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Photovoltaic performance and photostability of anthocyanins, isoquinoline alkaloids and betalains as natural sensitizers for DSSCs

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ABSTRACT

Natural dyes extracted from fruit (FBV) and root (RBV) of barberry (*Berberis vulgaris*) and fruit (FPA) and stalk (SPA) of pokeweed (*Phytolacca americana*) were used as sensitizers for dye-sensitized solar cells (DSSCs). All the extracts were employed without any modifications, such as purifications or addition of stabilizers. Anthocyanin and isoquinoline alkaloid were identified as the main components for FBV and RBV extracts, respectively, whereas betalain for FPA and SPA extracts. SPA and FPA displayed much broader absorption spectra than the others, which is beneficial to light harvesting capability. When tested in DSSCs, the highest power conversion efficiency (PCE) of 3.04% is obtained by SPA, and this followed by PCEs of 2.97, 2.35 and 2.01% for FPA, RBV and FBV, respectively. The lowest PCE for FBV can be attributed to poor electron transfer ability, which may cause reduced photocurrent and photovoltage. On the other hand, after 120 h of sunlight irradiation, FBV, RBV, FPA and SPA retained the PCE values as 91, 54, 63 and 69% of the initial efficiencies. The moderate photovoltaic performance with good photostability for the anthocyanin extract may favorable for low-cost and environmental-friendly DSSC applications.

1. Introduction

Dye-sensitized solar cells (DSSCs), which mimic the photosynthesis in plants (Sauvage et al., 2010), have been extensively studied in recent years owing to their cost-effectiveness and resource-unlimited attributes (O'Regan and Gratzel, 1991; Zeng et al., 2010). However, the power conversion efficiency (PCE) of DSSCs is lower than that of traditional silicon-based solar cells (Sharma et al., 2017). On the other hand, the silicon solar cells are not an option for portable power sources and integration into buildings because of their low performances under ambient light conditions and opacity (Apostolou et al., 2016; Fakharuddin et al., 2014). Unlike the silicon solar cells, DSSCs are very suitable for above-mentioned applications due to their working capability under ambient light conditions and tunable transparency (Fakharuddin et al., 2014).

The photovoltaic performance of DSSCs mainly depends on the molecular structure of the dyes used as sensitizers, which absorb sunlight and produce excitons (Abdou et al., 2013). Currently, commercially available ruthenium-based synthetic dyes, such as N719 and N3, have been widely used as sensitizers for DSSCs due to their intense charge-transfer absorption in the visible range of the solar spectrum, a long excitation lifetime and highly efficient metal-to-ligand charge transfer (Lai et al., 2008). However, these dyes have some disadvantages, such as high cost, resource scarcity, heavy metal toxicity, difficult synthesis and low synthetic yield, which limit their utilization in large scale DSSCs (Huang et al., 2016). Natural dyes have been considered as convenient alternative sensitizers for DSSCs because of their low-cost and environmental friendliness. However, the overall photovoltaic performance of natural DSSCs (NDSSCs) is lower than that of ruthenium-based dyes because of weak binding energy with TiO_2 thin film and poor absorption in the whole visible range (Chang et al., 2010; Maabong et al., 2015). Despite the lower efficiencies, the ratio of the PCE to the cost of the dye for NDSSCs is larger than that of ruthenium-based solar cells (Furukawa et al., 2009). Another problem is the low stability of NDSSCs due to photocatalytic degradation of natural dyes by TiO_2, which results in a decrease in the efficiency (Dumbrava et al., 2012). To overcome this instability, various approaches have been examined, including adjusting extracting conditions like solvent type, pH and temperature (Wongcharee et al., 2007; Calogero et al., 2012) and adding stabilizers, such as antioxidants (Dumbrava et al.,

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2012), sugar (Hemalatha et al., 2012) and tetraethyl orthosilicate (Hernandez-Martinez et al., 2013). However, these modifications result in an increase in the cost of solar cells.

Many studies show that the natural dyes as crude extracts such as anthocyanin (Akin et al., 2016; Phinjaturus et al., 2016), caroten (Hao et al., 2006; Shanmugam et al., 2013), chlorophyll (Sahare et al., 2015; Ganta et al., 2017) and betalain (Sengupta et al., 2015; Ramamoorthy et al., 2016) are effective sensitizers for low-cost NDSSCs. However, few studies have examined the stability of NDSSCs based on the crude extracts (Calogero and Di Marco 2008; Fernando and Senadeera 2008; Calogero et al., 2010; Suyitno et al., 2015). In this context, there is a need for examination of new natural dyes as crude extracts to achieve low-cost and stable NDSSCs. In this study, DSSCs were fabricated using natural dyes as crude extracts from fruit and root of barberry (*Berberis vulgaris*) and fruit and stalk of pokeweed (*Phytolacca americana*). To the best of our knowledge, this is the first study investigating the photovoltaic properties of these natural sources-based DSSCs. It is well known that anthocyanins and isoquinoline alkaloids are the main components for fruit and root of barberry (Rahimi-Madiseh et al., 2017), respectively, whereas betalains for fruit and stalk of pokeweed (Schliemann et al., 1996) (Fig. 1). Berberine as the main isoquinoline alkaloid of barberry root shows strong light absorption in the visible light range (380–470 nm) (Ravikumar et al., 2007) and is considered to be an alternative sensitizer. Optical and electrochemical properties of all the extracts seemed to be promising in terms of employing them as sensitizers in DSSCs. When tested in DSSCs, the highest PCE of 3.04% is obtained by stalk of pokeweed extract due to its broader absorption with respect to the others. However, after irradiation for 120 h, the stability of barberry fruit is found to be significantly higher than the others.

2. Experimental

2.1. Preparation of natural dyes

Fruits and roots of barberry (*Berberis vulgaris*) were collected from Artvin in Turkey, while fruits and stalks of pokeweed (*Phytolacca americana*) were taken from Sakarya in Turkey (Fig. S1). Approximately 15 g of the dried powdery roots of barberry were added into 200 mL of ethanol and refluxed by soxhlet for 8 h (El-Sayed et al., 2013; Sahin et al., 2013). The extract was then filtered with a filter paper. Fresh fruits of barberry and pokeweed were washed with distilled water and dried at 40 °C in an oven. Then 15 g of each sample was grinded into small pieces by a blender having a 200 mL 90% ethanol in it and then kept at room temperature in a place for three days (Hao et al., 2006; Sengupta et al., 2015; Lim et al., 2016). The solid residues in the extracts were filtered out to obtain pure dye solution. This procedure was also applied for stalks of pokeweed, except that the stalks were not grinded. The extracts were stable for at least 8 months when stored at +5 °C in the refrigerator.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.solener.2018.07.048.

2.2. Electrochemical measurements

A potentiostat/galvanostat (PARSTAT 2273, USA) was used for all electrochemical studies. Cyclic voltammograms (CVs) were carried out using a three-electrode system in which a glassy carbon electrode (GCE, 3 mm diameter), Pt disk and Pt wire served as the working, pseudo-reference and counter electrode, respectively, with 0.1 M tetrabutylammonium tetrafluoroborate/dichloromethane ($TBABF_4$/DCM) solution at scan rate of 0.050 V s^{-1}. The peak separation potential (ΔE_p) of ferrocene/ferrocenium (Fc/Fc^+) redox couple solution as an external reference under these conditions was 86 mV.

2.3. Fabrication of DSSCs

TiO_2 photoanodes were prepared on a fluorine-doped tin oxide-coated glass substrate (FTO) (Solaronix, TCO22–15, 15 Ω cm^{-2}) by the doctors' blade method. The preparation of the TiO_2 was similar to those described elsewhere (Hu et al., 2017; Karaca et al., 2018). Before device fabrication, the FTO substrates were cleaned by ultrasonic treatment in 0.1 M hydrochloric acid, acetone and isopropanol sequentially and then washed with deionized (DI) water and ethanol. After drying, an adhesive tape (Scotch™, 3 M) with a window of 0.196 cm^2 area and approximately 50 μm depth was applied to the conductive surface of the substrate. The tape-coated substrate was dipped into a 0.04 M aqueous titanium tetrachloride solution at 70 °C for 30 min and rinsed with DI water and dried. Then, a TiO_2 paste (Solaronix Ti-Nanoxide T/SP) was spread on this substrate. The tape was removed and the TiO_2 film was slowly annealed at 500 °C and exposed to the same temperature for 0.5 h in a furnace. After cooling, the spreading and heating processes were repeated to obtain double layer of TiO_2 film. The average thickness of the double layer TiO_2 film was ~12 μm measured by a surface profiler (KLA Tencor P6). Finally, the TiO_2 film was cooled to room temperature, again immersed into the titanium tetrachloride solution at 70 °C for 0.5 h and calcined at 500 °C for 30 min. After cooling 80 °C, the resultant photoanodes were soaked into the extract solutions at room temperature for 18 h. As a reference DSSC, the photoanode was also immersed in an ethanol solution containing 0.5 mM N719 (Solaronix, Ruthenizer 535-bisTBA) and 5 mM chenodeoxycholic acid (CDCA) for a prolonged time of 6 h. The Pt counter electrode was fabricated on another FTO substrate (Şişman et al., 2017; Günsel et al., 2017). Then, DSSCs were assembled in a sandwich structure using a sealing spacer (Solaronix, Meltonix 1170-25) and a redox couple (Solaronix, Iodolyte HI − 30). This structure was also sealed at 100 °C by pressing for photostability tests.

2.4. Characterization

Perkin-Elmer FT-IR spectrophotometer was used to analyze the functional groups in the extracts. UV–Vis studies were performed by a

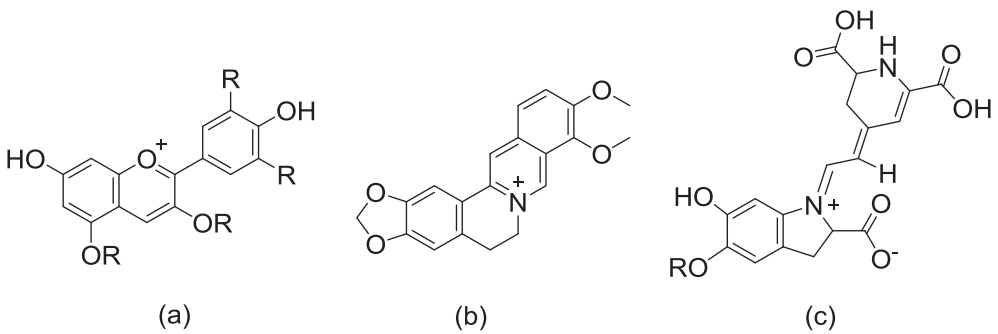

Fig. 1. General structure of anthocyanin (a), berberine-an isoquinoline alkaloid (b) and betalain (c).