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Performance and stability of low-cost dye-sensitized solar cell based crude and pre-concentrated anthocyanins: Combined experimental and DFT/TDDFT study

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ABSTRACT

The low cost DSSCs utilized by crude and pre-concentrated anthocyanins extracted from six anthocyanin-rich samples including mangosteen pericarp, roselle, red cabbage, Thai berry, black rice and blue pea were fabricated. Their photo-to-current conversion efficiencies and stability were examined. Pre-concentrated extracts were obtained by solid phase extraction (SPE) using C18 cartridge. The results obviously showed that all pre-concentrated extracts performed on photovoltaic performances in DSSCs better than crude extracts except for mangosteen pericarp. The DSSC sensitized by pre-concentrated anthocyanin from roselle and red cabbage showed maximum current efficiency $\eta = 0.71\%$ while DSSC sensitized by crude anthocyanin from mangosteen pericarp reached maximum efficiency $\eta = 0.97\%$. In addition, pre-concentrated extract based cells possess more stability than those of crude extract based cells. This indicates that pre-concentration of anthocyanin via SPE method is very effective for DSSCs based on good photovoltaic performance and stability. The DFT/TDDFT calculations of electronic and photoelectrochemical properties of the major anthocyanins found in the samples are employed to support the experimental results.

1. Introduction

Since first discovered by Grätzel el al. [1] in 1991, dye-sensitized solar cell (DSSC) has attracted much attention as a new promising solar to electric convertor because of its low production cost, easy fabrication, more environmental friendliness compared to conventional silicon solar cell. The DSSC is composed of nanocrystalline porous semiconductor electrode-adsorbed dye, a counter electrode and an electrolyte. Dye sensitizer plays a crucial role in absorbing sunlight and transforming solar energy into electric energy. Numerous organic and metal complexed compounds have been synthesized and utilized as molecular sensitizers in DSSCs. By far, DSSC utilized ruthenium (Ru) complex compounds as molecular sensitizer has been reached 11–12% overall efficiency [2–5]. Even though the DSSCs-based ruthenium complexes have provided a relatively high efficiency, but they are not yet suitable to be produced in large scale based on several disadvantages. For example, the noble metals serving as sensitizer are limited in amount and led to their high production cost. In addition, complicated synthetic method and toxicity due to incomplete degradation are considered to be the main drawbacks. To overcome this problem, organic dyes, especially natural pigments derived from different parts of various plants such as flower, fruit, leaf and wood are promising alternative

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ways to reduce production cost of solar cells and they have been widely studied and used to replace the ruthenium dye [6–26].

By far, it has been reported that the conversion efficiencies of 1.60 and 1.86 obtained from roselle and pomegranate [27], 2.3 from monascus [28] and 1.17 and 2.63% from mangosteen pericarp [29,30], respectively. From reviews, it is reported that almost of extracted pigment contain anthocyanins (Fig. 1) in different derivatives that show significant role enhancing DSSC efficiencies according to the active carbonyl (−C═O) and hydroxyl (−OH) groups which can generate and transfer electron during absorption of light [31]. Recently, Mozaffari et al. investigated the photovoltaic characteristics of DSSCs sensitized by crude and purified extracts from Siahkooti fruit as sensitizers [32]. It has been found that efficiency of DSSCs using purified and crude extracts of the fruit were 0.32% and 0.27%, respectively, indicating that purified extract performs on photovoltaic performance better than crude extract. On the same hand, it is interesting to note that concentration of the dyes plays a crucial role on photovoltaic performance of DSSCs.

The aim of this work was to study and optimize photovoltaic performance and stability as a function of the concentration and adsorption characteristics of the dyes on TiO_2 thin films. Solid phase extraction (SPE) using C18 cartridge was applied to pre-concentrate anthocyanin from the crude extracts. To this end, dye adsorption behavior on TiO_2 electrode were obtained and analyzed to better understand the relations between concentrations of the dye contain in extracted solutions and photovoltaic performances as well as stabilities their DSSCs. The DFT/TDDFT calculations were performed to support the experimental results.

2. Experimental method

2.1. Preparation of natural pigments and characterization

Extraction and pre-concentration of anthocyanin from the six samples were performed based on the following procedure [33]. The pre-concentration method is shown in Scheme 1. Fresh samples were cleaned with de-ionized water, air-dried and crushed into powder in a mortar. 50 g of powdered sample was put into a beaker, 300 mL of acidified methanol (0.01%v/v) was added and the mixture was kept overnight, stored at 4 °C and dark condition. The obtained solution was filtered out and centrifuged to get rid of any solid residues; thereafter a pure and clear pigment solution was obtained. The solvent was removed using vacuum rotary evaporator at 40 °C to get more concentrated crude extract. Further purification of clear solution was performed using SPE to achieve more concentrated anthocyanin. A small drop of crude extract was dropped into the C18 cartridge. 5 mL of acidified de-ionized water was dropped to elute soluble sugar followed by 5 mL of ethyl acetate was used for elution of undesirable polyphenolic compounds. The remaining anthocyanin in the cartridge was then eluted by acidified methanol. The pigment solutions obtained before and after pre-concentration were stored and refrigerated at 4 °C before UV–Vis characterization and used as sensitizer in fabrication of DSSCs. The absorption spectra of pigment solutions both before and after pre-concentration were measured by UV–VIS spectrophotometer (model: T80+, PG Instruments Ltd). Structure of some isolated anothocyanins were characterized by NMR (Varian Mercury Plus 400) and also comparison with the spectral data reported from literature.

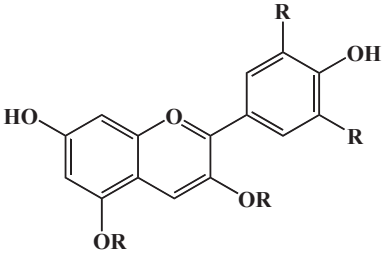

Fig. 1. Molecular structure of anthocyanins.

2.2. Fabrication of DSSCs

A fluorine-doped SnO_2 conductive glass (FTO) sheet resistance (15 Ω/cm^2; XinYan, China) was used as the current collector. The FTO plate was cleaned with acetone and distilled water to remove impurities. The cleaned FTO glass surface was coated with nanocrystalline TiO_2 (P25, Degussa) paste using screen-prints method working area 0.25 cm^2. The FTO/TiO_2 electrodes were then sintered at 500 °C for 1 h. The cooled down electrode was immersed in the dye extract solution for 24 h. The TiO_2/dye electrode was rinsed with de-ionized water to remove impurities and then with methanol to remove trapped water from the initial rinsing. The counter electrode was prepared by coating platinum catalyst onto FTO glass. The 5 mM hexachloroplatinic acid (H_2PtCl_6)(Aldrich) solution in isopropanol was spread on the FTO glass surface. The Pt-coated FTO electrode was the heated in a furnace at 500 °C for 30 min. The two electrodes were clipped together to make a sandwich type cell. The electrolyte was composed of 0.1 M LiI (Fluka), 0.05 M I_2 (Riedel-deHaën) solution in acetonitrile (Merck) and was injected into the space of electrodes then the space was filled through the capillary action.

2.3. Dye adsorption measurement

The experiment for adsorption behavior of dye on TiO_2 electrode were carried out by immersing the TiO_2 cell with an active area 4 cm^2 in a small chamber filled with a solution of crude or pre-concentrated anthocyanin [34]. The adsorption efficiency at time t was calculated from Eq. (1)

$$\%adsorption = \left(\frac{A_0 - A_t}{A_0}\right) \times 100 \quad (1)$$

where A_0 and A_t are the initial and any time absorbances determined at maximum absorption wavelength of each solution using a UV–Vis spectrophotometer after filtration through a 0.0015 μm membrane filter.

2.4. Measurement of DSSC efficiency and stability

The solar to electric conversion efficiency (the photocurrent–voltage; J–V curve) was measured using Peccell® model PEC-L11 solar simulator class A under 1.5 a.m. and 100 mW/cm^2 condition. Based on the J–V curve, the fill factor (FF) is defined as:

$$FF = \frac{(J_{max} \times V_{max})}{(J_{SC} \times V_{OC})} \quad (2)$$

where J_{max} and V_{max} are the photocurrent and photovoltage, respectively for maximum power output (P_{max}) while J_{SC} and V_{OC} correspond to the short-circuit photocurrent and open-circuit photovoltage, respectively. The overall energy conversion efficiency (η) is defined as:

$$\eta = \frac{(J_{SC} \times V_{OC} \times FF)}{P_{in}} \quad (3)$$

where P_{in} is the power of incident light. The overall efficiency for all