Development of TiO$_2$-based dye-sensitized solar cells using natural dyes extracted from some plant-based materials

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The need for a green and more environmentally friendly energy production has led to recent research into the use of natural products in the production photovoltaic cells. In this study, TiO$_2$-based dye-sensitized solar cells (DSSCs) were fabricated using photo-sensitizers made from ten natural dyes extracted from different plant parts (i.e. seeds, stalks, peels and flowers) of some selected plants and using candle soot carbon as a counter electrode. The chemical composition of the materials was determined using basic phytochemical screening assays. The extracted dye materials were characterized using UV and IR methods after which they were used in developing DSSCs. The DSSCs were then characterized under AM 1.5 illuminations to measure their photo-electrochemical properties. The dyes containing carboxyl and hydroxyl functional groups showed weak to large absorption under the visible light (400-700 nm) irradiation. The photo-electrochemical performance of the various cells gave an efficiency of as high as 0.18% with open circuit voltages ranging from 0.28 to 0.45 V and short-circuits photocurrent densities from 0.26 to 1.69 mA.cm$^{-2}$. Better efficiencies can be attained by improving the DSSC constructional parameters.

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Capsule Summary: Plants extracts have been found to be a good potential for solar photovoltaic technologies known as DSSC with the advantage of easy processing and sustainability of the materials.


INTRODUCTION

Energy and fuel crisis are of great concern all over the world. Natural sources of energy such as fossil fuels have been supporting global energy needs for decades. However, fossil fuels are depleting drastically with the demand for energy increasing everyday forcing countries to use much more of their natural resources. Besides, the combustion of fossil fuels emits tons of carbon dioxide which is considered as a pollutant and a major cause of global warming, hence, climate change (Solomon et al., 2009). With these concerns, there is an urgent need for sustainable, renewable and more environmentally friendly energy resource. Solar energy, hydro power, geothermal energy, biomass and wind energy are alternative sources of energy which are renewable though having individual advantages and drawbacks. Wind and hydro sources of energy face resource instability, as the
wind does not blow all the time at all locations and the sea tides are also unpredictable (Godfrey, 2004); geothermal and biomass energy sources cause environmental problems, as they require tempering with the earth's crust and the flora respectively (Godfrey, 2004). Solar energy is a reliable and sustainable resource as the sun shines all over the globe, which is easily accessible to even deprived areas and can be used as either a heating source or as electrical energy. Recently, engineering researches have been focused on converting solar radiation into electrical energy in an efficient and economical manner through devices known as solar photovoltaic devices (Azarpour and Suhaimi, 2013).

Generally, photovoltaic devices or solar cells are devices that directly convert sunlight or sun energy into electrical energy. The first generation of the solar cell consists of monocrystalline silicon solar cell. However, they are very expensive to fabricate as requiring high cost machinery and high purity process. Besides, silicon based solar cells are temperature sensitive (Pagels et al., 2009). A new generation of solar photovoltaic named dye-sensitized solar cells (DSSCs) drew researcher's attention as it seems to be solving the drawbacks of the conventional one (Bat et al., 2013; Grätzel, 2003; Sirimanne et al., 2006). The DSSC imitates the way in which plants harness solar energy. It is based on meso-porous nano-structured metal oxide semiconducting materials sensitized to the visible light by an absorbed dye molecule (Cavallo et al., 2017; El-Agez et al., 2012; Grätzel, 2003). The dye molecule plays the role of absorbing visible light and injecting electrons into the conduction band of the semiconductor material. The injected electrons move through the semiconductor film and reach the current collector. An electrolyte added to the system, is in charge of regenerating the dye (Ludin et al., 2015; Muthukumarasamy et al., 2011; Miettunen et al., 2008; Sma et al., 2010; Sirimanne et al., 2006). To date, the most efficient DSSCs were obtained using ruthenium bipyridyl complexes dyes which absorb a large portion of the solar spectrum (visible light especially), have excellent stability, easily absorbed by the semiconductor film and present very good electron injection ability (Boschloo and Hagfeldt, 2009; Hemmatzadeh and Mohammadi, 2013, Mathew et al., 2014; Omid et al., 2014; Shelke et al., 2013; Wang et al., 2010; Yu, 2012). However, ruthenium-based compounds are relatively expensive, and research showed that organic dyes with similar characteristics and even higher absorption coefficients are potential alternatives; solar cells with efficiencies of up to 9% have been reported to have been achieved using the organic dyes (Bessho et al., 2010; Gehlot and Sekar, 2010; Lan et al. 2012; Richhariya et al., 2017). These organic dyes present the advantage of fast charge transport and the possibility of using high viscosity electrolyte such as ionic and solid electrolytes (Furukawa et al., 2009; Kay and Grätzel, 1996; Lan et al., 2012; Noshin and Masoud, 2012; Omid et al., 2014). It was also observed that the organic dyes used in DSSCs resemble the dyes or pigments present in coloured natural materials such as plants’ parts and animals feathers (Kushwaha et al., 2013; Narayan and Raturi, 2011). Since then, intense research on natural materials based dye-sensitized solar cells have been done (Aal, et al., 2017; Abdel-latif et al., 2015; Hemalatha et al., 2012; Miettunen et al., 2008; Muthukumarasamy et al., 2011; Omid et al., 2014; Patrocinio et al., 2009; Prakash, 2012; Bessho et al., 2010; Gehlot and Sekar, 2010; Lan et al., 2012; Richhariya et al., 2017; Wongcharee et al., 2007).

The aim of this work was to explore the potential of naturally occurring dyes as sources of molecular sensitizers in the production of dye-sensitized solar cells (DSSCs). Natural dyes were extracted from sorghum stalk (Sorghum bicolor), Dawadawa or Dorowa fruit peels (Parkia biglobosa), Red onion peels (Allium cepa), Achiote seeds (Bixa orellana), yellow and pink Frangipani flowers (Plumeria rubra), Flamboyant tree flower (Delonix regia), Oleander flower (Nerium oleander), Thevetia flower (Thevetia peruviana) and White trumpet flower (Tabebuia rosea).

MATERIAL AND METHODS

Chemicals and reagents

All chemicals were of analytical grade and chemically pure. Ethanol (96%) was purchased from Central House Drug Ltd (India). Hydrochloric acid, picric acid, potassium mercury iodide, sodium hydroxide, hydrogen peroxide, ammonium hydroxide, acetic acid, benzene, bromine water, chloroform, acetic anhydride, sulphuric acid (concentrated), ferric acid (2.5%), acetic acid, iodine and potassium iodide crystals, and ammonia were all obtained from VWR ProLabo Chemicals (UK). Lithium iodide was purchased from SureChem Products Ltd (UK) and Sigma-Aldrich Corporation (USA); and Titanium dioxide (TiO₂) nanoparticle paste (Ti-Nanoxide T/SP) and ruthenium dye N719 were purchased from Solaronix S.A (Switzerland). The TiO₂ paste used is 100% anatase with a pore size between 15 to 20 nm in a medium of terpineol and organic binders with a concentration of about 18% by weight (Solaronix, 2013).

Apparatus and instruments

Basic laboratory tools, an oven, a UV light and a carbolite furnace were used throughout the experiment. For the photovoltaic properties test, some pieces of Indium doped Tin Oxide (ITO) coated glass (50 x 50 mm, 1.1 mm thickness, resistivity < 6Ω/cm²) were purchased from china; an AM 1.5 illuminations set up was made using a 50 W white LED lamp (100 mW/cm²), a solar irradiance meter, a lux meter (TASI-8721) and a decade resistance box ELC DR 06 GENTRAD (Philippines); some binding clips, a candle and a transparent tape. For the infra-red analysis, an Ultra Attenuated Total Reflectance Fourier Transform Infrared (UATR-FTIR) spectrometer Perkin Elmer Spectrum Version 10.03.09 (USA) was used. For the ultraviolet analysis, a Shimadzu UV mini-1240 spectrometer (USA) was used and for the elemental analysis, a Vario Macro CUBE elemental analyser (Germany) was used.
Fig. 1: A summarized dye-sensitized solar cells (DSSC) fabrication process

Fig. 2: A schematic diagram of a DSSC working principle
Sample collection and preparation

Samples were taken on campus (KNUST) and some were purchased from a local market in Kumasi, Ghana. The samples collected were dried in an oven at 50°C on a daily basis until a constant weight was observed. Then, the dried samples were milled with an electric blender and sieved using a 1 mm mesh. The samples were finally stored in plastic containers in a dried environment away from sunlight.

Phytochemical screening test

A 0.05g of dried dye powder was used in each of the phytochemical screening test for all the dyes. The tests for the presence of the following phytoconstituents were done: alkaloids (Hager’s test), coumarins, glycosides (Bromine water test), saponins (Froth test), sterols (Liebermann-Burchard test), tannins (Ferric chloride test), triterpenoids (salkowski’s test), flavonoids (alkaline reagent test), carotenoids and anthraquinones (Chien et al., 2014; Delgado-vargas et al., 2010; Kallo et al., 2018a; Taylor and Jimenez, 2012).

Extraction

A 10 g of dried dye powder was immersed in 100 mL ethanol for 48 h in a dark environment at room temperature (~28°C). Filtration was done using a 1 mm mesh and the solid residue was subjected to two further extraction processes using 70 mL and 40 mL ethanol respectively with 48h interval followed by filtrations and storage of the dye solutions together in the same container at the end. The resulting dye solution was left to dry at ambient temperature under ventilation for days well-protected from direct sunlight until a constant weight was observed. The final dried extract was stored in a fridge (T = 0-4°C) for further analysis.
Analyses

Different concentrations from 1 to 20 mg/mL of the individual extracts were prepared in ethanol and their UV spectra were taken. After the cell's fabrication, a piece of the dye-absorbed TiO$_2$ glass of 1x4 mm was inserted into the UV spectrometer in order to get the corresponding cell's absorption spectra. Dried powders of each of the samples were also analysed under FTIR spectrometer for their functional groups' identifications. Finally, a powder of the counter electrode was analysed under an elemental analyzer for its elemental composition.
DSSC fabrication process

Preparation of the electrolyte solutions

The electrolyte solution was prepared by mixing in acetonitrile an iodine solution of 0.05 M and an iodine salt solution (lithium iodide) of 0.5 M at a 1:1 volume ratio.

Preparation of the working electrode

Some pieces of ITO glass were cut to the desired size and the conductive sides were detected using a digital multimeter. A thin film of titanium dioxide paste was deposited by doctor blade method and was sintered at 450°C for 1 h in a carbolite furnace in ambient air. The pieces of glass were left to cool to room temperature and then were immersed into the various ethanol dye solutions for one (1) month. After absorption, the electrodes were rinsed with ethanol to remove unbounded dye molecules.

Preparation of the counter electrode

A candle was allowed to smoke for 5 minutes. Later, a piece of ITO glass was brought to cause hindrance to the candle smoke flow at an angle beyond 5° for the carbon from the smoke to be deposited onto the conductive side of the ITO glass till the glass was coloured black.

DSSC assembly

The individual working electrode was put on top of the counter electrode and two binding clips were used to close them firmly. The electrolyte was then added from the other side (top or down) and allowed to fill-in the gaps by capillary action.

Photo electrochemical tests

The fabricated dye-sensitized solar cells were illuminated under an LED projector lamp with an incident power of 100 mW/cm² and an illumination area of 1 cm². Current and voltage were measured using two HoldPeak HP-90EPC digital multimeters connected to a personal computer (PC) One measuring the voltages and the other measuring the corresponding currents (Fig. 1 and 2).

RESULTS AND DISCUSSION

The presence of phytoconstituents in the plant materials give an idea of the naturally occurring chemical compounds responsible for the colouring and other organoleptic properties of the materials (Ananda et al., 2014; Delgado-vargas et al., 2010; Stathalo, 2012). The phytochemical screening test was performed to ascertain the presence of certain secondary metabolites responsible for the pigmentation in plants. Results obtained from the phytochemical analysis in the study are shown in Table 1.

| Table 1: Results obtained from the phytochemical screening test of various plant materials |
|---------------------------------|--|--|--|--|--|--|--|--|--|--|
| Chemical Constituents          | Sor | Daw | Oni | Ach | FPY | FPP | Flamb | NO | Thev | WT |
| Alkaloids                      | +   | -   | +   | +   | +   | +   | +     | +  | +    | +  |
| Coumarins                     | +   | -   | -   | -   | +   | +   | +     | +  | +    | +  |
| Glycosides                    | -   | -   | -   | -   | -   | -   | -     | +  | +    | +  |
| Saponins                      | +   | +   | +   | +   | +   | +   | +     | +  | +    | +  |
| Sterols                       | +   | -   | -   | -   | -   | -   | -     | +  | +    | +  |
| Tannins                       | +   | +   | +   | +   | +   | +   | +     | +  | +    | +  |
| Triterpenoids                 | +   | +   | +   | +   | +   | +   | +     | +  | +    | +  |
| Flavonoids                    | -   | -   | -   | -   | +   | +   | +     | +  | +    | +  |
| Anthocyanins                  | -   | -   | -   | -   | +   | +   | +     | +  | +    | +  |
| Carotenoids                   | +   | -   | -   | -   | +   | +   | +     | +  | +    | +  |
| Anthraquinones                | +   | -   | -   | -   | -   | -   | -     | +  | +    | +  |

+ indicates present, - indicates absent

| Table 2: The elemental analysis results of candle soot carbon-based counter electrode |
|---------------------------------|--|--|--|--|--|--|--|--|
| Weight (mg) | Name | Method | Nitrogen (N) [%] | Carbon (C) [%] | Humidity [%] |
| 5           | C-dep Coal | 0.11±0.01 | 99.78±1.11 | 0 |
The results revealed the presence of anthocyanin, carotenoids and flavonoids and these results are in agreement with similar phytochemicals investigated in the plants extract. It was also added that these plants’ phytochemicals, mostly used in the textile for their dyeing property, have a potential use as sensitizers for energy collection (Delgado-vargas et al., 2010; Kallo et al., 2018a).

From the basic phytochemical analysis, the presence of the already identified compounds were confirmed by subjecting the crude extracts to UV-Visible spectroscopy (UV-Vis) and Fourier transform spectroscopy (FTIR) to get their absorption capabilities. The presence of the identified compounds was confirmed by the presence of their anchoring functional groups, such as carbonyl and hydroxyl functional groups (Figure 3-10) (Kallo et al., 2018a). The compound identified as having good binding functional groups and a large light absorption spectrum, are qualified to be used as photo-sensitizers for energy generation in dye-sensitized solar cells (Calogero et al., 2010; El-Agez et al., 2012; Kallo et al., 2018a). In order to confirm this assumption, it is imperative to make use of them in DSSC and see their performances. The performance of the various dyes extracts as photo-sensitizers was checked by making up different solar cells from which the cells’ individual photo-current and the corresponding potentials or voltages were measured and the various current-voltage curves (IV-curves) were plotted. A ruthenium dye cell was used as reference cell (Fig. 11). All these tests are requirements for a dye to be considered as a good photo-sensitizer.

The results obtained showed that all the crude dye extracts absorbed within the visible light region (400 – 700 nm) (see figure 3 and 5). This proves the colour we see out of the plant extracts dye, could be attributed to π-π * transitions of -C = C- and -C = N- and / or -N = N-chromophores present in these dyes (Kallo et al., 2018b). Chromophores are needed for electron charge generation. Besides, after the fabrication of the cells, the various TiO2-dye electrodes were passed through the UV spectrometer and it was noticed that the anodes were absorbing similarly to their corresponding initial dye extract on one hand and better than the anodes with the TiO2 alone on the other hand. That shows that those plant-derived dyes really enhanced the cell’s absorption ability as shown in figures 4 and 6 (Kallo et al., 2018b; Kushwaha et al., 2013).

From the FTIR spectra presented in figure 7 and 8, the following assignments were made: a broad peak signal from 3600 to 2900 cm⁻¹ shows the O–H stretching vibration followed by two sharp peaks between 2900 and 2800 cm⁻¹ showing the C–H stretch due to methyl and methylene groups. At around 1700 cm⁻¹ the carboxylic C=O group is seen. The sharp peaks between 1700 and 1500 cm⁻¹ are due to the alkene C=C stretch. Between 1400 and 1300 cm⁻¹ the C–H bending of the methyl groups is observed. Between 1350 and 1200 cm⁻¹ the C=O acyl and phenyl vibrations and between 1200 and 1000 cm⁻¹ symmetric and asymmetric vibrations of the C–O–C ester group are also observed.
Table 3: Results obtained from the phytochemical screening test of various plant materials

<table>
<thead>
<tr>
<th>Dyes extracts</th>
<th>Concentrations prepared (mg/mL)</th>
<th>$\lambda_{\text{max}}$</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$P_{\text{max}}$ (mW/cm$^2$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorghum stalk</td>
<td>1</td>
<td>538</td>
<td>1.69</td>
<td>0.34</td>
<td>0.18</td>
<td>0.31</td>
<td>0.18</td>
</tr>
<tr>
<td>Dasdawoda</td>
<td>10</td>
<td>450</td>
<td>1.22</td>
<td>0.33</td>
<td>0.12</td>
<td>0.29</td>
<td>0.12</td>
</tr>
<tr>
<td>Red onion</td>
<td>5</td>
<td>449</td>
<td>1.68</td>
<td>0.28</td>
<td>0.16</td>
<td>0.34</td>
<td>0.16</td>
</tr>
<tr>
<td>Achiote</td>
<td>10</td>
<td>432</td>
<td>1.28</td>
<td>0.35</td>
<td>0.16</td>
<td>0.35</td>
<td>0.16</td>
</tr>
<tr>
<td>Flamboyan</td>
<td>10</td>
<td>458</td>
<td>0.81</td>
<td>0.42</td>
<td>0.1</td>
<td>0.29</td>
<td>0.10</td>
</tr>
<tr>
<td>Yellow Frangipani</td>
<td>10</td>
<td>452</td>
<td>1.12</td>
<td>0.42</td>
<td>0.15</td>
<td>0.32</td>
<td>0.15</td>
</tr>
</tbody>
</table>
These results confirmed those obtained from the phytochemical screening test. Indeed, the dye materials contain mixtures of aromatic and phenolic compounds capable of bonding with the titanium dioxide through carboxyl and hydroxyl groups and they absorb visible light as shown by their UV spectra. The observed functional groups may be as a result of the compounds such as alkaloids, anthocyanin, triterpenoids, carotenoids, flavonoids, anthraquinones, coumarins, tannins and saponins (Table 1) as obtained from the phytochemical analysis. According to literature, the family anthocyanin is mostly responsible for the reddish attractive colour of most flowers and plants parts. Generally, cyanin 3-O-glucoside is responsible for the red colour of the flowers of the flamboyant tree (Muthukumarasamy et al., 2011; Boyo et al., 2013) and in that of the frangipani species (Shanmugam et al., 2013). Furthermore, the Achiote seed dye was found to contain norbixin and bixin which was determined to be the main pigments responsible for the colour present in the seeds (Oskam et al., 2010). Norbixin and Bixin are compounds classified under carotenoids. Many phytoconstituents exist at a time in a given plant material with one or two being in high quantity. This has an effect on the final colour of the material which makes the detection the minority phytoconstituents difficult.

The I-V curves presented in Figure 9, 10 and 11 were obtained by recording all photo-electrochemical parameters (Table 3) of the fabricated cells under illumination of 100 mW/cm². The short circuit current (Jsc) ranged from 0.26 mA/cm² (Thevetia peruviana) to 1.68 mA/cm² (Ruthenium dye N719).
mA/cm² (Sorghum bicolor) and the open circuit voltage (Voc) ranged from 0.28 V (Allium cepa) to 0.45 V (Nerium oleander). The maximum power was obtained from the cell of Sorghum bicolor with a value of 0.18 mW/cm². As compared to the reference cell from the ruthenium N719 dye, the crude plant extracts cells had an acceptable Voc but a very low Jsc which means they suffer from poor electron injection and charge separation (Sharma et al., 2017; Taya et al., 2012; Tributsch, 2004). The cell from sorghum dye had the highest Jsc probably due to its high content in anthocyanin as shown by the tests conducted (Phytochemical and IR tests) and as shown that anthocyanin is found to be a naturally occurring dye that is holding the highest efficiency (Boyo et al., 2013; Tributsch, 2004). Carotenoid dyes do have a reasonable performance but relatively lower than the anthocyanin. It was found that betalain dyes could even perform more than anthocyanin dyes (Calogero et al., 2017; Zhang et al., 2008).

The elemental composition of the counter electrode used in the DSSCs was investigated (Table 2). Three tests were run and a standard deviation of 1.11 was found. This shows that the material used for the cathode in this research is indeed made mostly of elemental carbon. The other percentage of impurity was assigned to come from the contamination of nitrogen from the air since the deposit was done in an atmospheric environment. Investigations on the smoke of a candle proved that the smoke is comprised in majority of ultrafine particles (<100 nm) of elemental carbon, organic carbon, a small amount of organic matter and inorganic compounds (Pagels et al., 2009).

CONCLUSIONS

In this work, ten (10) plants species were successfully investigated and used as natural photo sensitizers for dye-sensitized solar cells. All the dye extracts presented good characteristics for a dye to be used as photo sensitizer including visible light absorption and the presence of anchoring groups such as hydroxyl and carbonyl functional groups. As a result, the extract from Sorghum bicolor presented the widest visible light absorption spectrum from far ultraviolet to near-infrared (300–900 nm) and the highest efficiency of 0.18%. These results are reasonable for raw impurified dye extracts and especially using a basic and cheap constructional method. Efficiencies could increase significantly if the assembly conditions and methods of measurement were to be improved.

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REFERENCES


