

Carotenoid pigment as sensitizers for applications of dye-sensitized solar cell (DSSC)

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Abstract. A dye-sensitized solar cell is the third generation of solar cells that can convert solar energy into electrical energy using photo-electrochemical principles. Natural dye extracted from carotenoid pigments such as orange fruits, carrots, and tomatoes. The absorbance of dye and TiO₂ were characterized using UV-Vis spectrophotometer. The chemical bond contained TiO₂/dye were characterized using FTIR spectrophotometer. The efficiency of DSSC was calculated using I-V meter Keithley. The absorbance spectra results show that carotenoid dyes have peaked in the wavelength range of 400 nm-510 nm. The highest efficiency was obtained from tomatoes dye at 0.03% due to the interaction between TiO₂ and carboxyl -OH group. Adsorption of carotenoid dyes on the surface of TiO₂ can be used as the photosensitizer for DSSC.

1. Introduction

Dye-sensitized solar cell (DSSC) technology is a third-generation solar cell technology based on the dye that can convert solar energy into electrical energy using photo-electrochemical principles [1-5]. Components for assembling the DSSC consists of a transparent conductive glass substrate, a semiconductor having a wide band gap, photosensitizers, electrolyte, and a counter electrode [6]. The best semiconductor material often used in DSSC fabrication is TiO₂ [7]. The performance of photosensitizers adsorbed on the surface of TiO₂ is one of the important factors to determine the efficiency of the dye-sensitized solar cell [8, 9]. Natural dyes is one component that plays an important role in improving the performance of DSSC because it can be that convert solar energy into electrical energy. The natural dye can be fabricated in a simple, very cheap and environment-friendly.

Some fruits, plants, flowers, and leaves displayed various colours and contained several pigments, which can be simply extracted and then used as sensitizer because most of yellow, red, and orange plants contained a lot of carotenoid, which help in absorbing photon from sunlight in the visible region at the wavelength range of 400 nm-510 nm. Gomez-Ortiz *et al.* carotenoid have carboxyl group enable to bind to the interface of TiO₂ [10] because carboxyl groups at the ends of the chain of compounds which may be binding to Ti from TiO₂. The entire carotenoid is poly-isoprenoid have a system with single and double bonds conjugated [11] as has been reported [12], carotenoid molecules are highly reactive and degrades more quickly due to the small number of oxygen. Extraction of carotenoids is very difficult because there is no optimal solvent for preventing the degradation process. Gao *et al.* used a carotenoid dye with an efficiency of 34% on the stability of the light irradiation for 1 hour [13]. *Daucus carota* as



a carotenoid dyes for DSSC resulted the absorbance at the wavelength peak in 415 nm and 508 nm. The performance of DSSC based on *daucus carota* dye showed that the maximum voltage ($V_{\max}$) of 23.9×10^{-2} V and the maximum current (I_{sc}) of 3.3×10^{-5} A, and conversion efficiency was very low is $12.5 \times 10^{-4}\%$ [14]. In this work, a natural dye is extracted from carotenoid pigments such as orange fruits, carrots, and tomatoes. The aim of this work is to examine the chemical bond of a carotenoid dye on TiO_2 for the efficiency of the dye-sensitized solar cell.

2. Experimental

TiO_2 pastes were prepared using TiO_2 nano-powder in ethanol. The TiO_2 solution was stirred at 300 rpm for 30 minutes. TiO_2 pastes that have been formed are inserted into the bottle and stored in an area free from direct sunlight. The TiO_2 paste is deposited onto the FTO substrate glass with the active cell area $1 \text{ cm} \times 1 \text{ cm}$ by spin coating technique. TiO_2 films were annealed in a furnace at 400°C for 10 minutes.

The material used is natural dyes extracted from orange fruits, carrots, and tomatoes, and then cut into small cubes. Carotenoid dyes were dissolved in n-hexane solvent. It was kept for 24 hours. It were filtered using filter paper. The dye was evaporated using a rotary evaporator to get the more concentrated solutions. The working electrode was soaked in the dye solution for 24 hours. The dye solution and TiO_2 /dye layers were characterized using a UV-Visible spectrophotometer to determine its absorbance spectrum and TiO_2 /dye was characterized using a FTIR spectrophotometer to know the chemical bonds contained in TiO_2 /dye.

The electrode counter is made of transparent conductive glass (FTO) coated with a platinum catalyst. The working electrode and electrode counter are assembled, thus forming a sandwich structure (Figure 1). The electrolyte solution is dropped into the gap between the two electrodes. The DSSC was characterized using a *I-V* meter Keithley 2602A.

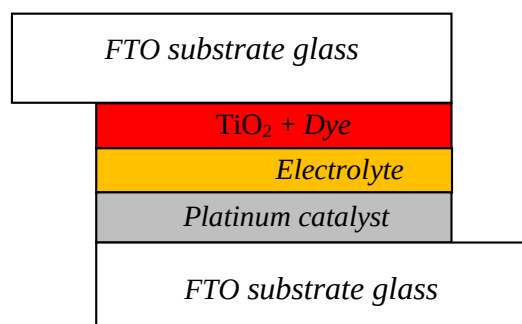


Figure 1. The structure of DSSC.

3. Results and discussions

3.1. Optical characteristics of carotenoid dyes

Characterization of the absorbance of the dye was examined using UV-Vis spectrophotometer. Figure 2 shows the absorbance peaks of orange fruit and tomatoes dye at 441 nm and 466.5 nm while the dye carrots at 433 nm and 472.5 nm. Absorbance peak difference is not significant because the three dye is in the wavelength range of 400-510 nm in the visible region which indicates the content of carotenoid pigments. High concentration of carotenoid dye causes the dye molecules are absorbed and reflected photons of light bulbs too much. The greater the wavelength used, the smaller the resulting absorbance values. It can be produced as white light at each wavelength can be selected more detail by the prism so that the spectrophotometer measurements imply the absorption of light energy away by a chemical system as a function of the wavelength of the radiation [15].

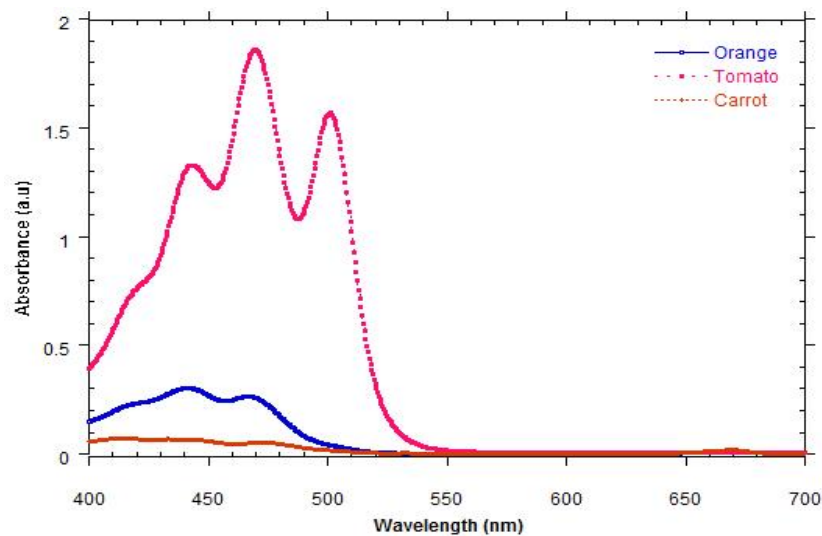


Figure 2. The absorbance spectra of carotenoid dyes.

3.2. Fourier transform infrared (FTIR) characterization of carotenoid dyes

Figure 3 shows the FTIR spectra of TiO_2 and the carotenoid dye. O-H stretching vibration of the carboxyl group appears on the three samples of tomatoes, carrots, and orange fruits. TiO_2 /dye of tomatoes at wavenumber 2395 cm^{-1} with transmittance of 84.8%, TiO_2 /dye of carrots at 2925 cm^{-1} and 2856 cm^{-1} with transmittance value of 81.8% and 84.7%, while for TiO_2 /dye of orange fruits appeared at 2924 cm^{-1} and 2854 cm^{-1} with transmittance of 73.7% and 78.5%. The two union monomers of carboxylic acids are capable of forming hydrogen bonds on two carboxyl groups. Therefore, the vibration of O-H in the carboxylic acid appears as a series of bands that are distributed over a very wide range ($3300\text{--}2500\text{ cm}^{-1}$). This resilient vibration occurs due to compression of the bond.

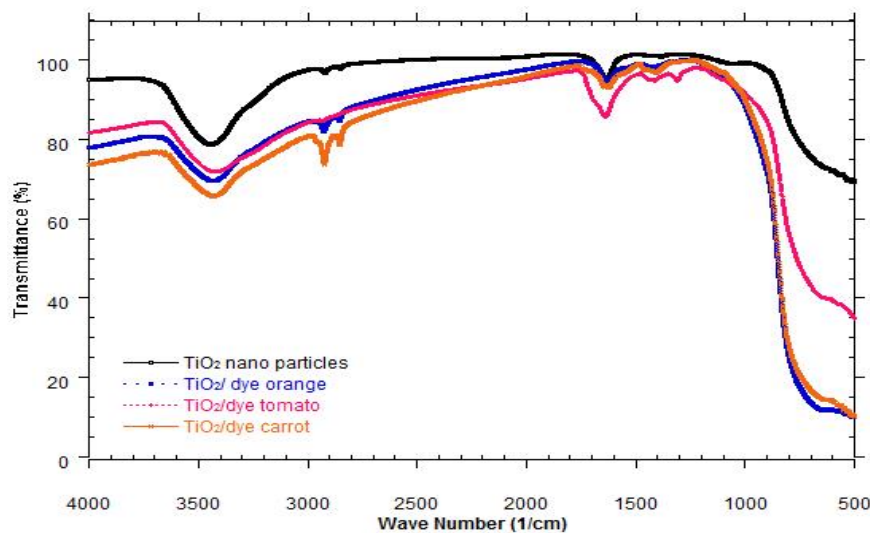


Figure 3. The FTIR spectra of carotenoid dyes.

TiO_2 /dye of tomatoes are capable of absorbing very large radiation due to the widened frequency in the lower direction. This is due to the tomato dye being absorbed into the more TiO_2 cavities. Vibrations that can absorb more radiation are caused by changes in the dipole moment in the molecule. The greater of the dipole moment, the resulting absorption is also more intense. $-\text{CH}_3$ and $\text{C}=\text{C}$ that appears in the infrared spectrum is estimated to come from carotenoid compounds. Carotenoid have carboxyl groups

at the end of the chain of compounds that enables to bind to the TiO_2 [10]. The entire carotenoid is polyisoprenoid have a system with a single bond and conjugated double bonds [11].

3.3. I-V characterization of DSSC

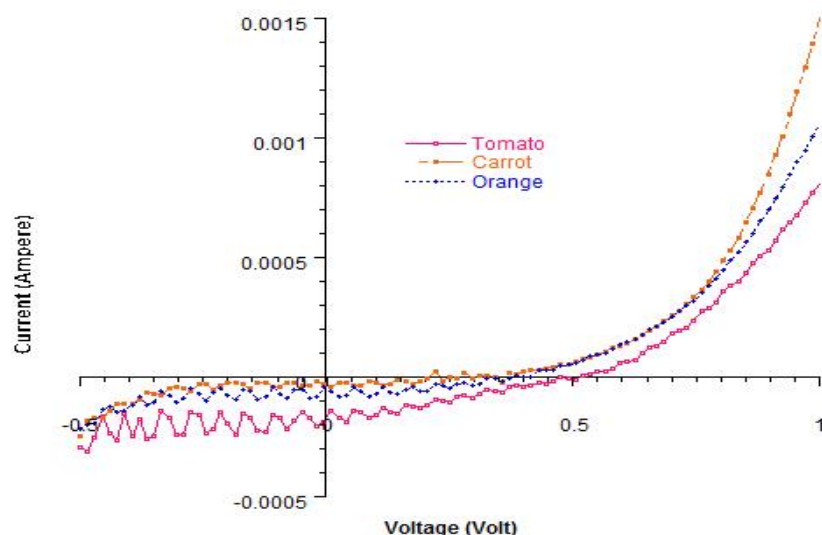


Figure 4. The I-V curve of the DSSC with carotenoid dyes.

Current-voltage characteristics of the DSSC fabricated using a light source $1000\text{W}/\text{m}^2$. Figure 4 shows sampled current-voltage characteristics of the DSSCs. Table 1 shows the results of current-voltage measurement of each dye extraction such as I_{sc} , V_{oc} , FF , and η . Table 1 shows the DSSC of tomato dye having an open-circuit (V_{oc}) voltage value higher than 0.51 V compared to the V_{oc} extract of orange fruits 0.37 V and carrots 0.36 V . The highest current density obtained by DSSC dye tomatoes of 0.00014 A . This current density value is greater than the current density of the orange fruits extract of 0.00006 A and carrots 0.00004 A . The differences that occur in the density of the cell flow may be due to the structural differences in the dye molecule and how quickly the charge is injected into the TiO_2 conduction band [16].

Table 1. Photoelectrochemical parameters of DSSCs based on carotenoid dyes.

Dye	I_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
Tomato	0.51	0.14	0.37	0.03
Orange fruit	0.37	0.06	0.58	0.02
Carrot	0.36	0.04	0.64	0.009

The efficiency of DSSC from each extract of tomato, orange fruits, and carrots was 0.03% , 0.02% , and 0.009% . The efficiency of tomato DSSC has a higher value compared to other DSSCs. This result is supported by a characteristic result from FTIR TiO_2/dye of tomato which has a value of transmittance of 84.8% in the range of $3500\text{--}2500\text{ cm}^{-1}$ wavenumbers. The FTIR analysis results support the efficiency of the tomato DSSC sample, although its efficiency value is still low probably because the dye molecules adsorbed on the TiO_2 surface are still low. The nanostructure of TiO_2 provides a pathway for electrons in order to maintain a high surface area during dye absorption process. Therefore, the unavailable bond between the dye and TiO_2 molecules during the electron transfer process causes a low-efficiency value [17, 18].

4. Conclusion

Based on research that the highest efficiency obtained by tomatoes dye was 0.03% in carotenoid pigment. This efficiency occurs due to the tomatoes dye binding to TiO_2 which is supported with the FTIR transmittance at wavenumber $3500\text{--}2500\text{ cm}^{-1}$ of 84.8%, resulting in the carboxyl O-H group stretching. The interaction between TiO_2 and dye causes the transfer of electrons from dye molecules to the TiO_2 conduction band. The amount of dye absorbed into the TiO_2 cavities is large, so the amount of light absorbed also rise.

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