CHAPTER 7

FABRICATION OF DYE-SENSITIZED SOLAR CELLS

7.1 INTRODUCTION

Chitosan as a host in polymer electrolyte systems has been successfully prepared. Their properties have been analyzed in the previous chapters. In this chapter, three systems of chitosan-based electrolyte with different conductivities have been used for fabrication of dye-sensitized solar cells. Natural and synthetic dyes have been used as sensitizer. Natural anthocyanin dyes have been extracted from black rice, blueberry and red cabbage.

7.2 CHARACTERISTICS OF DSSCS USING DYE EXTRACTED FROM BLACK RICE

7.2.1 UV-Vis studies of black rice

Figure 7.1 shows the absorption spectra of bare TiO_2 electrode, anthocyanin extracted from black rice in solution and anthocyanin adsorbed into the TiO_2 electrode. The anthocyanin dye clearly shows a broad absorption spectrum in the region of visible light (color from red (700 nm) to blue (400nm)). This indicates that anthocyanin has the potential to act as a good sensitizer for wide bandgap semiconductors [Hao *et al.*, 2006]. The absorption spectrum for black rice anthocyanin in solution shows a peak at wavelength, λ = 535 nm. Also, it can be observed that the absorption band of anthocyanin/TiO_2 is red-shifted towards higher wavelength (λ = 538 nm) compared to absorption band of anthocyanin in solution.

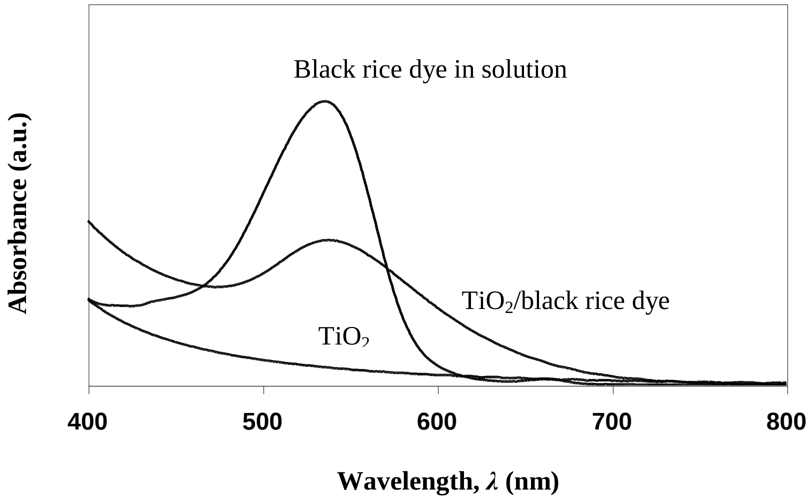

Figure 7.1: The absorption spectra of TiO_2 electrode, anthocyanin from black rice in solution and absorbed onto TiO_2 electrode

Figure 7.2 depicts the absorption spectrum of anthocyanin extracted from black rice at different pH. From the figure, it can be seen that the absorption peak increases with decreasing pH. The highest absorption peak intensity can be observed at pH 1 compared to pH 2, pH 3 and pH 4 as shown in the figure.

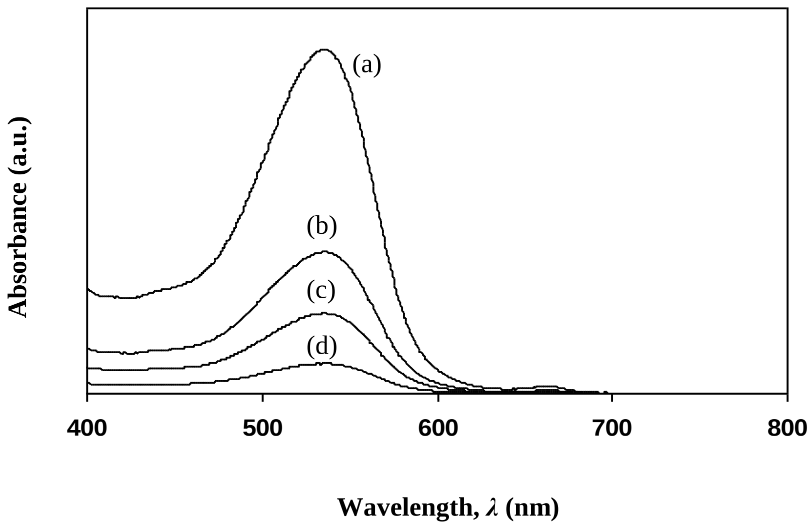

Figure 7.2: The absorption spectrum of anthocyanin extract of black rice solutions at pH a) 1, b) 2, c) 3 and d) 4

Figure 7.3 shows that complexation can occur between cyanidin-3-glucoside (from black rice) and TiO_2 particles.

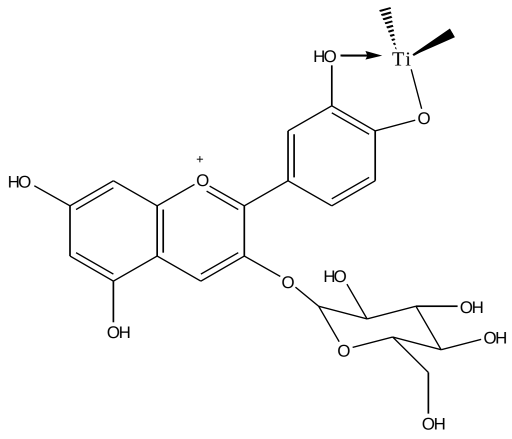

Figure 7.3: The binding between anthocyanin (black rice) molecule and TiO_2 particle

7.2.2 DSSCs utilizing black rice anthocyanin

7.2.2.1 Effect of electrolyte conductivity

Table 7.1 displays the performance of black rice DSSCs using ITO glass as counter electrode with different electrolyte compositions. The aim of this study is to investigate the relationship between electrolyte conductivity and short-circuit current density of the DSSC. In all solar cells, the anthocyanin solution used to soak the TiO_2 layer has a pH value of 3. Short-circuit current density, J_{sc} of 0.006 mA cm^{-2}, 0.007 mA cm^{-2}, 0.022 mA cm^{-2} and 0.032 mA cm^{-2} and open-circuit voltage, V_{oc} of 0.16 V, 0.20 V, 0.14 V and 0.24 V are obtained for DSSCs using Ch9, CIL1, CIL3 and CIL5 electrolytes respectively. The efficiency of the cells is observed to increase five times using CIL5 electrolyte. Referring to chapter 6, the conductivity of the electrolytes follows the order σ (Ch9) < σ (CIL1) < σ (CIL3) < σ (CIL5). From Table 7.1, it can be concluded that the performance of DSSCs is increasing with the conductivity of the electrolytes.

Table 7.1: Electrolyte composition, room temperature conductivity of electrolytes and their DSSCs performance. pH of dye solution is 3

Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	fill factor (*ff*)	P_{max} (mW cm^{-2})	η %
Ch9(+I_2)	0.006	0.16	0.16	0.0002	0.0002
CIL1(+I_2)	0.007	0.20	0.31	0.0004	0.0004
CIL3(+I_2)	0.022	0.14	0.19	0.0006	0.0006
CIL5(+I_2)	0.032	0.24	0.14	0.001	0.001

7.2.2.2 Effect of pH on dye

The performance of DSSCs at different pH of the dye solution for electrolyte with a fixed IL content of 50 wt. % is shown in Table 7.2. For this work, the electrolyte with the highest conductivity in Table 7.1 was employed. With addition of 2.2 wt% I_2, the composition of the electrolyte can be written as 26.9 wt. % chitosan-22 wt. % NH_4I(+ 2.2 wt. %I_2) + 48.9 wt. % IL. It is noted that a high J_{sc} of 0.065 mA cm^{-2} and high efficiency of 0.003% was obtained when the TiO_2 was soaked with pH 1 anthocyanin solution.

Table 7.2: The performance of DSSC with ITO counter electrode at different pH of the dye solution. Electrolyte is 26.9 wt. % chitosan-22 wt. % NH_4I(+ 2.2 wt. %I_2) + 48.9 wt. % IL

pH	J_{sc} (mA cm^{-2})	V_{oc} (V)	fill factor (*ff*)	P_{max} (mW cm^{-2})	η %
1	0.065	0.22	0.22	0.0029	0.003
2	0.044	0.22	0.15	0.0013	0.002
3	0.032	0.24	0.14	0.0010	0.001
4	0.027	0.18	0.15	0.0008	0.001

7.2.2.3 Effect of compact layer between TiO_2 and ITO surface

All the DSSCs in Tables 7.1 and 7.2 were fabricated without blocking layer coated on to the ITO glass. From the literature [Kim *et al*., 2005; Singh *et al*., 2008b], Ti(IV)bis(ethyl acetoacetato)-diisopropoxide serves as blocking layer prevents electron recombination losses to the oxidized electrolyte. In this work, the blocking layer consists of diisopropoxytitanium bis(acetylacetonate). The performance of DSSCs using Pt as counter electrode and anthocyanin at pH 1 as sensitizer with and without blocking layer is listed in Table 7.3. As can be seen, DSSC without blocking layer exhibited highest J_{sc} value of 0.17 mA cm^{-2} and efficiency of 0.01%. The DSSC with ITO blocking layer coating exhibited better performance compared to that without the blocking layer. The highest J_{sc} and efficiency of DSSC using anthocyanin dye extracted from black rice is 0.29 mA cm^{-2} and 0.04 %, respectively. However, the performance of DSSCs is still below par. The low performance of the DSSCs may be due to poor contact at the electrode-electrolyte interface. To improve electrode-electrolyte contact, the electrolyte was prepared in gel form for application in DSSC. It is expected that better contact will be created between electrode and electrolyte in gel form.

Table 7.3: V_{oc}, J_{sc} and *ff* of DSSC with platinum as counter electrode for dye solution at pH 1. Electrolyte is 26.9 wt. % chitosan-22 wt. % NH_4I(+ 2.2 wt. %I_2) + 48.9 wt. % IL

	J_{sc} (mA cm^{-2})	V_{oc} (V)	fill factor *ff*	P_{max} (mW cm^{-2})	η %
no blocking layer	0.17	0.20	0.31	0.011	0.01
with blocking layer	0.29	0.30	0.44	0.038	0.04

Figure 7.4 presents the *J-V* characteristics of DSSCs fabricated using CIL5 electrolyte in gel form.

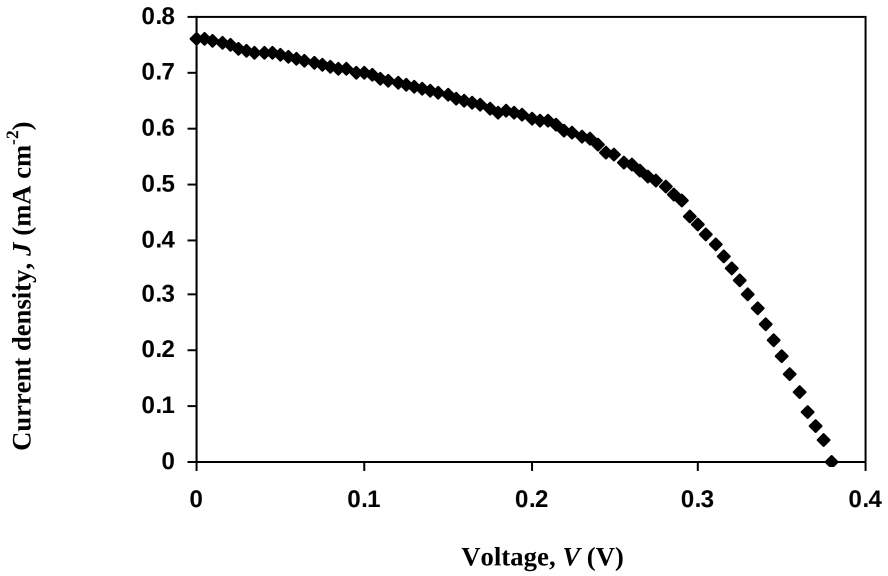

Figure 7.4: *J-V* characteristics of the DSSC for CIL5 electrolyte (in gel form)

J_{sc} of 0.76 mA cm^{-2}, V_{oc} of 0.38 V, fill factor, *ff* of 0.48 and efficiency of 0.14% were obtained. For comparison, conductivity of 27.5 wt. % chitosan-22.5 wt. % NH_4I-50 wt. % BMII (CIL5) in gel form is increased by one order of magnitude (1.51×10^{-4} S cm^{-1}) compared to the solid electrolyte with the same composition.

7.3 CHARACTERISTICS OF DSSCS USING DYE EXTRACTED FROM BLUEBERRY

7.3.1 UV-Vis studies of blueberry

Figure 7.5 depicts the absorption spectra of bare TiO_2 electrode, anthocyanin extracted from blueberry in solution and that adsorbed into the TiO_2 electrode, respectively. The maximum absorption spectrum of blueberry anthocyanin in solution shows at λ_{max} = 546 nm while anthocyanin adsorbed onto the TiO_2 electrode depicts maximum absorption at λ_{max} = 530 nm.

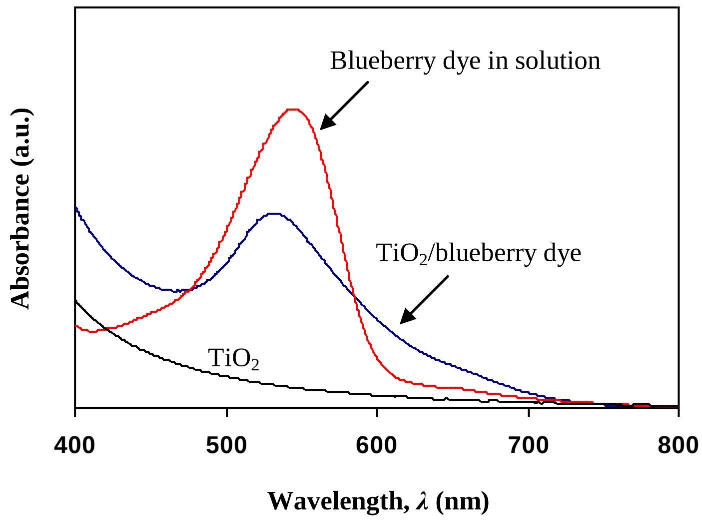

Figure 7.5: The absorption spectra of TiO_2 electrode, anthocyanin from blueberry in solution and absorbed onto TiO_2 electrode

In the spectrum of anthocyanin dye extracted from blueberry, the intensity of absorption peak of anthocyanin with pH 1 is slightly higher compared to that with pH 2 and much higher compared to that with pH 3 and pH 4, respectively as shown in Figure 7.6. Hence, in the fabrication of DSSC, anthocyanin with pH 1 was used.

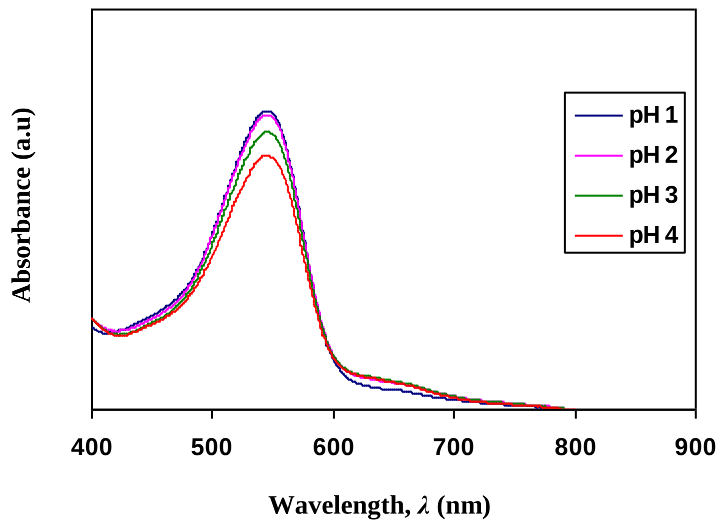

Figure 7.6: The absorption spectra of anthocyanin solutions at pH 4 to pH 1 extracted from blueberry

Figure 7.7 shows that complexation can occur between anthocyanin molecule (from blueberry) and TiO_2 particles.

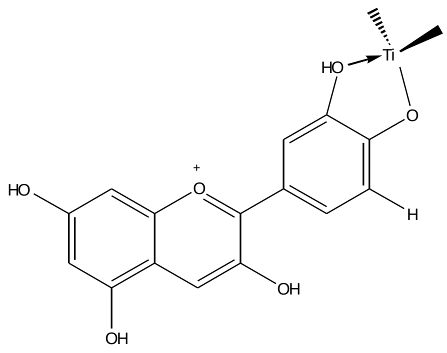

Figure 7.7: The binding between anthocyanin (blueberry) molecule and TiO_2 particle

7.3.2 DSSCs utilizing blueberry

J-V characteristics of ITO/TiO_2/dye/(27.5 wt.% chitosan-27.5 wt.% PVA)-45 wt.% $NH_4I(+I_2)$ (CV5($+I_2$))/Pt/ITO, ITO/TiO_2/dye/(16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO7($+I_2$)/Pt/ITO, and ITO/TiO_2/dye/27.5 wt.% chitosan-22.5 wt.% $NH_4I(+I_2)$-50 wt.% IL (CIL5($+I_2$)/Pt/ITO solar cells using blueberry anthocyanin solution as a dye sensitizer is illustrated in Figure 7.8.

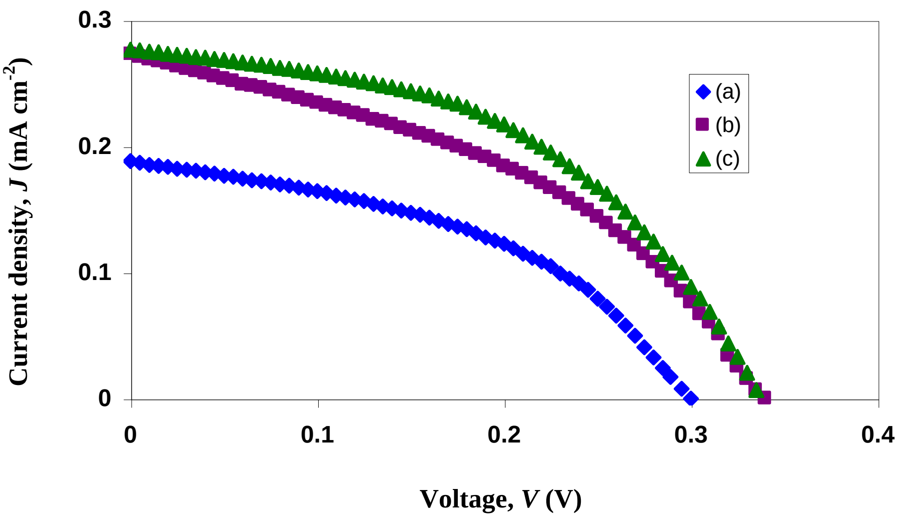

Figure 7.8: *J-V* curve of DSSCs using (a) CV5 electrolyte (b) CEO7 electrolyte and (c) CIL5 electrolyte. The dye solution is extracted from blueberry with pH 1

Short-circuit current density, J_{sc} of 0.19 mA cm^{-2}, 0.27 mA cm^{-2} and 0.28 mA cm^{-2} and open-circuit voltage, V_{oc} of 0.30 V, 0.34 V and 0.34 V were obtained for DSSCs using CV5, CEO7 and CIL5 electrolyte respectively and blueberry as the dye. Referring to chapter 6, the conductivity of the electrolytes follows the order σ (CV5) < σ (CEO7) < σ (CIL5). It can be observed that performance of the dye-sensitized solar cells is enhanced with the increase in conductivity of the electrolytes.

Similar trend of results has been obtained for ITO/TiO_2/dye/(27.5 wt.% chitosan-27.5 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO5($+I_2$))/ Pt/ITO, ITO/TiO_2/ dye/(23.0 wt.% chitosan-33.0 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO6($+I_2$))/Pt/ ITO and ITO/TiO_2/dye/(16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO7($+I_2$)/Pt/ITO solar cells using blueberry as dye sensitizer is shown in Figure 7.9. The conductivity of the electrolytes follows the order σ (CEO5) < σ (CEO6) < σ (CEO7). Performance of the blueberry DSSCs is summarized in Table 7.4.

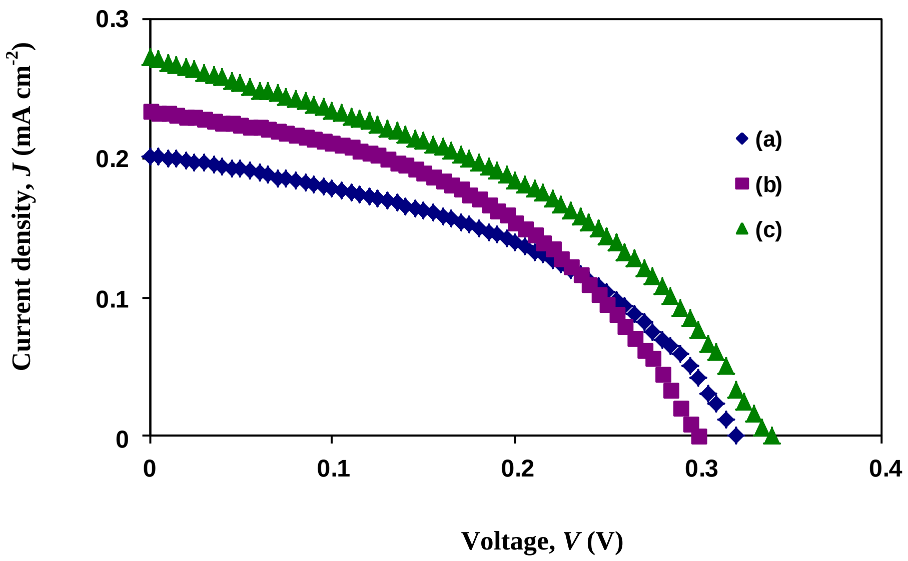

Figure 7.9: *J-V* curve of DSSCs using (a) CEO5 electrolyte (b) CEO6 electrolyte and (c) CEO7 electrolyte. The dye solution is extracted from blueberry with pH 1

Table 7.4: List of open-circuit voltage (V_{oc}), short circuit current density (J_{sc}) fill factor (*ff*), maximum power density (P_{max}) and efficiency (η %) for dye-sensitized solar cells (blueberry dye)

Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	fill factor (*ff*)	P_{max} (mW cm^{-2})	η (%)
CV5(+I_2)	0.19	0.30	0.43	0.025	0.02
CEO5(+I_2)	0.20	0.32	0.43	0.030	0.03
CEO6(+I_2)	0.23	0.30	0.44	0.030	0.03
CEO7(+I_2)	0.27	0.34	0.40	0.038	0.04
CIL5(+I_2)	0.28	0.34	0.46	0.044	0.04

Figure 7.10 presents *J-V* characteristics of dye-sensitized solar cell CIL5 electrolyte in gel form. As expected, the performance of dye-sensitized solar cell is improved using gel electrolyte. The cell exhibits short-circuit current density, J_{sc} of 1.178 mA cm^{-2}, open-circuit voltage, V_{oc} of 335 mV, fill factor, *ff* of 0.38 and efficiency, η of 0.15 %.

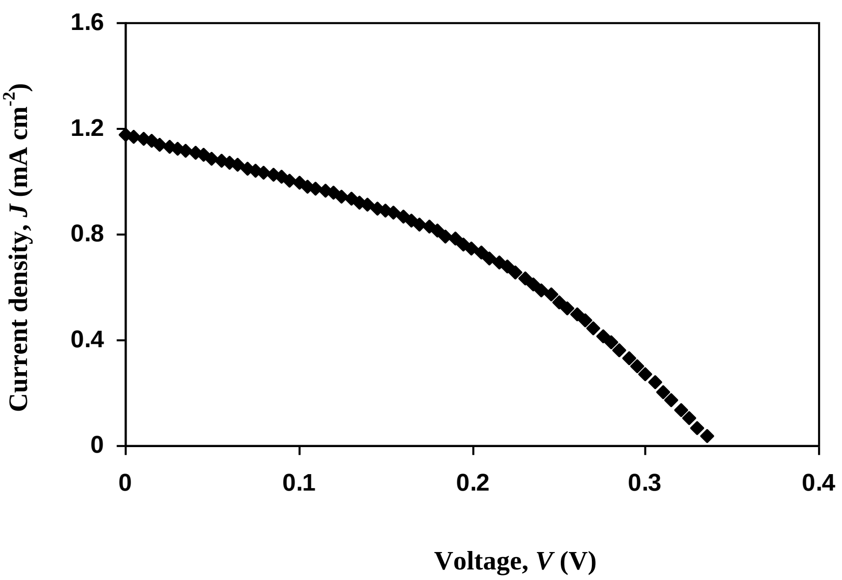

Figure 7.10: *J-V* characteristics of the DSSC for CIL5 electrolyte (in gel form).The dye solution is extracted from blueberry with pH 1

7.4 CHARACTERISTICS OF DSSCS USING DYE EXTRACTED FROM RED CABBAGE

7.4.1 UV-Vis studies of red cabbage

Figure 7.11 depicts the absorption spectra of bare TiO_2 electrode, anthocyanin extracted from red cabbage in solution and that adsorbed into the TiO_2 electrode. The absorption peak at about 550 nm is observed for anthocyanin solution extracted from red cabbage. Similar absorption peak has been reported by Furukawa *et al.* (2009). Upon adsorption of anthocyanin into TiO_2 photoelectrode, the peak has shifted towards lower energy indicating complexation has occurred between anthocyanin and TiO_2.

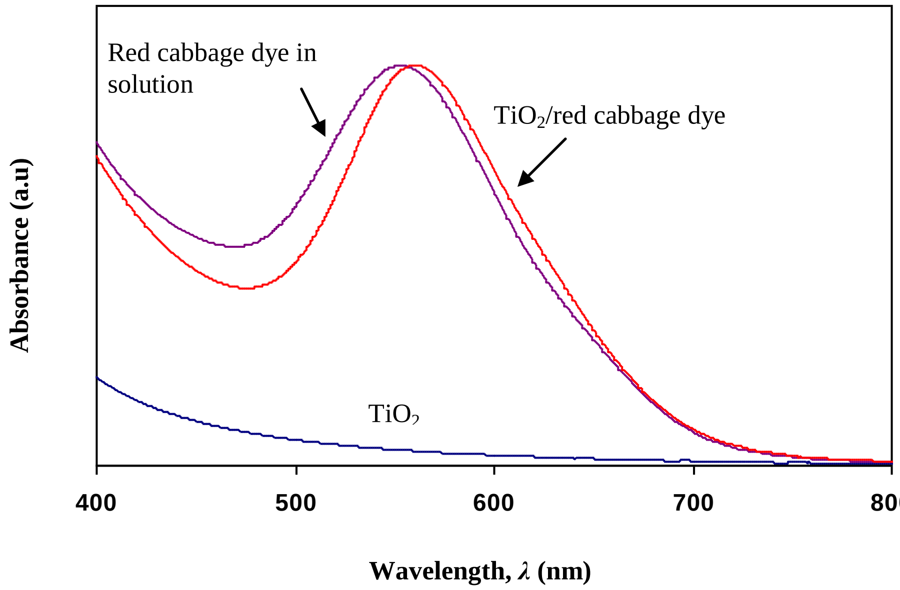

Figure 7.11: The absorption spectra of TiO_2 electrode, anthocyanin from red cabbage in solution and absorbed onto TiO_2 electrode

For the red cabbage anthocyanin dye, spectrum for dye with pH 1 clearly shows the highest absorption compared to that with pH 2, pH 3 and pH 4 as displayed in Figure 7.12. The higher intensity indicates that the anthocyanin dyes can absorb more light at pH 1.

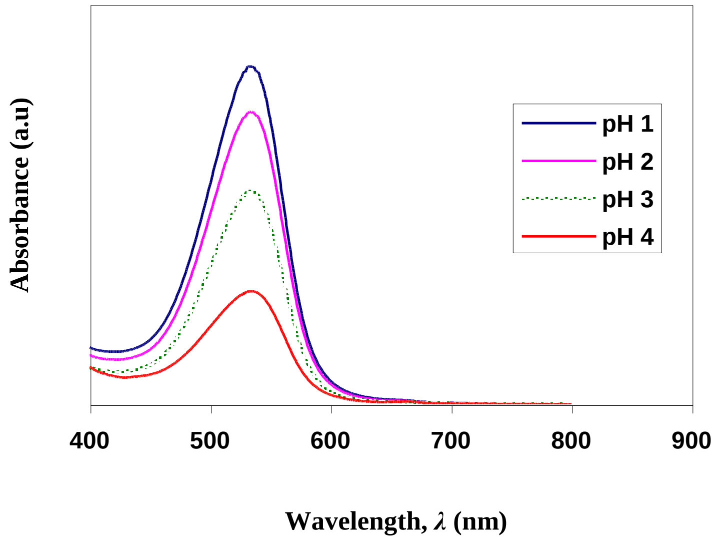

Figure 7.12: The absorption spectra of anthocyanin solutions extracted from red cabbage at different pH values

Figure 7.13 shows complexation between cyanidin-3-(sinapoyl)diglucoside-5-glucoside (from red cabbage) and TiO_2 particles.

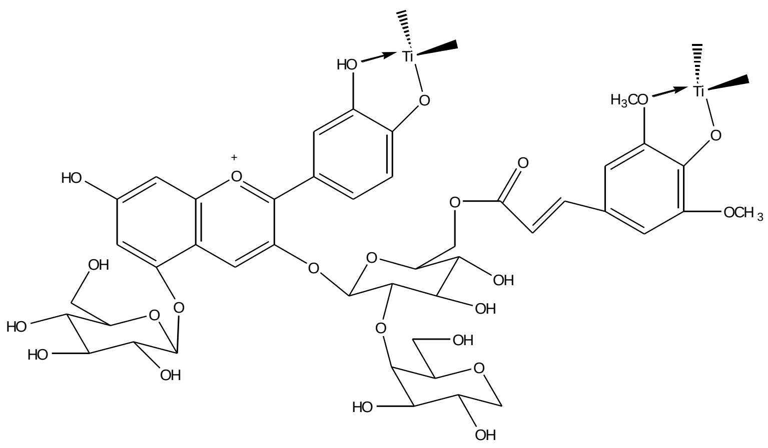

Figure 7.13: The binding between anthocyanin (red cabbage) molecule and TiO_2 particle

7.4.2 DSSCs utilizing red cabbage

J-V characteristics of ITO/TiO_2/dye/(27.5 wt.% chitosan-27.5 wt.% PVA)-45 wt.% $NH_4I(+I_2)$ (CV5($+I_2$))/Pt/ITO, ITO/TiO_2/dye/(16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO7($+I_2$))/Pt/ITO, and ITO/TiO_2/dye/27.5 wt.% chitosan-22.5 wt.% NH_4I ($+I_2$)-50 wt.% IL (CIL5($+I_2$)/Pt/ITO solar cells using red cabbage as a dye sensitizer is illustrated in Figure 7.14. Similar to blueberry anthocyanin dyes, the same trend of results has been obtained for ITO/TiO_2/dye/(27.5 wt.% chitosan-27.5 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO5($+I_2$))/Pt/ITO, ITO/TiO_2/dye/(22.0 wt.% chitosan-33.0 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO6($+I_2$))/Pt/ ITO and ITO/TiO_2/dye/(16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% $NH_4I(+I_2)$ (CEO7($+I_2$)/Pt/ITO solar cells using red cabbage as a dye sensitizer, see Figure 7.15. The conductivity of the electrolytes follows the order σ (CEO5) < σ (CEO6) < σ (CEO7). Performance of the red cabbage anthocyanin DSSCs is summarized in Table 7.5.

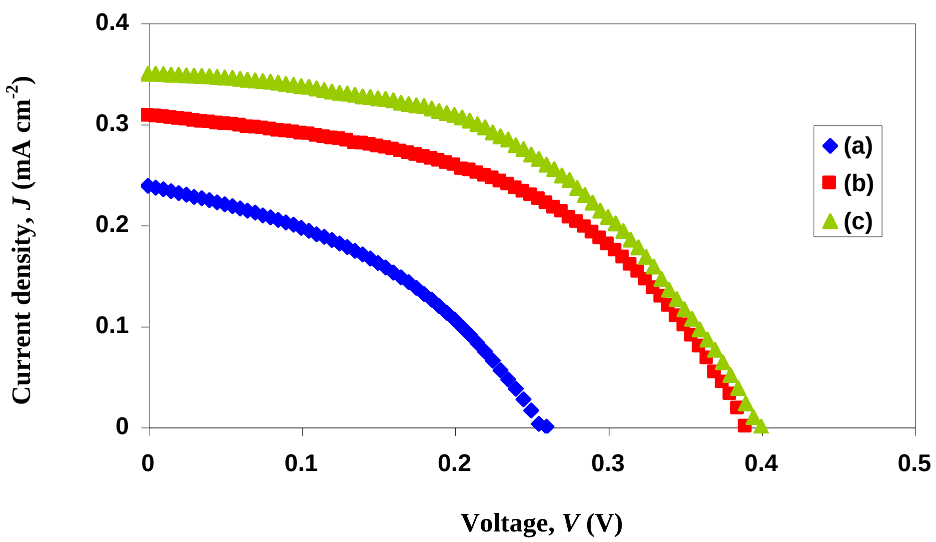

Figure 7.14: ***J-V*** **curve of DSSCs using (a) CV5 electrolyte (b) CEO7 electrolyte and (c) CIL5 electrolyte. The dye solution is extracted from red cabbage with pH 1**

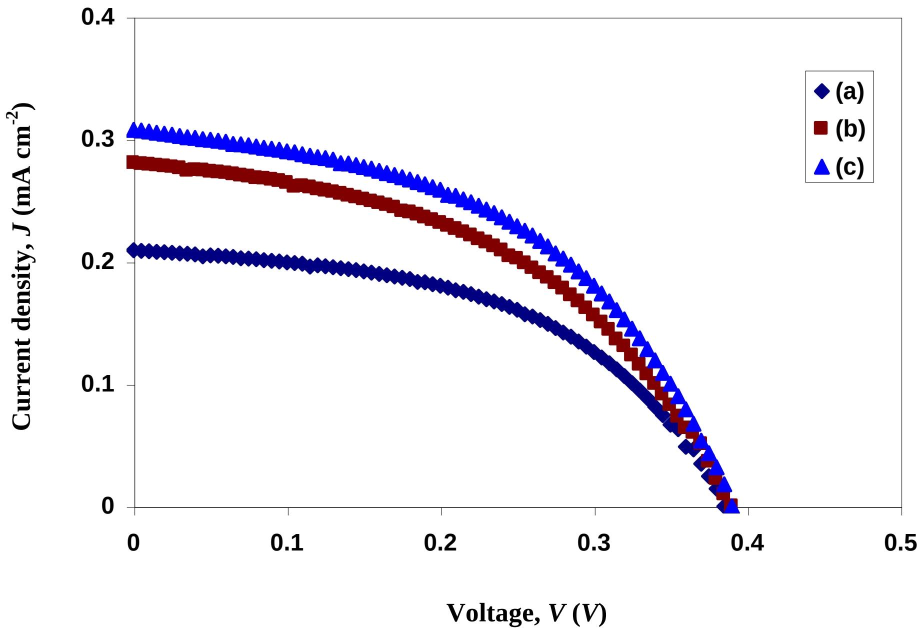

Figure 7.15: *J-V* curve of DSSCs using (a) CEO5 electrolyte (b) CEO6 electrolyte and (c) CEO7 electrolyte. The dye solution is extracted from red cabbage with pH 1

Table 7.5: List of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) fill factor (*ff*), maximum power density (P_{max}) and efficiency (η %) for dye-sensitized solar cells (red cabbage dye)

Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	fill factor (*ff*)	P_{max} (mW cm^{-2})	η (%)
CV5(+I_2)	0.24	0.26	0.39	0.024	0.02
CEO5(+I_2)	0.21	0.39	0.49	0.040	0.04
CEO6(+I_2)	0.28	0.39	0.46	0.50	0.05
CEO7(+I_2)	0.31	0.39	0.48	0.058	0.06
CIL5(+I_2)	0.35	0.40	0.48	0.067	0.07

Figure 7.16 shows *J-V* characteristics of dye-sensitized solar cell using CIL5 electrolyte in gel form. Similar to DSSC with blueberry dye, the performance of dye-sensitized solar cell using red cabbage dye is improved by using gel electrolyte. The cell

exhibits short-circuit current density, J_{sc} of 1.421 mA cm^{-2}, open-circuit voltage, V_{oc} of 0.31 V, fill factor, *ff* of 0.45 and efficiency, η of 0.2 %.

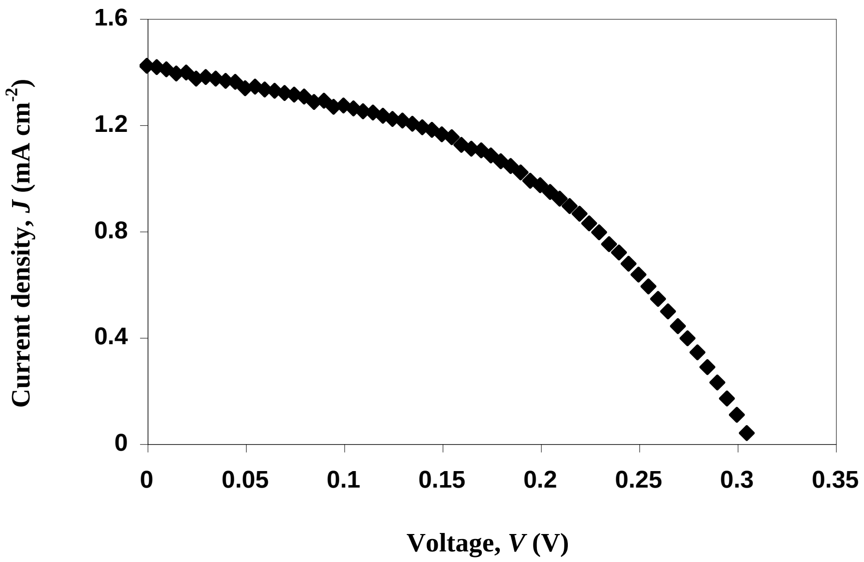

Figure 7.16: ***J-V*** **characteristics of the DSSC for CIL5 electrolyte (in gel form).The dye solution is extracted from red cabbage with pH 1**

7.5 CHARACTERISTICS OF DSSCS USING RUTHENIZER (N3) DYE

Figure 7.17 depicts *J-V* characteristics of dye-sensitized solar cell using *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (Ruthenizer 535) as sensitizer. The electrolyte used is 27.5 wt. % chitosan-22.5 wt. % NH_4I-50 wt. % BMII in gel form. Short-circuit current density, J_{sc} of 3.1 mA cm^{-2}, open circuit voltage, V_{oc} of 0.58 V, fill factor, *ff* of 0.41 and efficiency, η of 0.74 % was obtained. The absorption peak at 517 nm is observed in the spectrum of N3 dye that adsorbed into the TiO_2 electrode as shown in Figure 7.18. Also, it can be seen that the absorption of N3 dye is higher compared to anthocyanin from black rice, blueberry and red cabbage.

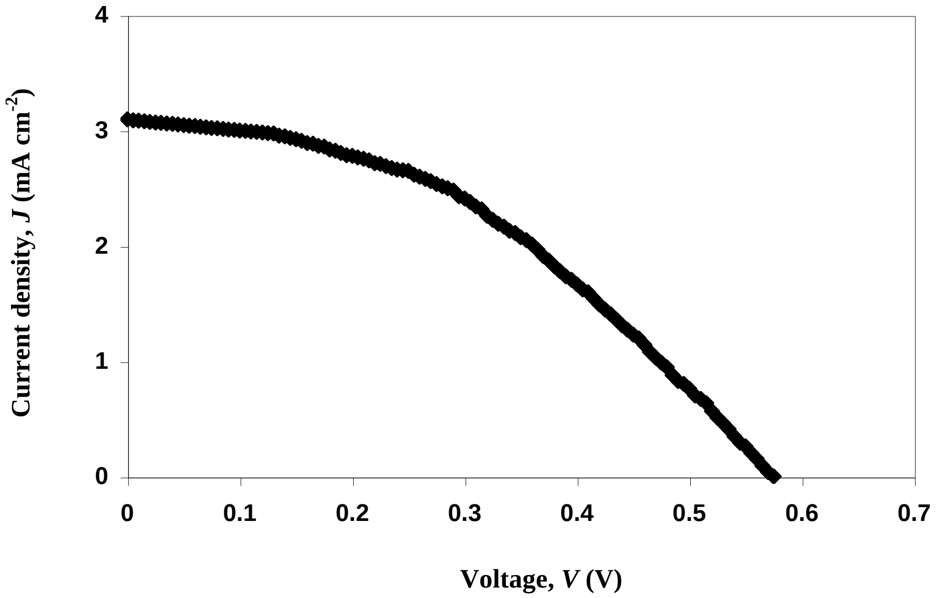

Figure 7.17: *J-V* characteristics of the ruthenium DSSC for 26.9 wt. % chitosan-22 wt. % NH_4I(+ 2.2 wt. %I_2) + 48.9 wt. % IL electrolyte (in gel form)

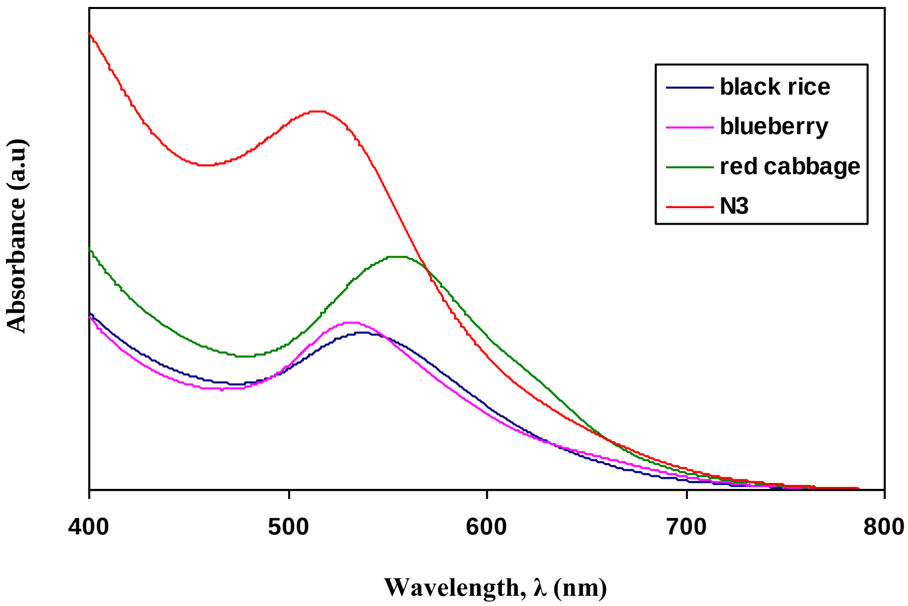

Figure 7.18: The absorption spectra of N3 dye, anthocyanin dye from black rice, blueberry and red cabbage absorbed onto TiO_2 electrode

Figure 7.19 shows the performance of ruthenium dye-sensitized solar cell using 11 wt. % chitosan-9 wt. % NH_4I-80 wt. % BMII electrolyte in gel form. Short-circuit current density J_{sc} of 4.55 mA cm^{-2}, open-circuit voltage, V_{oc} of 0.64 V, fill factor, *ff* of 0.4 and efficiency, η of 1.2 % was obtained. The conductivity of this electrolyte composition is 3.02×10^{-4} S cm^{-1}.

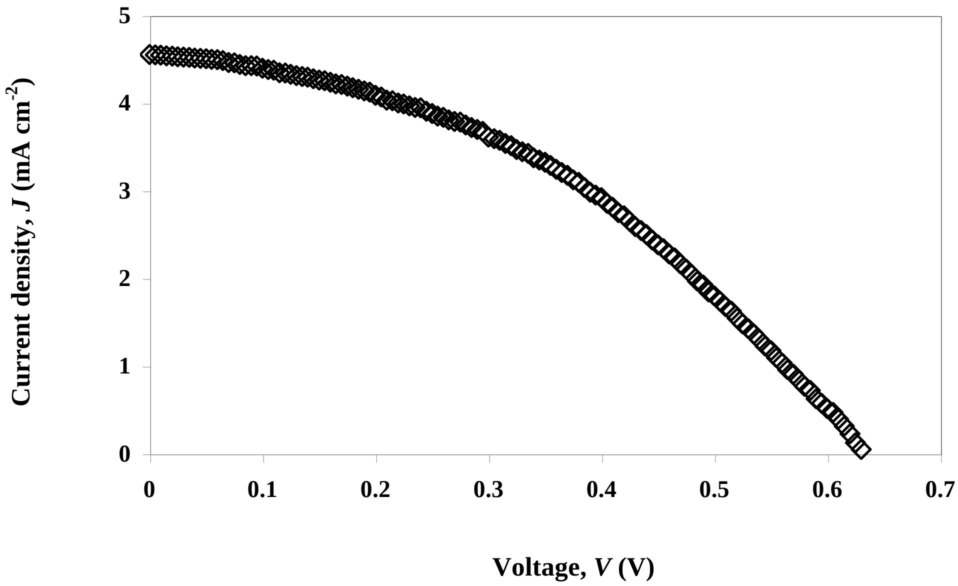

Figure 7.19: ***J-V*** **characteristics of the ruthenium DSSC for 11 wt. % chitosan-9 wt. % $NH_4I(+I_2)$ + 80 wt. % IL electrolyte (in gel form)**

7.5 SUMMARY

DSSCs using chitosan based electrolyte with different conductivity were fabricated. The DSSC utilizing the highest conducting CIL5 electrolyte exhibits best performance. Red cabbage dye exhibits better efficiency compared to blueberry and black rice. To improve the performance of DSSCs, electrolyte in gel form was used. The efficiency of 0.2% was obtained for DSSC using anthocyanin dye from red cabbage and CIL5 electrolyte. The performance of DSSC is further improved by using ruthenium sensitizer with efficiency 1.2%.