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Performance enhancement of dye-sensitized solar cells based on anthocyanin by carbohydrates

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Abstract

Dye-sensitized solar cells (DSSCs) were fabricated using anthocyanin extracted from red cabbage (*Brassica oleracea var. capitata f. rubra*). Carbohydrates were found to be excellent performance enhancers that functioned in a dose-dependent manner. Different types of carbohydrates generally had different enhancement capabilities in the order of oligosaccharide > disaccharide > monosaccharide > polysaccharide. The enhancement capability was also highly dependent on the constituents of carbohydrates. Two oligosaccharides, Isomalto-oligosaccharide (IMO) and xylooligosaccharide (XOS), showed the highest capability. The DSSCs sensitized with them as additives to anthocyanin exhibited a power conversion efficiency (η) over 1.6% (an improvement of 60%) with a short-circuit current (J_{SC}) of about 4 mA/cm^2, and open-circuit voltage (V_{OC}) around 630 mV. The mode of interaction of anthocyanin with extrinsic carbohydrates was proposed and discussed. The use of carbohydrates and a common coadsorbent deoxycholic acid (DCA) together could induce an additional enhancement, which boosted the efficiency up to 1.87% (an accumulative improvement of 90%). This study provided a choice of a promising and powerful enhancer for the DSSCs based on natural anthocyanins.

Keywords: Dye-sensitized solar cell; Anthocyanin; Carbohydrates; Oligosaccharides

1. Introduction

Tremendous research effort has been devoted to improving the power conversion efficiency (η) of dye-sensitized solar cells (DSSCs) following the breakthrough by Grätzel and his co-workers in 1991 (O'Regan and Grätzel, 1991). Since then, organometallic complexes based on ruthenium were found to provide the highest η, which rapidly climbed to more than 10% (Chiba et al., 2006; Nazeeruddin et al., 2001; Qin and Peng, 2012).

Nevertheless, ruthenium is a scarce element, which can become very expensive and inaccessible if widely used. Besides, ruthenium is a heavy metal and its threat to the

Abbreviations: CA, crude anthocyanin extract; DCA, deoxycholic acid; FF, fill factor; FOS, fructooligosaccharide; IMO, isomalto-oligosaccharide; IPF, impurity fraction; J_{SC}, short-circuit current density (mA/cm^2); PA, purified anthocyanin; V_{OC}, open-circuit voltage (mV); TBP, 4-tert-butylpyridine; XOS, xylooligosaccharide; η, light-to-electricity conversion efficiency.

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environment is a latent risk (Gaiddon et al., 2005; Yasbin et al., 1980).

Biological pigments can be decomposed naturally without any pollution. Besides environmentally friendly properties, their abundance in supply, easy accessibility and high absorption in the visible region all make them good candidates as alternative photosensitizers. Anthocyanins, a group of flavonoids found in fruits, leaves and flowers, are water-soluble plant pigments that usually carry vivid colors ranging from red to blue (Brouillard, 1983). Compared to ruthenium-based dyes, anthocyanins are metal free, nontoxic and widely available at very low expense. They also meet the criteria for photosensitizers by having enough hydroxyl groups to bind TiO_2 nanocrystallites tightly and being able to inject electrons into the TiO_2 conduction band at an ultrafast rate when excited with visible light (Cherepy et al., 1997; Hagfeldt et al., 2010).

There have been several studies on DSSCs using anthocyanins as photosensitizer (Aduloju and Shitta, 2012; Calogero and Di Marco, 2008; Chang and Lo, 2010; Furukawa et al., 2009; Hao et al., 2006; Luo et al., 2009; Polo and Murakami Iha, 2006; Wongcharee et al., 2007). The power conversion efficiency (η) from those studies, however, were generally quite low (0.5–0.6%). A few reports, extracting anthocyanins from specific plant species, demonstrated an efficiency around 1.1% (Kumara et al., 2006; Zhou et al., 2011). Great improvement is needed to make the DSSCs sensitized with natural pigments be able to compete in the future photovoltaic market.

In a previous report, the fabrication conditions that can boost η were explored using anthocyanin from red cabbage (Chien and Hsu, 2013). It was found that further purification of the anthocyanin extract led to a lower η. If the fraction that was separated from anthocyanin during purification was added back to the purified anthocyanin solution before constructing sensitized TiO_2 films, DSSCs regained most of its original performance, clearly indicating that there were yet unknown components in the crude extract that could help anthocyanin molecules in the conversion of light into electricity. In this study, the identity of the unknown compounds was determined. These natural compound were found to be a powerful enhancer for the DSSCs sensitized with anthocyanin.

2. Experimental

2.1. Materials

Fresh red cabbages (*Brassica oleracea* var. *capitata f. rubra*) were purchased from a local market. The electrodes were supplied by Taiwan DSC PV Ltd., Taiwan. TiO_2 with average particle size of 15–20 nm was coated onto FTO glass (thickness 2.25 mm, resistivity 7 Ω/square, average transparency higher than 80% in visible light range) as a porous layer (thickness 12 μm, active area 28.3 mm^2) of the anode, and a scattering layer (thickness 3 μm) consisted of bigger TiO_2 particles (~150 nm) was further coated on the porous layer by screen printing method. The cathode was FTO glass coated with nano-Pt. Oligosaccharides were purchased from Green Sun Organics Corp., Taiwan, and all other chemicals were from Sigma Aldrich Co. Deionized water was used throughout this study.

2.2. Water-based anthocyanin extraction

The leaves of red cabbage were washed thoroughly and dried by tissue paper. Deveined leaves were then sliced and homogenized by a blender (7012G, Waring Products, Inc.) which had been pre-cooled to 0 °C. The juice was obtained by pressing the slurry through a stainless steel sieve, followed by centrifugation at 16,000×g for 10 min at 4 °C (3–18 K, Sigma, with the rotor 12158-H) to remove cell debris and other undissolved substances. The supernatant was filtered first by gravity through a filter paper (Whatman, grade No. 2), and further through a syringe-driven membrane filter (Millipore, pore size0.22 μm). The filtrates, designated as the crude anthocyanin extract (CA), were stored at -20 °C until use. The whole procedure was conducted under dim light.

2.3. Anthocyanin concentration measurement

The concentration of anthocyanin was determined based on Wrolstad et al. (2005) using the following equation,

$$\text{Anthocyanin concentration (mM)} = A \times \text{DF} \times 103/\varepsilon \cdot l$$

where DF is the dilution factor, l is the light-path length (1 cm), ε is the molar extinction coefficient (L mol^{-1} cm^{-1}) which, in this case, equals to 26,900. A is the absorbance, given by

$$A = (A_{\max} - A_{700})_{\text{pH1.0}} - (A_{\max} - A_{700})_{\text{pH4.5}}$$

where $A_{\max}$ and A_{700} are the absorbance at the maximum and 700 nm measured at pH 1.0 or pH 4.5, respectively. The absorbance was measured by using a UV–VIS spectrophotometer (U-3210, Hitachi).

2.4. Purification of crude anthocyanin extract

Further purification was done as described by Ordaz-Galindo et al. (1999)using the BAKERBOND^{TM} spe Octadecyl disposable extraction column (J.T. Baker). CA (1 mL) was introduced to the column, which had been activated first with 1 mL of methanol and then 1 mL of 0.01% HCl (v/v). With anthocyanin being retained in the column, the eluate which contained compounds other than anthocyanin was designated as one aliquot of the impurity fraction (IPF). The column was then washed with 2 mL of 0.01% HCl (v/v). Anthocyanin was collected by eluting the column with methanol containing 0.01% HCl (v/v). To replace the solvent methanol with water, the eluate was