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Correlation between the Acidity of Butterfly Pea (*Clitoria ternatea* L.) Flower Extract and Carbon Nanotube Counter Electrode Concentration on the Efficiency of Dye-Sensitized Solar Cells (DSSC)

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Abstract
In this research, we reported the fabrication of dye-sensitized solar cells (DSSC) using butterfly pea (*Clitoria ternatea* L.) flower extract as a natural sensitizer, TiO_2 as the working electrode, carbon nanotubes (CNT) as the counter electrode, and a self-synthesized copper(I) thiocyanate (CuSCN) electrolyte. The extract was obtained by ultrasound-assisted extraction with methanol and adjusted to pH 2, 7 and 10, while the CNT concentration of the counter electrode was varied at 1, 2 and 3%. The anthocyanin content decreased from 23.75 mg/L at pH 2 to 11.19 mg/L at pH 10, and the extract absorbed visible light with a maximum at 550 nm. FTIR characterization showed O–H, C–H, C=C and C–O groups in the extract, together with Ti–O and In–O bands in the assembled photoanode, which indicates the interaction between the dye, TiO_2 and ITO glass. The Tauc plot showed that the band gap energy decreased from 3.03 to 2.98 eV when CNT was added. The performance of the DSSC was tested using a digital multimeter under indoor light, a 20 W halogen lamp, and outdoor sunlight. The highest photovoltaic efficiency of 0.29% was obtained from the DSSC with the pH 2 extract and the 3% CNT counter electrode under sunlight. The efficiency increased as the dye became more acidic and as the CNT concentration increased.

Keywords: Butterfly Pea, Anthocyanin, Carbon Nanotube, Counter Electrode, Dye-sensitized Solar Cell

Introduction

The growing demand for electricity has accelerated the development of sustainable energy sources, and solar energy is one of the most promising of them because it is abundant, clean and emits no greenhouse gases during operation [1]. The dye-sensitized solar cell (DSSC) is a third-generation photovoltaic device that offers simple fabrication, a lower cost than silicon solar cells, and the ability to harvest low-intensity indoor light [2]. Since it was introduced by O'Regan and Grätzel in 1991 [3], the DSSC has typically consisted of a dye-sensitized nanoporous TiO_2 photoanode, a redox electrolyte and a counter electrode. Upon illumination, the dye absorbs photons and injects the excited electrons into the TiO_2 conduction band, and the oxidized dye is then regenerated by the electrolyte so that the conversion cycle can continue [4].

The dye that acts as the light harvester largely determines the performance of a DSSC [5]. Ruthenium-based sensitizers are widely used, but they are expensive and harmful to the environment, which makes natural and sustainable alternatives attractive [5]. Natural dyes have a low production cost, are easy to prepare, are non-hazardous to the environment and can perform well under diffuse light [6]. Among them, anthocyanins are particularly interesting because they are biodegradable, non-toxic and abundant [7]. Anthocyanin molecules contain carbonyl and hydroxyl groups and a conjugated π-electron system that can bind strongly to the TiO_2 surface, which promotes electron transfer from the dye to the semiconductor and reduces charge recombination [8].

Butterfly pea (*Clitoria ternatea* L.) is a climbing plant with blue, purple or pink flowers that is commonly found in yards and rice-field areas. Its blue colour comes from anthocyanins of the ternatin group [9], and the flower also contains other flavonoids, terpenoids, tannins and steroids [10]. Together with its abundance, low cost and simple extraction, these features make the flower a promising natural sensitizer for DSSC [11, 12]. However, the structure of anthocyanin depends strongly on pH. The flavylium cation, which absorbs light most strongly, dominates at low pH, whereas the less stable quinoidal base and chalcone forms appear as the pH increases [13, 14]. The acidity of the dye solution is therefore expected to influence the dye

loading and the efficiency of the cell.

Besides the dye, the counter electrode, which catalyses the reduction of the redox species in the electrolyte, also governs the DSSC performance. Platinum, the conventional counter electrode, has a high catalytic activity but is expensive and scarce, which has driven the development of carbon-based alternatives [15]. Carbon nanotubes (CNT) are attractive because of their high electrical conductivity, large specific surface area and good chemical stability, which can accelerate electron transfer and reduce charge recombination at the electrode. [15, 16] In this work, a CuSCN electrolyte synthesized in our laboratory was used in place of the conventional iodide/triiodide electrolyte.

To the best of our knowledge, the effect of the dye acidity and of the CNT concentration has mostly been studied separately. This study therefore investigates the correlation between the pH of the butterfly pea extract (pH 2, 7 and 10) and the concentration of the CNT counter electrode (1, 2 and 3%) on the efficiency of DSSC, and relates the electrical performance to the UV–Vis, FTIR and band gap characteristics of the materials.

Experimental

Chemicals and Materials

DSSC used in this study were fabricated from indium tin oxide (ITO) glass, titanium dioxide (TiO_2), carbon nanotubes (CNT) and dried butterfly pea flowers. The chemicals used for the electrolyte were copper(II) sulfate ($CuSO_4$), potassium thiocyanate (KSCN), and sodium nitrate ($NaNO_3$). Other chemicals were methanol, ethanol, hydrochloric acid, acidic and basic buffer solutions, sodium carboxymethyl cellulose (CMC-Na), monoethanolamine (MEA), and demineralized water. All of these chemicals are analytical grade.

Instrumentals

This study used several tools such as an ultrasonic extractor, rotary evaporator, magnetic stirrer, analytical balance, vernier caliper, 20 W halogen lamp, lux meter, digital multimeter, UV–Visible spectrophotometer of Shimadzu, and Fourier transform infrared (FTIR) spectrometer of Shimadzu.

Dye extraction

Butterfly pea petals were cleaned, dried and soaked in methanol in an Erlenmeyer flask. A total of 100 g of dried flowers was extracted with 1500 mL of methanol using the ultrasound-assisted extraction (UAE) method for 1 hour at 50 Watt. The filtrate was separated with filter paper and concentrated using a rotary evaporator at 50 °C. CMC-Na (1 g) was added to the concentrated extract, which was then conditioned to pH 2, 7, and 10 by adding acidic and basic buffer solutions.

Photoanode preparation

ITO glass with a size of 2.5 cm × 2.5 cm × 1.1 mm was masked with black tape to define the coated area. The TiO_2 paste was spread on the ITO glass by the doctor blade method using a spatula and left to dry, and the coating was repeated until the layer was level with the tape (about 0.36 mm), as measured with a vernier caliper. The dried TiO_2-coated ITO glass was then soaked in the dye solution for 24 hours, rinsed with demineralized water to remove the excess dye, and dried at room temperature.

Counter electrode preparation

CNT dispersions of 1, 2 and 3% were prepared by dispersing 0.10, 0.20 and 0.30 g of CNT in 9.90, 9.80 and 9.70 mL of demineralized water, respectively, and stirring them with a magnetic stirrer for 1 hour at 80 °C. Each dispersion was deposited on a cleaned ITO glass by the doctor blade method until the surface was evenly covered and was left to dry.

Electrolyte synthesis

CuSCN was synthesized by precipitation at 4–6 °C. $CuSO_4$ and $NaNO_3$ were dissolved in demineralized water to form a homogeneous solution. In a separate beaker, KSCN was dissolved in demineralized water and added dropwise to the $CuSO_4$–$NaNO_3$ solution under magnetic stirring until a pale white CuSCN precipitate was formed. The precipitate was separated using a Buchner funnel, washed with ethanol, dried at 80 °C and stored as a powder.

DSSC fabrication

The electrolyte was dripped onto the counter electrode and spread so that it was absorbed over the whole TiO_2 surface. The dye-sensitized photoanode was then placed on the counter electrode with the coated sides facing each other to form a sandwich structure, and the two electrodes were fixed with binder clips.

Characterization

The absorption spectrum of the concentrated extract was recorded with a UV–Visible spectrophotometer in the range of 400–800 nm to determine the wavelength of maximum absorption (λ_{max}), and the anthocyanin content of each extract was determined spectrophotometrically at this wavelength. FTIR analysis was carried out on ITO glass, ITO glass coated with TiO_2, the pH 2 extract, and the assembled ITO/TiO_2/electrolyte/CNT/dye sample. The band gap energy of the TiO_2 + extract and TiO_2 + extract + CNT samples was calculated from the UV–Vis data using the Tauc plot method. The photovoltaic performance was measured with a digital multimeter: The open-circuit voltage (V_{oc}) was measured by connecting the multimeter in parallel to the cell terminals and the short-circuit current (I_{sc}) by connecting it in series. The cells were connected in parallel before the measurement and were tested under three light conditions: Indoor ambient light, indoor light from a 20 W halogen lamp, and outdoor direct sunlight. The light intensity was measured with a lux meter, and the efficiency (η) was determined from the maximum electrical power and the input power calculated from the measured light intensity.

Results and Discussion

Dye extraction

The butterfly pea extract obtained by UAE method had an intense blue-purple colour (Fig 1), which shows that the pigment was successfully extracted from the petals. Methanol is a polar solvent and dissolves the polar anthocyanin effectively, while the ultrasonic waves break the cell walls and enhance the mass transfer, so that the extraction time is shortened and less solvent is needed. After the filtrate was concentrated in the rotary evaporator at 50 °C, the extract became a deep blue-purple (Fig 1c).



Fig 1: (a) Ultrasound-assisted extraction, (b) butterfly pea extract after filtration and (c) concentrated extract after rotary evaporation

UV–Vis absorbance and anthocyanin content

The UV–Vis spectrum of the concentrated extract is shown in Fig 2. The extract absorbs light over a broad region of the visible spectrum with a maximum absorbance at 550 nm, so the dye is suitable to act as a sensitizer in DSSC. The measurement follows the Lambert–Beer law, in which the absorbance is proportional to the concentration of the absorbing species and to the path length of the light.

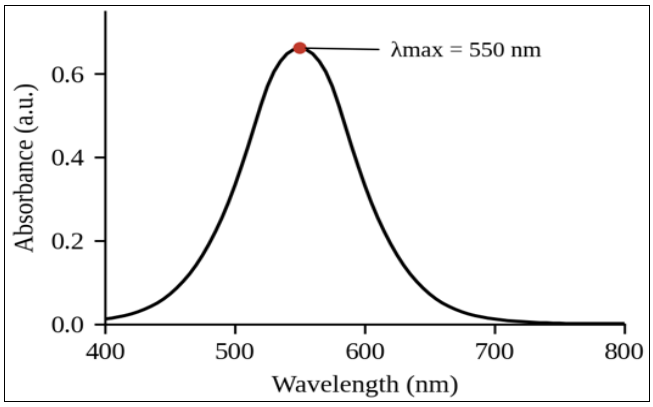


Fig 2: UV–Vis absorption spectrum of the butterfly pea extract

The anthocyanin content of the extract at each pH is given in Table 1. The highest content, 23.75 mg/L, was found at pH 2, followed by 17.08 mg/L at pH 7 and 11.19 mg/L at pH 10. In an acidic medium the anthocyanin is stabilized in the form of the flavylium cation, which has the strongest light absorption, whereas at basic pH the anthocyanin is converted into the quinoidal base and partly degraded, so the measured content becomes lower [13, 14]. Therefore, the use of a basic dye is better avoided in further work.

Table 1: Anthocyanin content of the butterfly pea extract

pH of the extract	Anthocyanin content (mg/L)
2	23.75
7	17.08
10	11.19

Electrolyte

CuSCN was used as the electrolyte that returns electrons to the dye after excitation by the light. It is a hole-transporting material with a high optical transparency, a good thermal stability and an energy level suitable for the extraction and transport of holes from the dye molecules to the electrode [17].

FTIR analysis

FTIR analysis was carried out to identify the functional groups in the ITO glass, the ITO glass coated with TiO_2, the pH 2 extract and the assembled sample (Fig 4 and Table 2).

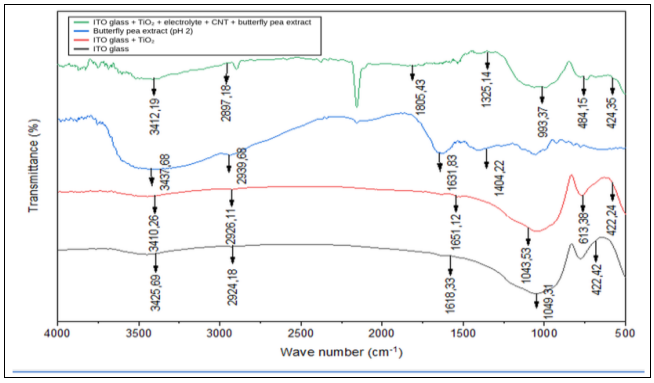


Fig 3: FTIR spectra of ITO glass, ITO glass + TiO_2, butterfly pea extract (pH 2) and ITO glass + TiO_2 + electrolyte + CNT + butterfly pea extract

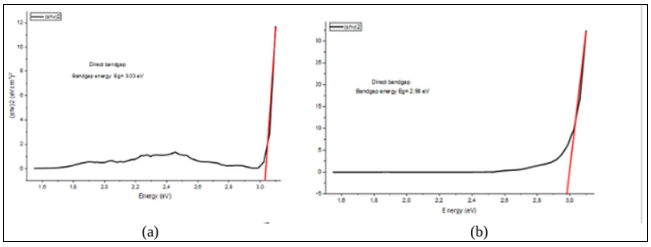


Fig 4: Tauc plots of (a) TiO_2 + butterfly pea extract (E_g = 3.03 eV) and (b) TiO_2 + butterfly pea extract + CNT (E_g = 2.98 eV)

The ITO glass shows an O–H vibration at 3425.69 cm^{-1}, which arises from water adsorbed on the glass surface, and a C–H vibration at 2924.18 cm^{-1}. The band at 1618.33 cm^{-1} is assigned to C=C; the Si–O vibration of the glass appears at 1049.31 cm^{-1}, and the In–O band of ITO appears at 422.42 cm^{-1}. After the deposition of TiO_2, the O–H band shifts to 3410.26 cm^{-1} and a new Ti–O band appears at 613.38 cm^{-1}, which confirms that TiO_2 was deposited on the ITO glass.

The pH 2 extract shows a broad O–H band at 3437.68 cm^{-1}, which is related to the hydroxyl groups of phenolic compounds, especially anthocyanin, and to hydrogen bonding with the solvent [18], together with C–H at 2939.61 cm^{-1}, C=C at 1631.83 cm^{-1}, which comes from the aromatic rings of anthocyanin, and C–O at 1404.22 cm^{-1}. In the assembled sample, all the main bands of the extract (O–H, C–H, C=C, and C–O) are detected together with those of ITO and TiO_2 (Si–O at 993.37 cm^{-1}, Ti–O at 484.15 cm^{-1}, and In–O at 424.35 cm^{-1}). The O–H band shifts from 3437.68 cm^{-1} in the extract to 3412.19 cm^{-1}, and the Ti–O and Si–O bands shift compared with the ITO/TiO_2 sample. These shifts indicate an interaction between the hydroxyl and carbonyl groups of the dye and the TiO_2–ITO surface, which supports the adsorption of the dye on the photoanode.

Table 2: FTIR wavenumbers (cm^{-1}) of the samples

Group	ITO glass	ITO/ TiO_2	Extract (pH 2)	Assembled sample
O–H	3425.69	3410.26	3437.68	3412.19
C–H	2924.18	2926.11	2939.61	2897.18
C=C	1618.33	1651.12	1631.83	1805.43
C–O	–	–	1404.22	1325.14
Si–O	1049.31	1043.53	–	993.37
Ti–O	–	613.38	–	484.15
In–O	422.42	422.42	–	424.35

Band gap energy

The band gap energy was calculated from the UV–Vis absorbance data using the Tauc plot method [19]. The band

gap energy of TiO_2 with the butterfly pea extract is 3.03 eV (Fig 5a), while that of TiO_2 with the extract and CNT is 2.98 eV (Fig 5b). A smaller band gap means that a lower energy is required to excite the electrons, so the decrease indicates that the addition of CNT improves the visible-light absorption of the sample. A strong interaction between TiO_2 and CNT, for example through Ti–O–C bonding, may provide an effective electron transfer pathway and suppress the recombination of electron–hole pairs, but this explanation should be confirmed by further structural characterization.

DSSC performance

The V_{oc} and I_{sc} of the DSSC prototypes were measured under the three light conditions, and the efficiency was calculated from the input power obtained from the measured light intensity (Table 3 and Fig 6).

The intensity of the light strongly affects the performance. Under indoor ambient light, the number of photons reaching the dye layer is small, so only a few electrons are excited, and the I_{sc} was only 0.2–0.5 µA with an efficiency of 0.02–0.07 ($\times 10^{-3}$ %). The 20 W halogen lamp, whose spectrum covers a wide visible range close to that of sunlight, raised the I_{sc} to 0.4–12.1 µA. Under direct sunlight, the I_{sc} reached 83.1–160.0 µA and the V_{oc} reached 0.402–0.597 V, more than two orders of magnitude higher than the indoor current. The highest efficiency was therefore found in the outdoor test, and the effects of the dye pH and the CNT concentration are discussed mainly on the basis of these results.

Table 3: Open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and efficiency (η) of the DSSC prototypes with different extract pH and CNT concentration under three light conditions

		Indoor light			Halogen lamp 20 W			Outdoor sunlight		
pH	**CNT (%)**	**V_{oc} (V)**	**I_{sc} (µA)**	**η ($\times 10^{-3}$ %)**	**V_{oc} (V)**	**I_{sc} (µA)**	**η ($\times 10^{-3}$ %)**	**V_{oc} (V)**	**I_{sc} (µA)**	**η ($\times 10^{-3}$ %)**
2	1	0.299	0.2	0.02	0.4430	0.4	0.04	0.5500	105.8	0.20
7	1	0.2895	0.2	0.02	0.3779	3.0	0.03	0.5598	95.0	0.18
10	1	0.3199	0.3	0.02	0.3400	12.1	0.02	0.4019	83.1	0.12
2	2	0.4255	0.3	0.04	0.4632	0.4	0.06	0.5973	120.0	0.25
7	2	0.4353	0.3	0.04	0.4734	3.0	0.05	0.5598	105.0	0.21
10	2	0.3523	0.4	0.04	0.4596	3.0	0.04	0.4914	87.6	0.16
2	3	0.3950	0.4	0.05	0.4908	9.9	0.12	0.5640	160.0	0.29
7	3	0.4987	0.4	0.06	0.5310	7.0	0.10	0.5601	130.0	0.23
10	3	0.5120	0.5	0.07	0.5147	6.9	0.11	0.5247	101.0	0.18

Effect of the dye pH: Under sunlight, the efficiency decreased with the increasing pH of the extract at every CNT concentration. For the 3% CNT counter electrode, the efficiency was 0.29 at pH 2, 0.23 at pH 7 and 0.18 at pH 10, so the pH 2 dye gave an efficiency about 61% higher than the pH 10 dye. This order is the same as the order of the anthocyanin content (23.75, 17.08 and 11.19 mg/L). The Pearson correlation coefficient between the anthocyanin content and the outdoor efficiency over the three pH values was 0.95, 0.995, and 1.00 for the 1, 2, and 3% CNT, respectively, although it is based on only three points and is therefore indicative. A more acidic dye contains more anthocyanin in the flavylium form, which absorbs more light and injects more electrons into the TiO_2 conduction band. At basic pH, the anthocyanin changes into the unstable quinoidal base and then into the chalcone form, which lowers the efficiency [13]. Under indoor and halogen light, the pH trend was not consistent (for example, the highest indoor efficiency at 3% CNT was found at pH 10), probably because the currents of 0.2–0.5 µA are close to the resolution of a handheld multimeter, so the effect of the pH can only be resolved reliably under sunlight.

Effect of the CNT concentration: At each pH, outdoor efficiency increased as CNT concentration rose from 1 to 3%; at pH 2, efficiency rose from 0.20 to 0.25 and 0.29, and Isc rose from 105.8 to 120.0 and 160.0 µA. A higher CNT loading increases the electrical conductivity and the catalytic surface area of the counter electrode, which lowers the resistance to electron transfer, accelerates the regeneration of the dye and decreases the chance of recombination, so that more electrons reach the counter electrode. [15, 16] Since the efficiency was still increasing at 3% CNT, the optimum concentration may lie above the range studied here.

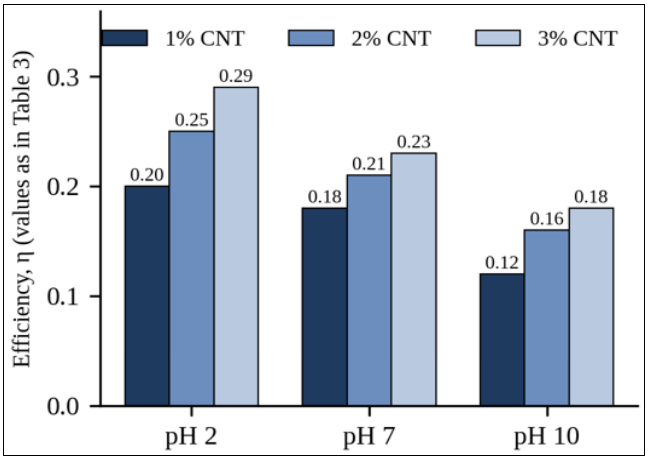


Fig 6: Outdoor efficiency of the DSSC with different extract pH and CNT concentration

Correlation between the dye pH and the CNT concentration: The two factors act in the same direction on different components of the cell: The pH determines how much light-absorbing anthocyanin is available on the photoanode, while the CNT concentration determines how efficiently the electrons are returned through the counter electrode. As a result, the best performance was obtained when the most acidic dye (pH 2) was combined with the highest CNT concentration (3%), giving an efficiency of 0.29% under sunlight, which is about 2.4 times the lowest value (0.12, pH 10 and 1% CNT). The absolute efficiency is still low, which may be related to the cracks in the TiO_2 layer, the limited light absorption range and photochemical stability of anthocyanin dyes, and the fact that the CuSCN electrolyte has not yet been optimized.

Conclusion

In summary, DSSC were fabricated using butterfly pea extract as the sensitizer, TiO_2 as the working electrode, a CNT counter electrode and a CuSCN electrolyte. The acidity of the dye affected the efficiency: The more acidic dye contained more anthocyanin (23.75 mg/L at pH 2) and gave a higher efficiency than the neutral and basic dyes. The CNT concentration also affected the efficiency, which increased from 1 to 3% CNT. The maximum efficiency of 0.29% was achieved by the DSSC with the pH 2 extract and the 3% CNT counter electrode under outdoor sunlight. The extract absorbs visible light with a maximum at 550 nm, FTIR confirmed the O–H, C–H, C=C and C–O groups of the dye and the Ti–O and In–O bands of the photoanode, and the band gap energy decreased from 3.03 to 2.98 eV with the addition of CNT.

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