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Pigment Extracts of Citrus Peels as Light Sensitizers for Dye-Sensitized Solar Cells

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Abstract
Dye-sensitized solar cells (DSSCs) were constructed with four natural pigments from *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* fruit peels as photo-sensitizers. Ethanol was maintained as an extracting solvent without any other purification. The UV-Vis absorption, Fourier Transform Infra-red (FT-IR) and Photo-luminescence (PL) spectroscopy characterization were done to analyze the natural dyes. The film of titanium dioxide (TiO_2) was prepared as a semiconducting photo-anode material. The net performance of the cells constructed with citrus peel extracts showed comparable efficiencies with the reported natural dyes. The DSSC constructed with the pigments from *citrus paradisi* peels exhibited the maximum efficiency of 0.63%.

1. Introduction

Solar energy, as the dominant energy source for all living creature on the earth, is appraised as the unrivalled solution to energy and environmental challenges as a renewable energy source. Nevertheless, utilizing solar energy from sunlight in a productive way remains a challenge. 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 [1].

As a novel renewable and clean solar- to- electricity conversion system, DSSCs proffer the hope of constructing photovoltaic cells showing better efficiency with reasonably inexpensive and facile process of fabrication, as a substitute to standard p-n junction photovoltaic cells [2, 3].

Generally, DSSC's are a photo-electrochemical system which consists of four main parts such as, the porous nano-crystaline wide band gap semiconductor electrode, sensitizer, counter electrode and electrolyte [3, 4]. The conversion into electric energy from sunlight occurs in DSSC due to sensitization of semiconductor photo-anode. Some of the significant characteristics that determine the efficiency of solar energy conversion from sunlight to electricity in DSSCs are 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 also the attachment of the molecules of dye unto the surface of the semiconductor porous layer [5, 6].

Common photo-sensitizer used in DSSCs can be categorized into two (2) types according to dye structure: inorganic dyes (metal complex such as polypyridyl complexes of ruthenium) and organic dyes (natural or synthetic organic dyes). Between the two, ruthenium polypyridyl complex synthetic inorganic dyes have been favorably employed as photo-sensitizers in DSSCs with high efficiency up to 11-13% [7, 8, 9, 10]. Since ruthenium dyes are extremely rare, expensive and undesirable considering its influence on the environment, there is significant interest in recent times 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]. Several natural occurring pigments like carotenoid [11, 12], chlorophyll [13, 14, 15, 16], anthocyanin [17, 18] and betalains [19] have been utilized successfully and reported as photo-sensitizers for DSSCs. Naturally occurring pigments used as photo-sensitizer proffers many advantages such as large absorption coefficient, highly light-harvesting efficiency, non-toxic, environmentally friendly, full biodegradable, availability and cheap cost [3, 19]. Recently, the usage of natural occurring materials in DSSC was investigated and reported with extracts from marine plant utilized as a photo-sensitizer, also as redox complex and counter electrode resulting to 1.40% efficiency [20].

In this work, natural pigments were extricated from fruit peels waste of *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo*. 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 studies of the extracted pigments of *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* in ethanol solution were primarily characterized by UV-Vis absorption, FT-IR and PL spectroscopy techniques. The TiO_2 nanoparticle as photo-anode material was structurally and compositionally characterized. The photo-electrochemical properties of DSSCs constructed with the natural pigments from fruit peels of *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* were studied.

2. Experimental Study

2.1. Preparation of Natural Photo-Sensitizers

Fresh fruits of *Citrus paradisi* (grapefruit)*, Citrus sinensis* (orange)*, Citrus limon* (lemon)*,* and *Citrus tangelo* (tangelo)*,* were purchased from nearby local farm in Ogbomoso, Nigeria. The peels from the fruits were taken and washed severally with distilled water, followed by vacuum-drying at 60^{o}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 out; 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. Construction 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.

0.2 g of the TiO_2 powder (Titanium IV oxide, anatase, J.T Baker) was ground inside a mortar in order to break the lumps into separate particles and a little amount of water (0.5 ml) and ethanol (7.5 ml) were introduced slowly with continuous grinding to lessen the aggregation of particles. After the powder had been evenly distributed by highly shear forces applied into the mixture, ethyl cellulose powder (0.1 g) was added into ethanol (1 ml) and then added to the mixture, thoroughly mixed to form uniform and homogenous mixture, and also 1 ml of terpineol was later introduced to the mixture until the uniform and smooth paste was acquired.

The smooth and homogenous paste 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^{o}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^{o}C in a furnace then cool down to 80^{o}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 constructed by sandwiched the dyed sensitized TiO_2 electrode and counter electrode formed with platinum together. The electrolyte was introduced within the region into the two electrodes. The properties of the constructed cells were then studied.

2.3. Characterizations and Measurements

The TiO_2 powder was characterized for structural characteristics using X'pert pro MPD PAN analytical X-ray diffraction (XRD) with CuαK radiation (λ = 1.5406 Å). The morphology and compositional of TiO_2 sample has been analyzed with scanning electron microscope, SEM (LEO 430i, Carl Zeiss).

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 4000 and 400 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 spectrofluorometer

(QM-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^oC, coupled with source measure unit (Kethley 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 TiO_2 Sample

The room temperature XRD characterization was performed to establish the phase evolution of the TiO_2 powder sample as shown in Figure 1. It is observed that XRD pattern corroborated well with reported reference reflection planes of TiO_2 anatase tetragonal phase (JCPDS file 71-1168). The mean crystallite size, D calculated from the highest diffraction peak along the <101> plane for TiO_2 sample is 39.10 nm.

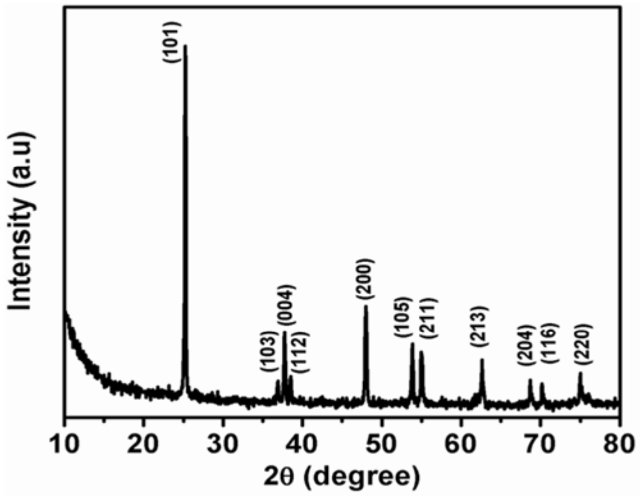

Figure 1. XRD structure of TiO_2 sample with their specific reflection planes.

3.2. Microstructural and Compositional Studies of TiO_2 Sample

The SEM microstructure and EDX spectra for TiO_2 sample are revealed in Figure 2. The particle morphology is observed to be spherical and homogenous with small cluster of the particles. The EDX result also shows a corresponding peak of titanium (Ti) and oxygen (O).

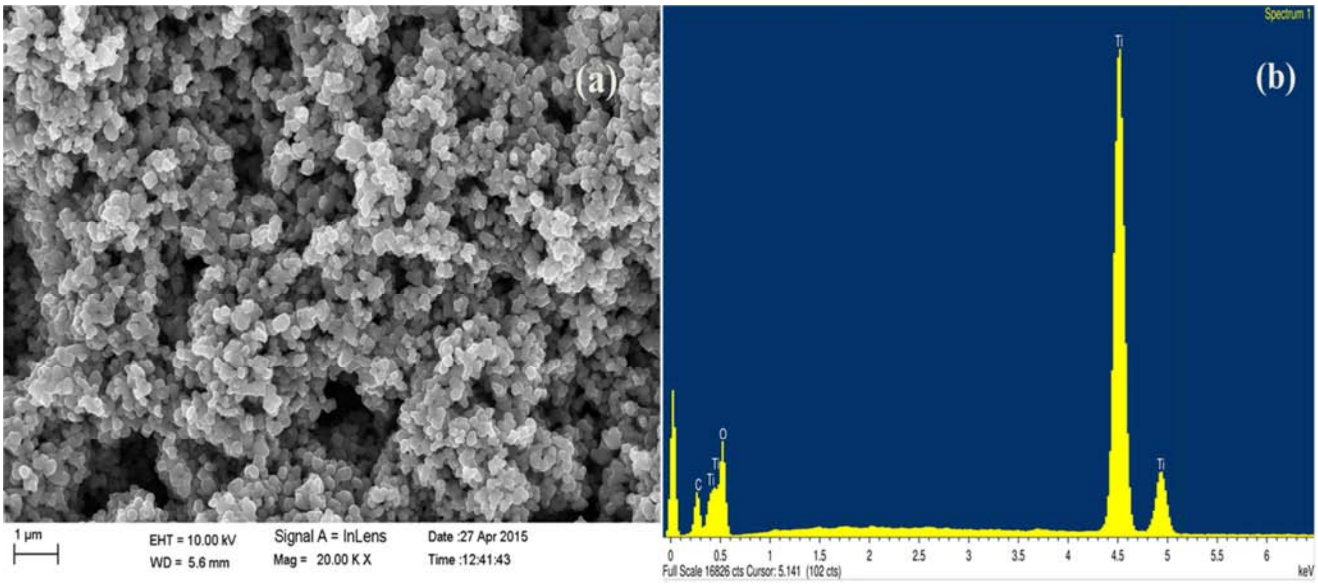

Figure 2. SEM and EDS images of TiO_2 sample.

3.3. Optical Absorption Studies of Natural Photo-Sensitizers

The UV-Vis optical absorption spectra of *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* in ethanol as a solvent are revealed in Figure 3. It is observed that all have similar absorbance peaks. Altogether, the four natural pigments show maximum absorption in the region around 666 nm and similarly, two very weak bands are observed at around 538 nm and 608 nm. The observed red band at 666 nm and weak bands located at 538 nm and 608 nm are in support of the reported data for chlorophyll derivative [21]. Many accessory pigments of non-chlorophyll like carotenoid do absorb light with chlorophyll and its derivative. Interestingly, the most dominant pigment here is pheophytin 'a' because major observed peaks are conforming to the reported band for pheophytin 'a' [16, 21].

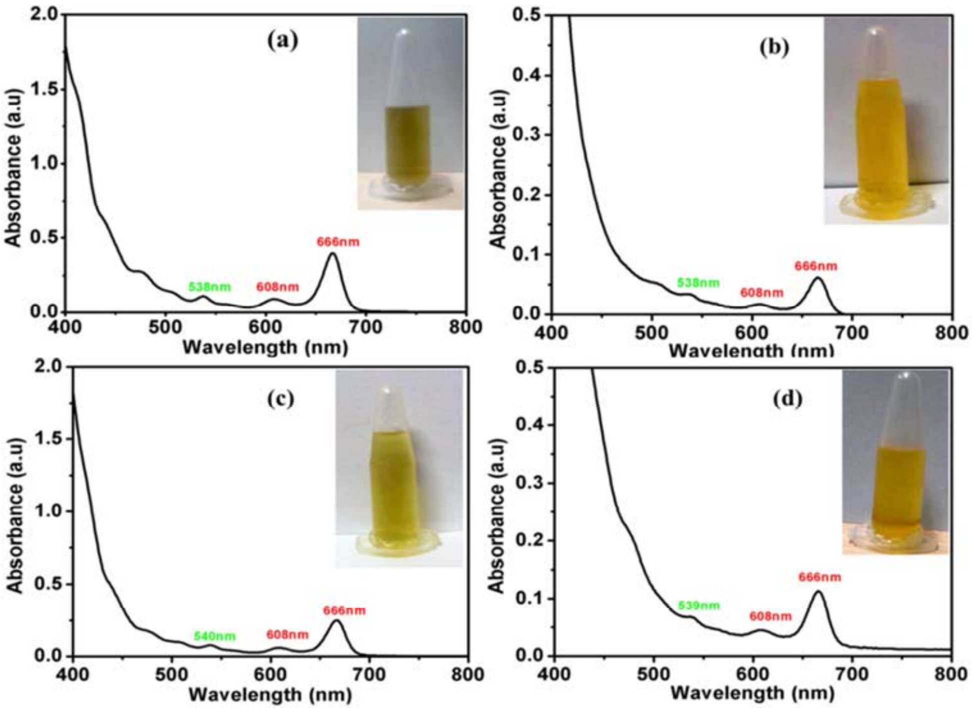

Figure 3. *UV-Vis absorption spectra for photo-sensitizer obtained from fruit peels (a) Citrus paradisi (b) Citrus sinensis (c) Citrus limon and (d) Citrus tangelo alcoholic extracts with the inset showing digital image of dye solution.*

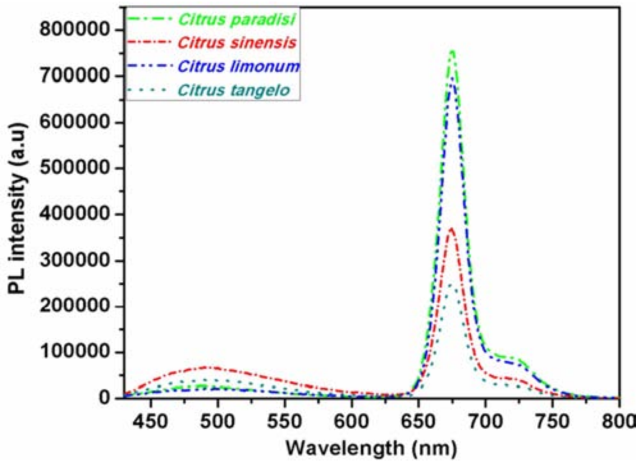

Figure 4. *The spectra of Fluorescence emission of natural dye obtained from citrus fruit peels.*

3.4. Photo-Luminescence Studies of Natural Pigments

The study of photoemission of all the extracted dyes is necessary because there may be possible correspondence between the phenomenon of photoelectron emission 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. Figure 4 shows the steady-state PL spectra of *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* dye extracts in alcohol. There is common fashion of maximum fluorescence intensity centered at 495 nm and 675 nm with an arm at 725 nm. The photoemission intensity of all the dyes at 675 nm with an arm at 725 nm indicates the characteristic response of pheophytin ‘a’. They all exhibited a little red shift compare to that of chlorophyll derivative. The chlorophyll and its derivative molecules may possibly aggregate in polar solvents and upon aggregation; their absorption and PL spectra describe bathochromic shift [22]. Also, emission intensity of all the dyes at 495 nm indicates the existence of other non-chlorophyll pigment with photoluminescence property. This result confirms that, there are other pigments present and it corroborates well with absorption spectra in Figure 3.

3.5. Fourier Transform-Infrared (FT-IR) Studies of Natural Photo-Sensitizers

The plotted FT-IR spectra of natural pigments from *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* fruit peels as revealed in Figure 5 exhibit major feature peaks of chlorophyll derivatives [23]. It is observed that all four dyes extracted have similar spectral shape. The strong and broad bands at 3420-3435 cm^{-1} are due to either –OH groups of water and alcohol or N-H band, a band at 1063 cm^{-1} corresponding to C-O-C vibrational mode of acid and carbohydrate groups; and two observed peaks at 2924 cm^{-1} and 2845 cm^{-1} correspond to asymmetric and symmetric –CH stretching modes respectively. Consequently, the point at 1618-1638 cm^{-1} corresponding to the double bond (C=C) stretching vibration and can be compared to the stretching mode of aromatic C=C in carotenoid or chlorophyll derivative [16]. The FT-IR spectra studies also establishes the existence of pheophytin ‘a’ in all the four fruit peels extracts, which is well corroborated with the UV-Vis absorption and PL spectroscopic results.

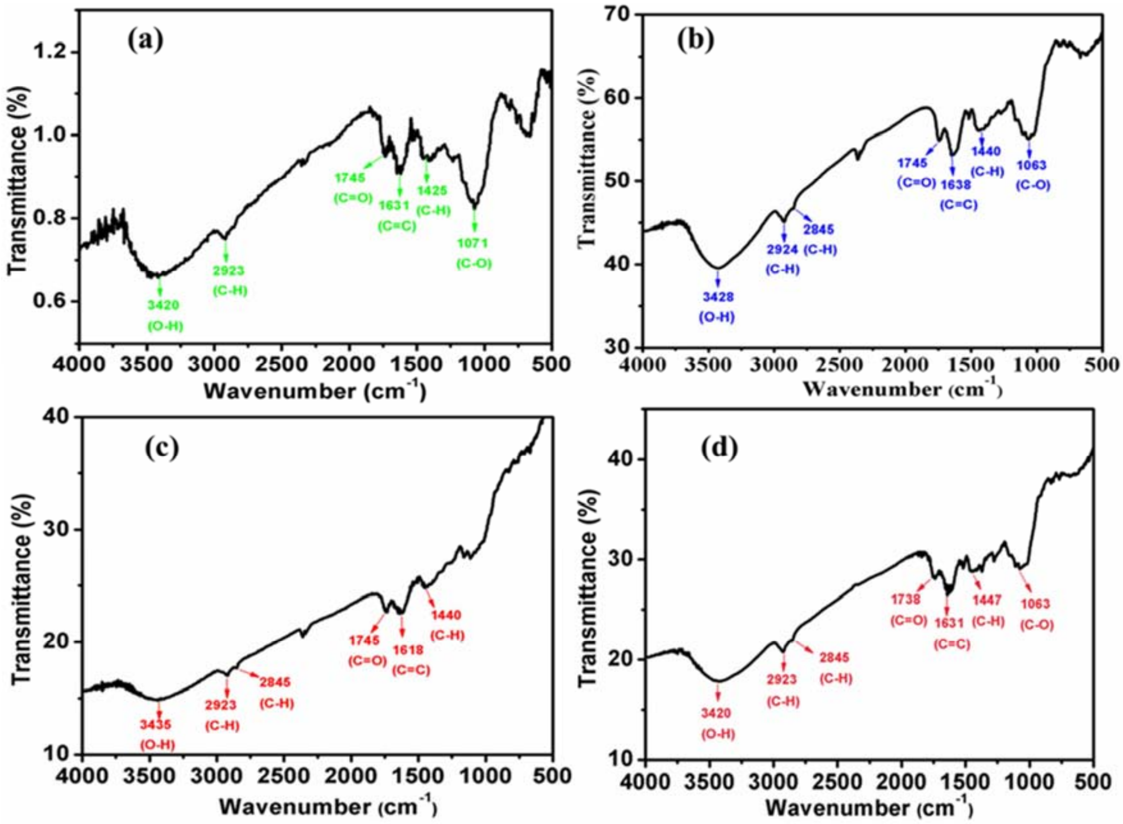

Figure 5. *FT-IR spectra of natural dye obtained from fruit peels (a) Citrus paradise (b) Citrus sinensis (c) Citrus limon and (d) Citrus tangelo.*

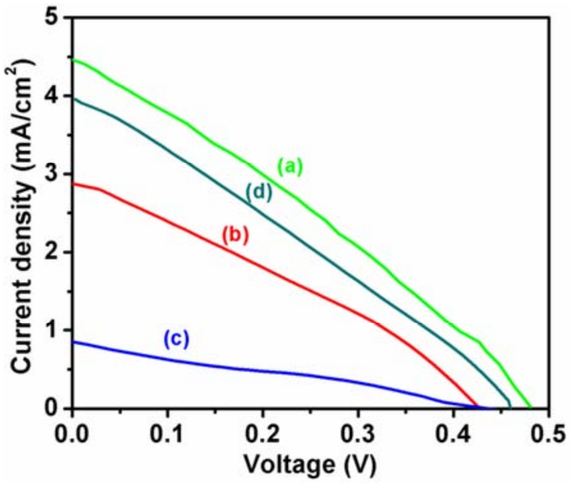

Figure 6. *Curves of current density versus voltage for DSSCs sensitized by (a) Citrus paradisi (b) Citrus sinensis (c) Citrus limon (d) Citrus tangelo alcoholic extracts.*

Table 1. *Photo-electrochemical parameters for natural dye DSSCs sensitized by Citrus paradisi, Citrus sinensis, Citrus limon and Citrus tangelo alcoholic extract.*

Natural Dye	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Efficiency, η (%) ± 0.05
Citrus paradisi	0.482	4.477	29	0.63
Citrus sinensis	0.428	2.885	29	0.36
Citrus limon	0.434	0.852	27	0.10
Citrus tangelo	0.459	3.971	28	0.51

3.6. Photovoltaic Performance

The cell performances of the natural sensitizers in 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 revealed in Figure 6 and the corresponding photo-electrochemical parameters for the constructed cells are summarized in Table 1. The efficiency of the DSSCs fabricated with natural pigments from *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* peels are 0.63%, 0.36%, 0.10% and 0.51%, respectively. The lower efficiency recorded from the solar cells constructed 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 TiO_2. Notably, TiO_2 photo-anode provides paths for the electrons conduction while better still maintaining better adsorption of dye at its surface area. Therefore the natural dyes used as photo-sensitizers in DSSC showed very low efficiencies compared to synthetic dyes because of non-existence of better interaction between the dye and TiO_2 surfaces through which electrons can move from molecules of excited dye to TiO_2 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 [5]. More molecules of dye available on the TiO_2 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 constructed cells. The DSSC constructed with *Citrus paradisi* dyes extract shows relatively higher Jsc and enhanced efficiency of 0.63% compared to *Citrus sinensis, Citrus limon* and *Citrus tangelo* dyes. From the above results, the *Citrus paradisi* natural extract may be worthy substitute for the solar cell application.

4. Conclusion

The natural photo-sensitizers from *Citrus paradisi, Citrus sinensis, Citrus limon* and *Citrus tangelo* fruit peels were successfully appraised 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 some other minor components. The FT-IR studies for the natural dye resemble the structural properties of pheophytin 'a' and minor component like carotenoid. The photovoltaic performance reveals that the maximum efficiency acquired for the constructed cell with *Citrus paradisi peels extract* is 0.63%, while the constructed cells efficiency with *Citrus sinensis, Citrus limon* and *Citrus tangelo* extracts are 0.36%, 0.10% and 0.51%, respectively. The higher efficiency observed for DSSC with *Citrus paradisi* is owing to better adsorption of dye molecules available to TiO_2 film and enormous charge transfer resistance at TiO_2-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 *Citrus paradisi* dye and more optimization of the cells.

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