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Dye-Sensitized Solar Cells Using Natural Dyes Extracted from Roselle (*Hibiscus Sabdariffa*) Flowers and Pawpaw (*Carica Papaya*) Leaves as Sensitizers

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Abstract: Dye-sensitized solar cells (DSSCs) were fabricated using natural dyes extracted from roselle flowers and carica papaya leaves extract as photosensitizers. The photovoltaic perfomance of the DSSCs were evaluated under 100 mAcm^{-2} light intensity. The roselle (*Hibiscus Sabdariffa*) extract sensitized solar cell gave a short circuit current density (*Jsc*) of 0.180 mAcm^{-2}, an open circuit voltage (*Voc*) of 0.470 V, a fill factor (*FF*) of 0.552, and an overall solar energy conversion efficiency (η) of 0.046%. Also, the pawpaw leaves extract sensitized cell gave a *Jsc* of 0.094 mAcm^{-2}, *Voc* of 0.433 V, *FF* of 0.544 yielding a conversion efficiency of 0.022%. The cell sensitized by the roselle extract shows better sensitization, which was in agreement with the broadest spectrum of the extract adsorbed on TiO_2 film. The sensitization performance related to interaction between the dye and TiO_2 surface is discussed.

Keywords: DSSCs, Natural Dyes, Dye Extracts, Sensitization

1. Introduction

The first attempt to develop photo-electrochemical cells was dated back to 1873 and 1970s as a result of tremendous effort to replicate photosynthesis process [1,2].

However, due to difficulties in electrons movement through semiconductor layer after sensitization, the efficiency of the ever first sensitized solar cells was ~ 0.01 %

The problem was solved by the concept of nanotechnology in the late 1980s [1]. The use of dye-sensitization in photovoltaic remained difficult to be implemented until a major breakthrough in the Laboratory of Photonics and Interfaces in the École Polytechnique Fédérale de Lausanne (EPFL) Switzerland in 1991. It was achieved by the successful combination of nanostructured electrodes and efficient absorbing dyes. The sensitized solar cell recorded a conversion efficiency greater 7% [3] and in 1993, it was enhanced to 10 % [4]. This solar cell is called the dye sensitized nanostructured solar cell or the Grätzel cell named after its inventor professor Michael Gratzel.

Dye-sensitized solar cells (DSSCs) belong to the third generation of photovoltaic devices which is used for the conversion of photon energy at specific wavelength into electrical energy. These solar cells technology are based on the photosensitization produced by the dyes on wide band-gap semiconductors with nanoporous nature through dye adsorption [5].

The sensitization approach helps the generation of electricity with energy greater than the energy of the bandgap of the semiconductor nanocrystalline film. The progress of the DSSC device was made possible with the light absorbing dye molecules adsorbed on the semiconductor. Many efforts have been channeled on sensitizer dye, since dye plays a crucial role in harvesting sunlight and transforming solar energy into electric energy. Several organic dyes and organic metal complexes have been employed to sensitize nanocrystalline TiO_2 semiconductors [6].

Naturally, most flowers and leaves show various colours and contain several pigments which are easily extracted and then employed in DSSCs [7]. The leaves of most green plants dye has been investigated in many studies [8, 9, 10]. Anthocyanins are natural compounds that give colour to fruits and plants [11]. Roselle extract is rich in anthocyanins. It was reported that anthocyanin obtained from roselle are delphinidin and cyanidin complexes [12, 13]. The chemical structure of cyanidin and delphinidin in the *Hibiscus Sabdariffa* dye is shown in figure 4.

In this research work, anthocyanins extracts of roselle flowers, and chrorophyll extract from carica papaya leaves were the natural dyes used as sensitizers in the formed DSSCs. The performances of the formed DSSCs shows that, the roselle extract has higher photosensitized performance as compared to the pawpaw leaves extract.

The *Hibiscus sabdariffa* dye (commercially known as Roselle) belongs to the family *Malvacae* and is present in abundance through-out the world and has attained prominence as a jute substitute [14].

Pawpaw, belongs to the family of caricaceae. It is not a tree but a herbaceous succulent plants that posses' self-supporting stems of spongy and soft wood [15].

2. General Composition, Function and Parameters of the DSSCs

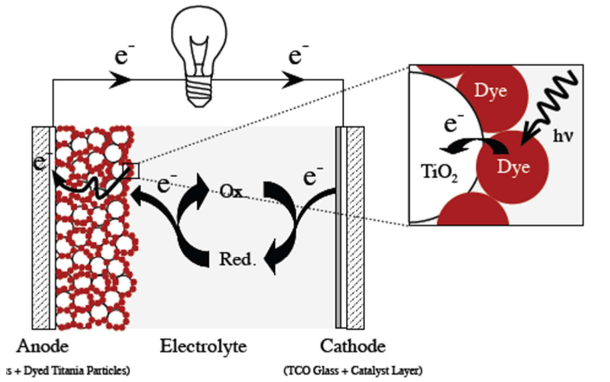

Figure 1. *Schematic of the structure of the dye sensitized solar cell [16].*

The cell is composed of four elements, namely, the transparent conducting and counter conducting electrodes, the nanostructured wide bandgap semiconducting layer, the dye molecules (sensitizer), and the electrolyte. The transparent conducting electrode and counter-electrode are coated with a thin conductive and transparent film (such as fluorine-doped tin dioxide (SnO_2)). The TiO_2 surface is stained with a dye. TiO_2 nanocrystals are used rather than a continuous layer to maximize surface area for light absorption. Between the electrodes is an electrolyte. Upon absorption of photons, dye molecules are excited as shown schematically in Figure 1. Once an electron is injected into the conduction band of the wide bandgap semiconductor nanostructured TiO_2 film, the dye molecule (photosensitizer) becomes oxidized. The injected electron is transported between the TiO_2 nanoparticles and then extracted to a load where the work done is delivered as an electrical energy. The electrons flow through the TiO_2 onto the electrode, through an electric circuit, and then to the counter electrode. The electrolyte carries electrons back to the dye from the counter electrode. Electrolytes containing redox ions is used as an electron mediator between the TiO_2 photoelectrode and the coated counter electrode. Therefore, the oxidized dye molecules (photosensitizer) are regenerated by receiving electrons from the ion redox mediator that get oxidized.

3. Materials and Methods

3.1. Preparation of the Natural Dye

The leaves of *carica papaya* were ground to small particles using blender with water as extracting solvent, and flowers of *Hibiscus Sabdariffa* were air dried till they became invariant in weight.

The dried flowers of *Hibiscus Sabdariffa* were left uncrushed because previous attempts proved failure to extract the dye from crushed samples due to jellification [17]. The method of heating in water (*Aq.*) was used to extract the dye. Distilled water was the solvent for aqueous extraction. 5 g of the sample (*Hibiscus Sabdariffa*) Flower was measured using analytical scale balance and dipped in 50 ml of the solvent heated to 100°C for 30 minutes after which solid residues were filtered out to obtain clear dye solutions.

3.2. DSSCs Assembling

The photoanode was prepared by first depositing a blocking layer on the fluorine doped tin oxide (FTO) glass (solaronix), followed by the nanocrystalline TiO_2 (solaronix). The blocking layer was deposited from a 2.5 wt% TiO_2 precursor and was applied to the FTO glass substrate by spin coating and subsequently sintered at 400°C for 30 minutes. The 9 μm thick nanocrystalline TiO_2 layer was deposited by screen printing. It was then sintered in air for 30mins at 500°C. The counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at 100°C and fired at 400°C for 30 minutes.

The sintered photoanode was sensitized by immersion in the sensitizer solution at room temperature overnight. The cells were assembled by pressing the photoanode against the platinum-coated counter electrodes slightly offset to each other to enable electrical connection to the conductive side of the electrodes. Between the electrodes, a 60 μm space was retained using two layers of a thermostat hot melt sealing foil. Sealing was done by keeping the structure in a hot-pressed at 100°C for 1min. the liquid electrolyte constituted by 50 mmols of tri-iodide/iodide in acetonitrile was introduced by injection into the cell gap through a channel previously fabricated at opposite sides of the hot melt adhesive, the channel was then sealed.

3.3. Characterization and Measurement

The current-voltage (*J-V*) data was obtained using a keithley 2400 source meter under AM1.5 (100 mw/cm^2)

illumination from a Newport A solar simulator. Scanning electron micrographs of the nanocrystalline TiO_2 films are taken with Carl Zeis SEM. The absorption spectra of the dyes was recorded on Ava-spec-2048 spectrophotometer. The cell active area was 0.5 cm^2. Thickness measurement was obtained with a Dektac 150 surface profiler. X-ray microanalysis was carriedout with INCA EDX analyzer.

4. Results and Discussion

Figure 2a. shows the SEM image of TiO_2 nanoparticles fabricated using screen printing method. The SEM micrograph shows that the TiO_2 nanoparticles produced have a mean particle size of about 20nm. It also reveals that the surface is porous and has agglomeration.

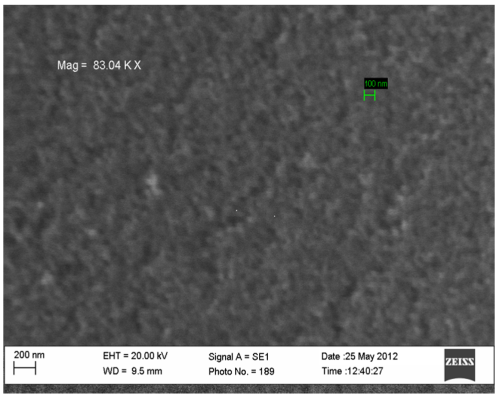

Figure 2a. *The Scanning electron microscope surface morphology of TiO_2 sample.*

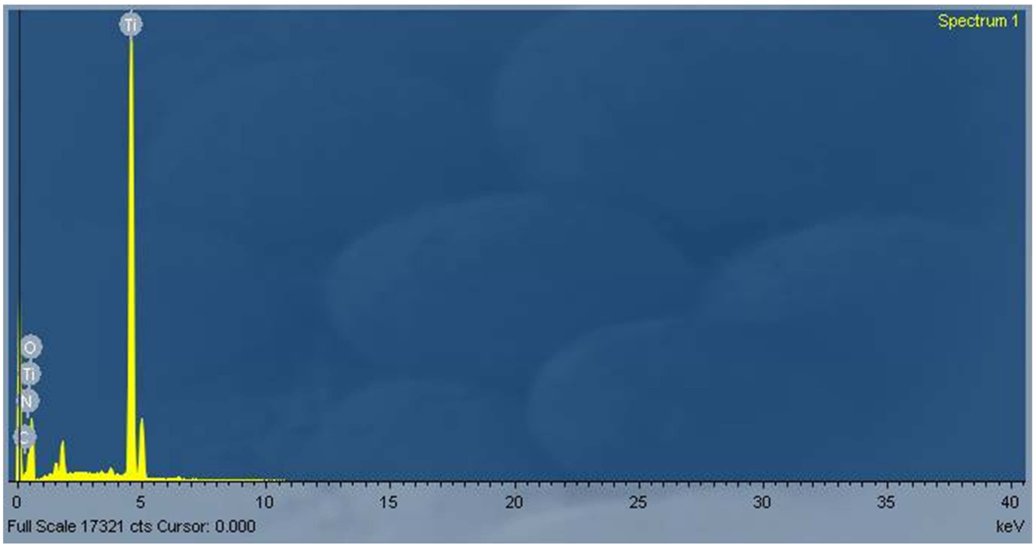

Figure 2b. *EDX image showing the elements present in the TiO_2 compound.*

Figure 2b presents the EDX Image of TiO_2. The elements present in the TiO_2 are Titania, Chlorine, Oxygen and Nitrogen. Nitrogen is present due to the blower that was used to dry the TiO_2 semiconductor.

Figure 3a shows the UV-VIS absorption spectra of roselle extract, and pawpaw leaves extract. It was found that the absorption peak of roselle extract is about 540nm (Fig 3b) while it was deduced that the *carica papaya* dye absorbs photons best at a wave length peak of 370nm (Fig 3a). The difference in the absorption characteristics is due to the different type of pigments (anthocyanin for roselle and chlorophyll for pawpaw) and colors of the extracts. After immersion of the TiO_2-coated electrode (photoanode) in the extracts, observable colors of TiO_2 films turned deep purple for the roselle extract but the film turned light green for the pawpaw extract. In the case of roselle extract, an absorption peak of the photoanode is broader than that of the dye solution (Figure 3(c)), with a shift to a higher wavelength (from 540 to 560 nm). The difference in the absorption peak is due to the binding of anthocyanin in the extract to the TiO_2 surface [18].

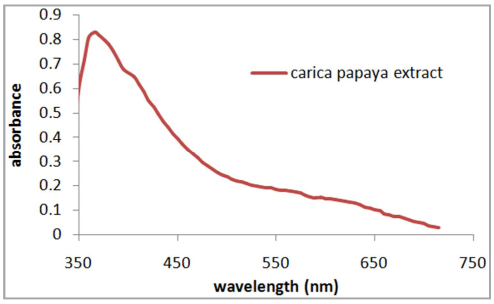

Figure 3a. *Absortion spectra of papaya extract.*

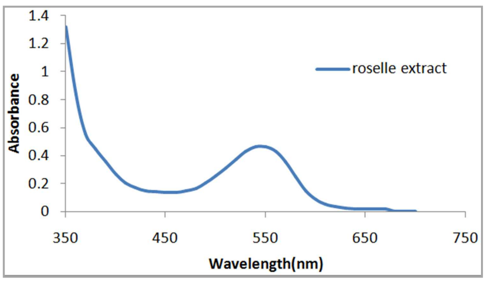

Figure 3b. *Absortion spectra of roselle extract.*

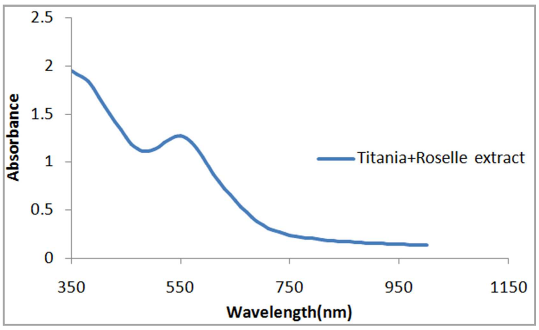

Figure 3c. *Absorption spectra of titania immersed in roselle extract.*

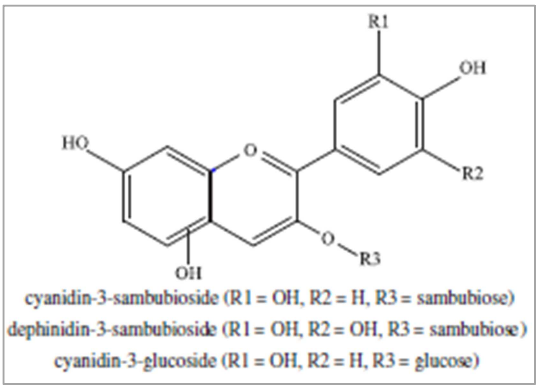

Figure 4. *Chemical structures of: cyanidin and delphinidin in roselle dye.*

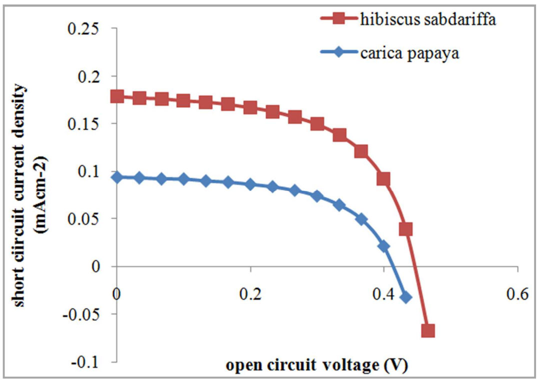

Figure 5. *Photocurrent density-voltage (J-V) curve under 100mWcm^{-2} light intensity.*

Figure 5 shows the *J–V* (current density–voltage) curves of the roselle and pawpaw leaf extract under illumination.

Based on the *J-V* curve, the *fill factor* (*FF*) and *solar cell efficiency* (η) were determined using equations (1) and (2) respectively.

$$FF = \frac{P_{max}}{P_{in}} = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}} \quad (1)$$

$$\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_{IRRADIANCE}} .100\% \quad (2)$$

Where V_{max} = maximum voltage (V);
J_{max} = maximum density (mA/cm^2);
J_{sc} = short density (mA/cm^2);
V_{oc} = *open circuit voltage* (V) and
$P_{IRRADIANCE}$ = light intensity (mW/cm^2)

From the effective absorption area of 0.5 cm^2 of the DSSCs, the averaged values of the light-to-current conversion efficiencies (η) of the DSSCs, shortcircuit photocurrent (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (*FF*) were recorded as presented in *Table 1*. Obviously, the efficiency of the cell sensitized by the roselle extract was significantly higher than that sensitized by the pawpaw leaf extract. This is due to a higher intensity and broader range of the light absorption of the extract on TiO_2 (Figure 3c), and the higher interaction between TiO_2 and anthocyanin in the roselle extract which leads to a better charge transfer. Moreover, anthocyanin in the roselle extract (cyanidin and delphinidin) has a shorter distance between the dye skeleton and the point connected to TiO_2 surface compared to the chrorophyll extract from *carica papaya* leaves that shows lower charge transfer effect due to the limited absorbance of the dye in the visible spectrum [19]. This could facilitate an electron transfer from anthocyanin in the roselle extract to the TiO_2 surface and could be accounted for a better performance of roselle extract sensitization [20].

Table 1. *Performance characteristics of DSSC under 100mWcm^{-2}.*

Sample	J_{SC}(mAcm^{-2})	V_{OC}(V)	*FF*	η (%)
Roselle	0.180	0.47	0.552	0.046
Pawpaw	0.094	0.43	0.544	0.022

When the results in this study is compared to a studiy performed under similar conditions by Ahmed *et., al* [21] who found *Jsc* of 0.17 mAcm^{-2}, *Voc* of 0.46 V, *FF* of 0.41 and η of 0.033% for *Hibiscus Sabdariffa* respectively, our result is alitle higher. Also when compared to Kimpa *et.al* [22], where the conversion efficiency of the DSSCs prepared by pawpaw leaf extract was 0.20%, with V_{OC} of 0.50 V, J_{SC} of 0.649 mA/cm^2 and *FF* of 0.605. Their result has better performance. These differences may be attributed to differences in concentrations of phytoconstituents in different parts of the plants for the *Hibiscus Sabdariffa* dye [17], and due to the extracting solvent used for the case of pawpaw (distilled water for our studies and ethanol for Kimpa *et., al*) [22].

5. Conclusions

Sensitization of a dye sensitized solar cell with extracts from roselle flowers was demonstrated. A similar cell sensitized with *carica papaya* leaves (containing a mixture of carothenoids and appreciable concentration of phenolic acid) extract shows a lower *Jsc, Voc, FF* and η. Using water as extracting solvent, the energy conversion efficiency (η) of the cells consisting of roselle extract and pawpaw leaves extract was 0.046%, and 0.022%, respectively. The roselle extract has higher photosensitized performance as compared to the pawpaw leaves extract. This is due to the better charge transfer between the roselle dye molecule and the TiO_2 surface which is related to a dye structure.

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