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Dye-sensitized solar cells fabricated with black raspberry, black carrot and rosella juice

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Abstract : In this work, dye sensitized solar cells (DSSC's) were constructed from black raspberry (*Rubus Ideaus*), black carrot (*Daucuscarota* L.) and rosella juice (*Hibiscus Sabdariffa L.*). In order to fabricate a DSSC the fluorine-doped tin (IV) oxide (FTO) thin films obtained by using spray pyrolysis technique were used as a substrate. TiO_2 films on FTO layers were prepared by doctor-blading technique. Platinum-coated counter electrode and liquid Iodide/Iodine electrolyte solution were used to fabricate DSSC's. The efficiencies of solar cells produced with black carrot, rosella and black raspberry juice were calculated as 0.25%, 0.16% and 0.16% respectively, under a sunny day in Kahramanmaraş-Turkey.

Keywords : Dye sensitized solar cell; black raspberry; black carrot; rosella juice.

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1. Introduction

One of the popular subjects among the clean energy sources is a photovoltaic power. After invention of dye-sensitized nanocrystalline TiO_2 solar cell made by O'Regan and Graetzel [1], dye sensitized solar cells (DSSC's) were developed very quickly since 1991 [1]. Simply, a DSSC comprises a working electrode consisting of a dye absorbed porous nanocrystalline TiO_2 layer on transparent and electrically conducting substrate SnO_2:F (FTO), a counter electrode consisting of a FTO substrate with a redox catalyst (thin Pt or carbon layer), and in between these electrodes an electrolyte solution with a dissolved I^-/I^-_3 redox couple. The working principle of the DSSC is that solar light passes through an electrically conductive glass electrode and dyes anchored to TiO_2 are irradiated. When a dye absorbs light one of the electrons in the dye transits from a ground state to an

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excited state. This excited electron makes a jump from dye to the conduction band of TiO_2 nanocrystals. The electrons flow from the TiO_2 and reach to glass electrode and then through the load they go back to the counter electrode. Then the electrolyte in the cell, such as iodine, is reduced to iodide by absorbing the incoming electrons, and iodide in the electrolyte is oxidized to iodine by donating the electrons to the dye. Hence, the circuit is completed. Ideally, nothing is consumed, and the cell is regenerating.

DSSCs are attractive for next-generation solar cells because the production cost of DSSCs is expected to be greatly reduced compared with conventional silicon solar cells. However, before they are put on the market, many things need to be done on DSSCs, such as increasing efficiency, achieving better durability and avoiding electrolyte loss caused by the leakage and or volatility of the electrolyte solution. Today, many efforts have been focused on improving the solar conversion efficiency of presently reported value of about 10%. One of the important factors in efficiency of DSSCs is the dye which is used as sensitizer in DSSC. Many different dye groups, such as organic dyes, organic metal complexes and natural dyes, are currently employed in DSSCs [2-4]. As the organic metal complexes, the Ru based dyes (known as N3 and N719) can be considered as the backbone of currently applied sensitizers in DSSCs [1,5]. The natural dyes extracted from fruits, flowers and leaves of plants, usually perform poorly in DSSC because of weak binding energy with TiO_2 film and low chargetransfer absorption in the whole visible range, but these dyes are very cheap, easy to prepare and environmentally friendly, comparing to ruthenium based complexes [6-8]. Photocurrents observed in DSSCs fabricated from natural pigments are ascribed to anthocyanines. Anthocyanins are natural compounds that give color to fruits, flowers and leaves of plants [9].

In this study, we prepared conducting FTO glass by using spray pyrolysis method and we used these FTO glass as a substrate in making of DSSC. As a natural sensitizer we used black raspberry (*Rubus Ideaus*), black carrot (*Daucuscarota L.*) and rosella (*Hibiscus Sabdariffa L.*) juice. These plants are abundant in many countries and rich in anthocyanins. In here, we used rosella juice to compare it to black raspberry and black carrot dyes.

2. Experimental works

2.1. Preparation of FTO glass :

Transparent conducting FTO films were prepared by using chemical spray pyrolysis technique. The experimental set up and the other experimental details are explained elsewhere [10]. The method of preparation of FTO films described in Ref. [11]. The starting solution was prepared by dissolving $SnCl_2$ (11gr.) in 5 ml of concentrated hydrochloric acid and this solution was heated at 90°C by stirring with a magnetic stirrer for 10 min. The fluorine doping was achieved by adding NH_4F, dissolved in 5 ml of distilled water, to the starting solution. 90 ml diluted methanol was added in order to complete the total volume of 100 ml. The glass substrates were cleaned by using deionized water, acetone and ethyl alcohol subsequently and dried in air and then immediately placed on a hot plate. The prepared solution was atomized at a frequency of 1.63 MHz by an ultrasonic nebulizer and by using dry air. The generated droplets with size 5–6 μm were carried onto heated glass substrates. The flow rate of air, used as a carrier gas, was about 2 ml/min. The time for the film deposition was about 5-8 min. The nozzle substrate distance was maintained at 5 cm and the substrate temperature was set to 400^0C and controlled within ±5^0C by using an iron–constantan thermocouple kept on the metallic hot plate surface.

2.2. Assembling of DSSC :

The black raspberry (*Rubus Ideaus*) juice was prepared by squeezing fresh fruits and the resulting solution was filtered in order to remove the pulps and some residual fragments. To obtain rosella juice dried rosella (*Hibiscus Sabdariffa L.*) fruits were soaked in water for 10-12 hours. Black carrot (*Daucuscarota L.*) juice was prepared in 0.01 HCl solution by using an extractor apparatus. The obtained solutions were protected from direct sunlight exposition and were stored at about 5^0C.

To prepare working electrode, first TiO_2 powder paste solution was prepared 3.5 g of TiO_2 nano powder P25 (Degussa) in 15 ml of ethanol. Then 0.5 ml of titanium (IV) tetra isopropoxide was added into the suspension and was mixed by hand until the suspension is uniform. The prepared TiO_2 powder paste was printed on masked and cleaned FTO glass by using doctor-blading technique using a glass slide. The film thickness was controlled by 3M adhesive tapes. These films were then sintered at 450 ^{0}C for 1 hour in air to form a porous nanostructured TiO_2, and cooled down to room temperature in the furnace. Finally, the nanostructured TiO_2 films were dipped into the prepared fruit juices used as dye solutions for 2 hour. Then the stained films were washed in water, and then ethanol.

The platinum coated counter electrode was prepared by using 5 mM hexachloroplatinic acid (H_2Ptcl_6) solution in isopropanol. Two to three drops of the solution were dropped on the FTO coated glass plates and after that they were sintered in air at 350-400 ^{0}C for 1h in furnace and cooled down to room temperature in the furnace.

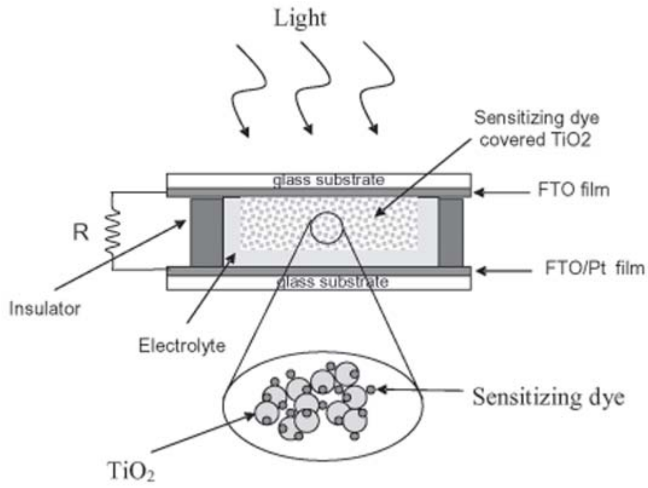

Figure 1. Schematic representation of a dye-sensitized solar cell.

The liquid electrolyte was prepared by mixing of 0.5M KI and 0.05M I_2 dissolved in ethylene glycol. One or two drops of this solution was placed between the working and counter electrode. Two binder clips are used to hold to electrodes together. Schematic representation of fabricated dye-sensitized solar cell was shown in Fig.1. Current–voltage (I–V) characteristics of produced cells have been carried out on sunny days of June and July between 12-13 pm in Kahramanmaras-Turkey. During the experiment, the outside temperature was measured around 33-35 ^{0}C and before I-V measurements, the cells were let to stabilize at the measured temperature for 10 minutes. The efficiencies of the cells were obtained by taking solar radiation in about 100 mW/cm^2 in Kahramanmaras. The sun light intensity was measured by using a light meter (C.E.M DT-1309) and the cell areas are calculated to be 1 cm^2.

3. Results and discussion

The sheet resistance and transmittance of the FTO layers obtained by spray pyrolysis technique were measured as 15-30Ω/ƒ}„Q, and 80%, respectively. UV–Vis transmittance spectra and X-ray diffraction (XRD) pattern of FTO films are shown in Fig.2. The using of the low sheet resistance and the high optical transmittance FTO films on glass substrate are favor of photoelectric conversion effect in the point of transfer of electrons and absorbance of sun light.

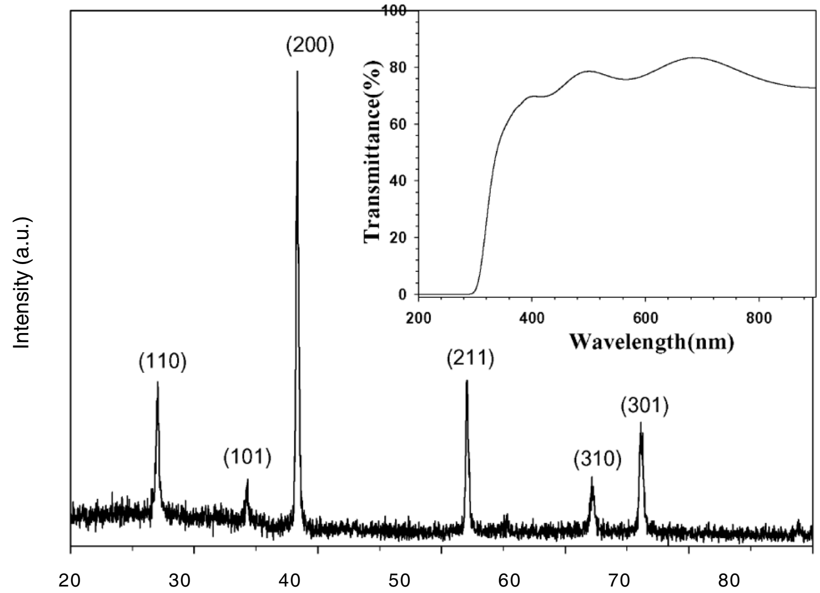

Figure 2. XRD pattern of SnO_2:F (FTO) film on glass substrate. Inset shows transmittance spectra for FTO film.

Figure 3 shows the XRD patterns of the TiO_2 nanocrystalline on the FTO glass after heat treatment at 450^{0}C for 1 h. Although some rutile phases of TiO_2 are detected from the XRD pattern, most of the peaks belong to anatase phase. Because TiO_2 powder (Degussa P-25) contains 80% anatase 20% rutile phase, some rutile phases also appear in the spectrum. In addition, the existence of peak at 25.9 of 2θ values corresponding to

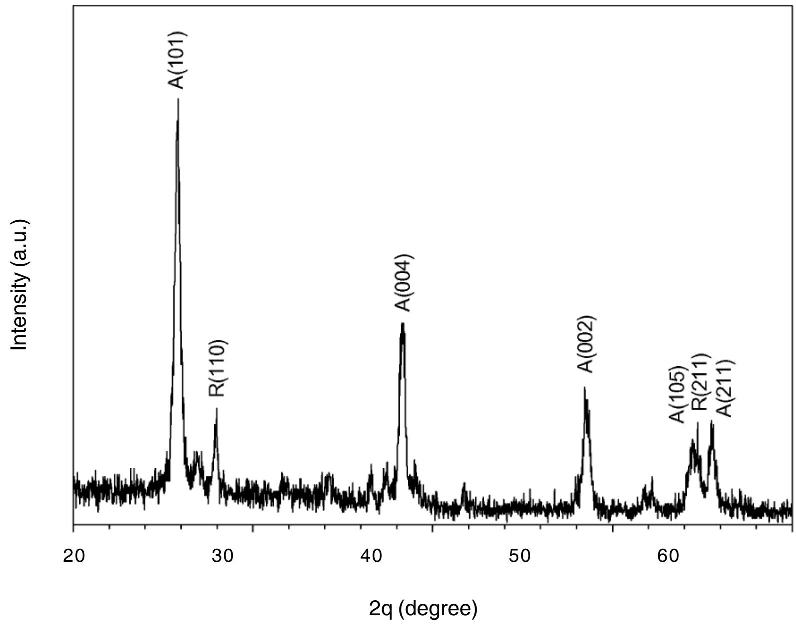

Figure 3. XRD pattern of TiO_2 on FTO glass after annealing at 450^0C for 1 hour in furnace. (A: Anatase, R: Rutile)

the anatase phase of TiO_2 with the lattice planes (101), shows that the film grows preferentially standard TiO_2 anatase phase. The anatase phase is preferred for the dye

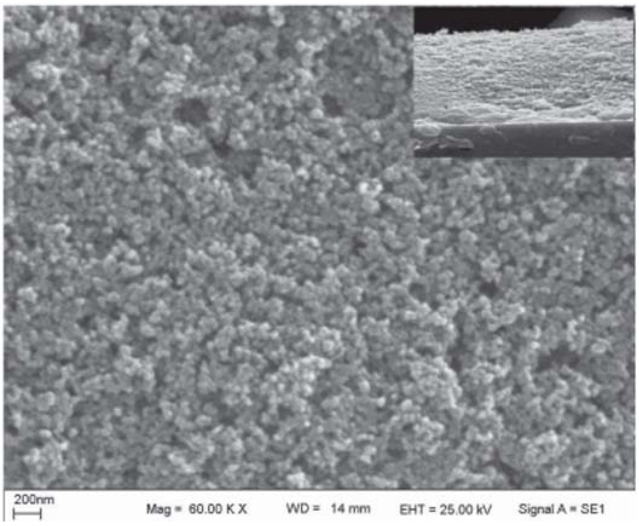

Figure 4. SEM photographs of porous TiO_2 films. Inset shows cross-section image of TiO_2 films

sensitized solar cell due to its larger band gap (3.2 eV compared to 3.0 eV for rutile.) From the full width at maximum height (FWMH) data, the average grain size was estimated to be about 26 nm by applying the Debye-Scherer Formula. This signifies that the formation of TiO_2 film is nano-sized. The scanning electron microscope (SEM) images shown in Fig.4 support the Debye-Schrerer results. In addition, the SEM picture also reveals the porosity of TiO_2 films. In this study, the thickness of TiO_2 films were measured 10-11 μm by using the cross-sections of SEM images.

The absorption spectra of black raspberry (*Rubus Ideaus*) , black carrot (*Daucuscarota L.*) and rosella (*Hibiscus Sabdariffa L.*) juice and their absorbances on TiO_2 films are

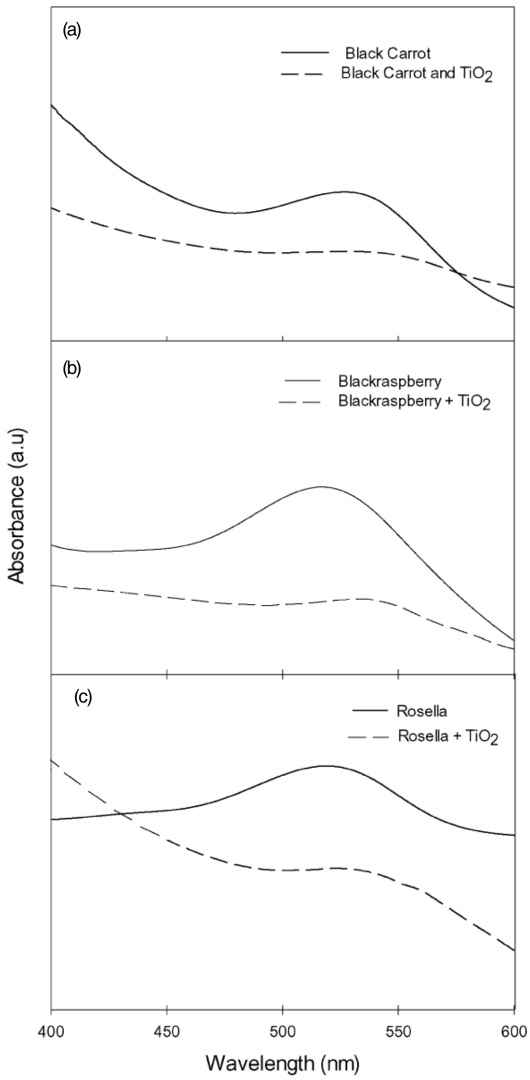

Figure 5. Absorption spectra of (a) black carrot, (b) black raspberry and (c) rosella juice and their absorbances on TiO_2 films.

given in Fig.5(a),(b), and (c) respectively. These spectra are referred to air. From Fig.5 it can be seen that the absorbance peaks are shown in about 520 nm for used fruit juices and peaks for juices absorbed onto TiO_2 are in about 540 nm. This absorbance shift between juices and absorbed juices by TiO_2 is due to complexation of anthocyanine in fruit juices with metal ions [12,13]. In other words, the spectra shows that the dyes obtained fruit juices are bound with the surface of TiO_2. The carbonyl and hydroxyl groups presented in cyanine based dyes in natural pigments are responsible to this binding.

The cell performances were examined by using the current-voltage curves as shown in Fig. 6. The fundamental results such as a conversion efficiency (η), an open circuit voltage (V_{oc}), a short circuit current density (J_{sc}) and a fill factor (FF) have been summarized in

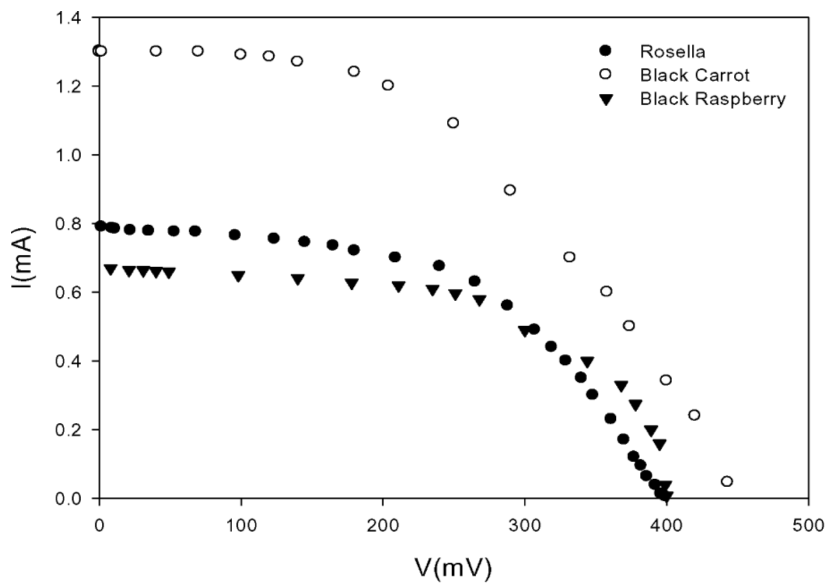

Figure 6. Current–voltage (I–V) characteristics of cell produced from (▼) black raspberry, (o) black carrot and (•) rosella juices.

the Table 1. The best solar conversion efficiency among the fabricated cells was obtained by black carrot juice. As seen in Table 1, the performance of the cell fabricated from black raspberry, and rosella juice are lower than that of the cell fabricated from black carrot juice, The reasons for this might be the large series resistance in the cell, absorbance of dye by TiO_2 film. In this study, the efficiency of cell obtained from rosella dye was measured 0.161. This result is lower than the result given by Wongcharee *et. al.* [6]. These different results might be arised from different cell components such as used liquid electrolyte solution and counter electrode.

4. Conclusion

DSSC's were constructed from natural dyes such as black raspberry, black carrot and rosella juice. The FTO thin films used as substrates for DSSC's were obtained by using

Table 1. Performance parameters of solar cell fabricated black raspberry, black carrot and rosella juices.

Sample	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
Black Carrot (Daucuscarota L)	1.302	400	0.47	0.25
Rosella (Hibiscus sabdariffa L.)	0.79	428	0.47	0.16
Black Raspberry (Rubus ideaus)	0.672	400	0.59	0.16

spray pyrolysis technique. TiO_2 films were deposited on FTO layers by the doctor-blading technique and platinum-coated counter electrode and liquid Iodide/Iodine electrolyte solution were used to fabricate for DSSC's. From the I-V curves, the efficiencies of solar cell produced with black carrot, rosella and black raspberry juice were calculated as 0.25%, 0.16% and 0.16% respectively, under a sunny day in Kahramanmaraş-Turkey.

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