Natural Light-harvesting Sensitizers for Dye Sensitized Solar Cell

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Abstract Natural pigments containing anthocyanidins extracted from 14 fruit samples were studied as possible sensitizers for the fabrication of dye-sensitized solar cell (DSSC). The Dyes extracted from pomegranate and berry families are reported as candidates for DSSC with a lead current between 0.5–3.98 (mA) and a voltage of 150–350 (mV), and so could be used as photosensitizers in the construction of affordable and low cost DSSC especially for educational purposes. Based on direct sunlight illumination, pomegranate dye had the maximum efficiency in energy conversion (0.22%) followed by, raspberry (0.16%), blackberry (0.14%), blueberry (0.05%) and red grape (0.02%).

Keywords Natural Fruit Dyes, Titanium-dioxide (TiO₂), Fluorine-Doped Tin-Oxide (ITO), Dye Sensitized Solar Cell (DSSC)

1. Introduction

1.1. Background

The high cost and environmental concerns in use of fossil fuels have piloted innovative techniques that aim to efficiently convert solar energy into electrical energy. Dye-Sensitized Solar Cell (DSSC) shows an economical and environmentally friendly credible alternate model to other forms photovoltaic devices [1]. Michael Grätzel first reported dye-sensitized solar cells in 1991 and has since then been a topic of great interest to many researcher in the scientific community [2]. Currently the highest reported performance for DSSC efficiency is about 13% [3]. Dyes employed in making DSSC usually consist of a transition metal complex of ruthenium or osmium [4]. The use of a natural product such as dye extracted from fruits insures the fabrication of inexpensive and eco-friendly solar cells.

1.2. Chemical Structure of a Dye-sensitized Solar Cell

Electron transfer from colored dyes to wide band gap semiconductors is of technological importance in photography as well as for photo-electrochemical energy conversion. Wide band gap semiconductors, such as TiO₂ and AgBr, could be sensitized to visible light using surface-adsorbed dye molecules [5]. DSSC is a photo-electrochemical cell inspired by the energy and electron-transfer mechanisms in natural photosynthesis and in the dye-sensitized silver halide emulsions used for photography [5-8]. It is made up of a photosensitized anode, an electrolyte, and a counter electrode [9-13]. The photosensitized anode consist of an optically transparent conducting substrate (typically Indium tin oxide) coated with a thin film of a wide band gap mesoporous semiconductor (usually TiO₂) on which the dye sensitizer get adsorbed [9-13]. The nanocrystalline nature of the TiO₂ not only provide a large absorption cross section (light harvesting) for the dye but also allows for a highly efficient charge transport of the photo-generated electrons through its particles and grain boundaries [14-18]. An iodide-triiodide (I⁻/I₃⁻) redox system is the electrolyte commonly used in DSSC and it insures the regeneration of electron charge. The counter electrode usually contains either graphite or platinum particles as a catalyst.

1.3. Natural Dye Sensitizers

The choice of dye is an important parameter in the fabrication of DSSCs and a huge variety of dyes, both organic and inorganic, have been utilized as the light harvesting elements in DSSCs [4]. The standard dye used in traditional dye sensitized solar cell (DSSC) is tris(2,2'-bipyridyl-4,4'-carboxylate)Ruthenium (II)(N₃ dye) [19] in which the carboxyl groups of the dye serve as an anchoring group on the semiconductor oxide substrate by chemisorption. Tri(cyanato-2,2',2''-terpyridyl-4,4',4''-carboxylate) Ru (II) (black dye), whose response extends 100 nm further into the, IR has also been routinely explored in DSSC

studies [20]. Aside metal based dyes, metal-free synthetic dyes, such as indoline dyes have also been exploited as solar cell dyes. Metal and other synthetic dyes are usually expensive and sometime toxic. Natural dyes are therefore an attractive alternative for the reason that they are less expensive, environmentally friendly and readily available. Natural dyes extracted from many plant sources have been used in DSSC with appreciable level of photocurrent and photo voltage characteristics. Combining a number of natural dyes for use as photosensitizers in DSSC has also been shown to improve photovoltaic performance. The main pigments responsible for light absorption in these dyes include anthocyanidins, carotenoids, and chlorophylls. These pigments absorb in the visible and near-infrared region and also have anchoring functional groups that interact favorably with the surface of the TiO_2 semiconductor [4]. Delphinidin, displayed in Fig. 1, like most anthocyanidins and other plant pigment possesses hydroxyl groups that ensure favorable interaction with TiO_2 . In this study, dye extract from 14 different fruits were analyzed as potential dye sensitizers for DSSCs. The optical properties of the fruit pigments were studied via absorption and emission spectroscopy and their average sizes via dynamic light scattering. The current and voltage responses were evaluated under three different conditions: Illumination under indoor light, halogen lamp and direct sun light.

Figure 1. Chemical structure of Delphinidin, an anthocyanidin presents in natural dyes.

2. Experimental Details

The electrodes were prepared according to a previously published procedure with some modification [2, 21]. To fabricate the anode, the conductive side of the fluorine-doped tin oxide (FTO) glass slides (resistance of $\sim 20 \Omega$) was spin-coated with a layer of TiO_2 and then heated over a hot plate for 60 min (Figure 2c). The TiO_2 paste was prepared by adding 3.5 ml of concentrated acetic acid to 0.8 g of titanium dioxide powder and vigorously stirring the mixture with a pestle and a mortar to obtain a white pasty colloid. The various fruit dyes as shown in Figure 2a were freshly prepared and purified by centrifugation. The TiO_2 electrode as displayed in Figure 2b were subsequently immersed in the freshly prepared homogenous fruit dye

extract for a minimum of 3 hours for proper and adequate adsorption of the fruit dye into the TiO_2 layer. After adsorption, the anode slides were rinsed with distilled water and again with acetone and then air-dried. The cathode was constructed by depositing carbon soot on the conductive side of the FTO glass slides (resistance of $\sim 20 \Omega$). This process carried out by placing the FTO slide over a lighted candle. To prepare the electrolyte, 127 mg of iodine crystals and 830 mg of potassium iodide were dissolved 10 ml of ethylene glycol to obtain a I/I^{-3} solution. The two conductive sides of the FTO were coupled together like a sandwich using a pair of binder clips followed by the addition of a few drops of iodine electrolyte in between the two slides to ensure connectivity.

Figure 2. Dye sensitized solar cell fabrication: (a) 14 samples used for the study; (b) TiO_2 slides immersed in the various fruit dye extract; (c) FTO slides coated with TiO_2 paste

3. Results and Discussion

UV/Vis Spectroscopy, Fluorescence Spectrophotometry and Dynamic Light Scattering were employed to analyze dye extract from 14 different fruits dye extract (pomegranate, red grape, blueberry, blackberry, lemon, mango, strawberry, grapefruit, lime, cherry, orange, kiwi, papaya and tangerine). The particle size, absorption and emission characteristics of four of these dyes (pomegranate, cranberry, blackberry, and raspberry) are presented and discussed in the following sections.

3.1. Absorption Spectra Analysis

An efficient DSSC requires a dye with a strong absorption in the visible region. To ascertain the strength of absorption of the various dyes, UV-Vis absorption measurements were carried out on the samples. Fig. 3a shows the absorption spectrum of dye extract from pomegranate with an absorption peak at 514 nm. The wavelength of maximum absorption for the cranberry dye as displayed in Fig. 3b was 511 nm. Fig. 3c shows the spectrum of the blackberry sample with an intense absorption broad band at 512 nm. The wavelength for maximum absorption for raspberry occurred at 511 nm in Figure 3d. The similarity in the wavelength of absorption of the different dyes could be attributed to the fact the dominate pigments in all these fruits are anthocyanidins.

Figure 3. Absorption spectrum of: (a) Pomegranate; (b) Cranberry; (c) Blackberry; (d) Raspberry

3.2. Emission Spectra Analysis

The fluorescence spectra of the various dyes were recorded from a wavelength of 350 nm to 800 nm. Emission is stimulated at various energized wavelengths and the

intensity of the discharged fluorescence is measured as a function of wavelength. The amplitude of the peaks seen in the emission spectrum is directly proportional to the number of photons that are emitted. A thorough understanding of the performance of DSSC could be obtained by examining the emission profile of the dyes used as sensitizers. The emission spectra with few deviations are similar to that of Anthocyanins - the active pigment in dye extract from the fruits.

Figure 4. Emission spectrum of: (a) Pomegranate; (b) Cranberry; (c) Blackberry; (d) Raspberry

Figure 4a displays the emission spectrum of the dye extract from the Pomegranate fruit. The peak maxima were observed at 412 nm and 603 nm. The emissions spectrum of dye extract of the cranberry fruit is shown in Figure 4b with intense emission occurring at 413 nm and 610 nm. The emission spectrum of extracted Blackberry dye as seen in Figure 4c shows intense peaks 398 nm and 606 nm. The Figure 4d illustrates the emissions spectrum of the raspberry dye sample. The raspberry dye spectrum exhibits intense peaks at 375 nm, 610 nm and 745 nm.

3.3. Particle Size Analysis

The size of dye particles provides information on the propensity of the dye to absorb or reflect light and thus crucial to the efficiency of the solar cell. Dye particles with uniform sizes get easily adsorbed to the TiO_2 and efficiently promote the transfer of electron. Particle size analysis of the dye extract from the fruits was carried out by Dynamic Light Scattering. The average particle size of the pigment from pomegranate dye extract 3 μm as displayed in Fig. 5a. It could be inferred from this measurement that the proclivity of pomegranate to absorb dye is very high. The average particle size of the dye extract from cranberry as shown in Fig. 5b was 1 μm . This is an indication that the cranberry dyes will be able to absorb high amounts of sunlight. Fig. 5c displays the particle size analysis of the blackberry dye. The blackberry sample particles were on the average about 3 μm in diameter. The cranberry dye is thus capable absorbing a large amount of light. The average particle size (3.5 μm) of the raspberry dye, as shown in Fig. 5d.

The performance of each of the 14 fruit dyes as a potent sensitizer was assessed via current and voltage output upon light irradiation of the dye-sensitized solar cell. The measurements were carried out under three different conditions (indoor light, halogen lamp, and direct sunlight) as displayed in Figure 6 a, b, and c. Major inconsistencies were observed when the experiments were conducted under indoor light (Fig. 6a) and also under a halogen lamp (Fig. 6b). Experiments carried out under direct sunlight (Fig. 6c) were more reproducible. The top five current-voltage producing fruit extract dyes based on their respective photocurrent and photo voltage values were pomegranate (3980 μA and 350 mV), blue berry (1150 μA and 280 mV), red grape (903 μA and 139 mV), raspberry (710 μA and 148 mV) and blackberry (452 μA and 202 mV). Based on the study (Figure 6c), Pomegranate dye had the highest efficiency in energy conversion (0.22%) followed by, raspberry (0.16%), blackberry (0.14%), blueberry (0.050%) and red grape (0.02 %).

Figure 5. Particle size analysis of: (a) Pomegranate; (b) Cranberry; (c) Blackberry; (d) Raspberry

Figure 6. Comparison data: (a) current and voltage data for 14 fruit dye samples under Indoor light; (b) current and voltage data under halogen lamp (c) current and voltage data for five best fruits dye under direct sun light

4. Conclusions

Natural dyes extracted from 14 different fruits were studied as potential sensitizers for DSSC. The dyes were characterized using Absorption Spectroscopy, Fluorescence Spectrophotometry and Dynamic Light Scattering. The photocurrent and photo voltages of the fruit dyes were also investigated. The Dye extract from the pomegranate fruit yielded the most significant conversion efficiency of 0.22 % with photocurrent of 3.98 mA and photo voltage of 350 mV. The wide availability, low cost, and biodegradability of pomegranate makes it a promising sensitizer for the fabrication of solar cells.

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