

Effects of Taiwan Roselle anthocyanin treatment and single-walled carbon nanotube addition on the performance of dye-sensitized solar cells

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Abstract. This study investigates the relationship between the performance of a dye-sensitized solar cell (DSSC) sensitized by a natural sensitizer of Taiwan Roselle anthocyanin (TRA) and fabrication process conditions of the DSSC. A set of systematic experiments has been carried out at various soaking temperatures, soaking periods, sensitizer concentrations, pH values, and additions of single-walled carbon nanotube (SWCNT). An absorption peak (520 nm) is found for TRA, and it is close to that of the N719 dye (518 nm). At a fixed concentration of TRA and a fixed soaking period, a lower pH of the extract or a lower soaking temperature is found favorable to the formation of pigment cations, which leads to an enhanced power conversion efficiency (η) of DSSC. For instance, by applying 17.53 mg/100ml TRA at 30 for 10 h, as the pH of the extract decreases to 2.00 from 2.33 (the original pH of TRA), the η of DSSC with TiO₂+SWCNT electrode increases to 0.67% from 0.11% of a traditional DSSC with TiO₂ electrode. This performance improvement can be explained by the combined effect of the pH of sensitizer and the additions of SWCNT, a first investigation in DSSC using the natural sensitizer with SWCNT.

Keywords: Dye Sensitized Solar Cell, Natural Sensitizer, Taiwan Roselle Anthocyanin, Single-Walled Carbon Nanotube

1. Introduction

Several alternatives to silicon-based photovoltaic (PV) cells have recently become available, and they may facilitate reduction of the cost of electricity generation via a PV cell. Among these alternatives, the dye-sensitized solar cell (DSSC), proposed by O'Regan and Grätzel [1], is an attractive alternative because of its properties, such as low production cost, the various choices of substrates that can be used, and low environmental impact during fabrication [2-3]. The dye sensitizer, which is used to harvest solar energy and generate excitons [2], is one of the major DSSC components. Therefore,



novel sensitizers were synthesized and applied in DSSCs to promote the absorption of the visible spectrum [4-11].

For the sake of reducing environmental pollution (or production cost) during fabrication of synthesized sensitizers, research on natural sensitizers extracted from plants has received substantial attention. For example, natural sensitizers such as anthocyanins extracted from Calafate and Jaboticaba [12], black rice [13], hibiscus flower [14], mulberry fruit [15], *Delonix regia* and Indian blackberry [16], chlorophylls extracted from pomegranate leaf [15] and shiso leaf [17], and betanin extracted from beet root [18] were prepared and applied in DSSCs. Moreover, Zhou et al. observed that for photo-electrochemical performance, rutin was the most effective sensitizer for DSSC among 20 natural extracts [19]. Wongcharee et al. investigated the effects of extracting temperature, extracting solvent, and pH of the extract solution on the performance of a DSSC [20].

Interestingly, Senthil et al. indicated that the anthocyanin pigment has hydroxyl groups in the molecule, and it can effectively chelate to the surface of a TiO_2 film [16]. Aside from this, the molecular structure of the Taiwan Roselle anthocyanin (TRA) (Figure 1(a)) [21] extracted from *Hibiscus Sabdariffa* Linnaeus (Figure 1(b)) which are planted in Taitung, Taiwan, lacks an electron, and this natural sensitizer may easily capture the electron from an electrolyte as it is applied in a DSSC. Therefore, research on the probable factors affecting anthocyanin stability during extraction (or soaking) and on enhancing the performance of a DSSC sensitized using anthocyanin from local Roselle are worthy of continued study. These are the motivations of this study.

The TRA was extracted from *Hibiscus Sabdariffa* Linnaeus as a natural sensitizer of the DSSC. The effects of the concentration of TRA in the natural sensitizer, the pH of the natural sensitizer solution, the soaking temperature, the soaking period, and the addition of the single-walled carbon nanotube (SWCNT) on the performance of the DSSC were investigated.

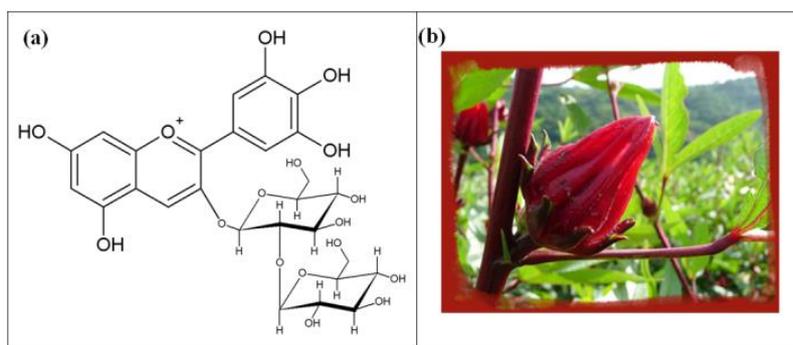


Figure 1. Schematic of the molecular structure of the TRA (a), the image of *Hibiscus Sabdariffa* Linnaeus (b).

2. Experimental

2.1. Preparing and measuring the natural sensitizer

The experiments of the natural sensitizer included: (1) preparing the powder of TRA (P_{RA}) and (2) preparing and measuring the solution of P_{RA} with different concentrations and pH values. The procedure of preparing the P_{RA} included the following steps: (1) the petals of *Hibiscus Sabdariffa* Linnaeus (Roselle) of Malvaceae, which had been planted in Taitung, Taiwan, were collected and cleaned using tap water; (2) these cleaned Roselle petals were placed in a freeze dryer (CT-5000D, Panchum Scientific Corp. Kaoshiung, Taiwan), and they were then ground into powder (P_{RP}); (3) 1 g P_{RP} was mixed with 50 ml de-ionized (DI) water in a beaker, and this mixture was stirred until it was uniformly mixed; (4) this uniformly mixed solution was placed in a fridge at a temperature of 5 °C for 24 h, so that the TRA could be fully extracted; (5) the TRA extract was separated from the other contaminants in the solution using a high-speed micro centrifuge (CF15RXII, Hitachi Koki Co., Ltd., Japan), and this extract was then placed in a freeze dryer to obtain P_{RA} .

The procedures of preparing and measuring the solution of P_{RA} included the following steps: (1) the P_{RA} with a preset mass was mixed with 200 ml DI water in a beaker, and this mixture was stirred until

the P_{RA} was fully dissolved in the DI water; (2) a filter paper was used to filtrate this solution of P_{RA} to obtain the natural sensitizer for a DSSC; (3) the pH of the natural sensitizer could be changed by adding the hydrochloric acid (HCl), and its pH value (Table 1) and absorbance of light were obtained using a pH meter (MP220, Mettler toledo, Switzerland) and a spectrophotometer (U-2001, Hitachi, Tokyo, Japan), respectively. Table 1 lists the test conditions of preparing the natural sensitizers.

2.2. Preparing TiO_2 (P-25) and TiO_2 (P-25)+SWCNT working electrodes

Titanium dioxide (TiO_2 , Uniregion Biotech P-25) particles of 20% rutile and 80% anatase with an average particle size of 21 nm were used in this study. Furthermore, a SWCNT with an inside diameter of 1.1 nm, a length of 0.5-100 μm , a density of 1.7-1.9 g/ml, and a resistance of $0.34 \times 10^{-4} \sim 10 \times 10^{-4}$ ohm/cm was procured from Sigma-Aldrich, USA, and it consisted of carbon nanotubes (> 90 VOL%), amorphous carbon (< 5%), Co (0.6%), Mg (1.2%), Mo (0.1%), and silicate (0.1%).

The procedure of preparing TiO_2 (P-25) and [TiO_2 (P-25)+SWCNT] working electrodes included the following steps: (1) a FTO (Fluorine doped tin oxide, $SnO_2:F$) glass substrate was immersed in the 0.05 M solution of $TiCl_4$ at a temperature of 70 for 30 min; (2) the colloids of the TiO_2 (P-25) and TiO_2 (P-25)+SWCNT were respectively prepared (Table 2), and these colloids were then homogenized in an ultrasonic homogenizer for 30 min; (3) the colloid of the TiO_2 (P-25) or [TiO_2 (P-25)+SWCNT] was deposited on the top of a FTO-glass substrate with the $TiCl_4$ treatment; (4) this substrate was then sintered at a temperature of 450 for 1 h (Table 3) in a high-temperature furnace (Thermolyne, 46100); (5) the surface of the TiO_2 (P-25) or [TiO_2 (P-25)+SWCNT] film on the FTO-glass substrate was modified by immersing this substrate in a 0.05 M solution of $TiCl_4$ at a temperature of 70 for 30 min; (6) the FTO-glass substrate with a TiO_2 (P-25) or [TiO_2 (P-25)+SWCNT] film was immersed into the solution of P_{RA} at a preset soaking temperature for a preset period; and (7) this substrate was then rinsed using ethanol. The area of the dye-covered TiO_2 (P-25) or [TiO_2 (P-25)+SWCNT] electrode of DSSC was 0.25 cm^2 . Table 4 lists the test conditions for soaking TiO_2 (P-25) and [TiO_2 (P-25)+SWCNT] electrodes in the natural sensitizer of TRA.

2.3. Assembling and testing the DSSC

A dye-covered working electrode with a layer of TiO_2 (P-25) or [TiO_2 (P-25)+SWCNT] and a counter electrode with a platinum (Pt) film were assembled to become an open cell. A liquid electrolyte was injected into the space between the two electrodes; the liquid electrolyte used herein was identical to that used in our previous work [3]. An AM 1.5 solar simulator (XES-310S, San-Ei Pioneer of Light Technology) was used to spotlight the DSSC, and a digital source-meter (Keithley 2400) was used to obtain the open-circuit photovoltage and the short-circuit photocurrent of the DSSC. Detailed calculations of the power conversion efficiency of the DSSC were described in our previous works [22-23].

Table 1. Test conditions of preparing the natural sensitizers.

Material	Concentration (mg/100ml)	Solution	pH Value
A1	8.52	200 mL DI water	2.33
A2	17.53		
A3	23.98		
A4	32.24		
A5	43.45		
A6	8.52		
A7	32.24		
A8	17.53		
A9			
A10			
A11	32.24		

Table 2. Test conditions of preparing the colloids.

	Solute		Solution		
	Particle	Mass (g)	Ethanol (mL)	Acetylacetone (mL)	Triton X-100 (mL)
B0	TiO ₂	1			
B1	TiO ₂	1	4	0.4	0.05
	+ SWCNT	0.002			

Table 3. Test conditions of preparing the TiO₂ and TiO₂+ SWCNT electrodes.

	Colloid	No. of layer daubed by spin coating	Sintering	
			Temp. (°C)	Time (h)
C0	B0	5	450	1
C1	B1			

Table 4. V_{OC}, J_{SC}, FF, η , and standard deviation of efficiency

Substrate	Dye	Soaking Temp. (°C) /Time (h)	V _{oc} (V)	J _{sc} (mAcm ⁻²)	FF (%)	η (%)	Standard Deviation of Efficiency (%)	
D1	A1		0.43	0.40	53	0.09	0.0083	
D2	A2		0.41	0.53	51	0.11	0.0071	
D3	A3	30/10	0.42	0.53	58	0.13	0.0122	
D4	A4		0.40	0.52	68	0.14	0.0083	
D5	A5		0.41	0.58	65	0.15	0.0109	
D6	C0	30/10	0.43	0.79	55	0.19	0.0083	
D7		50/10	0.41	0.72	62	0.19	0.0071	
D8		70/10	0.41	0.35	52	0.08	0.0083	
D9		30/10	0.44	0.98	51	0.22	0.0071	
D10	A7	50/10	0.41	0.90	51	0.19	0.0043	
D11		70/10	0.40	0.15	53	0.03	0.0050	
D12	A8	50/10	0.33	3.55	33	0.39	0.0109	
D13	A8	30/20	0.31	4.88	39	0.59	0.0192	
D14	C1	50/20	0.31	2.91	30	0.27	0.0112	
D15		A8	0.33	4.52	44	0.67	0.0071	
D16		A9	30/10	0.33	3.38	48	0.54	0.0109
D17		A4		0.42	0.96	53	0.22	0.0071

3. Results and Discussion

3.1. UV-visible absorbance of the natural sensitizer

Figure 2 shows the variations in the absorbance of the natural sensitizer of TRA with the wavelength of light in different concentrations of 8.52 (Test A1), 17.53 (Test A2), 23.98 (Test A3), 32.24 (Test A4), and 43.45 (Test A5) mg/100ml. Further, the pH value of these natural sensitizers is 2.33, which is the original pH of the TRA used in this study. The concentration of TRA influences the light absorbance of the natural sensitizer. For example, in the wavelength range of 300–700 nm, the

absorbance in Test A5 was the largest among the five tests. This can be attributed to the fact that the natural sensitizer with a higher concentration of TRA has a better capability of absorbing visible light.

In the absorbance spectra, the absorption peaks of TRA were at 320 and 520 nm (Figure 2). Chang and Lo showed that the absorption peaks of N719 dye and anthocyanin natural dye extracted from mulberry were at 518 and 543 nm, respectively [15]. Therefore, the absorption peak of TRA in the region of visible light obtained in this study is closer to that of the N719 dye, compared with the absorption peak of anthocyanin extracted from mulberry presented in [15]. Wongcharee et al. observed that in the region of visible light, the absorption peak of rosella flower extract is about 520 nm while those of blue pea flower extract are about 580 and 620 nm [20]. This difference is due to the fact that the anthocyanin obtained from blue pea flower is the ternatin structure, and the anthocyanin obtained from rosella flower is the complex of delphinidin and cyaniding [20].

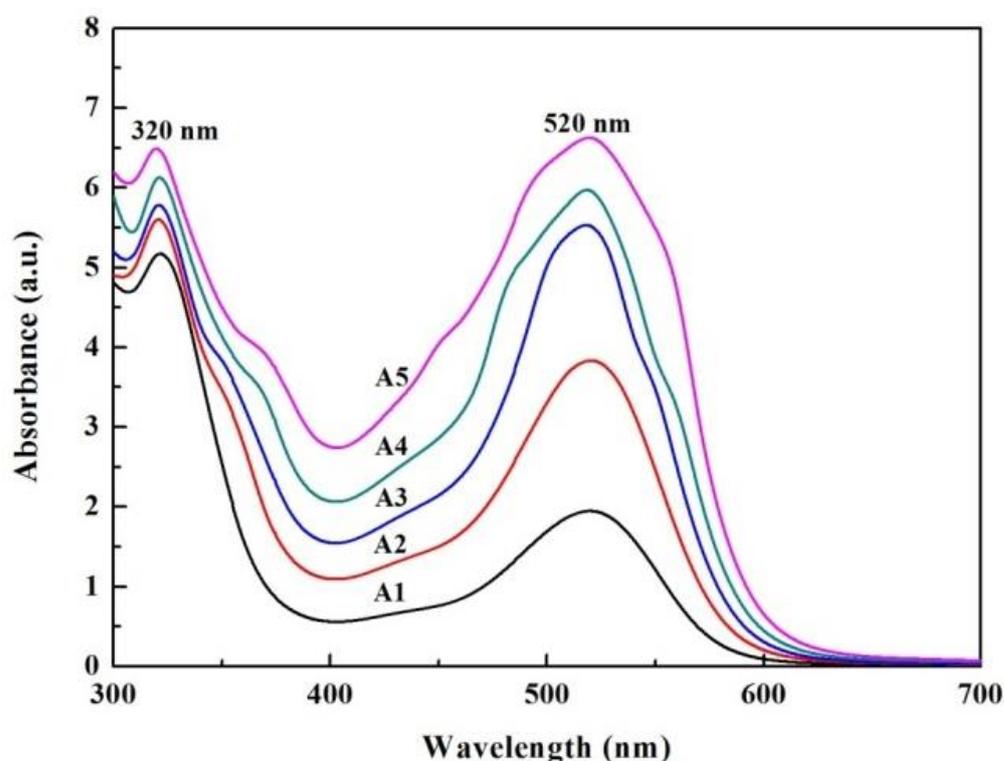


Figure 2. Variations in absorbance of TRA with the wave-length of light in Tests A1 to A5.

3.2. UV-visible absorbance of dye-covered working electrodes

Figure 3(a) shows the variations in absorbance of the TiO_2 +SWCNT electrodes of DSSCs in Tests D15 and D16 with the wavelength of light. The pH values of the natural sensitizer used to soak the working electrodes of DSSCs in Tests D15 and D16 were 2.0 and 2.2, respectively. These two working electrodes were soaked in the natural sensitizer with a concentration of 17.53 mg/100ml at 30 °C for 10 h. In the wavelength range of 400 – 800 nm, the absorbance of the working electrode of DSSC in Test D15 exceeded that of the working electrode of DSSC in Test D16. This can be attributed to the fact that the Roselle anthocyanin solution with a lower pH is more favourable for forming the pigment cations [24], and this may stabilize the natural sensitizer, in which more red color is observed.

Figure 3(b) shows variations in absorbance of the dye-covered TiO_2 +SWCNT electrode of DSSCs in Tests D12 and D15 with the wavelength of light. In Test D15, its working electrode was soaked in the natural sensitizer at 30°C, and the working electrode of DSSC in Test D12 was soaked in the

natural sensitizer at 50°C. These two working electrodes were soaked in the natural sensitizer with a concentration of 17.53 mg/100ml for 10 h, and the pH value of this natural sensitizer was 2.00. In the wavelength range of 400 – 800 nm, the absorbance of the working electrode with a soaking temperature of 30°C significantly exceeded that of the working electrode with a soaking temperature of 50°C. This can be attributed to the fact that the higher soaking temperature may cause the structural modification and color change of the natural sensitizer due to a rapid reactivity of the aglycone moiety in the Roselle anthocyanin [24]. Further, increasing the possibility of losing pigment cations due to raising the soaking temperature may also reduce the ability of the natural sensitizer in capturing electrons from an electrolyte.

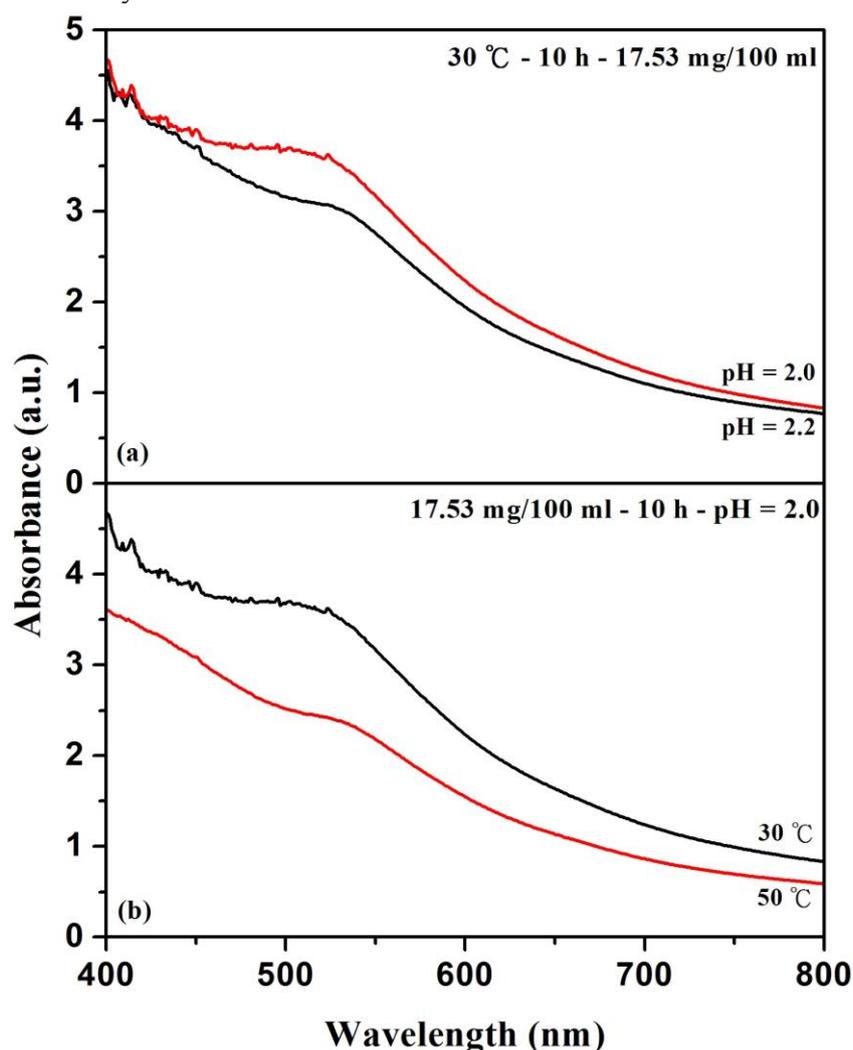


Figure 3(a)-(b). Variations in absorbance of the dye-covered working electrodes [TiO₂ (P-25)+SWCNT] of DSSCs with the wavelength of light. (a) Working electrodes of DSSCs in Tests D15 and D16; (b) working electrodes of DSSCs in Tests D12 and D15.

3.3. Voc, Jsc, η, and J-V Curve of DSSC

Table 4 shows the open-circuit photovoltage (Voc), the short-circuit photocurrent per unit area (Jsc), the fill factor (FF), the power conversion efficiency (η), and the standard deviation of efficiency of

the DSSC in Tests D1 to D17. Further, Figure 4 shows the variations in photocurrent density with photovoltage (i.e., J-V characteristics of DSSC) in Tests 12, 15, 16, and 17.

3.3.1 DSSC with a dye-covered electrode of TiO_2 (P-25)

The η of DSSC increased with an increase in the concentration of Roselle anthocyanin in the natural sensitizer. For example, at a fixed pH of the extract (2.33), as the concentration of TRA increased from 8.52 to 43.45 mg/100ml, the η of DSSC, whose TiO_2 (P-25) electrode had been soaked in the natural sensitizer for 10 h at 30°C, increased from 0.09% (Test D1) to 0.15% (Test D5). However, at a fixed concentration of 8.52 mg/100ml, a fixed soaking temperature of 30°C, and a fixed soaking period of 10 h, as the pH of the extract decreased to 2.00 from the original pH of the TRA (2.33), the η of DSSC substantially increased from 0.09% (Test D1) to 0.19% (Test D6), and the Jsc of the DSSC increased from 0.40 to 0.79 mAcm^{-2} . Apparently, a lower pH of the extract corresponds to a favorable condition to create more pigment cations [24], which may capture more electrons and enhance both Jsc and η of a DSSC.

Aside from this, increasing the soaking temperature may be unfavorable to the performance of DSSC. For example, at a fixed concentration of 8.52 mg/100ml, a fixed pH of the extract (2.00), and a fixed soaking period of 10 h, as the soaking temperature increased from 30 to 70°C, the η of DSSC substantially decreased from 0.19% (Test D6) to 0.08% (Test D8), and the Jsc of the DSSC decreased from 0.79 to 0.35 mAcm^{-2} . Therefore, at a fixed concentration of TRA and a fixed soaking period, either a lower pH of the extract or a lower soaking temperature can stabilize the natural sensitizer and then enhance the Jsc of the DSSC. Wongcharee et al. observed that the efficiency and stability of DSSCs can be enhanced by adjusting the extracting temperature and pH of the extracts [20].

3.3.2 DSSC with a dye-covered electrode of TiO_2 (P-25) +SWCNT

With the original pH of the TRA (2.33), a fixed soaking temperature of 30°C, a fixed soaking period of 10 h, and a fixed concentration of 32.24 mg/100ml, the η of DSSC substantially increased from 0.14% in Test D4 [DSSC with a TiO_2 (P-25) electrode] to 0.22% in Test D17 [DSSC with a TiO_2 (P-25)+SWCNT electrode], and the Jsc of the DSSC increased from 0.52 mAcm^{-2} (Test D4) to 0.96 mAcm^{-2} (Test D17). This result is due to the addition of SWCNT, whose good electric conductivity may enhance the Jsc of the DSSC. Zeng et al. observed that the carbon nano tubes (CNTs) provided a good electrical connection between the ZnO overlayer and the stainless steel substrate [25].

Interestingly, decreasing the pH of the TRA can significantly enhance the η of DSSC with a TiO_2 (P-25)+SWCNT electrode. For example, at a fixed soaking temperature of 30°C and a fixed soaking period of 10 h, although the concentration of natural sensitizer in Test D15 (17.53 mg/100ml) was smaller than that in Test D17 (32.24 mg/100ml), the η of DSSC substantially increased from 0.22% in Test D17 with the original pH of the TRA (2.33) to 0.67% in Test D15 with a pH of the natural sensitizer of 2.00. Moreover, the Jsc of the DSSC increased from 0.96 mAcm^{-2} (Test D17) to 4.52 mAcm^{-2} (Test D15). This can be attributed to the fact that the effect of pH might dominate over that of the concentration of TRA in the natural sensitizer. Aside from this, a natural sensitizer prepared under either a lower pH of the extract or a lower soaking temperature corresponds to a higher stability, which is favourable for creating a larger Jsc as the DSSC sensitized by the natural sensitizer is exposed to light.

At a fixed concentration of 17.53 mg/100ml, if the soaking process is under a lower pH of the TRA (such as 2.00) and a lower soaking temperature (such as 30), the η of DSSC slightly decreased from 0.67% (Test D15) to 0.59% (Test D13) as the soaking period increased from 10 to 20 h. However, if the soaking process is under a higher pH of the TRA (such as 2.20) and a higher soaking temperature (such as 50°C), a longer soaking period causes a rapid decrease in the Jsc and η of the DSSC. For example, in Test D14 the Jsc and η of the DSSC substantially decreased to 2.91 mAcm^{-2} and 0.27%, respectively. Markakis indicated that the Roselle anthocyanin is the delphinin-sambubiose, which is a

glycosylated polyhydroxy derivative of the flavylum salts, and the high reactivity of the aglycone moiety leads to the structural modification and the color change in the Roselle anthocyanin especially under an improper pH during a heat processing [24].

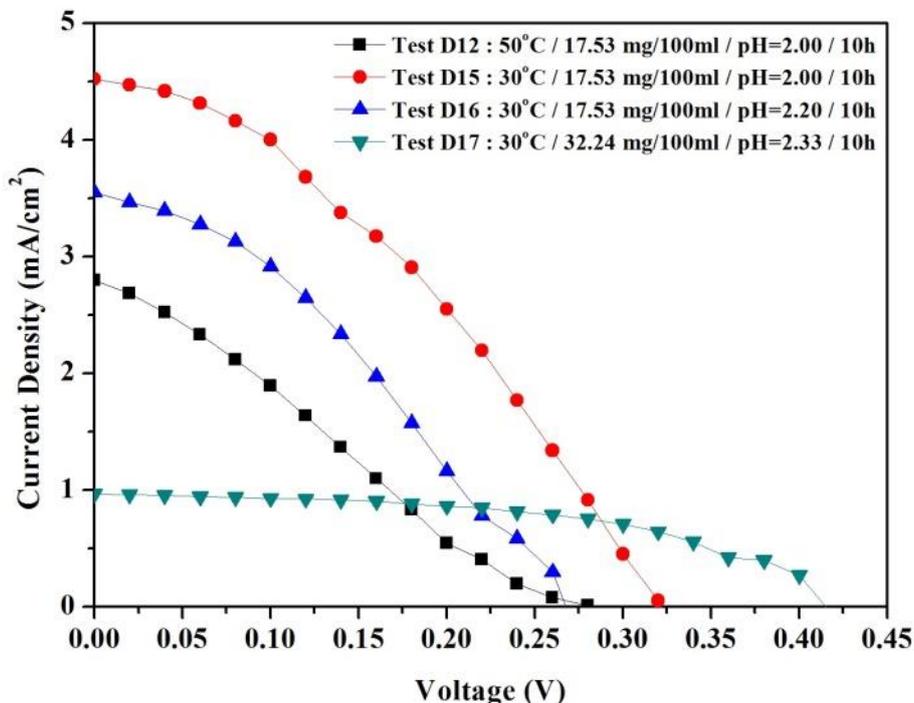


Figure 4. Variations in current density with voltage in Tests 12, 15, 16, and 17.

4. Conclusion

The TRA extracted from *Hibiscus Sabdariffa* Linnaeus planted in Taitung, Taiwan, was used as a natural sensitizer for sensitizing a DSSC. An absorption peak of TRA (520 nm) is close to that of the N719 dye (518 nm). At a fixed concentration of TRA and a fixed soaking period, the natural sensitizer of TRA prepared under either a lower pH of the extract or a lower soaking temperature corresponds to a higher stability of natural sensitizer, and it is favourable for creating a larger J_{sc} as the DSSC sensitized by the natural sensitizer is exposed to light. But, as the soaking process is under a higher pH of the TRA and a higher soaking temperature, a longer soaking period causes a rapid decrease in the J_{sc} and η of the DSSC. Importantly, the addition of SWCNT dramatically increases the η in a DSSC sensitized using TRA with a lower pH. Therefore, the optimum for preparing a DSSC with a TiO_2 +SWCNT electrode, which is sensitized using a natural sensitizer, is worthy of continued study.

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