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Utilization of natural pigment extracted from pomegranate fruits as sensitizer in solid-state solar cells

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Abstract

The juice extracted from pomegranate fruits containing cyanin (flavylium) is utilized as the light-harvesting analog in a dye sensitized solid-state photovoltaic cell. Strong chelation of flavylium with TiO_2 changes it to quinonoidal form. A higher incident photon to current conversion efficiency is observed in solid-state TiO_2|pomegranate piment|CuI solar cell compare to that of the cells (TiO_2|dye|CuI type) sensitized with other natural pigments.

Keywords: Cyanin; Chelation; Photovoltaic cells

1. Introduction

Sensitization of wide band gap oxide semiconductors was initiated in 1950s [1] and tremendous growth is seen in last few decades. A dye-sensitized electrochemical cell with a power conversion efficiency of 10% was fabricated by using nano-porous titana film by Gratzel and co-workers [2]. Fabrication of cost effective solar cells is a scientific challenge in the field of solar energy conversion. Several natural pigments have been utilized as sensitizers in photovoltaic cells due to their capability of injection of electron from excited pigments to the conduction band of anchored material [3–10]. Most pigments utilized in photovoltaic cells undergo in rapid photodegradation [3–5]. Natural pigment cyanin is known as more photo-stable than other pigments in the application of photovoltaic cells [5,6]. We have fabricated a solid-state solar cell using juice extracted from pomegranate fruits (rich with cyanin and derivatives) as a sensitizer in *n*-semiconductor|dye|p-semiconductor type solid-state cell by sandwiching pomegranate pigments in between CuI and TiO_2 layers. Photo-properties of TiO_2|pomgranate pigments|CuI cells are discussed.

2. Experimental

TiO_2 films of thickness of 5 μm were prepared by applying a colloidal solution of hydrolyzed titanium isopropoxide which contains TiO_2 powder (P-25 Degussa) on preheated conducting glass plates (Soloronix, Switzerland, with a conductivity of 16 $\Omega\,cm^{-1}$) as described elsewhere [10,11]. Pomegranate pigments were extracted by filtration the juice followed by squeezing pomegranate seeds coat in the laboratory. TiO_2 films were kept immersed in the juice extracted for 5–10 min at room temperature. CuI was coated on pomegranate pigments anchored TiO_2 electrodes as follows: CuI (1.2 g) was dissolved in 20 ml of acetonitrile and residual was separated. Triethylamine hydrothiocyanate was added to the CuI solution until concentration reaches 10^{-6} M. Small amount of this solution was spread on preheated (∼150 °C) pomegranate pigments coated TiO_2 electrodes. CuCNS was

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coated on sensitized TiO_2 films by spreading small amount from a solution prepared by digesting CuCNS in propylsulfide until photovoltage of the cell reaches its maximum. A thin layer of graphite was carefully applied on the top of CuCNS layer by painting smoothly from graphite granular. (Graphite layer on CuCNS makes proper contact with conducting glass.) TiO_2|pomegranate pigments|CuI(CuCNS) cells were fabricated by attaching a conducting glass plates on the top of the electrode as the back contact. Cells were characterized by illuminating with a monochromatic and polychromatic light (100 mW cm^{-2}). Illumination was carried out through the TiO_2 layer of the cell. Absorption spectra were obtained by UV–vis spectrometer (Shimadzu UV-3000) and IR spectrometer (JASCO FT/IR-410) respectively. The stretching and bending frequencies of cyanin was identified from frequency calculations performed on cyanidin molecule (model) using hybrid DFT methods employing the B3LYP hybrid functional within Gaussian'03 [12]. Cyclic voltometry of pomegranate pigments coated TiO_2 films was studied in 0.1 M ammonium perchlorate solution under the three electrode system. A SCE and Pt foil were used as the reference and the counter electrodes.

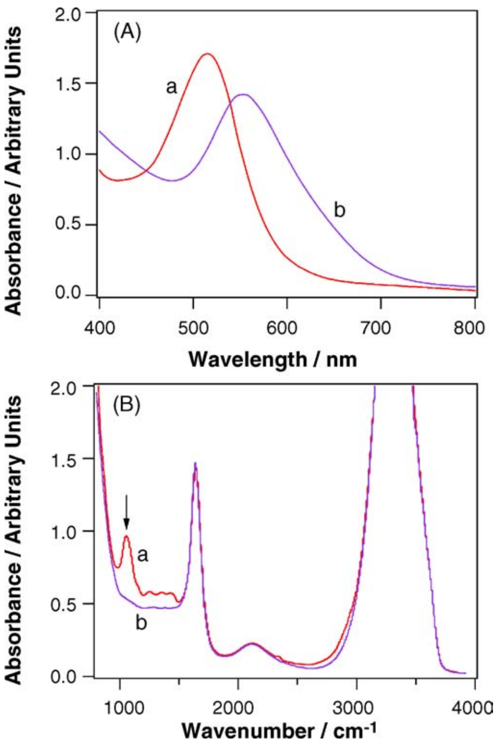
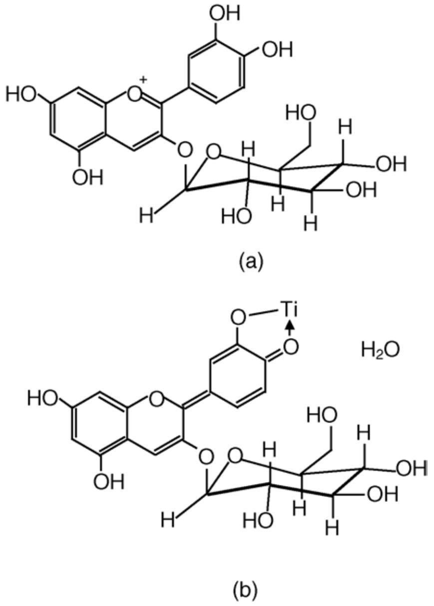


Fig. 1. (A) Absorption spectra for (a) pomegranate pigments and (b) pomegranate pigments coated on TiO_2 colloid. (B) FT-IR spectrum for (a) pomegranate pigments and (b) pomegranate pigments coated on TiO_2.

3. Results and discussion

The juice extracted from pomegranate fruits mainly contains cyanin derivatives and exists as flavylium at natural pH (∼3.4). Flavylium is red in color and strongly bond with Ti^{4+} via emanating H_2O molecule [5,6]. Absorption spectra for (a) pomegranate pigments and (b) pomegranate pigments coated on TiO_2 colloid are illustrated in Fig. 1(A). Pomegranate pigments exhibited an intense absorption band in visible region with a peak at 510 nm. Absorption of pomegranate pigments coated TiO_2 films has red shifted by 40 nm and exhibited the maximum at 550 nm. Chelation of flavylium with TiO_2 changes its form to quinonoidal and could be one of the reasons for the red shift in absorption spectrum [13]. This red shift in absorption spectrum in visible region and disappearance of the peak at 1050 cm^{-1} in IR spectrum [Fig. 1(B)] indicate complexation of pomegranate pigments with Ti^{4+} ions. The band at 1050 cm^{-1} is appear to be due to bending mode of the free hydroxyl group before making the bond with Ti. The structural diagram of flavylium and complexation of flavylium with TiO_2 are shown in Fig. 2. Pomegranate pigments chelate with Zn^{2+}, Sn^{4+} with a lower rate than that of with Ti^{4+} at room temperature.

Cyclic voltomogram of pomegranate pigments coated TiO_2 film is shown in Fig. 3. When the electrode potential swept toward negative direction a color change (purple to green) of the electrode was observed at potentials less than −0.8 V (versus SCE). Again purple color was appeared on the TiO_2 electrode when the electrode anodically polarized. Reduction and oxidation of the pigments attached to the TiO_2 electrode might be a reason. Similar color change was observed on pomegranate pigments coated TiO_2 films by immersing in basic and acidic solutions, alternatively. We have fabricated TiO_2|dye|CuI cells (a) before and (b) after applying −0.8 V (versus SCE) on pomegranate pigments coated TiO_2 electrodes and their IPCE spectra are shown in Fig. 4. The maximum IPC efficiency of 38% was observed



(a)

(b)

Fig. 2. The structure of flavylium (cyanadin 3-glucoside) and the mechanism of chelation with TiO_2.

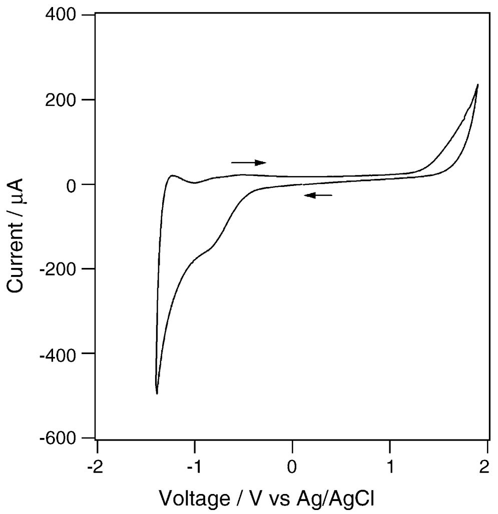


Fig. 3. *I–V* characteristics of pomegranate pigments coated TiO_2 electrode in 0.1 M ammonium perchlorate supporting electrolyte. Potential of the electrode was scanned from positive to negative direction and scan speed was $10\,mV\,s^{-1}$.

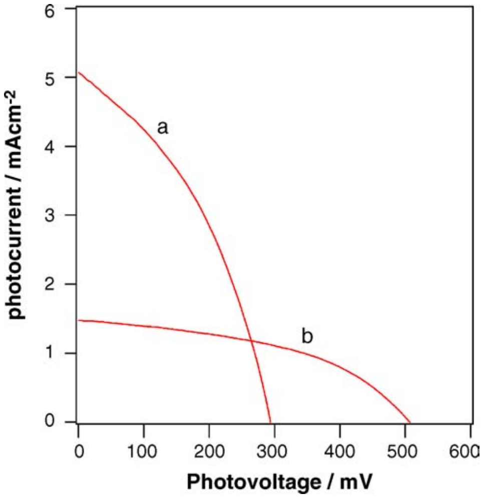


Fig. 5. *I–V* characteristics of (a) CuI|pomegranate pigments|TiO_2 cell and (b) CuCNS|pomegranate pigments|TiO_2 cell.

for the cells prepared by using natural pomegranate fruits juice at the wavelength of 570 nm (curve ‘a’, Fig. 4). This value is grater than that of values observed for TiO_2|dye|CuI type solar cells prepared by using other natural pigments (cyanidin [7], tannin [8], santalin [9] and Vitamin C [10]) is also higher than the IPCE value obtained as 20 % for the electrolytic cells (TiO_2|dye|electrolyte) sensitized with same pigments [5]. IPCE action spectrum of the cell fabricated by using a catholically polarized dyed TiO_2 electrode is shown as curve ‘b’ in Fig. 4. The IPCE action spectrum and the maximum have slightly red shifted compare to that of the cell with natural pigments. This may be due to changes in the structure (pigments). Current–voltage characteristics of TiO_2|pomegranate pigments|CuI cell is shown as curve ‘a’ in Fig. 5. We have observed a maximum photocurrent of $5 \pm 0.5\,mA\,cm^{-2}$ and a photovoltage of $300 \pm 40\,mV$ with a higher reproducibility (over 80%) for TiO_2|pomegranate pigments|CuI cells. Only very few number of dyes (or dye cocktails) are identified that produce higher photocurrent than pomegranate pigments in TiO_2|dye|CuI type solar cells [11]. However, TiO_2|dye|CuI solar cells with other natural pigments [8,9] produce higher photovoltage under similar conditions. TiO_2|pomegranate pigments|CuCNS solar cells were also fabricated by using CuCNS instead of CuI. Current–voltage characteristics of TiO_2|pomegranate pigments|CuCNS cell is shown as curve ‘b’ in Fig. 5. Considerable enhancement in photovoltage was observed when CuCNS is used as hole conducting material in these cells. Higher conduction band position of CuCNS (compared to CuI) favors higher open circuit voltage as observed [9]. The resulted lower photocurrent of TiO_2|pomegranate pigments|CuCNS cell may be due to high resistivity of the CuSCN film. The adsorbed water molecules are known to be degradated dye molecules in N|D|P type solid-state solar cells under illumination [7]. Pomegranate pigments exhibited an extended photo-stability in photoelectrochemical cells [6]. Such a pigments help to increase the stability of N|D|P type solar cells and make better understanding for future work.

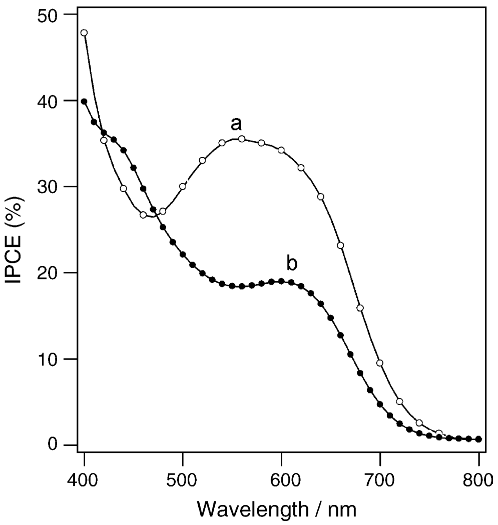


Fig. 4. IPCE action spectra for TiO_2|pomegranate pigments|CuI cells (a) before and (b) after passivation of pomegranate pigments coated TiO_2 electrodes at −0.8 V (vs. SCE) before preparing the cells.

4. Conclusion

A natural pigment was used as sensitizer in solid-state dye-sensitized solar cells. Pomegranate pigments sensitized TiO_2|dye|CuI cells exhibited a higher incident photon to photocurrent conversion efficiency than this type of cells with other pigments.

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