Synthesis of Dye-Sensitized Solar Cells Using Chromophores from West African Plants

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Abstract— The current study tested the hypothesis whether chromophores from common West African plants, including *Hibiscus sabdariffa* (roselle/zobo), *Cymbopogoncitratus* (lemongrass) and *Telfairiaoccidentalis* (ugu) could be used as photosensitizers to assemble dye-sensitized solar cells (DSSCs). We examined ZnO nanoparticle paste as an electron acceptor and I^-/I_3^- as electrolytes. The dye extracted from ugu showed the highest open circuit voltages (V_{oc}) as 149 mV and the photocurrent density (J_{sc}) as 104 μA cm^{-2}, and the power as 270μW under sunlight (~10,000 lux).

Index Terms—dye-sensitized solar cell, photosensitizer, anthocyanin, chromophore, ZnO nanoparticle, roselle/zobo, lemongrass, fluted pumpkin/ugu, natural dye, West Africa

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1 INTRODUCTION

THE global energy demand is constantly growing, while energy resources such as fossil fuel are constantly depleting. Therefore, there has been an urgent need to develop new ways of harnessing alternative, sustainable and environmentally friendly energy resources, including solar energy. Over the years, many new methods and designs have been developed in an effort to utilize solar energy for power generation. The most popular is the solar panel that is based on crystalline silicon technology. One major drawback to solar energy applications, however, is its high cost per watt electricity generated.

The largest source of energy on earth is solar energy. After reflection and absorption in the atmosphere, up to 100,000 terawatts (TW) gets converted to many other forms of energy upon reaching earth. The current global consumption of primary energy is about 13.7TW, meaning the sun is supplying 6,000 times what is being consumed globally. Nigeria has abundance of sunlight reaching an average solar radiation of 7.0kWh/m^2 (25.2MJ/m^2/day) in the far north and about 3.5kWh/m^2/day (12.6MJ/m^2/day) in the costal latitudes[1].

A Dye-sensitized solar cell (DSSC) uses a photoactive molecule [2] to generate electricity when exposed to sunlight. Although a relatively new technology, the use of DSSCs have exhibited efficiencies of up to 10.4% [3], and hence portray an encouraging process for the large scale conversion of the renewable solar energy into electricity. Grätzel cell is the most successful DSSC known and it uses Ru-polypyridyl based dyes absorbed on nanocrystalline films of TiO_2[4], [5]. Other nanoparticles of metal oxide semiconductors, including ZnO nanoparticles[6][7], [8], [9], [10], [11] have also been reported for DSSC application.

The basic principle ofDSSC to generate electricity is similar to that of plant photosynthesis to produce carbohydrates using sunlight, H_2O, and CO_2. In photosynthesis, a plant leaf is viewed as a photochemical cell that converts solar energy into biochemical energy. Using the photon energy, the chlorophyll in green leaves release electrons that trigger the subsequent reactions to complete the photosynthesis process [12]. Similarly in DSSCs, the basic variables necessary for a photovoltaic cell to operate include: (a) absorption of light by a photoactive molecule, (b) excitation of electrons and generation of electron holes, (c) separation of opposite charge carriers, and (d) separate extraction of those charge carriers through an external circuit.

A DSSC functions based on the sensitization of a wide band-gap metal oxide semiconductor by a monolayer of a molecular dye anchored on the surface of the metal oxide semiconductor.The dye absorbs light in the visible region (400–700nm)[12] of the electromagnetic spectrum. Excitation of electrons by sunlight occurs in the dye and the charges generated by photons are separated at the interface between the dye and the metal oxide. This crucial role played by the dye is why the dye is an essential variable in the assembly of a DSSC[13].

So far, the most efficient reported metal complex dyes are Ruthenium(II)-based [14] and Osmium(II)-based. The widely used Ru-polypyridyl complexes have good absorption, long excited lifetime, and highly efficient metal-to-ligand charge transfer. However, they have the disadvantage such as high cost and sophisticated preparation techniques.

The organic dyes are pigments extracted from organic molecules commonly found in natural dyes. Chromophores; including azo, nitro, triarylmethane, methine, anthroquinone, and phthalocyanine[12] are photoactive groups in a molecule that are responsible for plants pigmentation. These chromophores contain conjugated,

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resonance stabilized pi electrons and the change in energy between its two molecular orbitals fall within the visible region of the spectrum [15].

The leaves of *H. sabdariffa*, known as roselle or zobo, contain anthocyanin pigment. Anthocyanin contains three aromatic rings that electrons are conjugated. The electrons exist in the ground state and can be photo-excited with incident light to convert photons of light energy into mobile electrons that generate electricity. Apart from zobo plants, anthocyanin is also found in raspberries, black rice [16], and black soybeans. The leaves of *C. citratus*and *T. occidentalis* are commonly known as lemongrass and fluted pumpkin/ugu, respectively. Lemongrass like many other green plants contains chlorophyll. Fluted pumpkin (*T. occidentalis*) is mainly grown in Tropical West Africa where rainfall is high[17]. Ugu leaves contain high concentrations of the chlorophyll pigments which act as photosensitizers [18]. We hypothesized that these local plant chromophores in West Africa could be photosensitive and suitable for DSSCs application.

The current study determined photosensitivity of natural plant chromophores to generate electricity. We introduced ZnO nanoparticle pastes as the metal oxide semiconductor and iodide/triiodide as the electrolytes. We compared the efficiencies of the three chromophores by measuring open-circuit voltage ($\boldsymbol{V_{oc}}$), short-circuit current density ($\boldsymbol{J_{sc}}$), and power ($\boldsymbol{\mu W}$).

2 EXPERIMENTAL

All experiments were repeated triplicate, and a representative figure (Figure 2) and mean average value is shown (Table 1, 2).

2.1 Preparation of ZnO Paste

NanocrystallineZnO powder (1.0 g) and acetic acid (100 μl, 0.035 M) were grinded in a mortar to obtain a colloidal suspension with smooth consistency. Dishwashing detergent (50 μl) was added as a surfactant to the suspension.

2.2 Preparation of Redox Electrolyte

We used iodide and triiodide as the redox electrolyte and the mediator to generate electricity continuously. The I_2 and KI redox couple was added in distilled water. The KI (0.1M)made the I_2 (0.01M) stable in water[19]following the*disproportionation redox reaction* as in reaction equation (1).

$$I_2 + KI \rightarrow I^-(iodide) + I_3^-(triiodide) \quad (1)$$

As the electrons generated from the dye in the presence of photons travel through external circuit to perform work on the return journey from the external circuit, the carbon used in coating the cathode electrode serves as a catalyst in reducing tri-iodide ion with the two electrons from the dye to iodide ion for *electrolyte regeneration*[20] as in reaction equation (2).

$$I_3^- + 2e^- \rightarrow 3I^- \quad (2)$$

Because the dye gave out two electrons during illumination, it has electron holes that need to be filled. The iodide ion undergoes oxidation to provide the missing two electrons back to the dye[20] for *dye regeneration* as in reaction equation (3).

$$3I^- \rightarrow I_3^- + 2e^- \quad (3)$$

2.3Natural Dye Extraction

Three plants leaves (10.0 g), including *Hibiscus sabdariffa* (zobo), *Cymbopogoncitratus* (lemongrass) and *Telfairiaoccidentalis* (ugu) in 200 ml H_2O were heated at 100 ^{o}C for 30 minutes. The soaked plants were cooled and the residues were filtered to obtain the natural dye solutions. The pH of the three different plant extracts was determined using a pH meter.

2.4 Quantification of Natural Dyes Using UV/Vis Spectrophotometer

2.4.1 Preparation of Buffer Solution

The pH 1.0 buffer was prepared by dissolving KCl (1.86 g) in a beaker in H_2O (1 L). The KCl solution was adjusted to pH 1.0 by addition of concentrated HCl.

2.4.2 Preparation of Test Solutions

A modified single pH method [21] was used to measure concentrations of chromophores. Dye solution (10 mL) was diluted with pH 1.0 buffer (40 mL). The absorbance of the test portions (*H. sabdariffa* + buffer) was measured using a UV/Vis spectrophotometer. The concentrations of the dyes were calculated as equation (4).

$$C_{mg/L} = \frac{\mathbf{A}(\lambda \max)\, pH1}{\in \times b} \quad (4)$$

Where the $\mathbf{A(\lambda_{max})pH1}$ is the absorbance at λmax (520 nm) at pH=1, $\in$is the anthocyanin extinction coefficient (59.9$Lg^{-1}cm^{-1}$; 26900 $Lmol^{-1}cm^{-1}$, cyaniding 3-glucoside 449 g/mol), $\boldsymbol{b}$ is the path length (1 cm). The extinction coefficient of chlorophyll is 82–96 $Lg^{-1}cm^{-1}$ [22].

2.5 Preparation of Electrodes

2.5.1 PhotoanodeFabrication (Working Electrode)

A fluorine-doped tin oxide (FTO, $Sn_2O.F$) coated conducting glass (5 cm^2, Solaronix, Aubonne, Switzerland) was obtained and the conductive side of the glass was determined using a multimeter (resistance = 20-38 Ω). Three corners of the glass were taped to make a border with the conductive side facing up. ZnO paste (100 μL) was applied on the conductive side and spread evenly using a glass rod, followed by drying for 10 minutes before the tap was carefully removed without perturbing the ZnO layer. The ZnO coated glass was heated for at 150 °C for 30 minutes until the ZnO turned brown and then white, and allowed to cool. The ZnO coated conductive glass was immersed into the dye extracts to allow the dye to adsorb to the surface of the ZnO. The immersion/adsorption process was maintained for 10 minutes for complete adsorption. After the adsorption process, the photoanode was rinsed with distilled water/ethanol, and dried.

2.5.2 Graphite Cathode Fabrication (Counter Electrode)

On the other fluorine-doped tin oxide (FTO, $Sn_2O.F$) coated conducting glass (5 cm^2, Solaronix, Aubonne, Switzerland), graphite particles were applied on the conducting side using a pencil.

2.6DSSC Assembly and Parameter Analysis

The two fabricated electrodes were clamped together and the KI/I_2 electrolyte solution (50 μL) was applied onto the interface between the two plates. The electrolyte was allowed to cover the surface of the applied ZnO through capillary action. The photo-voltage under the projector light and sunlight was measured using a multimeter after forming a short circuit (Fig. 1.).

A multimeter was connected to each plate using alligator clips. The negative electrode was the ZnO/chromophore coated glass, while the positive electrode was the carbon coated glass. The current and voltage produced by illumination of sunlight (10,000 lux) and projector light (3,000 – 5,000 lux) were determined by measuring various parameters such as short-circuit density ($\boldsymbol{J_{sc}}$), open-circuit voltage ($\mathbf{V_{oc}}$), and power (**P**) using the following equations (5-7):

$$Current\ Density\ (Jsc)(\mu Acm^{-2}) = \frac{I}{A} \quad (5)$$

$$Voltage\ (Ohm's\ law)(V) = I \times R \quad (6)$$

$$Power\ (P)(\mu W) = V \times I \quad (7)$$

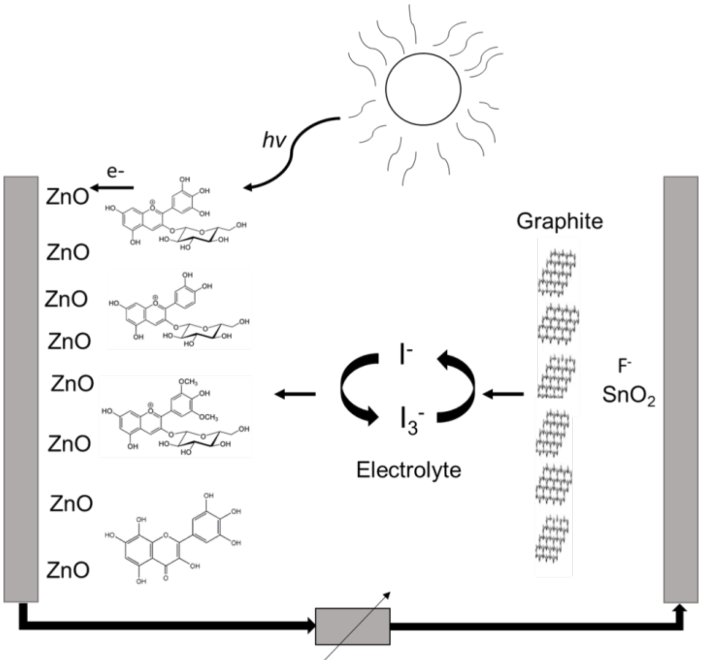

Fig. 1. Schematic of DSSC setup. Photons (*hv*) of light hitting the dye molecules give electrons (e^-) enough energy to escape the dye molecule and move to the ZnO nanoparticles, leaving a hole behind. The mediator electrolyte system (I^-/I_3^-) donates e^- to fill the hole. The traveling e^- powers a device connected on its travel path.

3 RESULTS AND DISCUSSION

To test the hypothesis of whether the chromophore from plants that include zobo, lemongrass and ugu can be used as a photosensitizer for DSSCs, we extracted the natural dyes that contain anthocyanin and chlorophyll. The pH of the fresh extracts were 3.02 (zobo), 4.95 (lemongrass), and 5.06 (ugu). Then we determined the concentration of the anthocyanin in the zobo using the UV/Vis pH differential quantification method (4). Using the abundant sunlight in West Africa, the solar cell as shown in Figure 1 was tested for the photovoltaic performance of each of the extracts from the three plants.

3.1 Chromophore Analysis

The UV/Vis spectroscopy showed that *H. sabdariffa* (zobo) absorbs maximum light at wavelength of 518.0 nm due to the red pigment, anthocyanin. The extracts from *C. citratus* and *T. occidentalis* absorb maximum wavelength of about 340.0 nm and 341.0 nm, respectively (Fig. 2.). The absorbance was measured for ugu (A=1.7), lemongrass (A=1.5), andzobo (A=1.4). The chromophore concentrations of ugu, lemongrass and zobo were calculated as 19 mg/L, 17 mg/L, and 23 mg/L, respectively.

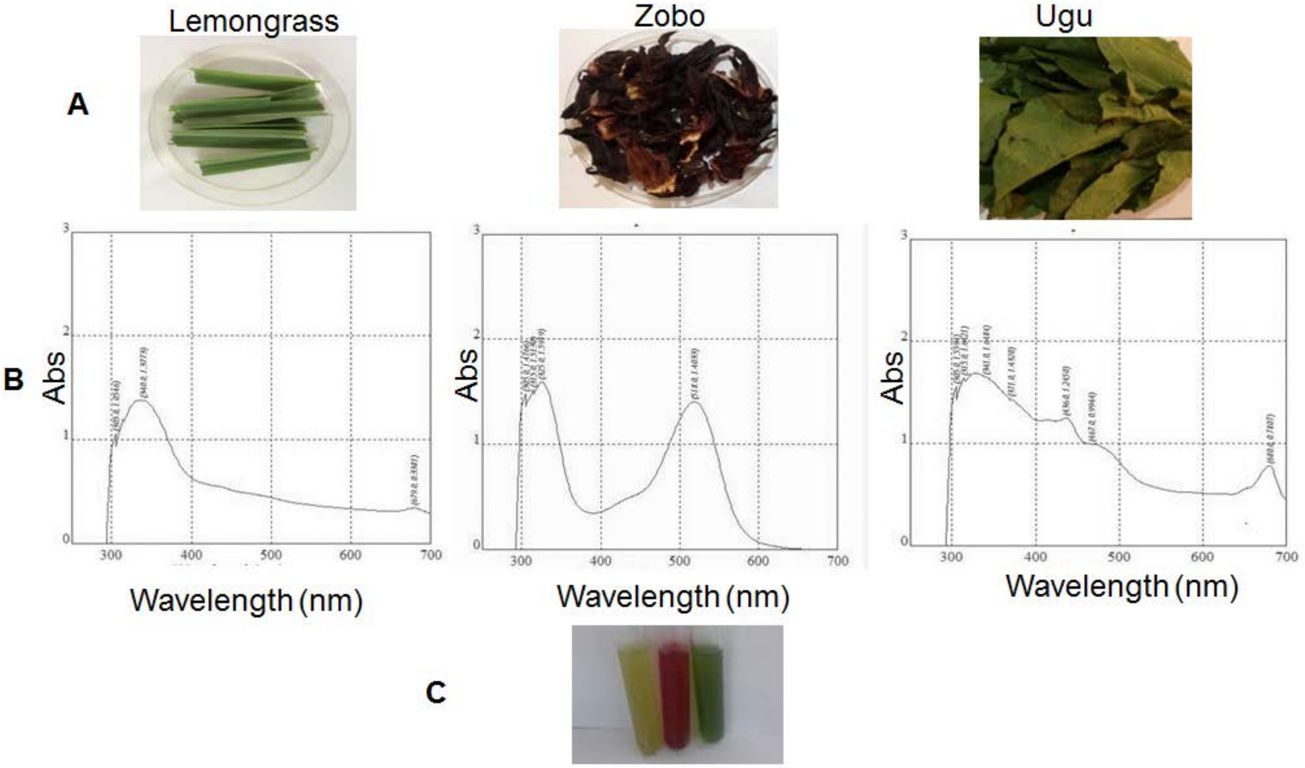

Fig. 2. (A) Dried leaves before extraction. (B) Absorption spectra of the three plants extracts with lemongrass (left; chlorophyll λ_{max} = 340.0 nm; Abs = 1.5), zobo (center; chlorophyll:λ_{max} = 325.0 nm, Abs = 1.5; anthocyanin:λ_{max} = 518 nm, Abs = 1.4), and ugu (right; chlorophyll λ_{max} = 341 nm; Abs = 1.7). (C) The extracted natural dyes of lemongrass (left),zobo (center), and ugu (right).

3.2 Photovoltaic Performance

The photovoltaic performance was measured under projector light and sunlight using a multimeter for three chromophores. Short-circuit density (J_{sc}), open-circuit voltage (**V_{oc}**), and power (**P**) were calculated from the measured current (***I***) and resistance (**R**). We found that the photovoltaic performance of each of the three extracts was higher under sunlight (Table 1) than under projector light (Table 2).

Table 1. Photovoltaic performance of extracts from zobo, lemongrass, and ugu underthe sunlight (10,000 lux).

Extract	***I*** (μA)	**R** (Ω)	**J_{sc}** (μA/cm^2)	**V_{oc}** (mV)	**P**(μW)
Zobo	116	1.21	4.64	141	16.3
Lemongrass	2600	10.4	72.4	27	70.2
Ugu	1810	82.5	104	149	270

Table2. Photovoltaic performance of extracts from zobo, lemongrass, and ugu leaves under projector light (3,000-5,000 lux).

Extract	***I*** (μA)	**R** (Ω)	**J_{sc}** (μA/cm^2)	**V_{oc}** (mV)	**P**(μW)
Zobo	25	925	0.76	18.0	0.34
Lemongrass	19	788	1.00	1.00	0.03
Ugu	32	39.6	1.28	25.0	0.80

Our results demonstrated that ugu extracts (*T. occidentalis*) produced the highest electricity among the three natural dyes under both sunlight and projector light. Other group reported the high electricity from anthocyanin-based solar cells [11]. From the UV/Vis absorbance results of the three extracts, ugu extracts that produced the highest electricity had the highest absorbance (1.7), followed by lemongrass (1.5), thenzobo (1.4). Our data imply that concentrations of the chromophore, pigments composition, the extinct coefficient, and light intensity may determine the photovoltaic performance.

The conditions of extraction of the dyes have been reported to have an effect on the performance of the dye as a photosensitizer in DSSCs. Variations in conditions that include extracting temperature, solvent, pH, and light intensity [23] may improve or diminish performance of the solar cell. The efficiency of rosella extract sensitized DSSC was improved from 0.37% to 0.70% when the aqueous dye was extracted at 50 ^{o}C instead of 100 ^{o}C and pH of the dye was adjusted from 3.2 to 1.0 [24].

4 CONCLUSIONS

The plant extracts from three plants commonly found in West Africa, including zobo, lemongrass, and ugu demonstrated the capability of serving as photosensitizers for solar cells. Solar cells using natural chromophores show the most promising future for electricity generation because such solar cells have lower environmental concern, lower maintenance cost, and readily available raw materials. Even though the electricity output for DSSCs is lower thanthat of thin film silicon solar cells, ongoing research on combining two or more dyes together could help obtain extended light absorption along the visible light spectrum.

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