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Photoelectrochemistry for Red Cabbage Extract as Natural Dye to Develop a Dye-Sensitized Solar Cells

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The aim of this work was to study the photoelectrochemical optimal conditions for red cabbage extract as natural dye to develop a dye-sensitized solar cells (DSSC). Red cabbage extract were characterized by various methods, such as electrochemical impedance spectroscopy (EIS), UV–Vis and cyclic voltammetry (CVs). DSSC is fabricated from a combination of relatively popular materials containing TiO_2 photoelectrode, natural dye, electrolyte containing I^-/I_3^- redox mediator, and counter electrode. The use of suitable pH for red cabbage improves the DSSC performance. The results showed that the increase of efficiency due to the purified and immersed time of natural dye content greatly increased the specific activity and total load volume.

Keywords: dye-sensitized solar cells (DSSC), red cabbage, natural dye, photoelectrochemistry.

1. INTRODUCTION

Dye-sensitized solar cell (DSSC), a device converting light energy to electrical energy, was firstly developed by Gratzel's group [1-3] and has widely known as a low-cost and easyassembly solar cell. It has the potential to become a new generation technology utilizing the nanoscale properties of the device. DSSC offers the selling points such as flexibility, lightweight, short energy payback time (<1 year), availability and low production cost. The use of a nanoscale semiconductor electrode with a high internal surface area led to a paradigm shift in the fields of photoelectrochemistry and photovoltaics in general. Indications of the possibilities to increase the roughness of the semiconductor surface so that a larger number of dyes could be adsorbed directly to the surface and simultaneously be in direct contact with a redox electrolyte. Titanium dioxide (TiO_2) 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 [4]. Electrons in dye molecules are excited and then injected to the conduction band of a wide-band gap n-type semiconductor, on which the dye molecules adsorb.

The light-harvesting efficiency for a monomolecular layer of dye sensitizer. Several thousands of dyes have been investigated, as well as hundreds of electrolyte systems and numerous types of mesoporous films with different morphologies and compositions. Early on in DSSC research, the classical dyes N3 and its salt analogue N719 and the black dye (N749) were developed. Here, natural dye sensitizers extracted from red cabbage were selected for DSSC. Anthocyanin from red cabbage is used mainly in food coloring and beverage industries as well as in making sweets and chewing gum [5-6]. Anthocyanins are a class of flavonoids responsible for the attractive bright red, purple, violet, and blue colours of most fruits, vegetables, flowers, leaves, roots and other plant storage organs [7-13]. Some report [14-15] shows employed anthocyanin dye from red cabbage as sensitizer in DSSC. As one of the crucial parts in DSSC, the photosensitizer should fulfill some essential characteristics. The red cabbage extracted absorption spectrum of the photosensitizer cover the whole visible region and even the part of the near-infrared (NIR) [16]. Natural dye of red cabbage extracted have anchoring groups to strongly bind on the semiconductor surface [17]. The plant extracted existed regeneration and redox potential of electrolyte. Photostable, electrochemical and thermal stability are also required. The most important, excited state level should be higher in energy than the conduction band edge of n-type semiconductor, so that an efficient electron transfer process between the excited dye and conduction band (CB) of the semiconductor can take place [18].

In this work, TiO_2 with natural dye as anode electrodes, cathode electrodes with iodide/triiodide electrolytes can be rather easily prepared by deposition of a thin catalytic layer of platinum onto a conducting glass substrate.

2. EXPERIMENTAL

2.1. Materials

P25 TiO_2 powder, Triton X-100 solution, Acetylacetone, PEG 20000, Propylene carbonate, were purchased from Sigma-Aldrich (USA). Lithium iodide (LiI), Potassium iodide (KI) and iodine (I_2) were obtained from Wako (Japan). Natural dye extracted from red cabbage. Indium tin oxide (ITO) (7 Ω/cm^{-2}) was purchased from Merck Display Technologies (MDT) Ltd (Taiwan). All other chemicals used were of analytical grade and used without further purification pH 7.0 (0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4) Phosphate buffer solutions (PBS) was used as supporting electrolyte. Aqueous solutions were prepared using doubly distilled deionized water and then deaerated by purging with high purity nitrogen gas for about 20 min before performing electrochemical experiments. Also, a continuous flow of nitrogen over the aqueous solution was maintained during measurements.

2.2. Apparatus

Cyclic voltammetry (CVs) was performed in an analytical system model CHI-1205A and CHI-627A potentiostat. A conventional three-electrode cell assembly consisting of an Ag/AgCl reference electrode and a Pt wire counter electrode were used for the electrochemical measurements. The working electrode were glassy carbon electrode (GCE) (area 0.07 cm^2) and ITO (area 0.25 cm^2). In these experiments, all the potentials have been reported versus the Ag/AgCl reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed using an IM6ex Zahner instrument (Kroanch, Germany). The power output measurements system by KEITHLEY 2400. UV–visible spectra were obtained using Hitachi U-3300 spectrophotometer (Japan). The atomic force microscope (AFM) images were recorded using a multimode scanning probe microscope (Being Nano-Instruments CSPM-4000, China).

2.3. Preparation of natural dye extracted and TiO_2/ITO modified electrodes

Fresh red cabbage, were cut into very small pieces and then extracted in a methanol/water (1:1 by volume) mixed solvent. Afterward, the solid residues were filtered out. Then, the dye solutions were concentrated by a rotary evaporator at 50 ^oC and finally stored at 4 ^oC before use [19]. The major part of red cabbage extract is anthocyanin derivatives. Anthocyanin connect sorbose and glucose to form rubrobrassicine as Fig 1.

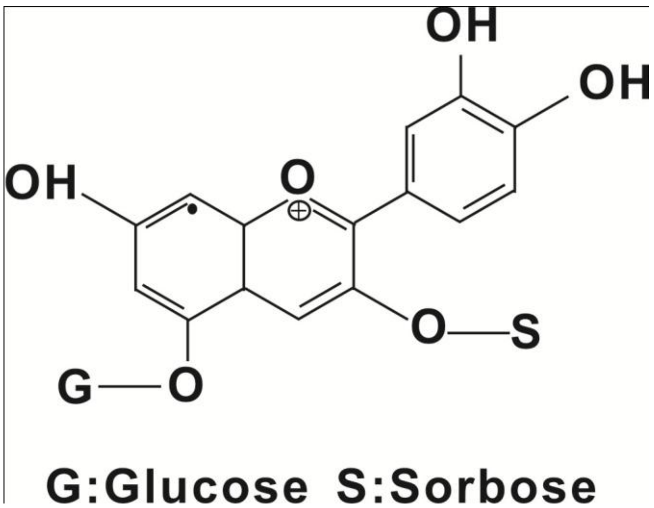

Figure 1. Red cabbage extract of anthocyanin derivatives.

Nano TiO_2 films on ITO substrates were deposited as follows, 9 g P-25 TiO_2 powder, 25 μl Triton X-100, 1 g PEG 20000, 50 μl acetylacetone and 18 ml doubly distilled deionized water were mixed well in a dried agate mortar for one hour [20-23]. The final mixture was stirred for an additional 2 days to obtain the desired TiO_2 paste. In prior to modification, ITO surfaces were cleaned and ultrasonicated in acetone–water mixture for 15 min and then dried. The above obtained TiO_2 paste solution was spin-coated on an ITO glass substrate at 1000 rpm for 10 s and 2000 rpm for 30 s. The formed film was annealed at 450 °C for 1 hour in atmosphere. These TiO_2 film coated on ITO were dried at room temperature for cooling several minutes. The TiO_2/ITO electrode was immersed in natural dye solution 6, 12, 18 and 24 h as an experimental control group. The electrolyte contains 0.1 M LiI, 0.05 M I_2, and 0.5 M propylene carbonate.

3. RESULTS AND DISCUSSIONS

3.1. UV-visible absorption spectra of natural dye

Studies investigating natural dye photosensitive have been mainly devoted to characterizing the effect of light on their colour stability. Natural dye can either increase in the presence of light depending on the state of DSSC.

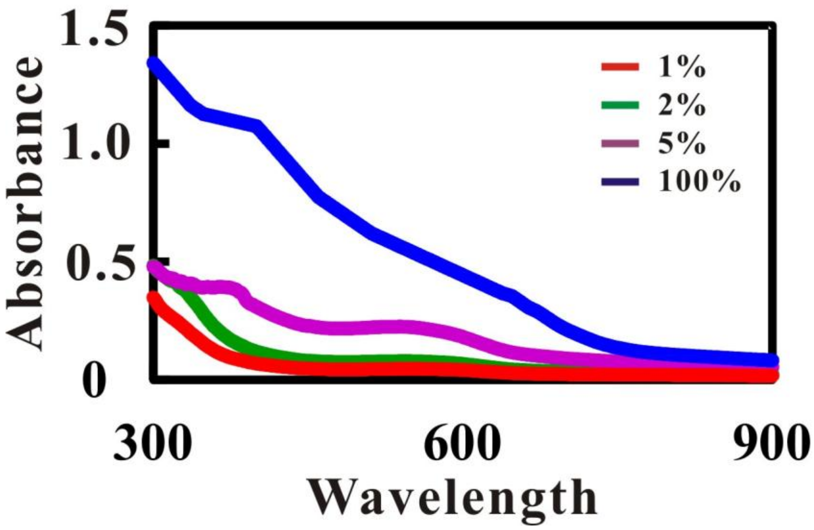

Figure 2. UV-visible absorption spectra of 1 %, 2 %, 5 %, 10 % and 100 % red cabbage extract in the presence pH 7.0 PBS.

Fig. 2 shows the UV–vis analysis, it was found that only the spectra of red cabbage dyes adsorbed on the photoanodes. The absorption spectra at different red cabbage extract quantities was measured spectrophotometer in 300–900 nm range. The 1 % (red line) of red cabbage extract was reported that flat absorb the wavelength and significant peak at 590 nm, and the intensity of 0.04. The 2% (green line) of red cabbage extract has peak at 586 nm, and the intensity of 0.07. The 5 % (purpule line) shows two peak at 562 nm and 379 nm, the intensity of 0.21 and 0.38. Absorbance and sharpness increases at highest red cabbage extract concentration showing at 100 % (blue line). Red cabbage extract shows highest background curve, two dramatic peak was found at 550 nm and 410 nm, the intensity of 0.54 and 1.02. The red cabbage dye provided the high efficiency photosensitive for DSSC.

3.2. Electrochemistry study of natural dye

Glassy carbon electrode was polished with 0.05 μm alumina on Buehler felt pads and then ultrasonically cleaned for about a minute in water. Finally, the electrode was washed thoroughly with double distilled water and dried at room temperature. After that electrode was immersed in different concentrations of red cabbage extract (a) 1 %, (b) 2 %, (c) 5 % and (d) 100 % in pH 7.0 PBS solution from -1.0 V to 1.6 V, scan rate 100 mVs^{-1} by cyclic voltammetric in Fig. 3.

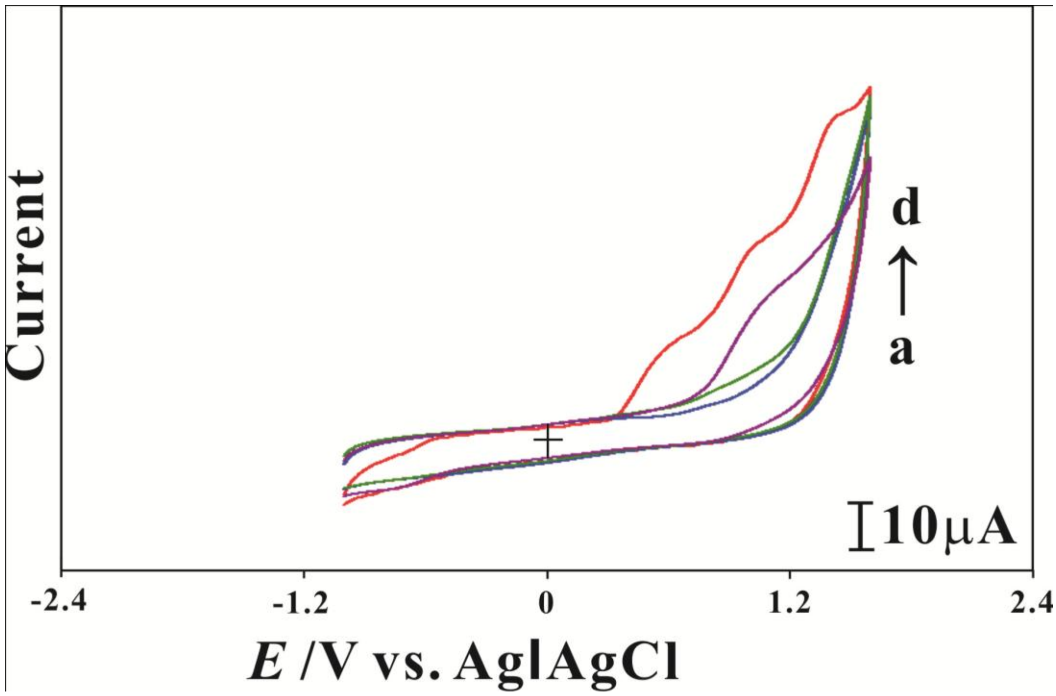

Figure 3. Cyclic voltammograms of (a) 1 %, (b) 2 %, (c) 5 % and (d) 100 % of red cabbage extract in the presence pH 7.0 PBS. The corresponding CVs have been obtained at 100 mVs^{-1} scan rate in the potential range of -1.0 to 1.6 V.

Curve (a) 1 % of red cabbage extract shows flatness graph. With increase concentrations of red cabbage extract from 2 % to 100 %, some irreversible peak current increased occur. Curve (d) 100 % of red cabbage extract shows highest background current was 21.11 μA, 42.19 μA and 72.55 μA at 0.58 V, 0.98 V and 1.38 V, we supposed that characterization of polyphenos [24-30]. The red cabbage extract have been already proved to be suitable present in this paper. This environmentally friendly dye of biological production provides rates of synthesis faster and can potentially be used in various human contacting areas such as cosmetics, foods, medical and DSSC applications.

3.3. Electrochemical impedance spectra (EIS) of natural dye

Electrochemical impedance spectroscopy (EIS), a relatively new and powerful method of characterizing electrochemical properties of materials and their interfaces, is now the method of choice for characterizing interfaces in which the physical and chemical behavior is dependent on several different processes occurring at different rates. Initially applied to the determination of the double-layer capacitance and in ac polarography, they are now applied to the characterization of electrode processes and complex interfaces. Analysis of the system response contains information about the interface, its structure and reactions taking place there.

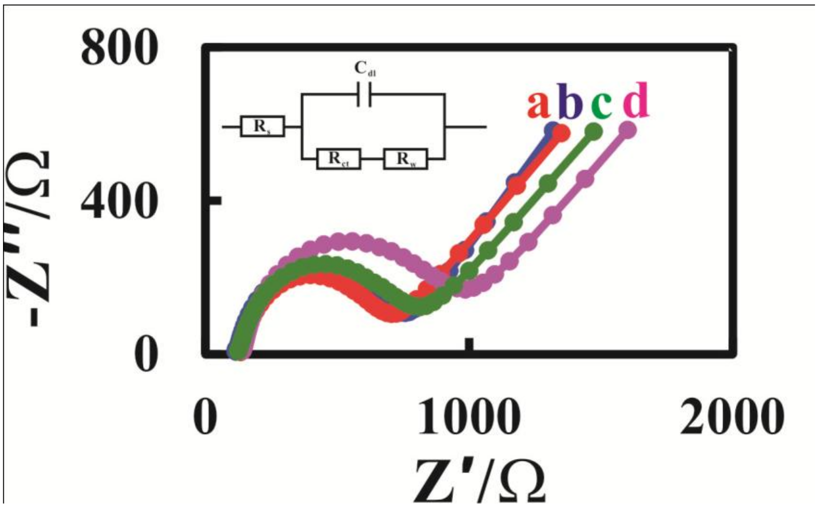

Figure 4. Electrochemical impedance spectroscopy (EIS) for (a) 0 %, (b) 1 %, (c) 2 % and (d) 5 % in the presence pH 7.0 PBS of equimolar 5 mM $[Fe(CN)_6]^{3-/4-}$. The insert displayed the equivalent circuit (Randles model) was used to fit Nyquist diagrams.

Fig. 4 shows the results of EIS for different concentrations of red cabbage extract in the presence pH 7.0 PBS of equimolar 5 mM $[Fe(CN)_6]^{3-/4-}$. The Faradaic impedance spectra, presented as Nyquist plots (Z″vs. Z′). The 0 % (curve a) of red cabbage extract exhibited almost a straight line with a very small depressed semicircle arc (R_{et} = 669 (Z′/ Ω)) represents the characteristics of diffusion limited electron-transfer process on the electrode surface. On the same conditions, the 1 % (curve b) of red cabbage extract shows like a depressed semicircle arc (R_{et} = 742 (Z′/ Ω)) clearly indicated the higher electron transfer resistance behavior comparing with 0 %. The 2 % (curve c) and 5 % (curve d) of red cabbage extract shows dispersed semicircle arc (R_{et} = 790 (Z′/ Ω)) and (R_{et} = 986 (Z′/ Ω)). The insert displayed the equivalent circuit (Randles model) was used to fit Nyquist diagrams. It constitutes a distributed element which can only be approximated by an infinite series of simple electrical elements.

Impedance methods are based upon the well-established theory of electronic AC circuit analysis with both instrumentation and data analysis techniques being analogous. The fundamental approach of EIS is the application of a spectrum of small-amplitude sinusoidal voltage excitations to interrogate the system of interest and the measurement of that systems' response. It will provide a way to monitor the H^+ process and long-term performance of red cabbage extract structures and could also provide a simple stability. EIS for different concentrations of red cabbage extract in the presence pH 7.0 PBS of equimolar 5 mM $[Fe(CN)_6]^{3-/4-}$ under illumination (light source, Xe lamp 100 $mWcm^{-2}$). The 0 % of red cabbage extract exhibited almost a straight line with a very small depressed semicircle arc (R_{et} = 667 (Z′/ Ω)). On the same conditions, the 1 % of red cabbage extract shows like a depressed semicircle arc (R_{et} = 740 (Z′/ Ω)). The 2 % and 5 % of red cabbage extract shows dispersed semicircle arc (R_{et} = 668 (Z′/ Ω)) and (R_{et} = 792 (Z′/ Ω)). All groups of resistance in each irradiation conditions reveals that the value decreased. The red cabbage extract provided the photosensitive for dye. The results showed individual resistance value in different concentrations conditions as in Table 1.

Table 1. Electrochemical impedance spectroscopy (EIS) of individual resistance value in different concentrations conditions.

Red cabbage extract (%)	Dark (Z'/ Ω)	Illumination (Z'/ Ω)
0	669	667
1	742	740
2	790	668
5	986	792

3.4. Photoelectric performances of DSSC

The performance of DSSC using Pt as the photocathode. Pt can be deposited using a range of methods such as electrodeposition, spray pyrolysis, sputtering, and vapor deposition. Best performance and long-term stability has been achieved with nanoscale Pt clusters prepared by sputtering. The electrolyte contains 0.1 M LiI, 0.05 M I_2, and 0.5 M propylene carbonate. The TiO_2/ITO electrode was immersed in natural dye solution 6, 12, 18 and 24 h as an experimental control group.

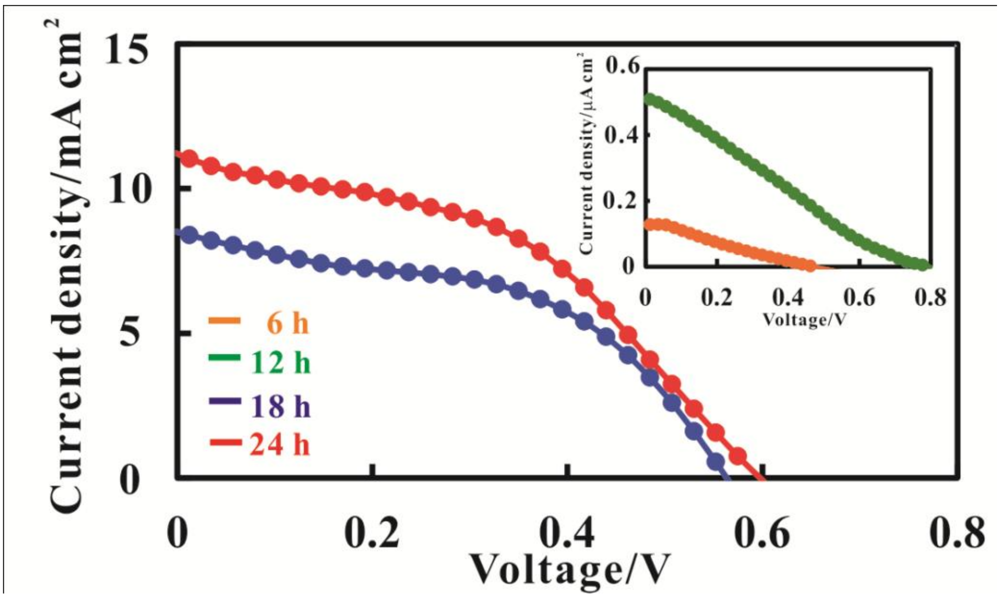

Figure 5. Photocurrent density-voltage curves of DSSC based on TiO_2/ITO electrode was immersed in natural dye solution 6 h, 12 h, 18 h and 24 h, respectively. Light source, Xe lamp 100 $mWcm^{-2}$, AM 1.5.

Fig. 5 shows the *J-V* characteristics of DSSC, TiO_2/ITO electrode was immersed various time in natural dye solution. The 18 h and 24h J_{sc} of 8.497 mA cm^{-2} and 11.2 mA cm^{-2}, V_{oc} of 0.56 V and 0.59 V were obtained. The inset shows 6 h and 12 h result. The adsorption modes of dyes on semiconductor surfaces are very important for the DSSC efficiency. The TiO_2/ITO electrode was immersed in natural dye solution 24 h shows highest efficiency photosensitive for DSSC. To construct workable and efficient DSSC, the dye must be adsorbed on the surface of the semiconductor intimately. Therefore, the first kind provides an approved strategy to accomplish a strong interlinkage between the dye and the semiconductor. Anthocyanin derivatives from red cabbage extract offer functional groups to adhere on semiconductor. Some studies reported that it requires that the dye should possess an anchoring group, which should react with surface hydroxyl groups of the semiconductor oxide to form chemical bonds. The standard anchoring group for sensitizers is carboxylic acid (-COOH). The binding modes can be determined by the molecular structure and adsorption environment [31]. The bidentate structure is superior to unidentate structure in the stability of the anchored dye and interfacial quantum yields of electron injection due to the intimate contact with the semiconductor surface [32]. Parameters such as V_{oc}, J_{sc}, *FF*, and η of DSSC immersed various time of red cabbage extract tabulated in Table 2.

Table 2. The photovoltaic parameters of DSSC based on TiO_2/ITO electrode was immersed in natural dye solution, respectively. Light source, Xe lamp 100 $mWcm^{-2}$, AM 1.5.

Time (h)	J_{sc} (μA cm^2)	V_{oc} (V)	*FF* (%)	η (%)
6	0.06	0.39	27.26	0.000007
12	0.51	0.79	23.71	0.00009
18	8497	0.56	48.05	2.3
24	11200	0.59	43.47	2.908

4. CONCLUSIONS

UV-Vis studies shows the absorption band of red cabbage extract solution. Absorption spectrum also shows that dye from red cabbage extract is found to be highly absorbing at high concentrations. CVs of red cabbage extract shows current at 0.58 V, 0.98 V and 1.38 V, we supposed that characterization of polyphenos. EIS of all groups resistance in each irradiation conditions reveals that the value decreased. The red cabbage extract provided the photosensitive for dye. The TiO_2/ITO electrode was immersed in natural dye solution 24 h shows highest efficiency photosensitive for DSSC. The adsorption modes of dyes on semiconductor surfaces are very important for the DSSC efficiency.

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