Application of Natural Plant Sensitizers with Polyaniline Electrode Couple in Dye-Sensitized Solar Cells

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Abstract— In the current study, we tested the hypothesis whether natural chromophores from common West African plants could be used as electron donors in dye-sensitized solar cells (DSSCs). Natural dyes were extracted from the leaves of seven common West African plants, including *Tamarindus indica* (tamarind), *Lawsonia inermis* (henna), *Cymbopogon citratus* (lemon grass), *Telfairia occidentalis* (ugu), *Hibiscus sabdariffa* (zobo), *Terminalia catappa* (tropical almonds), and *Magnifera indica* (mango). The solar cells were assembled using natural dyes and semiconducting metal oxide nanoparticles, including ZnO and TiO_2, which served as electron donor/acceptor deposited on transparent fluorine doped tin oxide (FTO) conductive glass as the photo-electrode. In addition, we introduced I^-/I_3^- electrolyte system, as well as a polyaniline/graphite couple as the counter electrode. The UV-Vis, IR spectroscopy, photovoltaic performance (open circuit voltage ***Voc***, short-circuit current density ***Jsc***, and output power ***P***) of the DSSCs under sunlight and projector light, and conductivity of the polyaniline were analyzed. The solar cell using henna extracts coupled with TiO_2 exhibited the highest generation of electricity showing open circuit voltage, current, short circuit current density and power as 214 mV, 3.24 mA, 216 μA/cm^2, and 693 μW, respectively, under the sunlight. The current study demonstrates that any plant chromophore could be used as a sensitizer in the solar cell and the cell efficiency could be enhanced by the incorporation of the conductive polymer into the counter electrode which increases the rate of dye regeneration, as well as using the specific chromophore/metal oxide combination with the optimum bandgap and wavelength for efficient electron excitation.

Index Terms— Conducting polymers, dye-sensitized solar cells, electricity production, metal oxide nanoparticles, natural sensitizer, polyaniline, renewable energy.

1 INTRODUCTION

ELECTRICITY is an essential energy to maintain the growth, development and progress of the human society. Sunlight is the largest renewable source of energy as there is an estimated 100,000 terawatt of absorption and reflection on earth which is 6,000 - 10,000 times more than the current global annual energy demand. The dye-sensitized solar cells (DSSCs) is one of popular methods of harnessing solar energy that has received an increasing interest due to many advantages over conventional silicon-based solar cells [1] [2] [3], including low cost, high efficiency, flexibility and easy fabrication [4] [5]. In general, the solar cells apply a photosynthetic-electrochemical principle at the molecular level [6], and consist of a photo-electrode, a dye sensitizer absorbed on the semiconducting material, a redox electrolyte system, and a counter electrode.

One part of the photoelectrode is a porous, wide band-gap metal oxide nanoparticle, including TiO_2 or ZnO (n-type) and NiO (p-type) [7]. A light harvesting chromophore is absorbed onto the metal oxide electrode to transfer excited electrons. A redox mediator that includes I^-/I_3^- is required as electrolyte to complete the circuit with the aim of charge diffusion between the electrodes and to prevent changes in electrochemical potential. The counter electrode is the significant issue of the solar cell as it transfers electrons from external circuit to the redox electrolyte system [8].

Dyes in the solar cells may contain a wide variety of inexpensive, biodegradable and non-toxic natural products, including anthocyanin, carotenoids, chlorophyll, hennotanic acid, tannin, saponin, alkaloids, phenols, flavonoids, gallic acid, ascorbic acid, citric acid, acetic acid, and terpenes [9]. Currently, the most widely used counter electrode is platinum [10]. However, platinum is rare and expensive. To assemble low-cost and efficient solar cells, it is inevitable to substitute platinum to inexpensive and efficient catalytic molecules. Such materials may include carbon black, carbon nanotubes, graphite, graphene and conductive polymers [11] [12] [13]. Conductive polymers, including polyacetylene and polyaniline are attractive alternatives to metals because they are lightweight, inexpensive, and functionally versatile. They have delocalized orbitals where the mobility of electrons can be enhanced through doping which essentially changes the number of electrons in the polymer by either removing or adding electrons to the molecule, making it easier for electrons to move around and transport charges. In polyaniline, acid protonation can be used as the doping method which helps make the emeraldine form of polyaniline highly stable and highly conducting by ten orders of magnitude [14].

Most of current research have focused on the enhancement of efficiency and cost reduction [15] to develop new dyes, employing photoanodes with different materials, and new electrolytes [4] [16] [17]. However, little attention has been

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given to counter electrodes, given the important role it plays in the DSSC functionality in terms of the efficient dye regeneration. In addition, we aimed to examine the hypothesis whether a wide variety of common West African plant materials could be used as the photosensitizers. The current study demonstrates that various natural dyes are indeed photosensitizers in the solar cell and also shows what degree conducting polymers may improve the efficiency of a DSSC based on their conductivity, easy synthesis, environmentally friendly properties, photoelectrical properties and the conductivity control.

2 EXPERIMENTAL

In this study, various extracting procedures, including ethanolic, aqueous, and alkaline techniques were introduced to solubilize the chromophore molecules from the leaves/flowers from the readily available West African plants. Infrared (IR) and Ultraviolet and visible light (UV-Vis) spectroscopy were used to analyze the photoactive compounds of the different dyes. Finally the photovoltaic parameters of the solar cells were determined using a multimeter.

2.1 Natural Dye Extraction

Seven natural dyes were extracted from the leaves of *Tamarindus indica* (tamarind), *Lawsonia inermis* (henna), *Cymbopogon citratus* (lemon grass), *Telfairia occidentalis* (ugu), *Hibiscus sabdariffa* (zobo), *Terminalia catappa* (tropical almonds), and *Magnifera indica* (mango) using solvent based methods (Fig. 1.). The raw materials were obtained locally in Yola Nigeria, then washed with distilled water to remove dust, air dried at room temperature for 48 hours, and grinded into fine powder.

For aqueous extraction of zobo, ugu and lemon grass dyes, 10g of each powder in 200 ml of distilled water were heated at 100°C for 30 minutes. The plants extracts were cooled and filtered to obtain the natural dye solution as the filtrate and stored at 4°C.

Fig. 1. The leaves or flowers of *Tamarindus indica* (tamarind), *Lawsonia inermis* (henna), *Cymbopogon citratus* (lemongrass), *Telfairia occidentalis* (ugu), *Hibiscus sabdariffa* (zobo), *Terminalia catappa* (tropical almond), and *Magnifera indica* (mango) are shown as common local plants in West Africa.

For ethanolic extraction, tamarind powder (33 g) was poured into a 500 ml solution of 50% (v/v) ethanol. The plants extract was placed in the dark for 48 hours, followed by filtration and the storage of greenish filtrate containing the natural dye. Ethanolic extraction was also applied for mango and tropical almond dyes. Each of mango and tropical almond powder (25g) were poured in 250 ml of 96% (v/v) ethanol. The mixture was thoroughly stirred continuously at 150 rpm at warm temperature (37±2 °C) and then filtered using a filter paper (Whatman No 1). The dark green natural dyes were obtained as the filtrate and stored at 4°C in the dark to avoid chromophore decomposition.

For the alkaline extraction of henna, a 0.3M NaOH solution was prepared by dissolving sodium hydroxide pellets (3.08g) in distilled water (250 ml). Henna powder (25g) was added into the NaOH solution (0.3M, 250 ml) to make the henna to NaOH solution ratio to be 1:10 (g/ml). The mixture was stirred continuously at 150 rpm at warm temperature (37±2 °C) and stored in the dark for 24 hours and then sieved using a muslin cloth filtered using Whatman No 1 filter paper to obtain a reddish brown dye which indicates the presence of Lawsone (2-hydroxy-1,4-naphthoquinone) known as hennotanic acid. The extracted solution (pH 9.8) was neutralized (pH 7.5) using a HCl (0.1M) solution to prevent side reaction of hennotanic acid in the dye extract in basic condition [17].

All concentrations of chromophores were measured using UV spectroscopy as previously reported [18] using a modified single pH method according to equation (1).

$$C_{mol/L} = \frac{A_{\lambda max}}{\in \times b} \quad (1)$$

Where A is the maximum absorption at λmax, ∈ is the chromophore extinction coefficient and b is the path length (1.0 cm).

2.2 IR and UV-Vis Spectroscopic Analyses

To analyze the phytochemical molecules of the dye extracts for the presence of alkaloids, flavonoids, tannins, phenolic compounds, glycosides, and saponins, IR and UV-Vis spectroscopy were applied. Each of the dried henna, tamarind and zobo powders (10 g) were dissolved in 20 ml of ethyl acetate, n-hexane, methanol and distilled water, respectively. Each mixture was filtered again to obtain the sample for the analysis. Each extract was measured using IR spectrometer (Buck Scientific IR Machine) and the absorbance of each extract in the UV-Visible region (200-800 nm) was measured using a UV-Vis spectrophotometer.

2.3 Preparation of the ZnO and TiO_2 Semiconductors

Nanocrystalline ZnO powder (1.0 g) and acetic acid (100 µl, 0.035M) 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. Separately, nanocrystalline TiO_2 (50 mg) and polyethylene glycol (PEG)

(100 mg) were measured in a ratio of 1:2 (w/w). The TiO_2 was located in a mortar and PEG was slowly added while grinding and mixing thoroughly until a homogeneous paste was obtained.

2.4 Synthesis of Polyaniline Conducting Polymer

The synthesis of polyaniline was carried out by chemical oxidative polymerization of aniline monomer [19]. A HCl solution (1 M, 200ml) was poured into the beaker and placed in an ice bath. Aniline (20 ml) was placed into the beaker and then $K_2Cr_2O_7$ (1.85 g) was poured into the mixture. The mixture was stirred for 30 minutes and then filtered to obtain the emeraldine salt residue which was left to dry in the oven at 90°C for 30 minutes. The dried emeraldine salt was then dissolved in 15 ml of dimethyl sulfoxide (DMSO).

2.5 Preparation of the Redox Electrolyte

The I^-/I_3^- redox electrolyte was prepared by dissolving 1g of iodine crystals and potassium in 15 ml of distilled water and then mixing thoroughly. The solution was stored in the dark to avoid decomposition.

2.6 Preparation of the Electrodes

Seven FTO conductive glasses (5cm × 5cm, Solaronix Aubonne, Switzerland) were obtained and labelled and a multimeter was used to determine the conducting sides of the glass. From the edges, 2 cm of two parallel ends of each of the glasses were taped to ensure that the paste does not spread out. To the glasses of the first set, ZnO paste (10 µl) was applied [20] while to other glasses, TiO_2 (100 µl) was applied on the conductive sides and spread evenly using the blade. Each conducting glass was dried for 5 minutes, then the tape was carefully removed. Each glass was sintered in an oven at 450°C for 30 minutes and allowed to cool to room temperature. The ZnO coated glasses were submerged into the zobo, lemon grass and dye extracts for 10 minutes. The TiO_2 coated glasses were submerged in the tamarind, henna, mango and tropical almonds extracts for 10 minutes. After a complete immersion/adsorption process, the photoelectrode was dried. On the second set of seven FTO conducting glasses, the conducting sides were also determined and graphite was applied to the entire surface using a lead pencil. Then, the polyaniline dissolved in DMSO was applied to the surface of the glass and spread homogenously across the glass surface.

2.7 Assembly and Photovoltaic Performance Test

Each of the seven pairs of electrode was clipped together using binder clips and a tiny slit was created at one of each electrode for connection purposes. The redox electrolyte (4 drops) was applied to each setup from the ends with the tiny slit and the electrodes were held together using a metal clips without the conducting parts touching the electrodes. Alligator clips were attached to the probe of the multimeter and the other side of the clip was connected to the cell and placed under sunlight (~10,000 lux), or projector light (~3,000 – 5,000 lux) to form a short circuit (Fig. 2.).

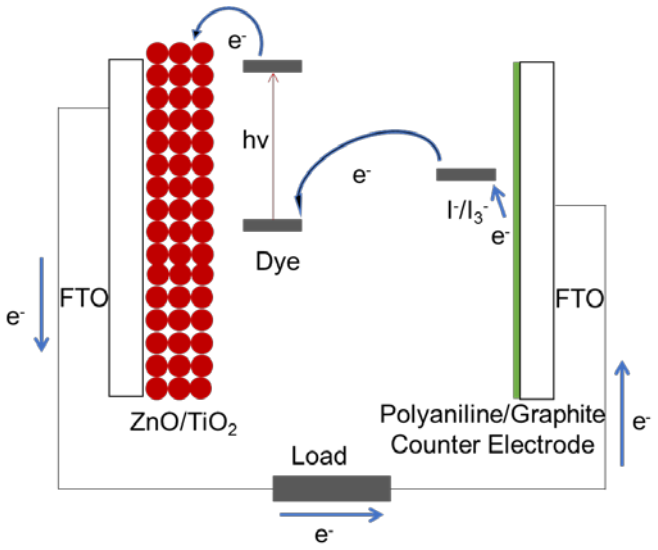

Fig. 2. Schematic diagram of a DSSC showing the flow of electron transfer. The working model of DSSC involves four distinct but sequential steps, including light absorption and dye activation, electron injection, electron reception, and interception reaction.

3 Results and Discussion

The solar cell parameters, including current (*I*), wavelength at the adsorption peak (λmax), open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and power (*P*) were determined using equations (2), (3), and (4). The wavelength was determined from adsorption spectra using UV spectroscopy, whereas the current was measured directly in triplicates using a digital multimeter to calculate the short-circuit density, open-circuit voltage and power, where A is the surface area of the FTO conductive glass.

$$J_{sc} = I/A \quad (2)$$

$$V_{oc} = I \times R \quad (3)$$

$$P = I \times Voc \quad (4)$$

3.1 Conductivity of Polyaniline

Polyaniline was doped with 1M HCl to facilitate a faster dye regeneration by electron transport required for a continuous functioning of the solar cell. The average conductivity of the polymer was 680 µS/cm. This high conductivity of the counter electrode is significant as it affects the rate of current flow in the solar cell, thus making the cell more efficient and stable.

3.2 UV-Vis and IR Spectroscopic Analysis

The absorption spectra of three extracts dissolved in n-hexane are shown in Figure 3. The figure shows for both henna and tamarind: (i) well defined absorption peaks at about 665nm, a characteristic absorption spectrum of chlorophyll *a* [21]; and (ii) peaks at 530nm, 556nm and 606nm, suggesting the presence of other pigments in the extracts. Similarly, the zobo extract shows a λ_{max} at about 518nm, a characteristic absorption spectrum of anthocyanin pigment [22].

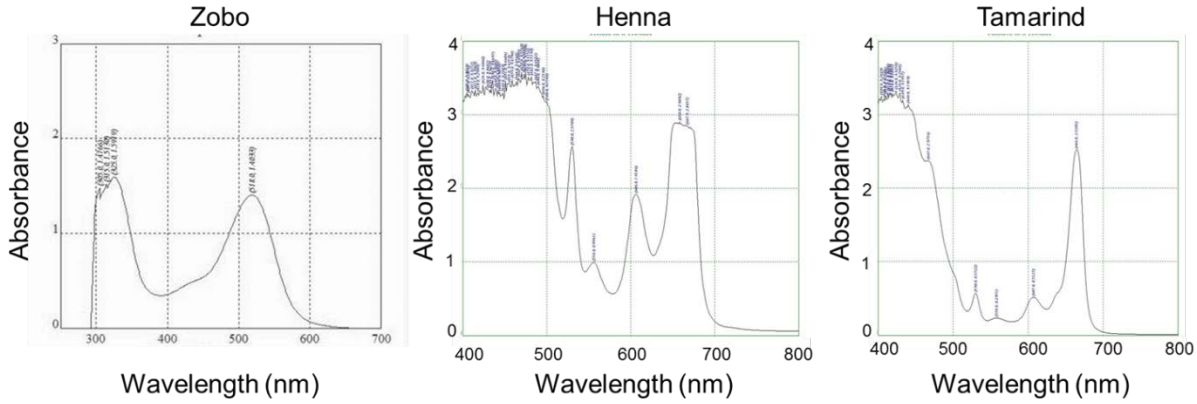

Fig. 3. UV-Vis Absorption spectra of zobo, henna and tamarind in n-hexane. All chromophores were analyzed using UV-VIS and IR spectroscopy in hexane, ethyl acetate, water, and methanol as solvents. Concentrations were calculated based on UV absorption spectra using specific molar absorptivity and A(λmax) values of 1.4, 2.8 and 2.5 for the zobo, henna and tamarind extracts, respectively.

The chromophore concentrations were calculated using equation (1) for zobo ($A_{\lambda max}$ = 1.4 and ϵ = 29,000 $Lmol^{-1}cm^{-1}$); tamarind ($A_{\lambda max}$ = 2.5 and ϵ = 33,000 $Lmol^{-1}cm^{-1}$); and henna ($A_{\lambda max}$ = 2.8 and ϵ = 80,000 $Lmol^{-1}m^{-1}$) [23]. The chromophore concentrations of zobo, tamarind and henna were calculated to be $4.8 \times 10^{-5} molL^{-1}$, $7.6 \times 10^{-5} molL^{-1}$, and $3.5 \times 10^{-5} molL^{-1}$, respectively.

The IR transmittance demonstrates the presence of electron-rich carbonyls, double and triple bond functional groups which are necessary for the photosensitization of the dye extracts as electron excitation by electrons. The henna, tamarind and zobo extracts showed peaks at 1740 cm^{-1}, the characteristic peak of double bonds, including C=O. In addition, the zobo extract showed a peak at 2926 cm^{-1}, well within the peak range of triple bonds, including alkyne and nitriles [24].

3.3 Photovoltaic Performance

All the photoelectrochemical parameters of the cells are presented in Table 1. Under the sunlight, the short circuit current density was ranged from 1.09 $\mu A/cm^2$ for the DSSC sensitized with mango to 215 $\mu A/cm^2$ with henna chromophore. The highest output power of 694 µW was obtained from the henna extract while the lowest power of 0.01 µW was obtained from the mango extract. The open circuit voltage was ranged from 280 mV with zobo to 0.89 mV with mango extract. The current study suggests that using polyaniline counter electrode would increase the efficiency showing that previous values of $\boldsymbol{I}$ (116 µA), $\boldsymbol{V_{oc}}$ (141 mV), $\boldsymbol{J_{sc}}$ (4.64 $\mu A/cm^2$), and $\boldsymbol{P}$ (16.3 µW) [18] were 87%, 99%, 212%, and 272% lower than our present zobo extract with polyaniline electrode, respectively. This proves that the presence of polyaniline significantly improves the performance of the solar cells.

In summary, our results demonstrated that the henna extracts produced the highest electricity among all the plants extracts in the study, even though all plants that contain chromophores could generate electric energy from light. High energy from henna extracts could be attributed to wide range of absorption

spectra which allows for the enhanced excitation of electrons [25], resulting in the formation of electron-hole pairs. Similarly, the high electricity production of tamarind can be associated to its riboflavin content, a substance that has been found to support photophosphorylation based on its photosensitivity [26]. Next, we noticed that the mango leaves extract produced the lowest electricity, suggesting that the dye may react with the light with a lower molar absorptivity.

The differences in photoelectric performance demonstrate that the concentration, pigment composition, extinction coefficient, conductivity of the counter electrode, and light intensity determine the photovoltaic performance. Further, variations in extracting temperature, solvent, and pH may affect the photosensitivity of the dye extract [27].

Table 1. Photovoltaic performance of all the extracts under projector light (3,000 - 5,000 lux) and sunlight (~10,000 lux). **S** = sunlight illumination, **P** = projector light illumination.

Plant Extract	I (μA)		V_{oc} (mV)		J_{sc} (μA/cm²)		*Power* (μW)	
	S	**P**	**S**	**P**	**S**	**P**	**S**	**P**
Henna	3,240	2,720	214	81	216	181	693	220
Ugu	1,810	32	149	25	122	2	270	0.8
Tamarind	1,220	510	110	33	81	34	134	17
Lemon grass	2,600	25	27	1.0	173	2	70	0.03
Zobo	217	19	280	18	14	1	61	0.34
Tropical almond	77	4	88	15	5	0.24	6.7	0.05
Mango	16	0.0	0.89	0.0	1.09	0.00	0.01	0.00

4 Conclusion

We conclude that common West African natural plant chromophores could potentially serve as photosensitizers in the assembly of the solar cell due to the presence of photoactive pigments, including chlorophyll, anthocyanins, and riboflavin. In addition, all plants sensitizers demonstrate an attractive alternative source of electrical energy because they are environmentally friendly, inexpensive, readily available and highly efficient.

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