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Utilizing Dye Sensitization Potency Of*BixaOrellana.L*seed And *PlumeriaRubra.L*flower In Dye Sensitized Solar Cell.

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Abstract: In this work, investigation on the performances of dye-sensitized solar cells (DSSCs) based on natural dyes extracted from ***Bixaorellana.L***seedand ***Plumeriarubra.L***flower was carried-out . The potency of the dyes' sensitization power in DSSC were examined using different solvents as extractors and the homogenous dye-extracts were characterized by UV-VIS absorption spectra. The photochemical cells were assembled using a TiO_2mesoporous film on FTO-coated glass andthe photovoltaic properties of the DSSCs were studied under an incident irradiation of 100 mW/cm^2. The best performance was found in the DSSC sensitized with ***Bixaorellana.L***seed extracted in Ethanolwith a solar energy conversion efficiency of 0.56%.

Keywords: Solar cells, solvent, photochemical, photovoltaic, mesoporous, efficiency

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I. INTRODUCTION

Reliable sources of Energy is the greatest challenge facing mankind in this century. Energy sources are grouped into two; nonrenewable sources such as fossil fuel and renewable sources such as wind and solar energy. Nonrenewablesources have been the energy sources for human society since pre-industrial era. However, this is being rapidly depleted by excessive consumption and its burning has caused and is still causing damage to the earth environment.

Renewable energy sources are considered clean alternatives to the traditional sources butwith oil, gasoline, and diesel prices increasing due to the massive dependence on fossil fuels, the world needs an alternative source of energy that is renewable, economical, environmentally friendly and socially acceptable. The availability , accessibility and sufficiency of such energy would in no small measure accelerates individual 's and nation's development therefore the supply should be secured and sustained

The use of dye-sensitization in photovoltaics remained ratherunsuccessful until a breakthrough in 1991 at the Laboratory ofPhotonics and Interfaces in EcolePolytechniqueFederale de Lausanne,Switzerland,whereGrätzel and his co-workers developed a solarcell by the successful combination of nanostructured electrodesand efficient charge injection dyes. This cell was then tagged dye sensitized nanostructured solar cell (DSSC) or Grätzel cell [1].

Due to its environmental friendliness, low cost, simple fabrication and reproducibility compare to the more established costly technologies based on hyper-pure crystalline Silicon and other crystalline thin-film solar cells, DSSC has attracted attention world wide.

Despite the fact that the cost of DSSC compared to the silicon solar cells is predicted to be at least five times lower, DSSC also have their limitations, these among other things include; low scalability, low efficiency, and low stability[2].

Another crucial parameter in the fabrication of DSSC is the sensitizing dye. Due to the dye significant role, considerable interest has been directed towards the development and improvement of new families of organic dyes and of metal complexes. So far, the most efficient dye is found to be Ru(II) [3,4] and Os(II) [5]. These complexes have a number of interesting features such as good absorption, long excited lifetime, and highly efficient metal-to-ligand charge transfer. The disadvantages of these complexes are high cost and sophisticated preparation techniques. Therefore, alternative organic dyes such as natural dyes are now been studied intensively.

In this study, six natural dyes extracted from *BixaOrellana .L* seed *(Bixaceae)* and *Plumeriarubra.L* flower*(apocynaceae*) using different solventswere examined. These *Bixa Orellana .L* seeds are inexpensive, have no nutritional use, and are abundant in Ado- Ekiti the present place of study.The absorption spectra of these dyes were carried out and the photoelectrochemical properties of the fabricated DSSCs using these extracts as sensitizers were investigated.

1.1. Chemicals and Materials

Fluorine doped Tin-Oxide (FTO)glass sheet of sheet resistance of 15Ω/sq.m and transmission > 80% (Xinyan Tech. Ltd, HongKong), Acetonitrile (CH_3CN, 99.9%, sigma Aldrich), Iodine(99%, G.P.R England),Sodium iodide (BDH),TiO_2 powder (P25,Degussa AG, a mixture of about 30% rutile and 70% anatase, sigma Aldrich), Ethanol (CH_3CH_2OH, 97%, Fluka), 2-propylene carbonate (99.5%,Fluka) ,$H_2PtC_{l6}.6H_2O$(BDH),and natural dye extracted from *Bixa Orellana .L* seed and *Plumeriarubra. L* flower.

All the purchased chemicals and solvents wereused as received / without further purification.

II. EXPERIMENT

2.1. Preparation of natural dye sensitizers

Generally, an efficient photosensitizer used for this purpose must fulfill certain requirementssuch as: an intense absorption in the visible region, Strong adsorption onto the semiconductor surface, efficient electron injection into the conduction band of the semiconductor, possessionof several O or –OH groups capable of chelatingto the Ti(iv) sites on the TiO_2 surface, be rapidly regenerated by the mediator layer toavoid electron recombination processes and fairly stable both inthe ground and excited states.All these qualities depend largely on the homogeneity of the natural dye extract [6]

With all these properties in mind, *Bixa Orellana .L* seed and *Plumeriarubra. L* flowerwere collectedfrom Ado-Ekiti city in Nigeria at noon time.Firstly, these samples werewashedwith pipe- bone water to get rideof dust particles. Thereafter, dried in the laboratory - in a dark place at room temperature for some days until the weight becomes invariant, then thedry-samples were crushed with a Kenwood- blender to obtain a fine powder.

For the extraction of dyes, 1.8 g of each powder was mixed with 50 ml solvent containing 1% HCl and the mixture stirred for 1hour to disperse the powder completely and then kept in the dark for a day . Later, the solution was filtrated by decantation followedby a glass filter to obtain clear solutions. In order to achieve a desired homogeneity the filtrate was centrifuged to obtain a homogeneous dye extract. The filtrate was covered with aluminum foiland kept in a dark place to prevent the dyefrom light exposure. The different solvents ultilized for the dye extractions at ambient temperature were ethanol, distilled water and mixtures of distilled water and ethanol mixed given six different dye extracts in all.

2.3. Preparation of photoanode

The transparent conducting oxide(TCO) on glass sheet adopted in this study is the Fluorine doped Tin-Oxide (FTO) glass.With the aid of a multimeter, the Conductive Side of the TCO was identified.It was first cut into sizes and cleaned in deconex detergent solution using anultrasonic bath for 25 minutes so as to leave no residual on the glass surface.it is thenrinsed with deionized water and ethanol to prevent traces of minerals on it and later dried using hot-air blower.

The required anatase phase- TiO_2 film on the FTO glass was prepared using a slot-coatingmethod .A consistent viscous slurry of titanium dioxide (TiO_2)was prepared by similar methods described elsewhere [7].

With the conductive sidefacing up, two parallel strips of scotch tape (♯810, thickness 50μm) wereapplied on the edges of the glass plate -this was used to;monitor the film thickness, to control the active area for dye absorption and when remove later leaves no trace of tape-glue on the TCO (‘‘Fig 2(a)’’).

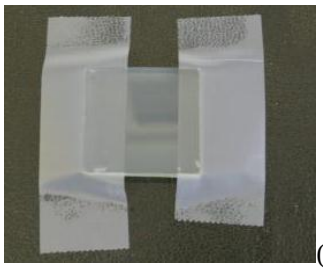
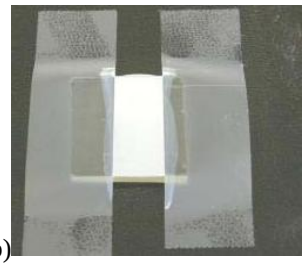
(a)  (b) 

Fig. 2photoanode sample prepared by slot-coating method; (a) positioning scotch tape on FTO glass, (b) homogenous film of TiO_2anatase phaseon FTO glass.

The prepared TiO_2 slurry was coated on the conductive glass by “slot-coating” method (i.e. sliding a pastewith a hard squeegee on the substrate to spread the paste across the substrate), this process was continued until the layer became homogenousas shown in ‘‘fig2(b)’’. After, the thick film formed was dried at room temperature, then tapes were removed carefully without scratching the TiO_2 coating. Theas-prepared TiO_2 film was sintered at 450^0C for 30 minutes in open furnace to enhancethe film/ TiO_2- particlescompactness and crystallinity as the vehicle of the paste burns away. After sintering, the filmswere allowed to cool in-step naturally to avoid glasscracking.

However at about 60^0C the sample was taken out of the furnace,immersed (face-down) into the extracteddye soluton for about 15 hours until the partially whitish colour of the film almost turn to the colour of the dye during adsorption.The film was taken out of the dye solution and rinsed with ethanol to remove unabsorbed dye and any otherresidues available on the surface.Finally, it was dried with hot-air dryer and stored in desiccator for later use (to avoid moisture absorption from ambient air).Furthermore , the left over dye solution was kept away from light and moisture in a sealed bottle to avoid degradation /for a later use.

2.3. Preparation of Platinum counter electrode

The counter electrodes were fabricated by spreading a drop of 5 mMchloroplatinic acidhexahydrate ($H_2PtC_{l6}.6H_2O$) in isopropyl alcohol onto the FTO surface, then subjected to heating at 450^0C for 30 minutes and then cool down in step. The thickness was measured using Profiliomterand found to be 32±1 μm.

In this study, Platinum (Pt) electrode was used because it is not venerable to corrosive attacks by theredox couple (I^{-1}/I^{-3}) and it enhances a reversible redox reaction to occur, at the sametime it maintain its transparency for photon entry.Furthermore, the catalytic activity of the counter electrode prepared was tested before continuingthe finalassemblyof the cell by Placing a drop of hydrogen peroxide on the counter- electrode (a 30% solution in water suffices). Bubbles were observed to evolve from the platinum surface indicating that active platinum layer is formed properly. It is later Clean with deionized water and ethanol to remove any trace ofhydrogen peroxide prior usage of the platinum electrode.

2.4The open cell configuration

Starting with the freshly made electrodes. The electrodes were put against each others such that the stained titania/photoanode is facing the platinum / counter-electrode i.e; The conductive sides of each electrode, face to face, forms the inside of the cell. Care was taken to slightly shift the two glass plates in order to leave room for electrical contacts. Thentwo similar clips were used to hold the electrodes together (‘‘Fig 3a’’). Immediately, the DSSC cell formed was filled with electrolytebefore getting damaged by ambient air.

The electrolyte solution used composed of 2ml acetonitrile (ACN), 8ml propylene carbonate (p-carbonate), 0.720 gm potassium iodide (KI), and 0.061 gm iodine(I_2).Few drops of the electrolyte was put at the interface of the two glass plates with a pipette (‘‘Fig3b’’), then tarry a little to allow the liquid to be drawn into the cell by capillary effect until the entire internal surface of the solar cell was wetted with electrolyte. Later, wipe off any excess liquid with a paper towel. The DSSC is now operational and will last until the electrolyte solvent evaporates.

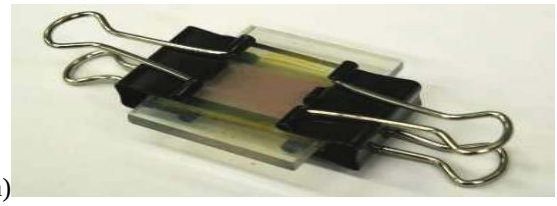
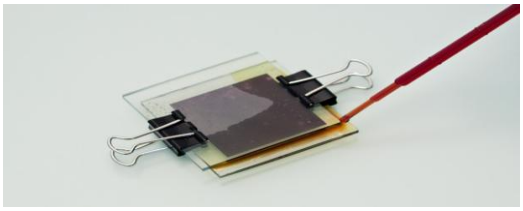
(a)  (b) 

Fig 3.(a)the assembled photoelectrochemical cell (b)pipette filling DSSC with electrolyte

2.5Measurements

The absorption spectra of the dye solutions were recorded using a double beam UV-VIS spectrophotometer, the absorption analysis was conducted in the wavelength range from 400 to 750 nm covering the UV-VIS range as shown in ‘‘fig.4 and fig. 5’’

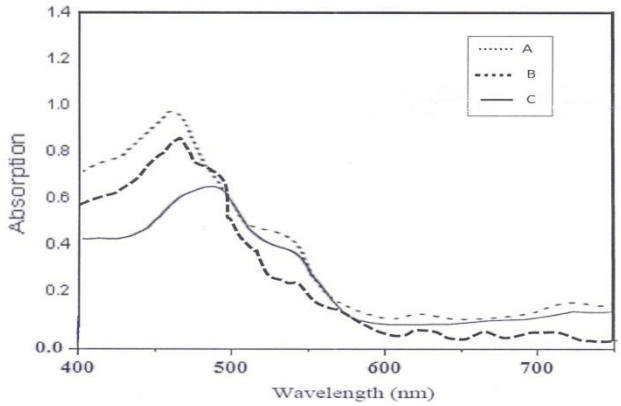


Fig. 4 electronic Spectra of *bixaorellana .l* seedextract using (A)ethanol, (B) 50% /50% water/ethanol, and (C) distilled water as solvents.

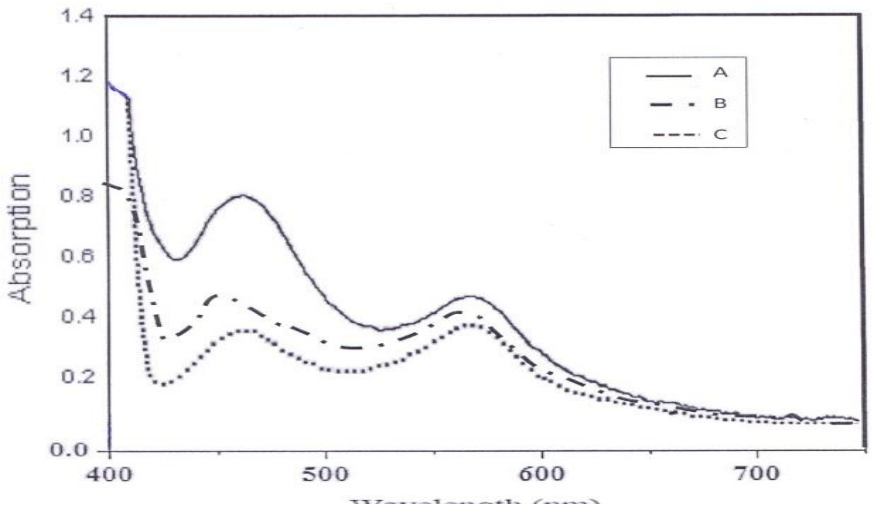


Fig. 5 electronic spectra of *plumeriarubra. l* flower extract using (A)ethanol, (B) 50% /50% water/ethanol, and (C) distilled water as solvents.

The thickness of the adherent and cracks-free film of TiO_2 prepared on FTO was determined byDekarkProfiliometer to be 8.20µm .

The I-V characteristic curves under simulated (AM1.5, 100 mW/cm^{-2}) /direct solar spectrum were conducted usingNewport/Oriel solar simulator, model 91160, with appropriatedfilters . The simulated AM 1.5 light intensity was also measured bythermopile detector model 70261 connected to a power meter model 70260 [8].Based on I-V curve, the fill factor (FF) can be calculated as ;

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} \quad (1)$$

Where*Im*and *Vm*are the photocurrent and photovoltage for maximum power output (*Pm*), *Isc*and *Voc*are the short-circuit photocurrent and open-circuit photovoltage, respectively.

The overall energy conversion efficiency (η) is defined as ;

$$\eta = \frac{FFI_{sc}V_{oc}}{P_{in}} \quad (2)$$

where*Pin*is the power of incident light.

III. Rsults and Discussion

3.1. Electronic spectra of Natural Dyes

Titanium dioxide is a white semiconductor that doesn't absorb visible light. Therefore, it is necessary to color, or sensitize ,thetitania electrode/photoanode with a dye that can absorb as much light as possible in the visible light spectrum. Green plants and their fruits investigated in this studies are fantastic source of naturaldyes that absorb visible light .

Although, Natural dyes are less toxic, less polluting, less health hazardous, non-carcinogenic , non-poisonous, environment –friendly,added to this, they are harmonizing colours, gentle, soft and subtle. However, the technology for the production of natural dyes could vary from simple aqueous to complicated solvent systems to sophisticated supercritical fluid extraction techniques depending on the product and purity required. In this study three solvents were adopted ;Ethanol,distilled water and 50% /50% water/ethanol as shown for the *Bixa Orellana .L* seed and *Plumeriarubra. L* flowerin ''fig4 and fig 5'' respectively.all the extracts showed an absorptionpeaks within the range 450 to 480 nm. These absorption peaks are closely related to the absorption peaksof anthocyanin as reported elsewhere[9,10] which indicates anthocyanin is the major components of the extracts.

The highest peaks of the two extracts were recorded for the Ethanol solvent, this indicates anthocyanin pigments arehighly soluble in 1% HClacidifiedethanol more than distilled water and equal volume of water and Ethanol solvents-a similar finding has been reported elsewhere[11].However, all the extracts showed abroad absorption peak in the visible region between 500 and 660nmwith a maximum absorption wavelength at 560 nm in *Bixa Orellana .L* seed.

3.2. Photoelectrochemical Properties

Photovoltaic tests of the fabricated DSSCs using these natural dyes as sensitizers were performed by measuring the I–V curve of each cell under 100 mW/cm^{2}irradiationas described ealier.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). All the photoelectrochemical parameters of the fabricated cells are presented in ‘‘Table 1’’.

Table 1. I-V Characteristics of *Bixa Orellana .L* seed and *Plumeriarubra. L* flowerbased solar cells at 100 mW/cm^{2}illumination.

S/N	Dye Source	Extracting solvent	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η%
A1	*Bixa Orellana .L* seed	ethanol	1.90	0.59	50	0.56
A2	-ditto-	water	1.60	0.46	38	0.28
A3	-ditto-	50%/50% ethanol/water	1.51	0.58	51	0.45
B1	*Plumeriarubra. L* flower	ethanol	0.49	0.51	60.4	0.15
B2	-ditto-	water	0.35	0.49	39	0.07
B3	-ditto-	50%/50% ethanol/water	0.64	0.44	48.5	0.13

The photoelectrochemical performance of the DSSCsbased on these dyes showed that the V_{oc} varied from0.44-0.59 V, the J_{sc}ranged from 0.35-1.90 mA cm^{-2}and the highest efficiency recorded is 0.56%. Therefore, the DSSCs sensitized with *Bixa Orellana .L* seed dye were found to have the best performance,

As depicted on ‘‘table 1’’, the DSSC sensitized with*Bixa Orellana .L* seed using ethanol as extracting solvent exhibit a conversion efficiency of 0.56% which declined to o.45% with 50%/50% ethanol/water solvent and 0.28% with water solvent shows that Ethanol is the best anthocyanin extracting solvent in plants. This result is equally reflected in the DSSC sensitized with *Plumeriarubra. L* flower as shown on the table.

IV. CONCLUSION

Dyes extracted from *Bixa Orellana .L* seedhave resulted in the DSSCs with highest efficiency.

This is expected because of the presence of deeper and darker coloration of the seeds extracts due to the presence of anthocyanins which have an increased absorption of light in visible spectra as depicted in ‘’fig.5’’[12]. The result leads us to believe that darker dyes are preferable candidates due to their increased absorption of visible light as compared to lighter ones(as observed in *Plumeriarubra. L* flower) leading to an increased photo current densities.Moreover, in this study it is found that extracting solvent has a crucial rule in the response of the cells.The DSSC sensitized with dye extracted with ethanol is found to have the best efficiency.

The resultsofourstudytherefore invokefurtherresearchinexploring different naturaldyesextracted with suitable solventsto improve theefficiency andstabilityof DSSC fortheuseinmarket.Therearegreatopportunitiesfor further development in regard to the reliability and repeatability of natural dyes as well as all other viable components employed in DSSC for the purpose of commercialization.

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