Natural dye extracts from fruit peels as sensitizer in ZnO-based dye-sensitized solar cells

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Abstract
As a result of twin problems of environmental pollution and continuous depletion of fossil fuels, a search for renewable and clean energy sources is necessary. This paper discusses the simple extraction techniques without any further purification of natural dyes from some fruit peels and their performance in DSSCs. Natural dyes extracted from fruit peels of Carica papaya, Citrus lanatus, Persea americana and Solanum melongena were used as sensitzers to fabricate ZnO-based dye-sensitized solar cells (DSSCs). The extracts of the natural dyes were characterized and studied using UV-Vis absorption spectroscopy, Fourier transforms infra-red (FTIR) and Photoluminescence (PL) spectroscopy. The photo-anode semiconductor material was prepared and characterized. The photo-voltaic characteristics of the fabricated DSSCs were measured under simulated solar light (power of incident light 100 mWcm\(^{-2}\) from Air Mass 1.5G). These studies indicated the presence of pheophytin 'a' in most of the extracts studied as the main pigments with other accessory pigments. The solar to electric conversion efficiencies for the pheophytin ‘a’ dye based solar cells are estimated as 0.017%, 0.013%, 0.010% and 0.011% for Carica papaya, Citrus lanatus, Persea americana and Solanum melongena, respectively. The dye extracts from Carica papaya exhibits higher photo-sensitized performance compared to the other extracts and this is due to the better charge transfer between the dyes of Carica papaya and ZnO photo-anode surface. Conversion of visible light into electricity was accomplished with natural dyes and ZnO-based DSSCs, resulting in excellent photo-electric properties compared to those in literature.

Keywords: Fruit peels, natural dye, pheophytin a, photoanode, DSSCs, conversion efficiency

1. Introduction
The considerable high attention and extensive research efforts have been devoted over the last decades to dye-sensitized solar cells (DSSCs). Since a new type of solar cells is developed in 1991, these have attracted considerable much attention due to their environmental friendliness and low cost of production [1]. DSSCs are regarded as promising low-cost solar cells with high light-to-energy conversion efficiency. Although, many photovoltaic cells that assure the conversion of solar energy from sunlight to electricity, have already been unfolded in the past years. However, their practicable implementation is still limited by two significant problems namely; conversion efficiency and cost [2,3].

DSSC’s are a photo-electrochemical system which consists of four main parts, such as, the porous nano-crystalline wide band gap semiconductor electrode, sensitizer, counter electrode and electrolyte [3,4]. The conversion of electricity from sunlight occurs in DSSC due to sensitization of semiconductor photo-anode. This is based on absorption of visible light characteristics of dye extract, the nature of the locality of the semiconductor conduction band relative to the dye excited state and the attachment of the molecules of dye unto the surface of the semiconductor porous layer [5,6].
The photo-sensitizer used in DSSCs can be divided into two (2) broadly types according to dye structure: metal complex such as polypyridyl complexes of ruthenium (inorganic dyes) and natural or synthetic organic dyes (organic dyes). Ruthenium polypyridyl complex synthetic inorganic dyes have been widely employed as photo-sensitizers in DSSCs with high efficiency up to 11-13% [7,8,9,10]. But ruthenium dyes are expensive, extremely rare, and undesirable considering its impact on the environment.

In recent times, there is significant interest toward the usage of extracted natural dyes from various plants, leaves, flowers and fruits as photo-sensitizer in DSSCs which sometimes are biodegradable and easily available [3,6]. Several natural occurring pigments like chlorophyll [11,12,13,14], carotenoid [15,16], anthocyanin [17,18] and betalains [19] have been successfully utilized and reported as photo-sensitizers for DSSCs. The photo-sensitizer from naturally occurring pigments proffer many advantages such as large absorption coefficient, highly light-harvesting efficiency, non-toxic, environmentally friendliness, full biodegradable, availability and cheap cost [3,19]. Usage of natural occurring materials in DSSC was recently investigated and reported with extracts from Citrus paradisi, Citrus sinensis, Citrus limon and Citrus tangelo peels utilized as a photo-sensitizer resulting to 0.63%, 0.36%, 0.10% and 0.51% efficiency, respectively [20].

In this study, natural pigments from fruit peels waste of Carica papaya, Citrus lanatus, Persea americana and Solanum melongena, were extracted. To the best of our knowledge, natural pigments from many of these fruits peels have not been previously reported as photo-sensitizers for DSSCs. The optical spectra characteristics of the extracted pigments of Carica papaya, Citrus lanatus, Persea americana and Solanum melongena in ethanol solution were primarily studied by using UV-Vis absorption, FT-IR and PL spectroscopy techniques. The ZnO nanoparticle as photo-anode material was structurally and compositionally characterized. The photo-electrochemical properties of DSSCs fabricated with the natural pigments from fruit peels of Carica papaya, Citrus lanatus, Persea americana and Solanum melongena were studied.

2. Materials and Methods

2.1 Preparation of natural photo-sensitizers

Carica papaya (pawpaw), Citrus lanatus (watermelon), Persea americana (avocado) and Solanum melongena (eggplant), were purchased from nearby market. The peels from the fruits were taken and washed severally with distilled water, followed by vacuum-drying at 60°C until the weight become invariant. The already dried peels were broken-down into fine powder. In a particular experiment, the natural photo-sensitizers in this research were extracted by dissolving fine powder of 1 g into ethanol of 50 ml and left undisturbed in the darkness for 48 hrs at room temperature. The residue was filtered and the resulting dye solutions were concentrated and then protected from exposure to direct light. The natural pigments were further analyzed and utilized as natural photo-sensitizers without any other purification.

2.2 Fabrication of DSSCs

A highly conducting fluorine-doped tin oxide (FTO) films deposited on glass plate were purchased (Solaronix, SA) with 8 Ω/sq resistance was employed as received. FTO substrates were washed in a beaker of solution of detergent inside ultrasonic bath for 30 min and then washed with mixture of acetone and ethanol for the next 30 min.

The smooth and homogenous paste was acquired using ZnO powder (May & Baker Ltd Dagenham, England) and was deposited unto surface of FTO glass by employing doctor blade method with an effective area of 1 cm × 1 cm. The sample was dried at 125 °C for 15 min in an oven. After repeating the process, the pre-selected thickness was achieved and finally, the sample was sintered for 1 hr at 450 °C in a furnace then cool down to 80 °C, before being immersed into natural dye solution kept at room temperature at a specific interval to guarantee complete sensitizer uptake. Platinum
nanoparticles-coated FTO and Iodolyte AN-50 which were purchased from Solaronix, SA were employed as counter electrode and electrolyte respectively, as supplied. The DSSCs were fabricated by sandwiched the dyed sensitized ZnO electrode and counter electrode formed with platinum together. The details of the cell fabrication and paste making are followed as reported elsewhere [21]. The properties of the fabricated cells were then studied.

2.3 Characterization and measurements

The ZnO powder was characterized for structural characteristics using X’pert pro MPD PANanalytical X-ray diffraction (XRD) with CuαK radiation (λ = 1.5406 Å). The morphology and compositional of ZnO powder sample has been analyzed with scanning electron microscope, SEM (LEO 430i, Carl Zeiss). The microstructure of the ZnO powder was analyzed by transmission electron microscopy (TEM; Tecnai G2 30ST operating at an acceleration voltage of 300 kV).

The UV-Vis absorption characteristics of the natural pigments were measured and the wavelength of all the measurements were scanned from 400-800 nm using UV-Vis-NIR spectrometer (Shimadzu UV-3600). The typical peaks of the natural pigments were measured between 400 and 4000 cm$^{-1}$ with a scan of 200 at interval on a NICOLET 380 FT-IR spectrometer. The room-temperature PL spectra for the natural pigments were taken on a spectrophotometer (Q-M-40, Photon Technology International, PTI) using a Xenon lamp (150 W) as an excitation source, at 420 nm and 2 nm wavelength and band-pass, respectively.

The photo-current (I) and photo-voltage (V) characteristics were obtained with solar simulator (Newport model No: 96000) at 100 mW/cm$^2$ (1 sun AM1.5) and 25°C, coupled with source measure unit (Keithley 2400). A mask was used for the measurement with the cell active area of 0.5 cm$^2$. The photo-electrochemical results presented were average of measurements taken on three repeated experiments for the sample under test.

3. Results and Discussion

3.1 X-ray Diffraction (XRD) studies of ZnO sample

The room temperature XRD characterization was performed to establish the phase evolution of the ZnO powder sample as shown in Fig. 1. It is observed that XRD patterns matched well with reported reference patterns of wurtzite ZnO (hexagonal phase, JCPDS file 75-0576). The mean crystallite size, D calculated from the highest diffraction peak along the <101> plane for ZnO powder sample is 34.2 nm.

3.2 Microstructural and compositional studies of ZnO sample

The SEM microstructure and EDX spectra for ZnO powder samples are revealed in Fig. 2. The particle morphology is spherical and homogenous in nature with small aggregation of the particles. In addition to spherical shape in ZnO nanoparticles, hexagonal structure could also be found. The EDX results also showed a corresponding peak Zinc (Zn) and Oxygen (O).

In order to strengthen structural characterization, TEM characterization was carried out on the sample of ZnO nanopowder. The TEM images of the sample in ethanol are displayed as shown in Fig. 3. A spherical shape nanoparticle was formed as shown in Fig. 3(a). The diameter of the nanoparticles varied in the range of 20 nm to 50 nm. The high-resolution transmission electron microscopy (HRTEM) image confirms the single crystalline nature of individual nanoparticles, where the spacing corresponds to (101) reflection as shown in Fig. 3(b). The selected area diffraction (SAED) pattern shown in Fig. 3(c) indicates (101), (102) and (200) planes of ZnO.

3.3 Optical Absorption Studies of Extracted Natural Photo-sensitizers

The UV-Vis optical absorption spectra of Carica papaya, Citrus lanatus, Persea americana and Solanum melongena in ethanol as a solvent are revealed in Fig. 4. Also the corresponding colour of the extracted natural dye is shown in the inset of Fig. 4. It is observed that, all the selected natural sensitizers have similar absorbance peaks. The two major intense absorption peaks of natural extract as shown in Fig. 4 (a-d) are centered mainly on wavelengths of about 411 nm, 666 nm; 410 nm, 666 nm;
411 nm, 665 nm and 411 nm, 666 nm for *Carica papaya*, *Citrus lanatus*, *Persea americana* and *Solanum melongena* nature dyes, respectively. The Soret bands for the entire extract (Fig. 4) exhibits bathochromic shift except *Citrus lanatus* extract, and in addition, three very weak bands were observed around 506 nm, 536 nm and 608 nm. The observed intense Soret and Q band, and weak bands located in the spectral range between the Soret and Qy bands are in accordance with the corresponding literature data reported for Pheophytin ‘a’ [14,22].

Figure 1. XRD structure of ZnO powder sample with their specific reflection planes
Figure 2. SEM and EDS images of ZnO powder sample

Figure 3: TEM images of ZnO nanoparticles (a) separated nanoparticles (b) HRTEM image of a single nanoparticle, and (c) SAED pattern.
The study of photoemission of all the extracted dyes is necessary because there may be possible correspondence between the occurrence of photoelectron emission characteristics and the photoelectric conversion of natural photo-sensitizers based DSSC. The steady-state PL measurements were conducted on all the alcoholic extracts of natural pigment. Fig. 5 shows the emission spectra of Carica papaya, Citrus lanatus, Persea americana and Solanum melongena dye extracts in alcohol. They all have identical trend of maximum emission intensity located at 674 nm with an arm at 726 nm and very low emission at around 480 nm with no emission in green region of the spectrum. Typically, chlorophylls and pheophytins have bright maximum fluorescence intensity between 670-700 nm and with a shoulder of approximately around 710-740 nm indicating their characteristics response [22,23]. The emission intensity of all the dyes exhibited a little red shift compared with that of the pheophtin ‘a’. The chlorophyll and its derivative molecules may tend to aggregate in polar solvents and upon aggregation, both absorption and PL spectra exhibit bathochromic shift [24,25]. The photoemission spectra agree well with the result of optical absorption spectra, indicating the main characteristic response of the pheophytin ‘a’ that masked all other non-chlorophyll that might be present.

3.5 Fourier Transform-Infrared (FT-IR) studies of natural photo-sensitizers
The plotted FTIR data of the natural dyes from Carica papaya, Citrus lanatus, Persea americana and Solanum melongena fruit peels shown in Fig. 6(a-d) exhibit most of the feature peaks of chlorophyll derivatives [22,24]. Chlorophylls and their derivatives have characteristic infrared band corresponding to N-H, C-H, C=O and C=C groups [12,13,14]. As observed from Fig. 6(a-d), N-H stretching vibration, saturated C=H vibration and C=H vibration are observed respectively at 3228 cm\(^{-1}\), 2923 cm\(^{-1}\) and 2845 cm\(^{-1}\) for all the four extracted dyes. The characteristic C=O band corresponding to the ketone in the cyclopentanon ring of pheophytin ‘a’ is observed between 1731 cm\(^{-1}\) and 1745 cm\(^{-1}\). Similarly the C=C vibrations of pheophytin ‘a’ is observed between 1631 cm\(^{-1}\)and 1646 cm\(^{-1}\). The FTIR spectral analysis also confirms the presence of pheophytin ‘a’ in all the four fruit peels extracts, which is well correlated with the UV-Vis and PL spectral results.

3.6 Photovoltaic Performance
The cell performances of the natural pigments of the photo-electrochemical solar cells were tested under 100 mW/cm\(^2\) illuminations (AM 1.5). The photo-current density-voltage (J-V) characteristic plots of the DSSCs sensitized with the four natural extracts are shown in Fig. 7 and corresponding photo-electrochemical parameters for the fabricated cells are summarized in Table 1. The open-circuit voltage (\(V_{OC}\)) varies from 0.303 to 0.373 V, and the short-circuit photocurrent density (\(J_{SC}\)) changes from 0.111 to 0.149 mAcm\(^{-2}\).

The efficiency of the DSSCs fabricated with natural pigments from Carica papaya, Citrus lanatus, Persea americana and Solanum melongena peels are 0.017%, 0.013%, 0.010% and 0.011%, respectively. Precisely, a higher open-circuit voltage (\(V_{OC} = 0.373 \text{ V}\)) and short-circuit photo current density (\(J_{SC} = 0.149 \text{ mAcm}^{-2}\)) were obtained from fabricated DSSC sensitized by Carica papaya extract, and its efficiency reached 0.017%. The energy conversion efficiency parameters of 0.017% for ZnO based DSSCs sensitized by extracts of Carica papaya is significantly higher than those of the DSSCs sensitized with other natural dyes in this work and showed a comparable performance to the ZnO based DSSCs prepared from other natural dyes used by other groups [21,26,27,28]. This is possibly due to a broader range of light absorption of natural dye adsorbed onto ZnO film, and higher...
interaction between ZnO and chlorophyll derivative (pheophytins) in these extracts which leads to a better charge transfer. Furthermore, pheophytins structure in the extracts of \textit{Carica papaya} may have the shorter distance between the dye skeleton and a point connected to ZnO surface compared to that of other extracts in this work. And this could facilitate an electron transfer from pheophytins molecules in the extracts to ZnO surface and may be accounted for a better performance of \textit{Carica papaya} extract. From this result, it is obvious that the interaction between the sensitizer and ZnO film

Figure 5: Fluorescence emission spectra of natural dye obtained from fruit peels
Figure 6: FTIR spectra of natural dye obtained from fruit peels (a) Carica papaya 
(b) Citrus lanatus (c) Persea americana and (d) Solanum melongena is significant in enhancing the energy conversion efficiency of DSSCs. Some of the natural dyes used in this work may have no or poor availability of bonds between the dye and ZnO molecules through which electrons can transport from excited dye molecules to the ZnO film [26]. The lower efficiency recorded from the solar cells fabricated from natural dye as photo-sensitizers is owing to the absence of some particular functional groups which may cause poor dye molecules adsorption onto the surfaces of ZnO.

The natural pigments employed as photo-sensitizers in DSSC exhibited very low efficiencies compared to synthetic dyes because of non-existence of better interaction between the dye and ZnO surfaces through which electrons can move from the part of molecules of excited dye to ZnO film [3,4]. The performance of short-circuit (Jsc), depends on the quality of molecules of dye adsorbed to photo-anode surface, structure of the dye, efficiency of light harvesting and the injection of electron capacity of dyes in DSSC [6]. More molecules of dye available on the ZnO surface produce more photon number from sunlight, which in turn generates faster electron injection. Also the fill factors for these cells are mostly lower than 30%. This is due to high resistance in the cell and it perhaps responsible for the poor performance of the fabricated cells. From the above results, the Carica papaya natural extract may be worthy substitute for the solar cell application.

Figure 7: Current density versus voltage curves for ZnO based DSSCs sensitized by (a) Carica papaya 
(b) Citrus lanatus (c) Persea Americana (d) Solanum melongena alcoholic extracts
Table 1: Photo-electrochemical parameters for natural dye DSSCs sensitized by *Carica papaya, Citrus lanatus, Persea americana* and *Solanum melongena* alcoholic extracts with ZnO as photo-anode

| Natural Dye          | $V_{OC}$ (V) | $J_{SC}$ (mA/cm²) | FF (%) | Efficiency, $\eta$ (%) ± 0.05 |
|----------------------|--------------|-------------------|--------|-----------------------------|
| *Carica papaya*      | 0.373        | 0.149             | 30.37  | 0.017                       |
| *Citrus lanatus*     | 0.333        | 0.140             | 26.78  | 0.013                       |
| *Persea americana*   | 0.303        | 0.111             | 29.51  | 0.010                       |
| *Solanum melongena*  | 0.321        | 0.126             | 28.24  | 0.011                       |

4. Conclusion

The natural pigments from *Carica papaya, Citrus lanatus, Persea Americana and Solanum melongena* fruit peels were successfully employed as natural photo-sensitizer in DSSCs. The UV-Vis absorption and PL properties of extracted pigments show maximum absorption and photoemission identical to the pheophytin ‘a’ along with small identifiable parts. The FT-IR data for the natural dye resemble that of structural properties of pheophytin ‘a’. The photovoltaic performance reveals that the maximum efficiency acquired for the fabricated cell with *Carica papaya* peels extract is 0.017%, while the fabricated cells efficiency with *Citrus lanatus, Persea Americana and Solanum melongena* extracts are 0.013%, 0.010% and 0.011%, respectively. The higher efficiency observed for DSSC with *Carica papaya* peels is owing to better adsorption of dye molecules available to ZnO film and enormous opposition to charge transfer at ZnO-dye-electrolyte interface. Hence the results acquired are encouraging and promising as a consequence of their natural abundance, simplicity of preparation and environmental conviviality. Therefore, further work is recommended to justify the constituents of *Carica papaya* dye and more optimization of the cells.

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