Effects of Oxalic Acid on UV-C Sensing Property of Tomato Thin-Film Based Photodetector

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Abstract. New concept of UV photodetector with self-powered and biodegradable features are needed to solve energy and environment. In this work, tomato thin-film was used as an active organic layer in UV photodetector. The effect of oxalic acid in the extraction of tomato juice on the formation of a solid thin film that dried at 120°C for 30 min has been investigated. The purpose of adding oxalic acid is to extract ascorbic acid from tomato. A comparison between tomato juice extracted with and without oxalic acid on the structural, chemical, optical, electrical and UV sensing properties of tomato thin-film have been investigated. The UV photodetector was consisted of a sandwich structure of glass substrate/tomato thin-film/interdigitated aluminium electrode. The photodetector operated at 5 V with tomato thin-film extracted from tomato juice with oxalic acid revealed the highest responsivity percentage difference (89.60%) in UV-C with quantum efficiency (η) of 1.0335x10⁻⁵ %, responsivity (R) of 2.1178x10⁻⁶ A/W, and detectivity (D*) of 1.1649x10²¹ Jones. While without oxalic acid, the highest responsivity percentage difference (70.6%) in UV-C was operated at 0 V.

1. Introduction

UV region of the electromagnetic spectrum covers the wavelength range between λ~10 nm and λ~400 nm. It is divided into the three spectral bands: UV-A (400–320 nm), UV-B (320–280 nm) and UV-C (below 280 nm). UV-C is very energetic and harmful to life but it has been filtered out by ozone layer. This type of UV is technological useful whereby it can be engineered out to kill bacteria and gems, fused for flame detection (fire alarm, missile warning or combustion engine control), forensic analysis, protein analysis and DNA sequencing, space observation (VUV/EUV ranges), and advanced lithography [1-4]. Currently, the most widely used semiconductor-based UV photodetector materials is either from inorganic based such as silicon (Si), wide and direct bandgap semiconductors such as SiC, III-nitrides compounds (AlN, GaN, InN), and selected II-V compounds or organic based synthetic polymer [5-7]. However, these materials are difficult to decompose and degrade when it is being disposed. Therefore, bio-organic materials have been considered as an active or passive material for this application [8,9].

In this work, tomato as a natural source of organic material has been chosen to be used as an active material and converted to a solid thin film for the use of UV sensing properties. The tomato (Lycopersicon esculentum) is a member of the Solanaceae family and is one of the most widely
consumed vegetables. Tomato is a major source of antioxidants and various vitamins, which are activated by UV radiation, transferring of electrons that involves either releasing or trapping of electrons may occur [10]. If an external voltage apply, the current will produce with respect to the UV radiation due to the electron transportation phenomenon would serve as a basis in the photodetector of this work. In order to use tomato as a solid-state UV photodetector, tomato juice must be extracted out from the fruit and the juice mixed with oxalic acid must then be formulated before it is deposited on a treated glass substrate and processed it into a solid and dried thin film. In this work, a systematic investigation has been performed in order to extract, formulate, and process the extracted tomato juice with and without oxalic acid into a functional solid thin film with the objective of using it as a sensing layer of UV-C radiation with no (self-powered) or minimum operating power that is able to address issue of electronic waste.

2. Materials and Methods

Firstly, the extraction process of tomato juice consisted of four stages, namely washing, homogenizing, centrifuging and vacuum filtering. A typical fresh tomato was between 38 and 56 g and it was washed with distilled water in order to remove dirt. Then, it was cut into half for seeds removal before homogenized in a food blender (Philips HR2061). After that, to prepare the acid, 2.1 g of oxalic acid (solid) were dissolved in 350 ml of deionized (DI) water in a glass beaker and stirred vigorously for 15 min. The oxalic acid were dissolved in deionized water and appeared as a transparent solution. After that, 50 g of tomato juice was mixed into the oxalic acid. And then, the homogenized solution were transferred into a centrifuged (Hettich Rotina 38) operated at 3000 rpm for 30 min in order to remove any fibres from the juice by passing through a filter paper (Whatman No. 1) using a vacuum filter. The extracted juice was collected in a plastic bottles and store in refrigerate condition at 5°C for further usage. The extracted tomato juice was then spin coated (3,000 rpm, 30 s) on a pre-cleaned glass substrate and dried at 120°C for 30 min in an oven (air ambient). Then, an array of Al interdigital electrode was thermally evaporated via a shadow mask. Detail of this has been reported in Ref.[10]. An atomic force microscope (AFM) (Nanonavi SPA400-DFM, SII Nanotechnology) was used to investigate surface topography of the dried tomato thin film. Chemical functional groups and absorbance characteristics of dried tomato thin-film was obtained from Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer Spectrum 1) and UV-Vis spectrophotometer (Cary 50-Varian), respectively. MProbe 20, based on diffusive spectral reflectance technique was employed to obtain the thickness and refractive index of the sample. UV sensing property was characterized from the metal-insulator-metal test structure using UV-B = 302 nm and UV-C = 254 nm radiation sources with intensity of 0.0018 and 0.0013 A/cm², respectively. The current-voltage (I-V) and current-time (I-t) characteristics of the photodetector was measured from an Agilent HP4156C Precision semiconductor parameter analyzer (SPA).

3. Result and Discussion

Table 1 compares the root-mean square surface roughness, physical thickness and refractive index (n) value of tomato thin-film with and without oxalic acid. Using the same processing condition, except with addition of oxalic acid, the thickness of tomato thin-film is approximately 3 times thinner than the thin-film without addition of oxalic acid. The thinner film is slightly smoother on its surface and higher n value than its counterpart. The higher n value indicates that the thin-film tomato is relatively denser when oxalic acid is added during the extraction process.

Table 1. A Comparison of Thickness, Root-Mean Square (RMS) Surface Roughness, and Refractive Index (N) Value of Tomato Thin-Film With and Without Oxalic Acid Dried At 120°C.

| Sample            | Thickness (nm) | RMS Surface Roughness (nm) | Refractive Index (n) |
|-------------------|----------------|---------------------------|----------------------|
| with oxalic acid  | 6.30           | 10.3500                   | 0.7052               |
| without oxalic    | 19.21          | 11.5300                   | 0.6912               |
Chemical functional groups available in tomato thin-film with and without oxalic acid were identified by Fourier Transform Infrared (FTIR) Spectroscopy. Figure 1 (a) shows the absorbance spectra of tomato thin-film with and without oxalic acid. Tomato thin-film without oxalic acid shows chemical function groups associated to the three main vitamin groups, namely Carotenoids (lycopens), Phenolic, and Ascorbic Acid (Vitamin C) as well as lipids. This has been reported in Ref: [10]. The similar absorbance spectra at approximately same wavenumber except for the variation in intensities of the absorbance has been revealed in tomato thin-film with oxalic acid. In general, the intensity of absorbance spectra of tomato thin-film with oxalic acid is lower than tomato thin-film without oxalic acid. This may due to difference in the amount being tested. As shown in Table 2, sample with oxalic acid is thinner hence; the intensity is lower in the FTIR measurement. In addition, there are a few absorbance spectra located at wavenumber below approximately 1380 cm⁻¹ are not detectable in tomato thin-film with oxalic acid if compared with its counterpart. These spectra are assigned to ascorbic acid [11]. Chakraborty et al. (2013) proved that by adding oxalic acid in tomato juice, concentration of ascorbic acid can be reduced [11]. Figure 1 (b) shows the absorbance spectra as a function of wavelength (λ) measured by UV-Visible spectrophotometry. According to the result, a distinct absorbance spectrum is recorded in the range of λ = 200 to 340 nm for the two samples, except with a lower intensity being recorded by the sample with oxalic acid. The lowering in intensity may be attributed to difference in the thickness of the thin-film as oxalic acid sample shows a thinner layer. As reported by Yao et al. (2004), phenolic compounds (quercetin and kaempferol) in the tomato is governing the absorption of UV in this particular wavelength [12].

Dark and UV respond on test structure consists of tomato thin-film with and without oxalic acid was measured and their current density (J) – voltage (V) responds was recorded (Fig. 2). The dark current density with respect to the applied voltage (5 to -5 V) is compared with the current density when illuminated with two different wavelengths (254 and 302 nm) within the UV range. In general, the trend of respond between dark and UV illumination is the same for tomato thin-film with and without oxalic acid with lower J being recorded at shorter wavelength and higher J at longer wavelength with respect to dark condition. Comparing the J-V results obtained from these two samples, there is variation in the differences between dark and UV responds of the current density values. These variation is translated into R and D*, which will be reported in the subsequent paragraphs.

Table 2. Assignment of Chemical Functional Groups of Respective Absorbance Spectra.

| Chemical Compound in tomato | Functional | 120°C (without oxalic acid) | 120°C (with oxalic acid) | References |
|-----------------------------|------------|---------------------------|-------------------------|------------|
| Phenol (Vitamin group)      | 3420-3250cm⁻¹ (-OH) | 3399.93 | 3392 | [13] |
|                             | 1400-1440cm⁻¹    |          |      |          |
| Ascorbic acid (Vitamin group)| Carboxylic acid, (OH bending and 1063-1015cm⁻¹ (primary alcohols) | 1063.93 | 1068.89 | [14] |
| Lycopene (Vitamin group)    | CH- out of plane(lycopens), 2990-2850cm⁻¹ (C-CH₃, -CH₂-) | 779.91 | - | [10] |
| Lipid                       | 1870-1620cm⁻¹ (C=O) | 2919.5 | 2929.6 | [10] |
| Carbonyl compound           |             | 1630.93 | 1634.69 | [10] |

**Figure 1.** (a) FTIR absorbance spectrum and (b) UV-Visible absorbance spectrum of tomato with and without oxalic acid at 120°C drying temperature. The result of sample without oxalic acid has been presented in Ref:[10].
The performance of UV sensing properties for the tomato thin-film with and without oxalic acid based UV photodetector was determined from the J-V results (Fig. 2). Figures 3 compares the R and D* values obtained from photodetector with tomato thin-film with and without oxalic acid and measured at -5 V (Fig. 3 (a)), 5 V (Fig. 3 (b)) and 0 V (Fig. 3 (c)) that had been illuminated by UV light of 254 and 302 nm, respectively. According to the result, the R and D* values are higher for tomato thin-films with oxalic acid if compared with its counterpart when measured under illumination of both wavelength at 5 V (Fig. 3 (a)), -5V (Fig. 3 (b)) and 0 V (Fig. 3 (c)). However, when the photodetector measured by longer wavelength (302 nm), a reversed trend is being observed only at 5 V. In order to identify a tomato thin-film based UV photodetector that can be selectively and sensitively detecting a specific wavelength for a particular application, the results presented in Fig. 4 can be used as a guide. In the figure, the percentage differences between R values for both samples showed only the UV-C region (254 nm), is calculated based on the results presented in Figs. 3. (a,b,c). The percentage differences between R values of λ = 254 nm and 302 nm (ΔR %) are calculated based on the following equation:

\[ \Delta R = \frac{R_{254nm} - R_{302nm}}{R_{302nm}} \times 100 \]  

(Eq. 1)

Where, \( R_{254nm} \) and \( R_{302nm} \) are the responsivity obtained from \( \lambda = 254 \text{ nm} \) and \( 302 \text{ nm} \), respectively. The photodetector prepared with oxalic acid is selectively and sensitive to UV-C (254 nm), which is similar to the photodetector prepared without oxalic acid. The only difference is the operating voltage of the photodetector with the former one operating at 5 V and the latter one working at 0 V. This indicates that the chemical functional groups that responsible for the sensing property are different with tomato thin-film prepared by additional of oxalic acid is having purer amount of phenolic compounds while without oxalic acid the thin film is having additional of ascorbic acid. With these differences, the operating voltage is affected. The external quantum efficiency of photodetector with tomato thin-film with and without oxalic acid dried at 120°C illuminated with 254 and 302 nm is compared and shown in Fig. 5. In general, the efficiency of the photodetector prepared with oxalic acid is much higher if compared with those without oxalic acid when the photodetector is illuminated with shorter wavelength (254 nm). This is totally different when the photodetector is illuminating with wavelength of 302 nm. In order to investigate the respond time of the photodetector, tomato thin-film with oxalic acid dried at 120°C and measured at 5 V had been performed. The photodetector was illuminated with a 302-nm UV light for a 5 periodic on and off cycle with an interval of 15 seconds each. The current density as a function of time (J-t) responding to the cycles is presented in Fig. 6 (a). When the photodetector prepared with oxalic acid is exposed to UV light, the J value increases and reaches a relatively stable value before starting to decay when the light is switched off. When the light is switched off the current density decreases substantially until it is stabilized for photodetector prepared with oxalic acid but its counterpart reveals a rapid increment in current density until it is plateau off gradually. By consecutively switching on and off the UV light, the on-off ratio of current density are decreasing with no significant changes of the current density when the UV light is switched off. The extracted respond times for raising (Fig. 6 (b)) and falling (Fig. 6 (c)) for the five cycles are presented in Table 3. The average times for raising and falling (with oxalic acid) are 0.048 s and 0.043 s, respectively if compared with its counterpart, the respective average times are relatively fast.

Figure 2. J-V characteristic of thin-film tomato (a) without oxalic acid and (b) with oxalic acid based UV photodetector. The result of sample without oxalic acid has been presented in Ref.[10].
The result of sample without oxalic acid has been presented in Ref.[10]. The percentage in positive and negative region shows a higher responsivity of the photodetector with respect to the shorter (254 nm) wavelength. The result of sample without oxalic acid has been presented in Ref.[10].

Figure 5. External quantum efficiency value of thin-film tomato with the applied voltage 5V, -5V and 0V under UV light of (a) 254 and (b) 302 nm. The result of sample without oxalic acid has been presented in Ref.[38].

Table 3: The Extracted Respond Times For Raising and Falling (Fig. 9) For The Five Cycles of Thin-Film Tomato Based UV Photodetector.

| Sample          | Cycle | Raise time ($t_r$) | Decay time ($t_d$) |
|-----------------|-------|-------------------|-------------------|
| With oxalic acid| 1st   | 0.052 s           | 0.040 s           |
|                 | 2nd   | 0.036 s           | 0.032 s           |
|                 | 3rd   | 0.058 s           | 0.051 s           |
|                 | 4th   | 0.049 s           | 0.049 s           |
|                 | 5th   | 0.043 s           | 0.041 s           |
|                 | Average | 0.048 s     | 0.043 s           |
4. Conclusion

In this work, tomato juice has been extracted, formulated, and processed into a solid thin film deposited on a glass substrate for the use of detecting UV radiation, in particular UV-C. The effects of oxalic acid to form a solid thin film on the structural, optical, chemical, and UV detecting properties have been investigated. The device extracted by adding with and without oxalic acid at 120°C, the highest responsivity percentage difference (89.60%) in positive region (UV-C) is recorded in photodetector with tomato thin-film with oxalic acid dried at 120°C and measured at 5 V with quantum efficiency ($\eta$) of 1.0335x10^{-5}%, R of 2.1178x10^{-6} A/W, and D* of 1.1649x10^{21} Jones. While a self-powered (V = 0 V) UV photodetector that was able to detect UV-C can be produced by drying the tomato thin-film without oxalic acid at 120°C with external quantum efficiency of 2.53x10^{-7}%. Because the total concentration of phenolic compounds in the extracted tomato juice will be much higher. If the tomato is extracted without using oxalic acid, treatment of glass substrate is capable to produce a UV sensing properties that can sense UVC. When the oxalic acid is added during the extraction, the sensing property is able to detect UVC. The change of chemical functional groups with respect to the effect of oxalic acid have been evaluated with the identification of three groups of vitamins and lipids. The electrical property of the dried tomato thin-film with respect to the chemical functional groups and antioxidant activity when illuminating under UV-C wavelengths had been proposed. The response time for raising and falling for all testing less than 0.3 s observed in this work enables the tomato thin-film been used as a UV photodetector at this specific wavelength. Hence, the quick response and stability enable the obtained tomato thin-film device to be used as UV sensing properties of the photodetector.

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