UV-Vis NIR spectrophotometer.

2.3. Preparation of the TiO_2 /Dye Electrode. The ITO glass ($2.5 \times 2.5 \text{ cm}^2$) was cleaned with distilled water and acetone to remove impurities. The cleaned ITO surface was coated

with commercially available nanocrystalline TiO_2 paste using the doctor-blade method. The ITO/ TiO_2 electrodes were sintered at 500°C for 1 hour. The thickness of the TiO_2 layer was controlled using adhesive tape of thickness $100\ \mu\text{m}$. When the temperature of the TiO_2 electrodes reached 100°C during cooling, the electrodes were immersed in the anthocyanin dye solution for 24 hours. The white TiO_2 film will change color when dye is absorbed. The TiO_2 /dye electrode was washed with water to remove impurities and then with ethanol to remove trapped water from the initial washing.

2.4. Preparation of Pt Counter Electrode. To prepare platinum catalyst coated on ITO glass substrate, $5\ \text{mmol L}^{-1}$ hexachloroplatinic acid solution in isopropanol was spread on the ITO conducting surface. The Pt-coated ITO counter electrode was then heated in a furnace at $723\ \text{K}$ for 30 minutes.

2.5. Fabrication of Natural Colorant-Sensitized Solar Cells (DSSCs). Natural colorant-sensitized solar cells with active area about $0.16\ \text{cm}^2$ were fabricated by sandwiching the electrolyte between TiO_2 /dye electrode and Pt counter electrode. The J - V characteristics of the dye-sensitized solar cells were obtained under white light illumination ($100\ \text{mW cm}^{-2}$) using Keithley 2400 source meter.

3. Results and Discussion

3.1. Characteristics of DSSCs Using Dye of Black Rice

3.1.1. UV-Vis Studies of Black Rice. Figure 1 shows the absorption spectra of bare TiO_2 electrode, anthocyanin solution extracted from black rice and that of the TiO_2 electrode after being soaked in anthocyanin solution. The absorption spectrum for the anthocyanin dye in solution shows peak at wavelength $\lambda = 535\ \text{nm}$. It can be observed that the absorption band of anthocyanin/ TiO_2 is red shifted towards higher wavelength ($\lambda = 538\ \text{nm}$) compared to that of the anthocyanin in solution. The shift towards lower energy can be attributed to complexation between anthocyanin and metal ions, Ti^{4+} [50]. Similar behavior has also been observed by Sirimanne and Soga [51]. It can be observed that TiO_2 does not strongly absorb in the visible region. Absorbance of TiO_2 increases as the ultraviolet region is approached. After soaking TiO_2 with black rice anthocyanin, absorbance significantly increased, but the absorbance of the TiO_2 /anthocyanin complex is lower than that of the untreated anthocyanin solution. This shows that TiO_2 is sensitized by the anthocyanin dye.

It is known that anthocyanin extracted from black rice contains cyanidin-3-glucoside and peonidin-3-glucoside [52]. The chemical structure of anthocyanin mainly present in black rice is illustrated in Figure 2(a). Figure 2(b) shows that the complexation occurs between anthocyanin molecule and TiO_2 particles. It can be seen that TiO_2 particles can form bonding with hydroxyl group in cyanidin-3-glucoside and both hydroxyl and methoxy groups in peonidin-3-glucoside.

FIGURE 1: The absorption spectra of TiO_2 electrode, anthocyanin solution from black rice, and anthocyanin adsorbed onto TiO_2 electrode.

Anthocyanins are glycosylated polyhydroxyl derivatives of 2-phenylbenzopyrylium salts or better known as flavylium salts. They are made up of three six-membered rings, that is, an aromatic ring bonded to heterocyclic aromatic ring that contains oxygen and carbon which is also bonded to another aromatic ring. It is said that anthocyanins can exist in various chemical forms, that is, quinonoidal base, flavylium cation, carbinol or pseudobase, and chalcone, which depend on the pH of the solution [53]. Figure 3 depicts an example of different molecular structures of cyanidin-3-glucoside which are pH dependent. At pH 1, anthocyanins mainly present as flavylium cations which are red in colour whereas quinonoidal base in blue colour exists at pH values between 2 and 4. At pH values between 4 and 6, anthocyanins can exist in four chemical forms, that is, flavylium cation, anhydrous quinonoidal base, carbinol base, and chalcone. Carbinol base has no colour whereas the colour of chalcone is pale yellow. The equilibrium between the quinonoidal bases and carbinol has to take place via the flavylium cation. Carbinol pseudobase and chalcone are two main species present at pH values between 5 and 6. The absence of conjugated double bond between the second and the third aromatic ring in the carbinol form does not allow it to absorb visible light. Degradation of anthocyanins occurs at pH above 7. The stability of anthocyanins is dependent on pH [54]. According to the literature [21, 55], it is known that the flavylium cation is the stable form of anthocyanin. The oxonium ion in flavylium form is said to assist in the absorption of photons in the visible range [56]. This is supported by the absorption spectra of black rice anthocyanin in solution as depicted in Figure 4(a). From the figure, the highest absorption peak intensity can be seen at wavelength of $535\ \text{nm}$ for the anthocyanin solution with pH 1. Consequently, it can be concluded that the flavylium ion is predominant and more stable at pH 1 compared to other pH values. Figure 4(b) presents the absorption spectra of black rice extract adsorbed on TiO_2 electrode at various pHs. The results obtained are in accordance with the absorption

FIGURE 2: (a) Chemical structure of cyanidin-3-glucoside and peonidin-3-glucoside present in black rice. (b) The binding between anthocyanin molecule and TiO₂ particle.

TABLE 2: V_{oc} , J_{sc} , FF , and η of DSSC with platinum as counter electrode for black rice dye solution at pH 1. Electrolyte is 26.9 wt. % chitosan-22 wt. % NH₄I(+ 2.2 wt. % I₂) + 48.9 wt. % IL.

	V_{oc} (mV)	J_{sc} ($\mu A\ cm^{-2}$)	FF (%)	η (%)
No blocking layer	195	172	31	0.01
With blocking layer	270	288	44	0.03

spectra of anthocyanin in solution (Figure 4(a)). It is noted that, at pH = 1, the black-rice-sensitized TiO₂ has the maximum absorbance at $\lambda = 538\text{ nm}$. This indicates that the flavylium ion can form bonding with Ti⁴⁺ ion more effectively [57]. Hence, anthocyanin extract of black rice solution at pH 1 was used to soak the TiO₂ photoelectrode overnight. The soaked TiO₂ photoelectrode was then used in the fabrication of ITO/TiO₂/anthocyanin dye/polymer electrolyte/counter electrode junction solar cell.

3.1.2. DSSCs Utilizing Black Rice Dye. The performance of DSSCs using Pt as the counter electrode, with and without compact blocking layer, is tabulated in Table 2. In the literature [58, 59], Ti(IV) bis(ethyl acetoacetato)-diisopropoxide has been used to prepare the blocking TiO₂ layer, and it is reported that this layer prevents electron recombination losses to the oxidized electrolyte. Recombination of electrons in the TiO₂ conduction band and electrolyte will cause the

occurrence of dark current at the electrode-electrolyte interface and deteriorate the performance of DSSC. In addition, it is understood that recombination of electrons in TiO₂ with the oxidized dye has significant effect on the performance of natural DSSC [57, 60]. In this work, diisopropoxytitanium bis(acetylacetonate) is used to prepare the blocking layer. From Table 2, it can be observed that the DSSC with blocking layer coating exhibits better performance with efficiency of 0.03% compared to that without the blocking layer ($\eta = 0.01\%$). According to Calandra et al. [61], platinum which is very compatible to I⁻/I₃⁻ redox couple helps to ensure fast reduction of the triiodide, I₃⁻ ion, and, thus, making the dye regeneration process more efficient. Also, platinum is said to help in reducing the overpotential for the triiodide reduction and thereby minimizes the energy loss [62]. Calogero and co-workers [57] reported the improvement on performance for DSSC based on eggplant sensitizer with blocking layer compared to that without blocking layer.

The highest J_{sc} and efficiency of DSSC obtained using Pt counter electrode and anthocyanin dye extracted from black rice are $288\ \mu A\ cm^{-2}$ and 0.034%, respectively. Hao et al. [19] has reported J_{sc} of $1.14\ mA\ cm^{-2}$ for DSSC sensitized by anthocyanin dyes (extracted from black rice) with liquid electrolyte. This is about four times higher compared to that in the present work. The low performance of DSSCs in this work may be due to the low ionic conductivity of the electrolyte which is only $3.43 \times 10^{-5}\ S\ cm^{-1}$. Other than

FIGURE 3: Various chemical forms of cyanidin-3-glucoside.

that, the contact issue at the electrode-electrolyte interface is also another probable reason why the performance of DSSCs in the present study is low. To improve the electrode-electrolyte contact, the electrolyte was prepared in gel form for application in DSSC. A better contact is expected between the electrode and electrolyte in gel form. Conductivity of the electrolyte in gel form has also been further improved by increasing the IL content up to 80 wt. % and by blending chitosan with PEO. The conductivity of 27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII gel electrolyte doubled upon the addition up to 80 wt. % BMII. The conductivity of chitosan-based gel electrolyte with 80 wt. % BMII increased by about four times when blending chitosan and PEO in wt. ratio 30 : 70. Figure 5 shows the J - V characteristics of DSSCs fabricated using various compositions of electrolyte in gel form. J_{sc} of $762 \mu\text{A cm}^{-2}$ and V_{oc} of 380 mV were obtained. Parameters such as V_{oc} , J_{sc} , FF , and η of DSSC employing different compositions of electrolyte in gel form are tabulated in Table 3. The conductivity of 27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII in gel form is increased by one order of magnitude compared to that of the solid electrolyte with the same composition. From Table 3, it can be noted clearly that V_{oc} , J_{sc} , FF , and η of DSSCs have significantly been increased with the use of electrolyte in gel form.

3.2. Characteristics of DSSCs Using Dye of Red Cabbage

3.2.1. UV-Vis of Red Cabbage. For the sake of comparison, the pH of red cabbage anthocyanin was also set to 1. The absorption spectra of anthocyanin extracted from red cabbage in solution and adsorbed onto the TiO_2 electrode are depicted in Figure 6. An absorption peak at about 550 nm is observed. Similar absorption peak has been reported by Furukawa et al. [63]. The absorption peak for TiO_2 -anthocyanin absorbance shifted towards lower energy indicating that complexation has occurred between the anthocyanin and TiO_2 . The carbonyl and hydroxyl groups in anthocyanin molecule can be bound to the surface of TiO_2 film as proposed by Hao and coauthors [19]. It can be observed that the absorption intensity for the TiO_2 photoelectrode soaked with red cabbage anthocyanin is only slightly lower than the intensity of absorption for the anthocyanin solution.

Figures 7(a) and 7(b) exhibit the chemical structure of anthocyanin mainly present in red cabbage and its complexation with TiO_2 particles. Cyanidin-3-(sinapoyl)diglucoside-5-glucoside is the prime species found in red cabbage [29]. As can be seen from Figure 7(b), the cyanidin-3-(sinapoyl)diglucoside-5-glucoside structure in red cabbage is able to interact with two Ti^{4+} ions.

TABLE 3: V_{oc} , J_{sc} , FF , and η of black rice anthocyanin DSSCs using various compositions of electrolyte in gel form.

Composition	Conductivity, σ ($S\ cm^{-1}$)	J_{sc} ($\mu A\ cm^{-2}$)	V_{oc} (mV)	FF (%)	η (%)
27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII	1.51×10^{-4}	762	380	48	0.14
11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII	3.02×10^{-4}	900	365	45	0.15
11 wt. % (chitosan : PEO, wt. ratio 30 : 70)-9 wt. % NH_4I -80 wt. % BMII	5.52×10^{-4}	1213	400	47	0.23

TABLE 4: V_{oc} , J_{sc} , FF , and η of DSSC employing red cabbage anthocyanin and different electrolytes in gel form.

DSSCs	Acid	Composition	Conductivity, σ ($S\ cm^{-1}$)	J_{sc} ($\mu A\ cm^{-2}$)	V_{oc} (mV)	FF (%)	η (%)
a	HCl	27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII	1.51×10^{-4}	1421	305	45	0.20
b	Tartaric	27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII		1429	475	32	0.22
c	HCl	11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII	3.02×10^{-4}	1588	450	41	0.29
d	Tartaric	11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII		2090	610	30	0.38
e	Tartaric	11 wt. % (chitosan : PEO, wt. ratio 30 : 70)-9 wt. % NH_4I -80 wt. % BMII	5.52×10^{-4}	2523	395	39	0.39
f	Tartaric	11 wt. % phthaloyl chitosan-9 wt. % NH_4I -80 wt. % BMII	5.86×10^{-4}	3472	365	34	0.43
g	Tartaric	11 wt. % (phthaloyl chitosan : PEO, wt. ratio 30 : 70)-9 wt. % NH_4I -80 wt. % BMII	6.24×10^{-4}	3503	340	39	0.46

TABLE 5: DSSC properties sensitized with natural dyes.

Dye	Electrolyte	J_{sc} ($\mu A\ cm^{-2}$)	V_{oc} (mV)	P_{max} ($mW\ cm^{-2}$)	FF (%)	η (%)	Ref.
Blue pea	Liquid	1630	404	—	57	0.05	[20]
Rosella	Liquid	370	372	—	33	0.37	[20]
Red cabbage	Liquid	4700	525	1.51	61	—	[31]
Red cabbage	Liquid	680	520	0.25	70	0.5	[63]
Black rice	Liquid	1140	551	0.327	52	—	[19]
Black rice	Liquid	1287	550	0.24	33	0.24	[64]
Blackberries	Liquid	10600	330	1.469	42	1.46	[10]
Red yeast rice	Liquid	6100	570	2.29	66	2.3	[65]
Spinach leaves	Liquid	9400	530	—	—	2.6	[57]
Red turnip	Liquid	9500	480	—	—	1.75	[57]
Skin of eggplant	Liquid	3400	350	0.48	40	0.48	[50]
Wild Sicilian prickly pear	Liquid	9400	350	—	38	1.26	[60]
Skin of jaboticaba	Liquid	2600	660	1.10	62	—	[66]
Fructus lycii	Liquid	530	689	—	46.6	0.17	[67]
Marigold	Liquid	510	542	—	83.1	0.23	[67]
Chinese rose	Liquid	900	483	—	61.9	0.27	[67]

3.2.2. DSSCs Utilizing Red Cabbage Dye. All the black rice anthocyanin DSSCs were fabricated with dyes prepared using hydrochloric acid (HCl) to adjust pH of the anthocyanin solution. The performance of DSSCs using HCl and tartaric acid to adjust pH of anthocyanin solution extracted from red cabbage is tabulated in Table 4, and Figure 8 depicts the J - V characteristics of DSSCs. For all the DSSCs utilizing red cabbage anthocyanin, electrolytes in the form of gel

were used. From Table 4, the red cabbage anthocyanin DSSC employing 27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII gel electrolyte and HCl as the agent to adjust pH exhibits higher J_{sc} and η compared to black rice anthocyanin DSSC with the same electrolyte composition in gel form and HCl as pH adjuster (see Table 3). The better performance of the DSSC employing red cabbage anthocyanin may be due to the structural differences between

FIGURE 4: The absorption spectra of anthocyanin (a) in ethanol solution and (b) on TiO_2 extracted from black rice at pH (i) 1, (ii) 2, (iii) 3, and (iv) 4.

FIGURE 5: J - V characteristics of black rice DSSC with electrolytes having (a) 27.5 wt. % chitosan-22.5 wt. % $\text{NH}_4\text{I}(\text{I}_2)$ + 50 wt. % IL (b) 11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII, and (c) 11 wt. % (chitosan:PEO, wt ratio 30:70)-9 wt. % NH_4I -80 wt. % BMII electrolyte (in gel form).

FIGURE 6: The absorption spectra of anthocyanin extracted from red cabbage.

anthocyanins from the two sources. It is understood that there is an increased charge density at the catechol end of anthocyanin molecule upon complexation with Ti^{4+} ion and, thus, enables electronic coupling for charge injection [57]. As can be seen in Figure 7(b), the molecular structure of cyanidin-3-(sinapoyl)diglucoside-5-glucoside in red cabbage provides two binding sites with Ti^{4+} ions compared to cyanidin-3-glucoside or peonidin-3-glucoside found in black rice (Figure 2(b)). Therefore, it can be inferred that the strong electronic coupling for charge injection occurs in cyanidin-3-(sinapoyl)diglucoside-5-glucoside of red cabbage which leads to better performance.

Other than blending chitosan with PEO, modification of chitosan by the method of phthaloylation can increase the ionic conductivity of the electrolyte which in turn improves the DSSC performance. The conductivity of 11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII gel electrolyte is almost doubled for the same gel electrolyte composition, but using phthaloyl chitosan as polymer host. The J_{sc} of DSSC employing 11 wt. % phthaloyl chitosan-9 wt. % NH_4I -80 wt. % BMII gel electrolyte is ~ 1.7 times higher than J_{sc} of DSSC utilizing 11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII gel electrolyte. Efficiency of the former DSSC is also higher than that of the latter. From the table, it can be observed that the use of tartaric acid as pH adjustment agent resulted in higher efficiency of DSSCs. It can be seen clearly that DSSC using tartaric acid as pH adjustment agent and phthaloyl chitosan-PEO blend electrolyte in gel form exhibits the highest short-circuit current density and efficiency. The V_{oc} and J_{sc} of DSSC with red cabbage as sensitizer and phthaloyl chitosan-PEO blend electrolyte in this work are comparable to the V_{oc} (525 mV) and J_{sc} ($4700 \mu\text{A cm}^{-2}$) of DSSC employing red cabbage and liquid electrolyte obtained by Calogero and Marco [50]. Furukawa et al. [63] reported that η of 0.50% was achieved by red cabbage DSSC under illumination of 50 mW cm^{-2} .

Tartaric acid is one of the most concentrated naturally occurring organic acids in grapes and wine. It mainly acts as an acidity adjuster in foods. Since tartaric acid is a diprotic

FIGURE 7: (a) Molecular structure of cyanidin-3-(sinapoyl)diglucoside mainly found in red cabbage and (b) complexation between anthocyanin molecule and TiO_2 particles.

organic acid, it is able to donate two protons, H^+ , per acid molecule when dissolved in solvent. Tartaric acid has twice the number of available hydronium ions compared to that of hydrochloric acid which helps in the absorption of photons in the visible region. Hence, tartaric acid is more suitable to serve as pH adjuster. Since ethanol was used in the solvent extraction of anthocyanin and being an organic acid, tartaric acid is more soluble in ethanol compared to HCl. This is an added advantage to tartaric acid as a pH adjuster.

To gauge the performance of the best DSSC obtained from this work, comparison with reported DSSCs using natural dyes was carried out. Table 5 lists the performance parameters of various DSSCs using natural dye found in the literature. Although the best DSSC obtained from this work uses gel polymer electrolyte of conductivity $\sim 10^{-4} \text{ S cm}^{-1}$, its efficiency is comparable to some of the reported DSSCs using liquid electrolyte.

4. Conclusions

UV-Vis studies show the shift of the absorption band of TiO_2 immersed in anthocyanin solution indicating the occurrence of complexation between anthocyanin and Ti^{4+} ions.

Absorption spectrum also shows that anthocyanin dye from black rice is found to be highly absorbing at pH 1, and; thus, the TiO_2 photoelectrode was soaked in anthocyanin dye at this pH. The conductivity of the electrolyte influences short-circuit current density of the cell. Anthocyanin (from black rice) dye-sensitized solar cell with platinum as counter electrode exhibited the J_{sc} of $172 \mu\text{A cm}^{-2}$ and V_{oc} of 195 mV. The performance of ITO/ TiO_2 /anthocyanin dye/26.9 wt. % chitosan-22 wt. % NH_4I (+2.2 wt. % I_2) + 48.9 wt. % IL/Pt cell was improved by coating a diisopropoxytitanium bis(acetylacetonate) layer on the ITO glass. J_{sc} increased from $172 \mu\text{A cm}^{-2}$ to $288 \mu\text{A cm}^{-2}$. The utilization of electrolyte in gel form improves the performance of DSSC. Black rice anthocyanin DSSC employing gel electrolyte of composition chitosan-PEO blend (wt. ratio 30:70) doped with 9 wt. % NH_4I (+ I_2) and 80 wt. % IL exhibited J_{sc} of $1213 \mu\text{A cm}^{-2}$, V_{oc} of 0.4 V, and η of 0.23%. A similar DSSC, but using red cabbage anthocyanin at the same pH (also adjusted with HCl), exhibited better performance with efficiency of 0.29%. The better performance of the red cabbage anthocyanin DSSC compared to black rice DSSC is attributed to the structural differences between the two anthocyanins. The cell fabricated using red cabbage anthocyanin as dye sensitizer

FIGURE 8: J - V characteristics of the red cabbage DSSCs for sample (a) HCl as pH adjuster and 27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII gel electrolyte, (b) tartaric acid as pH adjuster and 27.5 wt. % chitosan-22.5 wt. % NH_4I -50 wt. % BMII gel electrolyte, (c) HCl as pH adjuster and 11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII gel electrolyte, (d) tartaric acid as pH adjuster and 11 wt. % chitosan-9 wt. % NH_4I -80 wt. % BMII gel electrolyte, (e) tartaric acid as pH adjuster and 11 wt. % (chitosan:PEO, wt. ratio 30:70)-9 wt. % NH_4I -80 wt. % BMII gel electrolyte, (f) tartaric acid as pH adjuster and 11 wt. % phthaloyl chitosan-9 wt. % NH_4I -80 wt. % BMII gel electrolyte and (g) tartaric acid as pH adjuster and 11 wt. % (chitosan : PEO, wt ratio 30:70)-9 wt. % NH_4I -80 wt. % BMII gel electrolyte.

and phthaloyl chitosan-PEO blend electrolyte in gel form as the electrolyte exhibits a J_{sc} of $3503 \mu\text{A cm}^{-2}$ and η of 0.46%. The use of tartaric acid to adjust pH on red cabbage anthocyanin improves the DSSC performance. This may be due to its diprotic nature.

Acknowledgments

The authors would like to thank the University of Malaya for the financial support through PS353/2009A and PS325/2009C Grants to carry out this research work. M. H. Buraidah and S. N. F. Yusuf thank the Ministry of Education Malaysia and the University of Malaya for the scholarship and tutorship awards, and M. M. Noor thanks the International Islamic University Malaysia (IIUM) for the study leave awarded.

References

- [1] M. Grätzel, "Dye-sensitized solar cells," *Journal of Photochemistry and Photobiology C*, vol. 4, no. 2, pp. 145–153, 2003.
- [2] S. Karuppuchamy, J. M. Jeong, D. P. Amalnerkar, and H. Minoura, "Photoinduced hydrophilicity of titanium dioxide thin films prepared by cathodic electrodeposition," *Vacuum*, vol. 80, no. 5, pp. 494–498, 2006.
- [3] C. Longo and M. A. De Paoli, "Dye-sensitized solar cells: a successful combination of materials," *Journal of the Brazilian Chemical Society*, vol. 14, no. 6, pp. 889–901, 2003.
- [4] K. M. Lee, W. H. Chiu, H. Y. Wei et al., "Effects of mesoscopic poly(3,4-ethylenedioxythiophene) films as counter electrodes for dye-sensitized solar cells," *Thin Solid Films*, vol. 518, no. 6, pp. 1716–1721, 2010.
- [5] J. Wu, Q. Li, L. Fan et al., "High-performance polypyrrole nanoparticles counter electrode for dye-sensitized solar cells," *Journal of Power Sources*, vol. 181, no. 1, pp. 172–176, 2008.
- [6] Q. Li, J. Wu, Q. Tang et al., "Application of microporous polyaniline counter electrode for dye-sensitized solar cells," *Electrochemistry Communications*, vol. 10, no. 9, pp. 1299–1302, 2008.
- [7] T. Denaro, V. Baglio, M. Girolamo et al., "Investigation of low cost carbonaceous materials for application as counter electrode in dye-sensitized solar cells," *Journal of Applied Electrochemistry*, vol. 39, no. 11, pp. 2173–2179, 2009.
- [8] K. Imoto, K. Takahashi, T. Yamaguchi, T. Komura, J. I. Nakamura, and K. Murata, "High-performance carbon counter electrode for dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 79, no. 4, pp. 459–469, 2003.
- [9] T. N. Murakami and M. Grätzel, "Counter electrodes for DSC: application of functional materials as catalysts," *Inorganica Chimica Acta*, vol. 361, no. 3, pp. 572–580, 2008.
- [10] H. Zhu, H. Zeng, V. Subramanian, C. Masarapu, K. H. Hung, and B. Wei, "Anthocyanin-sensitized solar cells using carbon nanotube films as counter electrodes," *Nanotechnology*, vol. 19, no. 46, Article ID 465204, 2008.
- [11] G. Calogero, F. Bonaccorso, O. M. Maragò, P. G. Gucciardi, and G. Di Marco, "Single wall carbon nanotubes deposited on stainless steel sheet substrates as novel counter electrodes for ruthenium polypyridine based dye sensitized solar cells," *Dalton Transactions*, vol. 39, no. 11, pp. 2903–2909, 2010.
- [12] M. Y. Yen, C. Y. Yen, S. H. Liao et al., "A novel carbon-based nanocomposite plate as a counter electrode for dye-sensitized solar cells," *Composites Science and Technology*, vol. 69, no. 13, pp. 2193–2197, 2009.
- [13] G. Calogero, P. Calandra, A. Irrera, A. Sinopoli, I. Citro, and G. Di Marco, "A new type of transparent and low cost counter-electrode based on platinum nanoparticles for dye-sensitized solar cells," *Energy and Environmental Science*, vol. 4, no. 5, pp. 1838–1844, 2011.
- [14] K. Kalyanasundaram and M. Grätzel, "Applications of functionalized transition metal complexes in photonic and optoelectronic devices," *Coordination Chemistry Reviews*, vol. 177, no. 1, pp. 347–414, 1998.
- [15] M. K. Nazeeruddin, S. M. Zakeeruddin, J. J. Lagref et al., "Stepwise assembly of amphiphilic ruthenium sensitizers and their applications in dye-sensitized solar cell," *Coordination Chemistry Reviews*, vol. 248, no. 13-14, pp. 1317–1328, 2004.
- [16] C. Klein, M. K. Nazeeruddin, P. Liska et al., "Engineering of a novel ruthenium sensitizer and its application in dye-sensitized solar cells for conversion of sunlight into electricity," *Inorganic Chemistry*, vol. 44, no. 2, pp. 178–180, 2005.
- [17] P. Wang, B. Wenger, R. Humphry-Baker et al., "Charge separation and efficient light energy conversion in sensitized mesoscopic solar cells based on binary ionic liquids," *Journal of the American Chemical Society*, vol. 127, no. 18, pp. 6850–6856, 2005.
- [18] Y. Amao and T. Komori, "Bio-photovoltaic conversion device using chlorine-e6 derived from chlorophyll from Spirulina adsorbed on a nanocrystalline TiO_2 film electrode," *Biosensors and Bioelectronics*, vol. 19, no. 8, pp. 843–847, 2004.
- [19] S. Hao, J. Wu, Y. Huang, and J. Lin, "Natural dyes as photosensitizers for dye-sensitized solar cell," *Solar Energy*, vol. 80, no. 2, pp. 209–216, 2006.

- [20] K. Wongcharee, V. Meeyoo, and S. Chavadej, "Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers," *Solar Energy Materials and Solar Cells*, vol. 91, no. 7, pp. 566–571, 2007.
- [21] Ø. M. Andersen, T. Fossen, K. Torskangerpoll, A. Fossen, and U. Hauge, "Anthocyanin from strawberry (*Fragaria ananassa*) with the novel aglycone, 5-carboxypyranopelargonidin," *Phytochemistry*, vol. 65, no. 4, pp. 405–410, 2004.
- [22] A. Olea, G. Ponce, and P. J. Sebastian, "Electron transfer via organic dyes for solar conversion," *Solar Energy Materials and Solar Cells*, vol. 59, no. 1, pp. 137–143, 1999.
- [23] Q. Dai and J. Rabani, "Unusually efficient photosensitization of nanocrystalline TiO₂ films by pomegranate pigments in aqueous medium," *New Journal of Chemistry*, vol. 26, no. 4, pp. 421–426, 2002.
- [24] P. M. Sirimanne, M. K. I. Senevirathna, E. Premalal, P. K. D. D. P. Pitigala, V. Sivakumar, and K. Tennakone, "Utilization of natural pigment extracted from pomegranate fruits as sensitizer in solid-state solar cells," *Journal of Photochemistry and Photobiology A*, vol. 177, no. 2-3, pp. 324–327, 2006.
- [25] A. A. Gitelson, M. N. Merzlyak, and O. B. Chivkunova, "Optical properties and nondestructive estimation of anthocyanin content in plant leaves," *Photochemistry and Photobiology*, vol. 74, no. 1, pp. 38–45, 2001.
- [26] S. H. Nam, S. M. Chang, and M. Y. Kang, "Screening of mutagenicity and antimutagenic activity against chemical direct mutagens of ethanolic extracts from colored rice bran," *Journal of the Korean society of Agricultural Chemistry and Biotechnology*, vol. 45, pp. 195–202, 2002.
- [27] C. Hu, J. Zawistowski, W. Ling, and D. D. Kitts, "Black rice (*Oryza sativa* L. *indica*) pigmented fraction suppresses both reactive oxygen species and nitric oxide in chemical and biological model systems," *Journal of Agricultural and Food Chemistry*, vol. 51, no. 18, pp. 5271–5277, 2003.
- [28] Z. Xu, J. Wu, Y. Zhang, X. Hu, X. Liao, and Z. Wang, "Extraction of anthocyanins from red cabbage using high pressure CO₂," *Bioresource Technology*, vol. 101, no. 18, pp. 7151–7157, 2010.
- [29] G. J. McDougall, S. Fyffe, P. Dobson, and D. Stewart, "Anthocyanins from red cabbage—stability to simulated gastrointestinal digestion," *Phytochemistry*, vol. 68, no. 9, pp. 1285–1294, 2007.
- [30] N. Chigurupati, L. Saiki, C. Gayser, and A. K. Dash, "Evaluation of red cabbage dye as a potential natural color for pharmaceutical use," *International Journal of Pharmaceutics*, vol. 241, no. 2, pp. 293–299, 2002.
- [31] D. Zhang, N. Yamamoto, T. Yoshida, and H. Minoura, "Natural dye-sensitized solar cells," *Transactions of the Materials Research Society of Japan*, vol. 27, no. 4, pp. 811–814, 2002.
- [32] S. Furukawa, H. Iino, K. Kukita, and K. Kaminosono, "Effects of pH of dyes on characteristics of dye-sensitized solar cells," *IEEE Transactions on Fundamentals and Materials*, vol. 130, no. 2, pp. 136–140, 2010.
- [33] O. A. Ileperuma, M. A. K. L. Dissanayake, S. Somasunderam, and L. R. A. K. Bandara, "Photoelectrochemical solar cells with polyacrylonitrile-based and polyethylene oxide-based polymer electrolytes," *Solar Energy Materials and Solar Cells*, vol. 84, no. 1–4, pp. 117–124, 2004.
- [34] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [35] H. Gerischer, "Electrochemical photo and solar cells principles and some experiments," *Journal of Electroanalytical Chemistry*, vol. 58, no. 1, pp. 263–274, 1975.
- [36] J. Wu, P. Li, S. Hao, H. Yang, and Z. Lan, "A polyblend electrolyte (PVP/PEG+KI+I₂) for dye-sensitized nanocrystalline TiO₂ solar cells," *Electrochimica Acta*, vol. 52, no. 17, pp. 5334–5338, 2007.
- [37] S. A. Mohamad, M. H. Ali, R. Yahya, Z. A. Ibrahim, and A. K. Arof, "Photovoltaic activity in a ZnSe/PEO-chitosan blend electrolyte junction," *Ionics*, vol. 13, no. 4, pp. 235–240, 2007.
- [38] S. A. Mohamad, R. Yahya, Z. A. Ibrahim, and A. K. Arof, "Photovoltaic activity in a ZnTe/PEO-chitosan blend electrolyte junction," *Solar Energy Materials and Solar Cells*, vol. 91, no. 13, pp. 1194–1198, 2007.
- [39] V. C. Nogueira, C. Longo, A. F. Nogueira, M. A. Soto-Oviedo, and M. A. D. Paoli, "Solid-state dye-sensitized solar cell: improved performance and stability using a plasticized polymer electrolyte," *Journal of Photochemistry and Photobiology A*, vol. 181, no. 2-3, pp. 226–232, 2006.
- [40] S. A. Haque, E. Palomares, H. M. Upadhyaya et al., "Flexible dye sensitised nanocrystalline semiconductor solar cells," *Chemical Communications*, vol. 9, no. 24, pp. 3008–3009, 2003.
- [41] O. A. Ileperuma, M. A. K. L. Dissanayake, and S. Somasundaram, "Dye-sensitized photoelectrochemical solar cells with polyacrylonitrile based solid polymer electrolytes," *Electrochimica Acta*, vol. 47, no. 17, pp. 2801–2807, 2002.
- [42] P. Wang, S. M. Zakeeruddin, J. E. Moser, and M. Grätzel, "A new ionic liquid electrolyte enhances the conversion efficiency of dye-sensitized solar cells," *Journal of Physical Chemistry B*, vol. 107, no. 48, pp. 13280–13285, 2003.
- [43] N. Yamanaka, R. Kawano, W. Kubo et al., "Dye-sensitized TiO₂ solar cells using imidazolium-type ionic liquid crystal systems as effective electrolytes," *Journal of Physical Chemistry B*, vol. 111, no. 18, pp. 4763–4769, 2007.
- [44] D. Kuang, P. Wang, S. Ito, S. M. Zakeeruddin, and M. Grätzel, "Stable mesoscopic dye-sensitized solar cells based on tetracyanoborate ionic liquid electrolyte," *Journal of the American Chemical Society*, vol. 128, no. 24, pp. 7732–7733, 2006.
- [45] Q. Dai, D. B. Menzies, D. R. MacFarlane et al., "Dye-sensitized nanocrystalline solar cells incorporating ethylmethylimidazolium-based ionic liquid electrolytes," *Comptes Rendus Chimie*, vol. 9, no. 5-6, pp. 617–621, 2006.
- [46] D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, and M. Forsyth, "Pyrrolidinium imides: a new family of molten salts and conductive plastic crystal phases," *Journal of Physical Chemistry B*, vol. 103, no. 20, pp. 4164–4170, 1999.
- [47] E. I. Cooper and E. J. M. O'Sullivan, *Proceedings of the Eight International Symposium on Molten Salts*, R. J. Gale, G. Blomgren, and H. Kojima, Eds., The Electrochemical Society Proceedings Series, The Electrochemical Society, Pennington, NJ, USA, 1992.
- [48] J. Wu, Z. Lan, S. Hao et al., "Progress on the electrolytes for dye-sensitized solar cells," *Pure and Applied Chemistry*, vol. 80, no. 11, pp. 2241–2258, 2008.
- [49] A. K. Arof, M. H. Buraidah, L. P. Teo, S. R. Majid, R. Yahya, and R. M. Taha, "Characterizations of chitosan-based polymer electrolyte photovoltaic cells," *International Journal of Photoenergy*, vol. 2010, Article ID 805836, 7 pages, 2010.
- [50] G. Calogero and G. D. Marco, "Red Sicilian orange and purple eggplant fruits as natural sensitizers for dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 92, no. 11, pp. 1341–1346, 2008.
- [51] P. M. Sirimanne and T. Soga, "Fabrication of a solid-state cell using vitamin C as sensitizer," *Solar Energy Materials and Solar Cells*, vol. 80, no. 3, pp. 383–389, 2003.

- [52] S. N. Ryu, S. Z. Park, and C. T. Ho, "High performance liquid chromatographic determination of anthocyanin pigments in some varieties of black rice," *Journal of Food and Drug Analysis*, vol. 6, no. 4, pp. 729–736, 1998.
- [53] A. Bakowska, A. Z. Kucharska, and J. Oszmiański, "The effects of heating, UV irradiation, and storage on stability of the anthocyanin-polyphenol copigment complex," *Food Chemistry*, vol. 81, no. 3, pp. 349–355, 2003.
- [54] A. Castañeda-Ovando, Ma. d. L. Pacheco-Hernández, Ma. E. Pérez-Hernández, J. A. Rodríguez, and C. A. Galán-Vidal, "Chemical studies of anthocyanins: a review," *Food Chemistry*, results obtained are in accordance with vol. 113, no. 4, pp. 859–871, 2009.
- [55] G. Fan, Y. Han, Z. Gu, and F. Gu, "Composition and colour stability of anthocyanins extracted from fermented purple sweet potato culture," *Food Science and Technology*, vol. 41, no. 8, pp. 1412–1416, 2008.
- [56] J. M. R. C. Fernando and G. K. R. Senadeera, "Natural anthocyanins as photosensitizers for dye-sensitized solar devices," *Current Science*, vol. 95, no. 5, pp. 663–666, 2008.
- [57] G. Calogero, G. Di Marco, S. Caramori, S. Cazzanti, R. Argazzi, and C. A. Bignozzi, "Natural dye sensitizers for photoelectrochemical cells," *Energy and Environmental Science*, vol. 2, no. 11, pp. 1162–1172, 2009.
- [58] J. H. Kim, M. S. Kang, Y. J. Kim, J. Won, and Y. S. Kang, "Poly(butyl acrylate)/NaI/I₂ electrolytes for dye-sensitized nanocrystalline TiO₂ solar cells," *Solid State Ionics*, vol. 176, no. 5-6, pp. 579–584, 2005.
- [59] P. K. Singh, K. W. Kim, and H. W. Rhee, "Development and characterization of ionic liquid doped solid polymer electrolyte membranes for better efficiency," *Synthetic Metals*, vol. 159, no. 15-16, pp. 1538–1541, 2009.
- [60] G. Calogero, G. Di Marco, S. Cazzanti et al., "Efficient dye-sensitized solar cells using red turnip and purple wild Sicilian prickly pear fruits," *International Journal of Molecular Sciences*, vol. 11, no. 1, pp. 254–267, 2010.
- [61] P. Calandra, G. Calogero, A. Sinopoli, and P. G. Gucciardi, "Metal nanoparticles and carbon-based nanostructures as advanced materials for cathode application in dye-sensitized solar cells," *International Journal of Photoenergy*, vol. 2010, Article ID 109495, 15 pages, 2010.
- [62] C. H. Yoon, R. Vittal, J. Lee, W. S. Chae, and K. J. Kim, "Enhanced performance of a dye-sensitized solar cell with an electrodeposited-platinum counter electrode," *Electrochimica Acta*, vol. 53, no. 6, pp. 2890–2896, 2008.
- [63] S. Furukawa, H. Iino, T. Iwamoto, K. Kukita, and S. Yamauchi, "Characteristics of dye-sensitized solar cells using natural dye," *Thin Solid Films*, vol. 518, no. 2, pp. 526–529, 2009.
- [64] B. Yulianto, W. Septina, K. Fuadi, F. Fanani, L. Muliani, and Nugraha, "Synthesis of nanoporous TiO₂ and its potential applicability for dye-sensitized solar cell using antocyanine black rice," *Advances in Materials Science and Engineering*, vol. 2010, Article ID 789541, 6 pages, 2010.
- [65] S. Ito, T. Saitou, H. Imahori, H. Uehara, and N. Hasegawa, "Fabrication of dye-sensitized solar cells using natural dye for food pigment: Monascus yellow," *Energy and Environmental Science*, vol. 3, no. 7, pp. 905–909, 2010.
- [66] A. S. Polo and N. Y. Murakami Iha, "Blue sensitizers for solar cells: natural dyes from Calafate and Jaboticaba," *Solar Energy Materials and Solar Cells*, vol. 90, no. 13, pp. 1936–1944, 2006.
- [67] H. Zhou, L. Wu, Y. Gao, and T. Ma, "Dye-sensitized solar cells using 20 natural dyes as sensitizers," *Journal of Photochemistry and Photobiology A*, vol. 219, no. 2-3, pp. 188–194, 2011.