Optical Properties of Some Selected Fruit Juices and their Usage in Photovoltaic Cells as a Sensitizer

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Abstract: Use of natural pigments in photo-electrochemical cells, as a sensitizer is a cost effective approach compared to that of ruthenium based metal centered dyes. Different pigments extracted from fruits were utilized as a sensitizer in solar cells. However, ruthenium based metal centered dyes exhibit much higher power conversion efficiency in dye-sensitized solar cells, due to excellent matching of band gap with HUMO, LOMO levels of dye and charge transfer process.

Keywords: photo-electrochemical solar cells, photosensitization, quinonoidal, cole-cole plot.

1. Introduction

The history of photovoltaic began with the investigation of photo-effects on silver halides in 19th century. Becquerel demonstrated the first photovoltaic cell, which was composed of silver chloride coated metal electrode immersed in an electrolyte in 1838 [1]. Significant progress in sensitization process was ascertained after another few decades by Gerischer and Tributsch [2]. The major breakthrough in dye-sensitized solar cells was the usage of highly porous titanium dioxide film with a large photoactive area by a Swiss research group in 1991 [3]. Since then several hundred research publications have been aroused in the field of dye sensitization. Most of these investigations were based with ruthenium based metal centered dyes. Several environmental problems are encountered in the usage of with ruthenium based metal centered dyes in this type of solar cells. Hence, scientists have chosen environmentally friendly sensitizers (organic dye and natural pigments) in the fabrication of sensitized solar cell [4,5]. However, efficiencies of these cells are much lower than ruthenium based solar cells. In this viewpoint, finding a stable, environmentally friendly organic dye or natural pigment is one of the scientific hurdles. In this manuscript, we discussed the properties of different types of pigments extracted from natural fruits and their applications in sensitized solar cells.

2. Experimental Section

2.1 Preparation of screen printing TiO₂ pastes

2.1.1. Nano-crystalline TiO₂ paste

An amount of 12 g of acetic acid was added to 58.6 g of titanium iso-propoxide while stirring at room temperature. The mixture was poured into 290 ml water, as quickly as possible, with vigorous stirring (700 rpm). The hydrolysis reaction was stirred for one hour. 5.4 ml of 65% nitric acid was added to the mixture and heated from room temperature to 78 °C, within 40 min, and peptized for 75 min. Water was added to the mixture up to 370 ml. The suspension was kept in a titanium autoclave and heated to 250 °C for 12 h. 2.4 ml of 65% nitric acid was added and the particles dispersed with a 200 W ultrasonic titanium probe at a frequency of 15 pulses per sec. The resultant colloid was concentrated with a rotary-evaporator. The solution was centrifuged and washed with ethanol three times to produce a precipitate of TiO₂ in ethanol. An amount of 16 g of TiO₂ precipitate was mixed with 64.9 g of a solution of terpineol and ethyl cellulose in ethanol. The precipitate was well mixed and rotary-evaporated.

2.1.2. Micro-crystalline TiO₂ paste

400 nm particles (in aqueous solution) are transferred into ethanol by centrifuging and removing supernatant then topping up with pure ethanol. 5 parts of 400 nm titania paste and 1 part of 18 nm titania paste were mixed with 3.5 parts of ethyl cellulose and 30.5 ml of terpineol. The mixture was rotary-evaporated until ethanol is removed.

2.2 Preparation of TiO₂ films

Conducting glass plates (FTO) were cut into 1 x 2.5 cm² pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO (1 x 1 cm²) was covered with 3M-tape and placed horizontally on a hotplate facing the conducting side to air. Temperature of the hotplate was gradually increased up to 450 °C. A solution of titanium disopropoxide bis(acetylacetonate) (Sigma-Aldrich) in isopropanol (1:9) was sprayed over the FTO quickly at the thermal equilibrium at 450 °C and allowed to reach to room temperature by disconnecting power of the hotplate. This procedure results compact nano-crystalline TiO₂ layer on FTO. The microcrystalline TiO₂ paste was coated on the compact TiO₂/FTO substrates by screen-printing. The TiO₂ coated films (0.5 cm x 0.5 cm) were backed at 450 °C for 30 min. Finally TiO₂ substrates were wetted from a 0.05 M TiCl₄ (aq) in 20% HCl is diluted from a 2.0 M stock solution and again backed at 450 °C for another 30 min.

2.3 Pigment coating procedure on TiO₂ film

Different types of natural pigments were extracted by squeezing the ripe fruits. The juice was concentrated at 60°C in atmospheric condition. Pigment was coated on TiO₂ electrodes as follows: TiO₂ coated glass plates were kept immersed in a mixture of pigment solution. The temperature of the pigment was maintained as 40 °C. The amount of
pigment on TiO$_2$ electrodes was controlled by varying the immersion time in the pigment solution.

2.4 Assembling of the cell

2.4.1. Preparation of Pt coated electrodes

10 mM H$_2$PtCl$_6$ in isopropanol solution was prepared. One drop of this solution was put onto the conductive side of FTO electrode and allows drying. FTO counter electrode (active side up) was inserted into ceramic tube, gradually heated up to 400 °C leave for 15 min., allowed to cool electrode. A hole with a diameter of 1 mm was made on the Pt coated FTO electrode.

2.4.2. Preparation of electrolyte solution

An electrolytic solution was prepared by maintaining 0.03 M iodine, 0.5 M 4-tertbutylpyridine, 0.6 M 1-butyl-3-methylimidazolium iodide and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile/valeronitrile 85:15 by volume.

2.4.3. Sealing of the cell

A rectangular hole with the dimension of 0.5 cm x 0.5 cm was made at the center of 1 cm x 1 cm Surlyn film (thickness is 25 μm). This film was placed on the dye coated TiO$_2$ film as the rectangular hole superimpose with the dyed TiO$_2$ film (0.5 cm x 0.5 cm). A Pt coated FTO electrode hole with a diameter of 1 mm was placed on this TiO$_2$ electrode with the Surlyn film and heated by applying pressure on glass electrodes as Surlyn film melts and adhesive with two electrodes. The electrolyte was filled in to the device from the back hall and hall was sealed.

2.5 Measurements

Absorption spectra of dye solutions and dye coated TiO$_2$ films were measured by using UV-VIS-NIR spectrometer (Jasco V-570). Morphology of the cell was studied using scanning electron microscope. Photo-effects of the cell were studied by illuminating the cell through TiO$_2$ layer. The variation of photocurrent of the cell with the wavelength was measured using monochromator (Jasco) coupled with single-phased lock-in amplifier (NF Instrument-5600 A), under constant photon energy illumination mode. Current-voltage characteristics were recorded with a solar simulator (Wacom) coupled with semiconductor parameter analyzer (Hewlett Packard HP 4145B), under 1.5 AM condition. Scan speed was maintained as 0.01 V/min. The interfacial electrical properties of the cells were studied natural bias under a three-electrode configuration with the same electrolyte, by using a multi-channeled potentiostat (Princeton Applied Research) coupled with a computer. The charge transfer resistance at the electrolyte–electrode interface was evaluated from EClab software.

3. Results and Discussion

TiO$_2$ electrodes used in the present experiment are prepared as producing maximum photo-performance, as reported previously [6]. These TiO$_2$ electrodes are composed with three components, namely (a) dense TiO$_2$ layer, (b) nano-
crystalline TiO$_2$ layer and (c) meso-porous TiO$_2$ layer. These three layers can be easily distinguished by the nature of the morphology of the layers. The morphology of each TiO$_2$ layer is shown in Fig. 1. The cross-sectional image of the electrode is also shown image d in Fig. 1. The average thickness of the electrode was evaluated as 20 μm from a thickness meter (Fig. 2).

Capability of using different types of natural fruit juices extracted from pomegranate (Punica granatum), red-flesh dragon (Hylocereus costaricensis), prickly pear cactus (Opuntia), and red ginger lily (Etlingera Elatior) was used as sensitizer in photovoltaic cells. These fruit juices can keep several hours without fermentation in atmospheric condition. However, concentrated fruit juices were able to keep several weeks under refrigerator. Absorption spectrum of natural fruit juice (a) pomegranate (b) red-flesh dragon (c) prickly pear cactus and (d) red ginger lily is shown in Fig. 3.
These fruit juices absorb different regions of visible light due deference in to their structures. Absorption properties of fruit juices (A) pomegranate (B) red-fleshed dragon (C) prickly pear cactus and (D) red ginger lily as (a) natural, (b) acidic and (c) basic solutions were studied under acidic and basic media and results are shown in Fig. 4. Natural pomegranate juice absorbs visible light with a maximum at 510 nm (curve a in Fig. 4(A)). However, addition of several drops of acid to the natural juice enhanced the intensity of absorption maximum by several fractions (hyperchromic shift) (curve b in Fig. 4(A)). However, a bathochromic shift with a magnitude of 100 nm was observed in the absorption spectrum of basic pomegranate juice compare to that of the natural juice. Absorption spectrum for natural juice of red-flesh dragon fruit (a) natural (b) acidify and (c) basic juices is shown in Fig. 4(B). A significant reduction in absorption properties (hypochromic shift) of acidify medium was observed. This result is contrast with the result observed by adding acid in to pomegranate juice. No significant change was observed in the absorption by adding acid into prickly pear cactus juice (curve b in Fig. 4 (C)). A shift and split with a reduction in the intensity in the absorption band were observed by adding base in to red-flesh dragon, prickly pear cactus fruit juice (curves c in Fig. 4(B&C). Red ginger lily fruit juice also behaves as a similar manner to that of pomegranate juice, with the acid and base treatments. However, an un-predictable enhancement in the absorption band was observed by adding base in to methanol extraction of red ginger lily fruit juice (curve c in Fig. 5). Absorption spectrum of (a) natural pomegranate (b) red-fleshed dragon fruit (c) prickly pear cactus and (d) red ginger lily is shown in Fig. 6 (A). Though intensity of characteristics peaks varies, characteristic peaks were situated at 3400, 2930, 1639 and 1053 cm$^{-1}$ in FTIR
in acidic medium.

Mechanism for chelation of cyanadin ranges of 1 glucoside bonds with metal ions via bidentately in the pH [14]. Recently, it has been confirmed that cyanadin with TiO$_2$ eye. C juice coated TiO$_2$ electrodes exhibited purple juice. Acidified and natural pomegranate juices coated TiO$_2$ juice on TiO$_2$ flesh dragon, prickly pear cactus and red fruit juices on TiO$_2$ We have made an attempt to coat acidified, natural and basic pomegranate juice coated TiO$_2$ electrodes was feeble except pomegranate juice. No detectable deviation on the FTIR spectrum was observed for acid added juice curve a in Fig. 6(B)) compare to that of natural juice (curve b in Fig. 6(B)). It is known that dye molecules behave in different manner in different environments, probably due to enforcement of Van der Waals interaction between dye molecules and solvents depending on their polarity [9].

![Scheme 1: Structure of (a) acidified, (b) natural and (c) basic pomegranate juice](image1)

The composition and structure of red-flesh dragon, prickly pear cactus and red ginger lily is not known, to the best of our knowledge. However, pomegranate fruit juice contains with several anthocyanins, and other phenolic compounds [10]. Cyanadin 3 glucoside is the most known compound in pomegranate fruit juice. These molecules mainly composed from benzopiril group and phenolic group [11]. Color of the compound strongly depends on the numbers of substituents in phenolic rings [12]. Molecular structure of (a) flavylium form (acidify), (b) quinonodial form (natural) and (c) basic forms of cyanadin-3-glucoside are shown in scheme 1 [13].

![Scheme 2: Chelation of cyanadin-3-glucoside with TiO$_2$](image2)

We have made an attempt to coat acidified, natural and basic fruit juices on TiO$_2$ electrodes. Degree of absorption of red-flesh dragon, prickly pear cactus and red ginger lily fruit juice on TiO$_2$ electrodes was feeble except pomegranate juice. Acidified and natural pomegranate juices coated TiO$_2$ electrodes exhibited purple color and basic pomegranate juice coated TiO$_2$ electrodes exhibited green color for naked eye. Chelating of flavylium form of cyanadin-3-glucoside with TiO$_2$ results quinonodial form of cyanadin-3-glucoside [14]. Recently, it has been confirmed that cyanadin-3-glucoside bonds with metal ions via bidentately in the pH range of 1-3 [15]. Therefore, we propose following mechanism for chelation of cyanadin-3-glucoside with TiO$_2$ in acidic medium.

![Figure 7: IPCE Spectrum for the cells prepared by using (a) acidified and (b) basic pomegranate fruits juice.](image3)

When the electrode potential of pomegranate juice coated electrode swept toward negative direction a colour change (purple to green) of the electrode was observed at potentials less than −0.8 V (versus SCE). Again purple colour was appeared on the TiO$_2$ electrode when the electrode is anodically polarized. Reduction and oxidation of the pigments attached to the TiO$_2$ electrode might be a reason. Similar colour change was observed on pomegranate pigments coated TiO$_2$ films by immersing in basic and acidic solutions, alternatively.

![Figure 8: Current–voltage characteristics of TiO$_2$|pomegranate|electrolyte cell (a) acidified and (b) basic pomegranate fruits juice](image4)

The maximum IPCE (incident photon to current conversion efficiency) of 38% was observed for the cells prepared by using acidified pomegranate fruits juice at the wavelength of 570 nm (curve a, Fig. 7). IPCE action spectrum of the cell fabricated by using a basic pomegranate dye coated TiO$_2$ electrode is shown as curve b in Fig. 7. Clear red shift with a magnitude of 50-60 nm was observed in the absorption spectrum of pomegranate juice (acid or natural) coated TiO$_2$ electrode compare to that of the basic pomegranate juice coated TiO$_2$ electrode. The maximum IPCE of 19% was observed for the cells prepared by using basic pomegranate fruits juice at the wavelength of 610 nm (curve b, Fig. 7).
observed a maximum photocurrent of $8 \pm 0.5$ mA cm$^{-2}$ and a photovoltage of $300 \pm 40$ mV with a higher reproducibility for TiO$_2$|pomegranate pigment|electrolyte cells and results are compared with the cell prepared with Ru-metal centered dye with same configuration. Approximately two times greater photo-performance is observed for Ru-metal complex based photovoltaic cells compared to that of pomegranate juice based cells [3,16].

![Nyquist diagram of TiO$_2$|pomegranate pigment|electrolyte cell](image)

**Figure 9:** Nyquist diagram of TiO$_2$|pomegranate pigment|electrolyte cell

Fig. 9 represents the Nyquist diagram of pomegranate pigment coated electrode. A typical Nyquist diagram for glass-based DSCs normally features three semicircles. The semicircle corresponding to the higher range of frequencies (the left semicircle, with diameter R$_1$), the middle range of frequencies (the middle semicircle, diameter R$_2$) and the lower range of frequencies (the right semicircle, diameter R$_3$) represent $I_y$ transport in the electrolyte, electron recombination at the TiO$_2$|electrolyte interface together with electron transport in the TiO$_2$ network and the redox reaction at the platinum counter electrode, respectively [16]. The high frequency intercept with the real axis is the ohmic resistance (R$_o$) and is related with the sheet resistance of the substrate of the working electrode. Values of R$_o$ – R$_2$ were evaluated as 14, 10, 35 and 18 Ω from the ECLab software.

4. Conclusion

Capability of using different types of natural fruits juices as sensitizer in photovoltaic cells was studied. The maximum photo-performance was observed for the cell prepared with pomegranate juice among tested natural pigments extracted from fruits.

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References


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