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Photovoltaic Solar Cell Based on Chlorophyll Dye Pigments Obtained from *Brassica oleracea*

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ABSTRACT

In this work, dye sensitized solar cell employing commercial TiO_2 *as photoanode was fabricated using natural dye pigments obtained from Brassica oleracea (Green Cabbage) as photosensitizer. UV-VIS spectrophotometry was used to determine the optical properties of the dye. Experimental results shows that for this cell, the open-circuit voltage* (V_{OC}) *was found to be 0.246 V, the short-circuit current density* (J_{SC}) *was 0.193 mA/cm*^{2}*, fill factor (FF) was obtained as 0.413 and power conversion efficiency* (η) *was 0.0196%. Absorption spectra for the extract show small peaks at 336 and 605 nm, with optimal peak at 665 nm. The result suggests that while a Brassica oleracea-sensitized solar cell is possible, it is a poor source of chlorophyll and has limited viability as a photosensitizer for the manufacture of DSSCs.*

Key Words: *Photovoltaic, Brassica oleracea, Chlorophyll,* TiO_2*, DSSC, Natural dyes.*

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1. INTRODUCTION

Global energy requirements and consumption is steadily increasing with experts and analysts predicting an even higher energy demand in the near future. Generating enough energy to meet this increasing global demand has become of a key worry to governments all over the world. Renewable energy sources can not only help solve the looming crisis, but can aid developing countries grow economically and do same without degrading the environment. Renewables remain the world's fastest growing energy source and as such continue to attract the attention of experts in the energy sector [1]. The various alternative energy sources include biomass, wind energy, hydro-power, solar energy and geothermal energy. Most photovoltaic solar cells are typically made of semi-conducting material such as Silicon. Other materials include Cadmium Telluride (CdTe), Copper Iridium Selenide (CIS), and Copper Iridium Gallium (di) Selenide (CIGS). Conventional solar panels comprise of a lot of silicon-based solar cells which require faultless and pure silicon crystals for the manufacture of each cell. The process of producing and growing flawless silicon crystals is complicated, energy intensive and time consuming, making these crystals expensive to manufacture on a small scale. However, since its invention in 1991 by Michael Grätzel and Brian O'Regan, Dye Sensitized Solar Cells (DSSCs) have proven to be a very promising alternative to silicon-based solar cells due to availability of low-cost raw materials and ease of manufacture [2].

The operating principles of the cell as illustrated in Figure 1 can be summarized into the following stages: (1) Passage of electron through a cycle of excitation upon absorption of light energy (Photons). (2) Injection of emitted electron into the semiconductor conduction band. (3) External work done by electron upon loading. (4) Regeneration of dye to initial state by electron transfer from electrolyte and electrolyte-dye reduction. (5) Regeneration of oxidized electrolyte at the counter electrode.

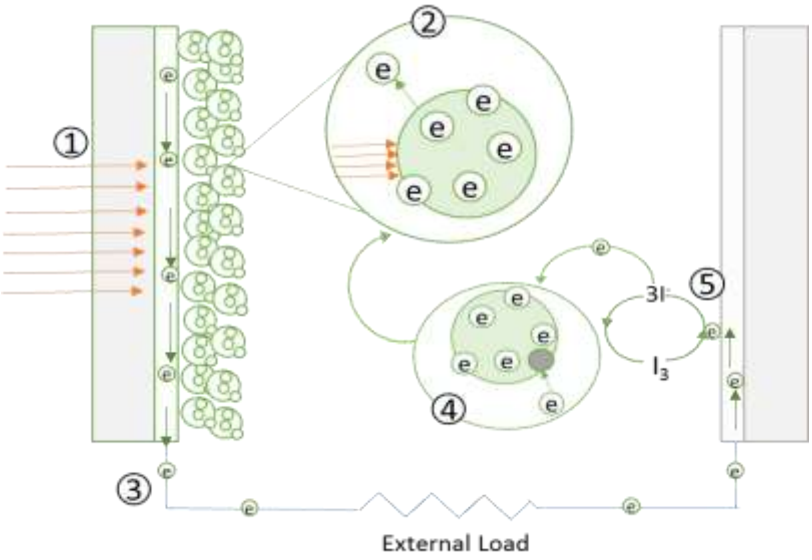

Figure 1 Operating principles of the cell.

A typical configuration of a DSSC consists of the several components including Transparent Conducting Oxide (TCO) coated glass substrate, semiconductor, photosensitizer, electrolyte and counter electrode, arranged in sequence. The most commonly used semiconductor in DSSCs is TiO$_2$. Titanium dioxide (TiO$_2$) is a white powdery solid that is often used as a white pigment in wall paint, food colours, tooth paste, and sunscreen. It is inexpensive, available, non-toxic, chemically and structurally stable with a wide band gap of 3.0 – 3.2 eV [3].

Due to the limited ranges of optical absorption of the TiO$_2$ semiconductor (mostly in the ultraviolet regions), various dyes have been explored in order to extend the absorption of solar radiation to the visible and near-infrared (NIR) regions of the spectrum. Inorganic complexes, like Ruthenium (N3 and N-749) dyes have shown good photovoltaic conversion efficiency, with over 10% efficiency reported [4]. However, due to several drawbacks, such as high cost, limited availability, complex synthesis process and toxicity of these inorganic materials, new dye materials, especially natural dyes are been developed to serve as alternatives to these compounds [5]. Natural dyes have the advantage of low cost, abundance and environmental safety. Various works have been done using natural dye sensitizers. Reference [6] and co-workers produced as cell using a natural dye extract from *Lonchocarpus cyanescens*, obtaining an efficiency of 0.37%. Other dye extracts that have been studied include *Hibiscus sabdariffa* [7]; *Papaya* leaves [8], among many others. Organic dyes, however, have so far shown lower conversion efficiencies than metal complexes.

In this work, chlorophyll dye extract, obtained from *Brassica oleracea* (also known as Green cabbage) was used to fabricate DSSCs, using commercial TiO$_2$ as semiconducting material. Green cabbage is a leafy, flowering food plant belonging to the *Capitata* cultivar group of the species *Brassica oleracea* of the mustard family *Brassicaceae* (or *Cruciferae*). This leafy head vegetable was originally native to the Mediterranean regions of Europe but is now a common staple food all over the world.

2. MATERIALS AND LABORATORY REAGENTS

The materials and laboratory reagents used in this work are listed as follows: Acetic acid 99.5% (CH_5COOH), Acetonitrile (CH_2CN), Ethanol 99.8% (C_2H_5OH) (BDH Poole England), Titanium dioxide powder (TiO$_2$) (Qualikems Ltd., India), Potassium Iodide (KI) (Burgoyne Burbidges & Co., India), Iodine (I_2) pellets (Chem Light Chemicals, India), Cabbage Leaves and FTO glass slides was obtained from (Sigma-Aldrich, USA). All reagents were used without further purification.

3. EXPERIMENTAL METHODS

3.1 Dye Preparation:

Freshly washed Cabbage leaves were cut into smaller pieces and dried at room temperature away from direct sunlight. The dried leaves were pulverized using an electric blender so as to reduce the surface area and 10g of the substance was weighed using an electronic weighing balance. 100 mL of ethanol was added to the powder and agitated using a magnetic stirrer for 1 hour to obtain a homogenous mixture. The mixture was allowed to stand for 24 hours. Filtration of the extract to obtain dye pigment was done using filter paper and the dye extract was stored in a labelled sample bottle. Figure 2 provides images of the dye preparation process.

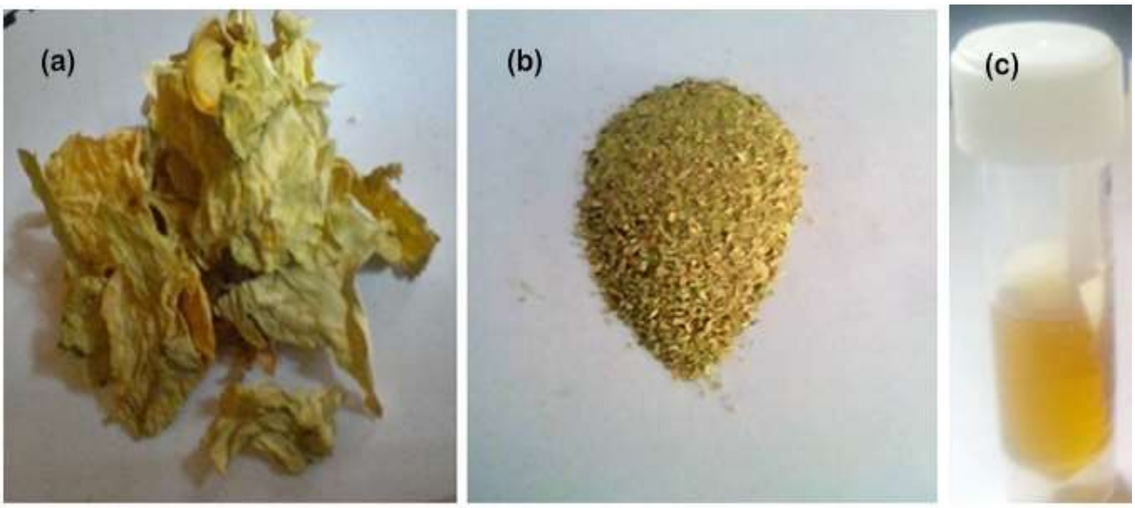

Figure 2 (a) Dried *Brassica oleracea* leaves, (b) Crushed sample and (c) Dye extract.

3.2 Electrode Preparation:

FTO glass slides (Sigma-Aldrich) measuring (50 × 25) mm with surface resistance of 10 Ω/m^2 were first cut into suitable sizes and then lightly washed with detergent, rinsed in distilled water and finally ethanol. The slides were subsequently dried in an oven at 70^0C for 10 minutes before coating with the TiO_2 layer. The colloidal paste was prepared by adding 6g of titanium dioxide to a mortar. A few drops of 0.035M acetic acid was added to the TiO_2, in 1 mL increments and ground in a circular motion for about 1-2 minutes, until a total of 7 mL of acid was used. The resulting suspension was allowed to equilibrate for 10 minutes.

An area of 3 cm^2 was marked out using transparent tape. 2-3 drops of the TiO_2 paste was deposited onto the conductive side of the glass substrate and spread out evenly on the surface with the edge of a microscope slide using Doctor Blade technique. The deposited TiO_2 film was allowed to dry at room temperature for 30 minutes and then sintered in a furnace by heating to 450^oC for another 30 min.

3.3 Counter Electrode Preparation:

Coating of the conductive side of the counter electrode was done using the procedure described by [8] with minor variations. This involved moving the piece of glass substrate slowly from side to side over a candle flame to deposit carbon soot for at least 45 seconds. The glass was heated in an oven at 100^0C for 15 minutes and subsequently cooled to room temperature.

3.4 Cell Assembly:

The photoanode consisting of electrode coated with a thin film of TiO_2 semiconductor was submerged face-down in a petri dish containing about 5 mL of a dye solution and allowed to soak for 24 hours for adequate sensitization to take place. The electrode was rinsed with distilled water, then ethanol so as to carefully remove excess dye particles. Both components were clamped together using binder clips and a few drops of the KI/I_2 electrolyte solution was introduced into the interface between the plates. The electrolyte was allowed to cover the surface of TiO_2 semiconductor by capillary action and the subsequent sandwiched DSSCs were obtained.

4. RESULTS AND DISCUSSION

4.1 Optical characterization:

The absorption spectra for the dye pigments is presented in the Figure 3.

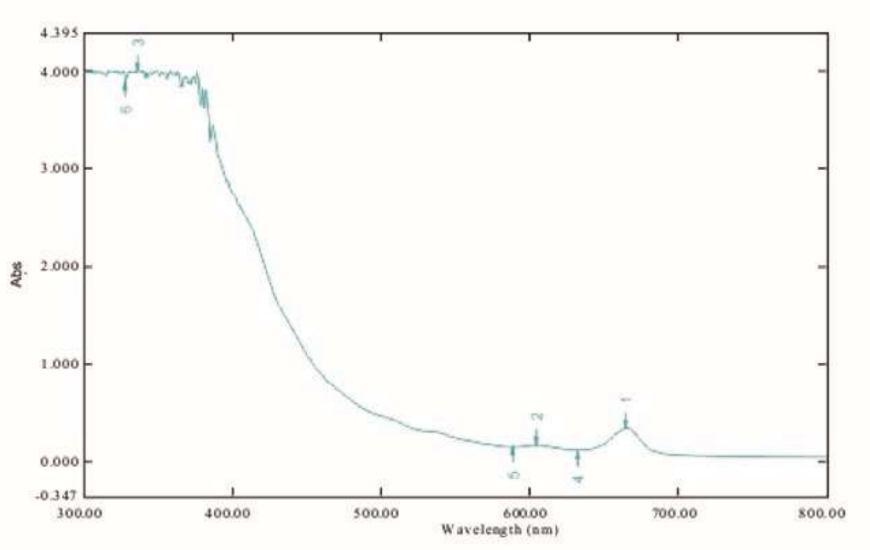

Figure 3 Absorption spectra of *Brassica oleracea* extract.

The chlorophyll extract shows peak values at 336 nm, 605 nm and optimal peak value of 665 nm. The wavelength corresponds mostly to the colour red in the visible light spectrum and is slightly different from the peaks observed in the work of [9], in which a peak values of 436 nm and 670 nm was reported. This observation indicates that the pigments contained in *Brassica oleracea* consists mainly of two chlorophyll types, namely type-a chlorophyll molecules and type–b molecules. The spectra results however shows low absorption peak values though the extract sample was undiluted when absorption analysis in the spectrophotometer was being carried out. . The low values obtained may be attributed to the method of preparation of the specimen, which involved a drying process. This, however, is inconclusive as [10] suggests that some plant containing chlorophyll pigments showed improved quality of extract and cell efficiencies when pigments were extract from dried samples as opposed to fresh ones. The analysis result obtained here is comparable to the work of [11], which also documents low chlorophyll values for *Brassica oleracea*. This observation suggests that *Brassica oleracea* may not be a good source of chlorophyll dye and as such may not be suitable for use in the manufacture of DSSCs.

4.2 Photovoltaic Characterization:

The current density-voltage and power curves are displayed in figures 4 and 5.

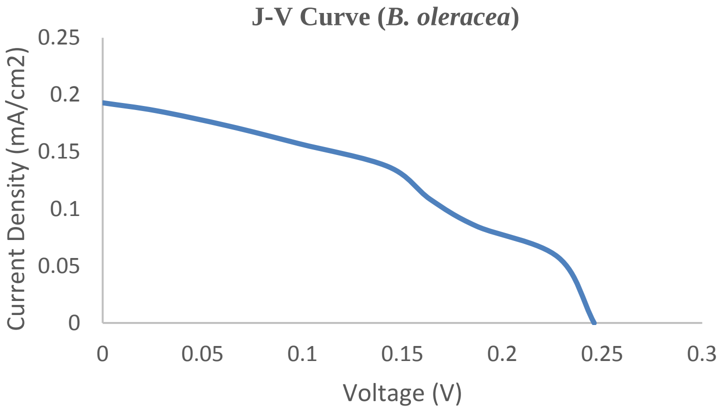

Figure 4 J-V Curve for *B. oleracea*-dyed cell.

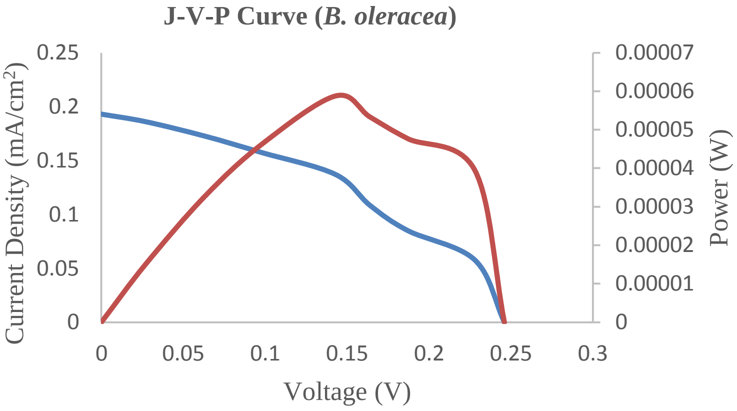

Figure 5 J-V-P Curve for *B. oleracea*-dyed cell.

The J-V plot for green cabbage dye DSSC shows a deviation from an ideal curve line. The plot line may be indicative of the unstable output observed during the analysis, hence the low values of voltage recorded. This may be attributed to very little dye pigments being absorbed on the surface of the TiO_2 coated electrodes. It is clear that the efficiency of this cell sensitized by the *Brassica oleracea* extract is low. This could be as a result of low intensity and narrow range of the light absorption of the extract and the poor interaction between the TiO_2 semiconductor and chlorophyll pigments in the *Brassica oleracea* extract, leading to a reduced charge transfer within the cell. The highlights of the important cell parameters are shown in table 1.

Table 1 Parameters of Photovoltaic Characterization.

Cell Type	**J_{MAX} (mA/cm^2)**	**V_{MAX} (V)**	**J_{SC} (mA/cm^2)**	**V_{OC} (V)**	**Fill Factor (FF)**	**Efficiency % (η)**
Cabbage	0.137	0.143	0.193	0.246	0.413	0.0196

5. CONCLUSION

Dye sensitized solar cell (DSSC) using commercial TiO_2 as photoanode was successfully fabricated with chlorophyll dye pigments extracted from *Brassica oleracea* as sensitizer. The research findings indicate that *Brassica oleracea* is a poor source of chlorophyll pigment with optical analysis showing a narrow absorption band for the extract. Low chlorophyll content of extract, inefficient charge injection into the TiO_2 structure and poor electron collection due to low regeneration kinetics between dye molecules and electrolyte could be responsible for the low power conversion efficiency observed in the cell. It is unclear if the mode of preparation of sample before dye extraction had any impact on the quality and quantity of chlorophyll extracted from the plant. Further studies in this direction may be required.

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