Original Research Article

Photoelectrochemical Performance of a dye sensitized solar cells based on natural pigments with distilled water as extracting solvent.

Abstract

Four natural dyes, extracted from natural materials such as flowers, and leaves, were used as sensitizers to fabricate dye-sensitized solar cells (DSSCs). The photoelectrochemical performance of the DSSCs based on these dyes shows that the open circuit voltages (*Voc*) varies from 0.433 to 0.470 V, and the short circuit photocurrent densities (*Jsc*) ranges from 0.044 to 0.138 $mAcm^{-2}$, the fill factors (*FF*) and the cell efficiencies (η) also vary from 0.400 to 0.570 and 0.021 to 0.065 %. The DSSC sensitized with *Hibiscus Sabdariffa* flowers extract was found to be superior to those obtained from other dyes. The DSSC gave a *Jsc* of 0.138 $mAcm^{-2}$, *Voc* of 0.470 V, *FF* of 0.504 , and η of 0.065 %. The sensitization performance related to interaction between the dye and TiO_2 surface is discussed.

Key Words: Natural Pigments, DSSCs, Photoelectrochemical Performance, TiO_2

1. Introduction

At present, the main method of utilization of solar energy is the conversion of solar energy into other energy sources. In 1954 the silicon solar cell developed by Bell marks that human can make solar energy converts into electrical energy for use, which is epoch-making significance [1]. However, it is not suitable for large-scale civilian since this type of battery has the more stringent requirements for raw materials and production process. Although the subsequent development of polysilicon and amorphous silicon solar cells is relatively simple in production process, high prices still can't meet the large-scale use.

In 1991, Professor Grätzel reported a new low-cost chemical solar cell using organic dye absorbed nanocrystal titanium dioxide (TiO_2) film as the photoanode, known as Grätzel cells or dye-sensitized solar cells (DSCs) which gave a photoelectric conversion efficiency of 7% under simulated sunlight irradiation [2]. The DSSC promises extremely cheap photovoltaic energy production by combining the advantages of none vacuum processing, extremely low costs components, low embodied energy of production, potentially high efficiencies and superior perfomance compared to silicon solar cells under diffuse light conditions.

Never the less, the technology still suffers from a number of technical challenges that has hindered large-scale deployment, notably, difficulty in scale-up, low efficiencies and stability. Advances in the synthesis of materials and experimental tools have led to an improvement of more than 12% [3]. Because of the simple production process, much lower cost relative to silicon cells and the lifetime of more than 15 years, this type of cells provides a feasible approach for large-scale utilization of solar energy [4].

Natural dyes have become a viable alternative to expensive and rare organic sensitizers because of its low cost, easy attainability, abundance in supply of raw materials and no environment threat. Various components of a plant such as the flower petals, leaves and bark have been tested as sensitizers. The nature of these pigments together with other parameters has resulted in varying performance.

In this study pigments from *Bougainvillea spectabilis (B S), mangifera indica leaves* known as mango *(M L), Hibiscus sabdariffa (H S)* commonly known as Roselle, and *Ocimum Gratissimum* commonly known as Scent Leaves *(S L),* were extracted and used as sensitizers. The results from the sensitization perfomance shows that, the DSSC sensitized with the extract of H S outperformed the other DSSCs sensitized with other natural dyes in this paper. All the photoelectrochemical performance were measured and characterized for all the above sensitizers.

1.1 Principles and Operation of a DSSC

Dye-sensitized solar cells are prepared in a sandwich arrangement and are comprised by two electrodes, the photoanode and the counter-electrode, Fig. 1. The photoanode is a conducting glass covered by a mesoporous and nanocrystalline TiO_2 film, sensitized by the dye-sensitizers. The counter electrode is a conducting glass covered by a thin film of catalyst, such as platinum or graphite. Between these electrodes is placed a mediator layer, usually a solution of I^{3-}/I^{-} in nitriles.

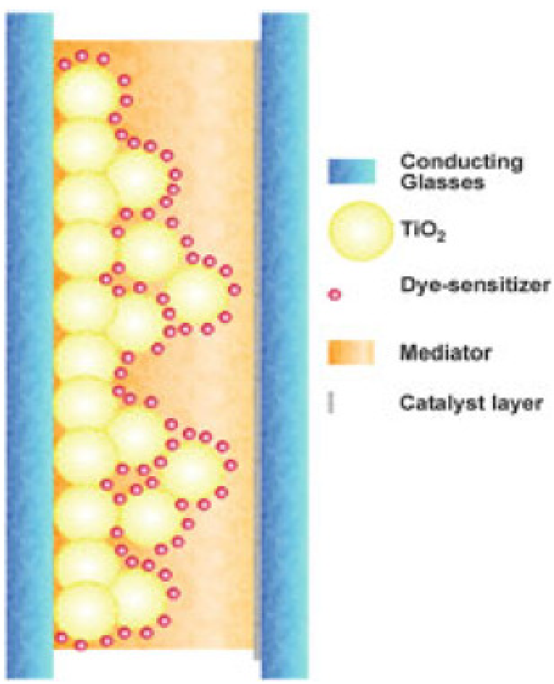

Fig. 1 Schematic arrangement of a dyesensitized solar cell

In order to promote the energy conversion, the sunlight is harvested by the dye-sensitizers leading to an excited-state capable of inject an electron into the semiconductor conducting band. The oxidized dye is immediately regenerated by the mediator and the injected electron percolates through the semiconductor film, reaches the conducting glass and flows by the external circuit to the counter electrode. The counter electrode is responsible for regenerating the oxidized specie of the mediator, reducing it by a catalyzed reaction using electrons from the external circuit. Since there is not a permanent chemical change for dye-sensitized solar cells, the estimated lifetime of these devices is 20 years [5].

2. Experimental section

2.1 *Natural Dyes Extraction*

Fresh leaves, and flowers of plants including, *Mangifera Indica, Bougamvillea spectabillis, Ocimum gratissimum and, Hibiscus sabdariffa,* were collected. The collected leaves of Mango, *Ocimum gratissimum* and the flower of *Bougamvillea* were grinded to small particles using a blender with 50 ml deionized water as extracting solvent. The solution was filtered to separate the solid from the pure liquid. Also the collected flowers of the hibiscus sabdariffa were air in a shade to prevent pigment degradation till they became invariant in weight. The dried flowers of *Hibiscus* were left uncrushed because previous attempts proved failure to extract the dye from crushed samples due to jellification [6]. The method of heating in water was used to extract the dye. Distilled water was the solvent for aqueous extraction. 5 g of the *sabdariffa* sample was measured using analytical scale balance and dipped in 50 ml of the solvent heated to 100 ^{O}C for 30 min after which solid residues were filtered out to obtain clear dye solutions.

2.2 Preparation of TiO_2 paste

The TiO_2 films was prepared using a modified sol–gel method, in which 2 g of P25 TiO_2 (Degussa, Japan) powder was dissolved in 10 ml of deionized water mixed with 0.2 mol of Triton-X 100 and 0.4 g of acetaldehyde, then vibrated ultrasonically for 1 day.

2.3 DSSCs Assembly

All the materials were first cleaned and rinse with distilled water and dried.
The photoanode was prepared by first depositing a blocking layer on the FTO glass (solaronix), followed by the nanocrystalline TiO_2. 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 ^{O}C for 30 mins. The 9 μm thick nanocrystalline TiO_2 layer was deposited by screen printing. It was then sintered in air for 30 mins at 500 ^{O}C. the counter electrode was prepared by screen printing a platinum catalyst gel coating onto the FTO glass. It was then dried at 100 ^{O}C and fired at 400 ^{O}C for 30 mins. The sintered photoanode was sensitized by immersion in the sensitizer solution at room temperature overnight. Sensitization was achieved by immersing the photoanode in the extracts. 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 50 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 ^{O}C for 1 min. the liquid electrolyte constituted by 50 mmol of tri-iodide/iodide in acetonitrile was introduced by capillary action into the cell gap through a channel previously fabricated at opposite sides of the hot melt adhesive, the channel was then sealed.

2.4 Characterization

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. The film morphology was obtained by scanning electron microscope (Carl Zeis SEM). The absorption spectrum of the dyes were recorded on Ava-spec-2048 spectrophotometer in the region of 350–700 nm. The cell active area was 0.5 cm^2. Thickness measurement was obtained with a Dektac 150 surface profiler.

3. Results and Discussion

Fig. 3.1. shows the representative UV–vis absorption spectra for the aqueous extracts of H S, B S, S L, and M L. The extracts of H S exhibits an absorption peak of 550 nm. This absorption is attributed to the presence of anthocyanins. The chemical adsorption of these dyes is accepted to occur because of the formation of bond with the surface of nanostructured TiO_2. In the extract of *Bougainvillea spectabilis* [Fig. 3.1 (B S)] the absorption peak was found around 370 nm, which can be associated to the presence of indicaxanthin, and betacyanin pigment.
The extract of *mangifera indica* leaves and *Ocimum gratissimum* [Figs. 3.1(M L) and (S L)] shows absorption peaks at 360 nm and 390 nm.

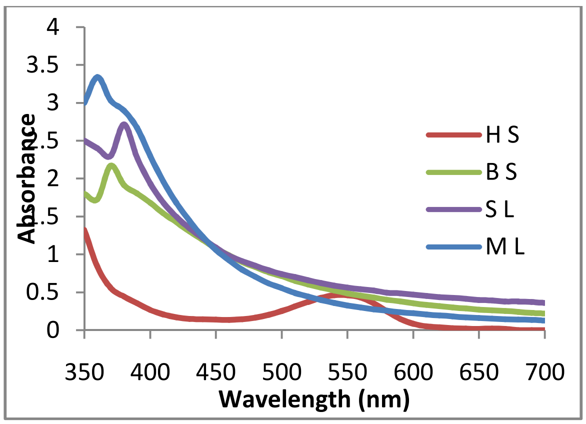

Fig. 3. 1 *shows the UV–vis spectra of H S, B S, S L, and M L extracts*

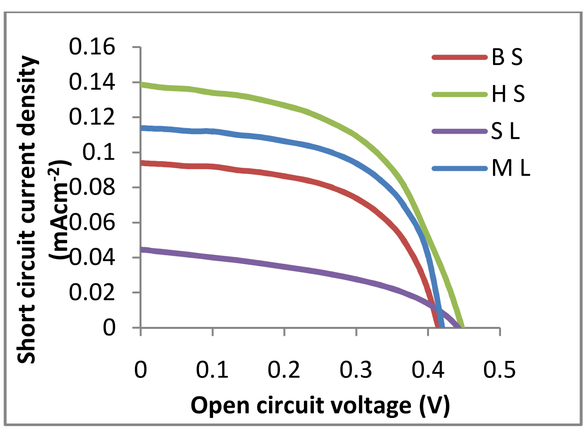

Fig. 3.2 *The photocurrent density–voltage (J –V) curves with different natural pigment*

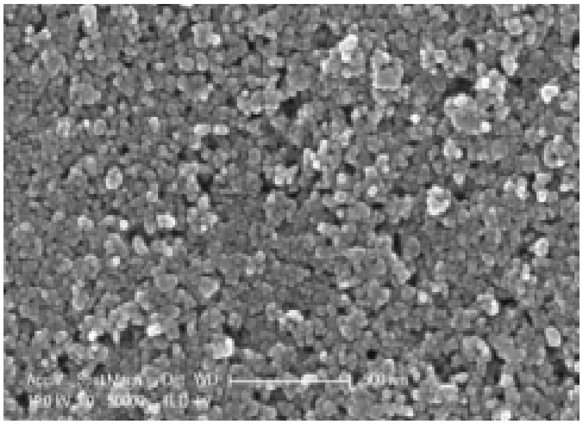

Fig. 3.3. *The Scanning electron microscope surface morphology of TiO_2 sample.*

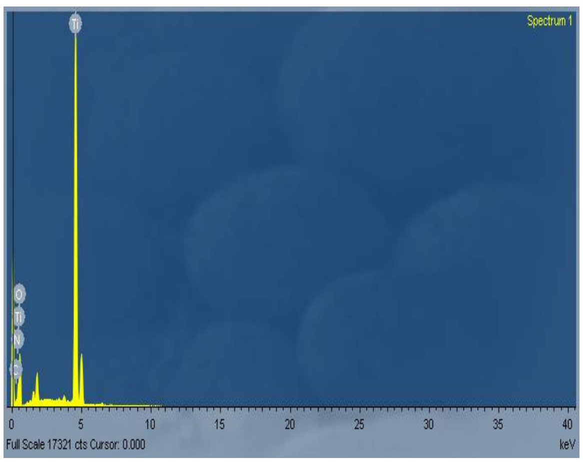

Fig 3.4. *EDX Image Showing the Elements Present in the TiO_2 Compound*

Fig. 3.4 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.

Fig. 3.3 shows the SEM micrograph morphology of TiO_2 film. From the figure, it shows that the TiO_2 nanoparticles produced have a mean particle size of about 15 nm. It also reveals that the surface is porous and has agglomeration.

The typical *J–V* curves of the DSSCs using the sensitizers extracted from mango leaves, *bougainvillea*, scent leaves and *hibiscus sabdariffa* flowers are shown in **Fig. 3.2**.
Based on the *J-V* curve, the *fill factor* (*FF*) and *solar cell efficiency* (η) were determined using equations (1) and (2) respectively.

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

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

Where V_{max} = maximum voltage (V);

J_{max} = maximum current (mA/cm^2);

J_{sc} = short current (mA/cm^2);

V_{oc} = *open circuit voltage* (V) and

$P_{IRRADIANCE}$ = light intensity (mW/cm^2)

Photovoltaic tests of DSSCs using these natural dyes as sensitizers are summarized in **Table 1**. From the effective area of 0.5 cm^2 the performance of the natural dyes as sensitizers in DSSCs was evaluated by short circuit current (*Jsc*), open circuit voltage (*Voc*), fill factor (*FF*), and energy conversion efficiency (η).

As displayed in **Table 1** and **Fig. 3.2**, the fill factors of these DSSCs varies from 0.400 to 0.570. The *Voc* varies from 0.433 to 0.470 V, and the *Jsc* changes from 0.044 to 0.138 mAcm^{-2}. Specifically, a high *Voc* (0.470 V) and *Jsc* (0.138 mAcm^{-2}) were obtained from the DSSC sensitized by the *Hibiscus sabdariffa* extract; the efficiency of the DSSC reached 0.065 %. These data are significantly higher than those of the DSSCs sensitized by other natural dyes in this work.

This is due to broader absorption range of the sensitizers, higher interaction between TiO_2 nanocrystaline film and the pigment extracted from *Hibiscus sabdariffa* which leads to a better charge transfer [7].

It was once reported that DSSCs based on anodes containing Hibiscus Sabdariffa and Bougainvillea *spectabilis* extracts shows a photoelectrochemical perfomances of (*Jsc*= 0.23 mAcm^{-2}, *Voc*= 0.44 V, *FF*=0.49 and η= 0.07 %) [6] and (*Jsc*= 0.088 mAcm^{-2}, *Voc*= 0.2 V, *FF*=0.374 and η= 0.0066 %) [7]. When compared to our results with H S extract sensitized DSSC, it is in agreement with Mphande and Pogrebnoi **[6]**, and when compared to Yirga *et.,al* [7] a 5.7 % improvement in shortcircuit current density of the B S extract sensitized DSSC was observed. The differences in the *hibiscus sabdariffa* DSSC might be attributed to the differences in concentrations of phytoconstituents in different parts of the plant [8].

The low conversion efficiency observed with DSSC sensitized with extract of *Ocimum gratissimum* was due to the presence of aggregated dyes or non-injecting dyes at the surface of the TiO_2 that leads to small solar to electricity conversion efficiency [9]. This is because there are no available bonds between the dye and TiO_2 molecules through which electrons can transport from the excited dye molecules to the TiO_2 film [10]. This result indicates that the interaction between the sensitizer and the TiO_2 film is significant in enhancing the energy conversion efficiency of DSCs

4. Conclusions

Four dyes obtained from nature, including flowers, and leaves of plants

Table 1. *Photovoltaic performance of DSSCs with different sensitizers under 100mWcm^{-2}*

Sample	**J_{sc}(mAcm^{-2})**	**V_{oc}(V)**	**FF**	**η (%)**
H S	0.138	0.470	0.504	0.065
S L	0.044	0.466	0.400	0.021
M L	0.114	0.433	0.570	0.049
B S	0.093	0.433	0.550	0.040

were used as sensitizers in DSSCs. The photoelectrochemical performances of the DSSCs based on these dyes shows that the *Voc* ranged from 0.433 to 0.470 V, and *Jsc* was in the range of 0.044 to 0.138 mAcm^{-2}. The DSSC sensitized by *Hibiscus Sabdariffa* extract offered the highest conversion efficiency of 0.065 % among the four extracts. The results obtained are encouraging and should prompt more detailed studies to uncover the exact mechanisms involved.

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