The Optical Properties of Cassiasiamea (Kassod) Plant Natural Dye-Doped Nanocrystalline -TiO_2 and the Photovoltaic Efficiency On DSSC

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ABSTRACT

This research was carried out to investigate the optical characteristics of nanocrystalline titanium dioxide doped with Cassiasiamea (Kassod) plant natural dye. Cassiasiamea (Kassod) plant dye was local dye extracted from a local plant which is very common in Nigeria. The sensitized nanocrystalline titanium (iv) oxide of Cassiasiamea (Kassod) plant natural dye was found to have a reduced energy band gap and hence could absorb incident solar radiation beyond the ultraviolet region. Spectrophotometer system – UV 752 Axion Medical Ltd., UK was employed to determine the optical spectrum, while the Tauc model was used to obtain the optical energy band gap.

The transmittance spectrum was shown, while the nature of the absorbance of dyed TiO_2 was studied. The behavior of the absorption coefficient of dyed TiO_2 was also investigated. The Current/Voltage and Voltage/Power Performances of TiO_2-based DSSCs using Cassiasiamea (Kassod) plant natural dye extracts was investigated and the solar simulation result of DSSCs developed in this research show (I_{sc}) = 1.44 mA, (V_{oc}) = 0.524 V, FF(%) = 65.30 %, and MPPT(mW) = 0.492 mW , while the conversion efficiency ɳ(%) of the dye sensitized solar cell was 0.492%.

(Keywords: nanocrystalline, optical, spectrophotometer, conversion, sensitized)

INTRODUCTION

In recent years, optical properties of semiconductor material have been of great interest as catalysts and other applications because of their unique textural and structural characteristics [1]. Scientist have developed much interest on the important of metal oxides such as TiO_2, ZnO, SnO_2, and VO_2 [2]. Due to the stability of semiconductor material such as titanium, its chemical structure, biocompatibility, physical, optical and electrical properties have become a well-known research area in physics [2, 3].

Titanium (iv) oxide exists in three forms; anatase, rutile, and brookite [1]. Anatase type TiO_2 has a crystalline structure with dipyramidal shape that corresponds to the tetragonal crystal structure and is used mainly as a photo catalyst under UV irradiation. Rutile type TiO_2 has a tetragonal crystal structure with prismatic habit. This type of titania is mainly used as white pigment in paint. Brookite type TiO_2 has an orthorhombic crystalline structure. Titanium dioxide, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells, and even as a food coloring agent and in toothpastes production [1, 2, 4, 7].

The range of absorption spectrum of a semiconductor material is important for its uses. The useful semiconductors for photo catalysis have a bandgap values comparable to photons energy of visible light, having a value below 3.5eV [6, 3]. The bandgap values for the three crystalline forms of TiO_2; anatase, rutile, and brookite are 3.20eV (tetragonal), 3.02eV (tetragonal), and 2.96eV (orthorhombic), respectively [3,4,5].

Different doping methods have been adopted to modify the electrical characteristics of TiO_2 nanoparticles to achieve new or improved catalytic characteristics and other chemical and physical properties [8, 9, 11, 13].

The present energy and environmental crisis has attracted the interest of exploring renewable energy sources. Dye sensitized solar cells based on nanocrystalline TiO_2 appears to be one of the most promising technologies as a low cost alternative to conventional semiconductor solar cells [10, 12, 16]. This concept was invented in 1988 by Brian O'Regan and Michael Gratzel at UC Berkeley [14]. The dye-sensitized solar cell is based on a semiconductor formed between a photon-sensitized anode and an electrolyte, a photo electrochemical system.

Dye sensitized solar cells (DSSC) are the most efficient third generation solar technology available, absorbing more sunlight per surface area than standard silicon based solar panels [13]. Dye sensitized solar cells work even in a low light condition such as non-direct sunlight and cloudy skies [17]. DSSC technology is attempting to replicate the ability of plants to turn sunlight into useful energy as seen in photosynthesis [18]. Since their invention in 1988 as reported by Gratzel et al. [18], the DSSCs have been attracting a significant attention of the researchers due to their substantial possibilities to fabricate low-cost, environmentally friendly, large-area photovoltaic devices [3, 21].

The main idea in DSSC development is to separate the light absorption process from the charge collection process thereby resembling natural light harvesting procedures in photosynthesis, by combining dye sensitizers with semiconductors [3,14,16]. This behavior enables the use of wide band gap metal oxide-semiconductors such as TiO_2. Natural pigments that are freely available in plant leave, flowers, and fruits of natural plants includes chlorophyll, carotene, and cyanin [20-21].

In this work, we investigated the optical properties of an FTO TiO_2 film doped with Cassiasiamea natural dye. UV-VIS spectrophotometer system – uv 752 was used to obtain the optical absorption spectrum of the doped film while Tauc model was used to determine the optical band gap [16-20].

Arduino software was used to run the UV spec, Scanning Electron Microscope (SEM), x-ray diffractometer (XRD), Four Point Probes used in testing the functionality of FTO and solar simulator model 4200-scs semiconductor characterization system. The transmittance spectrum was shown while the mesoporous nature of the film was studied using SEM analysis [15]. The behavior of the extinction coefficient was also studied. The current voltage characteristics of DSSC fabricated with the sensitized TiO_2 electrode were also presented.

The working electrode is a mesoporous film of TiO_2 nanoparticles (size ~20 nm) with a thickness of about 10 μm, on a Fluorine-Doped Tinoxide (FTO) coated glass substrate. Dye-molecules are adsorbed at the surface of TiO_2. The TiO_2 framework acts as electron acceptor and transport medium [17-20].

MATERIALS AND METHODS

Preparation of Natural Dyes

The soda lime glass was carefully cleaned using wool and piranha solution to remove any dirty particles on the soda lime glass. The leaves of a plant was provided and its botanical name obtained from Botany Department as *Cassia siamea* (Kassord Plant). Natural dye was produced from the leave of this plant called Cassiasiamea (Kassord Plant) for other analysis to be carried out in this research.

While preparing the dye, the method and the record of the data obtained from the following parameters were noted, weight of the leave, timing for grinding and centrifuging, and ratio of water and methanol solvent. Five grams (5g) of the leave was measured using weighing balance. Mixture of water and methanol 60ml (50:50 ratios) was measured using cylinder and grinded using electronics grinder. The five (5g) of leave and sixty ml (60ml) of water and methanol (50:50 ratios) was poured inside a grinder. The grinder was connected to the source and allowed to grind the leave and the solvent (50:50 ratios of water and methanol) for five (5) minutes. At the end of the grinding, the solution was filtered, and the dye separated and poured into a cylinder. The filtrate was further filtered by placing the solution on centrifuge machine for 3 minutes. After filtration, the natural dye from the leaf was on top of the cylinder while the waste product was at the bottom of the cylinder. The dye was carefully transferred to a small container and kept in a dark cupboard to avoid absorption of incident photon in open space [3].

Deposition of Electrode

Florine doped tin oxide thin films were deposited on the soda lime glass substrates (Axion

Medicals UF) via chemical vapor deposition (CVD) method. 60% of tin (IV) chloride ($SnCl_4$) and 40% of hydrofluoric acid was deposited on the cleaned soda lime glass as precursors and nitrogen gas was used as a carrier gas. Nitrogen gas was fed from a cylinder through a pressure regulator (Glook scientific) set at 0.5 Bars and then through a mass flow controller (Alicat Scientific).

The active area of 10mm by 35mm fluorine doped tin oxide (FTO) glass substrate was identified and covered with masking tape to control the thickness of the TiO_2 film. The flow rate is set at one (L) liter per minute and then through a bubbler containing $SnCl_4$ (anhydrous). A separate gas stream at one (L) liter per minute is bubbled through the hydrofluoric acid precursor.

The two gas streams converge on the substrate maintained at 550^0C by means of a thermocouple and temperature controller (Rex C-900). A chemical reaction takes place leading to the deposition of a transparent and conductive FTO thin film. The deposition time is varied between one minute and five minutes to generate films of a transparent and conductive. FTO generate films of different conductivities and transparency.

Thermal Treatment

The Cassiasiamea doped -TiO_2 electrode was allowed to dry naturally for about 15 minutes before removing the adhesive tapes. The edges were cleaned with ethanol. Using an electric hot plate, the film was subjected to thermal annealing at 200^oC for 10 minutes. Immediately after annealing, the electrode was sintered for about 30 minutes at 550^oC using thermocouple and temperature controller (Rex C-900).

Sensitization of Dyes

The thermally treated electrode was soaked in dyes for 12 hours (overnight) into a solution of the Cassiasiamea doped dye. After dye sensitization, the substrate was rinse with water and dried at 50^0C for 15 minutes and kept in dark in an airtight case till the time the solar cell will be assembly.

The presence of dye in the substrate allowed the cell to absorb photon energy even in the infrared region of the spectrum (low light condition). The resulting solar cell was able to sense and absorb photon energy of the smallest light that shines within the room and environments.

Optical Measurements

Spectrophotometer system – UV 752 Axion was used to obtain the optical absorption spectrum for the dyed working electrode. This measurement was carried out at room temperature before storing the dyed nc-TiO_2 electrode. The spectrometer was computerized and used to carry out the measurement. The result was displayed as graph of optical absorbance (arbitrary units) versus wavelength (nm). The Tauc equation was employed to have a quantitative estimate of the optical band gap of the film [1, 3].

$$\alpha = (hv - E_g)^{\frac{n}{2}} \qquad \textbf{(1)}$$

where α is the absorption coefficient, υ is the frequency, h is the Planck's constant, E_g is the band gap energy, while n carries the value of either 1 or 4.

The band gap energy could be obtained from a straight line plot of α^2 as a function of $h\upsilon$; and by extrapolation of the straight line portion of the plot on the energy axis will also give band gap energy. If a straight-line graph is obtained from n=1, it indicates a direct transition between the states of the semiconductor, whereas the transition is indirect if a straight line graph is obtained from n = 4

The transmittance spectrum was determined. If the spacing between the points is constant, and the conducting film thickness is less than 40% of the spacing, and the edges of the film are more than 43 times the spacing distance from the measurement point, the average resistance of the film or the sheet resistance is given by equation (2).

$$R_S = K\frac{V}{I} \qquad \textbf{(2)}$$

where K = 4.53 which is π/ln2 and k is the extinction coefficient and λ is the wavelength of the radiation.

RESULTS AND DISCUSSIONS

The Absorbance of Liquid and Solid Samples of Kassod Dyed TiO_2

The optical absorption spectrum, Figure 1, shows that the Kassod dyed TiO_2 working electrode noticeably absorbed light beyond the UV region. The natural dye greatly improved the absorbance of the wide–band gag titanium (iv) oxide which alone cannot absorb visible light.

The absorbance of liquid and solid samples of Kassod plants is shown in Figure 1.

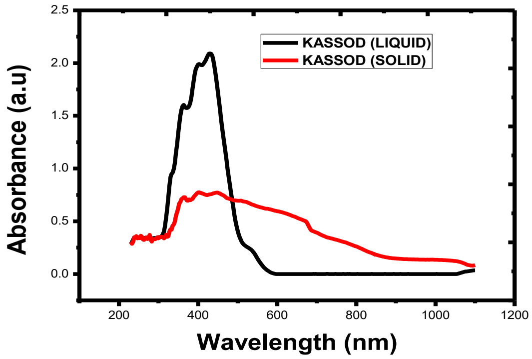


Figure 1: The Plot of Absorbance as a Function of Wavelength for Kassod (Liquid and Solid Sample).

It was noticed that as the wavelength increases the absorbance decrease in all the samples. The liquid samples recorded the highest absorbance and they absorb more cells compared to the solid samples. The liquid sample recorded absorbance above 2.0 a.u while the solid sample as an absorbance within 0.1 – 0.27. From the plot the solid sample absorbance will be suitable for solar application while the liquid sample will be for photovoltaic application.

Determination of Kassod Plant Band Gap of Dyed TiO_2

Figure 2 illustrates the plot of $(ahv)^2$ vs. eV for the doped TiO_2 film. The optical band gap estimated from the intercept of the tangent to the plot was 2.53 eV which is lower than the band gap for the crystal structures in titanium dioxide. This implies that the process of dye sensitization has led to band gap narrowing which was necessary for the doped TiO_2 to visible light as represented in Figure 2. Kassod Plant synthesized on FTO 2.53 eV. From the Figure, it is observed that the absorption coefficient squared increases exponentially with photon energy. The range of the band gap energy makes the material useful for fabrication of blue and green light emitting devices, photocell window layer and light emitting laser diode.

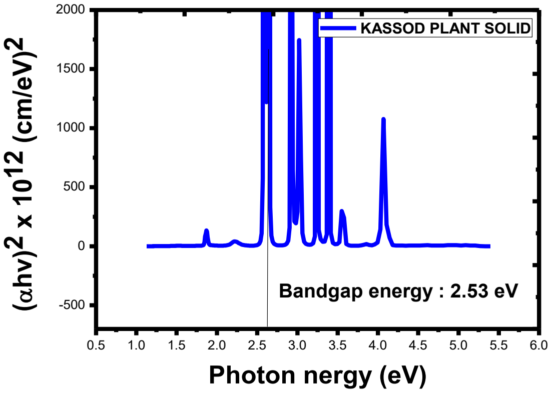


Figure 2: The Plot of Absorption Coefficient Square as a Function of Photon Energy for Kassod.

UV Transmittance Analysis of Dyed TiO_2

Figure 3 represents the transmittance spectrum. The transmittance of the Cassiasiamea (kassod plant) - doped nanocrystalline.

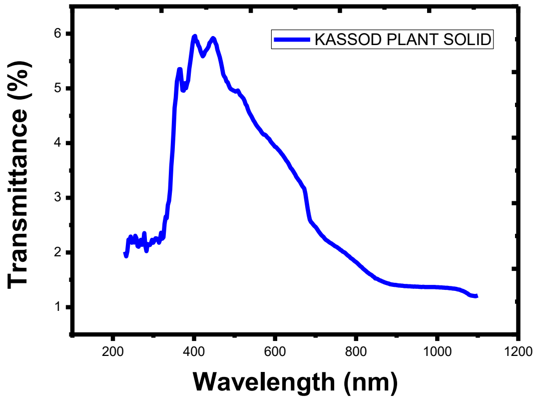


Figure 3: The Plot Transmittance (%) as a Function of Wavelength for Kassod Plant.

Absorption Coefficient Spectra of Kassod Dyed TiO_2 Film

The absorption coefficient spectra of Kassod films showed that the films have a sharp edge at the lower energies.

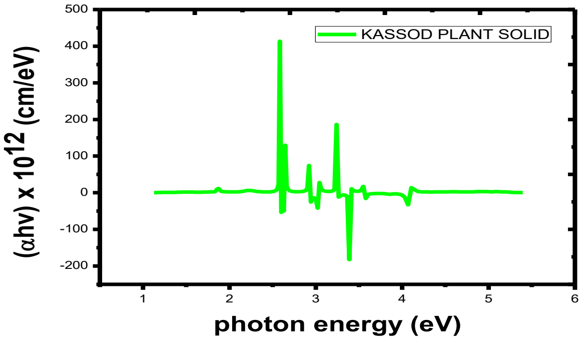


Figure 4: The Plot of Absorption Coefficient as a Function Photon Energy for Kassod Plant Solid.

The absorption coefficient spectra of Kassod films is shown in Figure 4. The films have a sharp edge at the lower energies. This is because these light energies below the band gap (3.0eV and above) do not have sufficient energy to excite an electron into the conduction band from the valence band. Consequently, the light was not absorbed. But, as the photon energy increased sufficiently to about 3.25eV, the absorption coefficient increases with the photon energy. Materials with higher absorption coefficients more readily absorbs photons which excite electrons into the conduction band.

Current/Voltage and Voltage/Power for Kassod Dyed TiO_2

The current density plots as a function of the voltage for the DSSCs for some of the dyes are shown in Figure 5.

The efficiency of a solar cell is determined as the fraction of incident power which is converted to electricity and are defined by the follow up equations.

$$P_{max} = V_{OC} I_{SC} FF \quad (3)$$

$$\eta = \frac{V_{OC} I_{SC} FF}{P_{in}} \quad (4)$$

$$n = maximum\ power\ output = \frac{maximum\ power\ output}{maximum\ power\ input} = \frac{1m\ Vm}{A\ x\ E} \quad (5)$$

$$FF = \frac{1_m V_m}{V_{OC} I_{SC}} \quad (6)$$

where;

V_{OC} is the open-circuit voltage, ISC is the short-circuit current; FF is the fill factor and η is the efficiency, and P_{in} is incident power.

The graphical results of photovoltaic parameters for DSSCs plant dye as photosensitizer are illustrated in Figures 5(a) and (b) for current/voltage and voltage/power relationship, respectively.

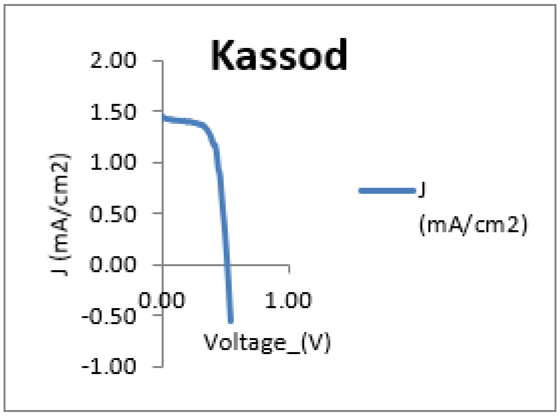
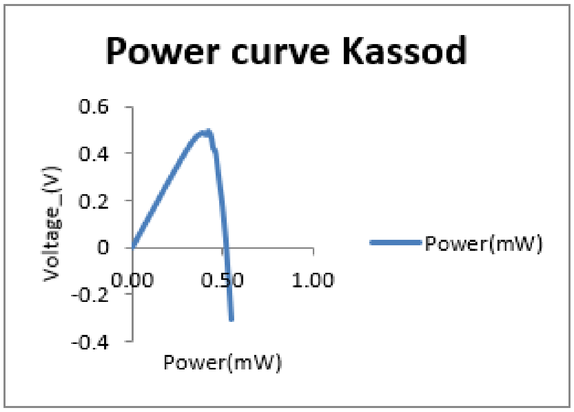


Figure 5(a): Current/Voltage for Kassod Plant.



Figures 5(b): Voltage/Power for Kassod Plant.

CONCLUSION

The Kassod plant natural dye extracts revealed good absorbance. The efficiency of a solar cell and incident power converted to electricity was determined using Equation 2.

Ideally, an excellent dye should absorb very well for all wavelengths below 920 nm. The DSSCs fabricated using these natural dyes overall photocurrent conversion efficiencies of η 0.492%. However, the Kassod plant outperformed the others probably due to the dye molecules' ability to anchor more firmly to the surfaces of the TiO_2. Moreover, the solar cell fabricated using the Kassod plant dye exhibited high shunt 10 resistances which implies that there were less alternative paths for current leakage in the cell. One of the greatest challenges to TiO_2 DSSCs is its ability to strongly adsorb dye molecules.

Optical characterization using Spectrophotometer system – UV 752 shows that the sensitized titanium dioxide electrode could absorb light both in the ultraviolet and visible region. Using the Tauc model, the optical band gap of the dyed TiO_2 was found to be 2.53eV which is lower than the band–gap of the three crystal structures in TiO_2. Hence, the Cassiasiamea-doped nanocrystalline -TiO_2 dye can be used as photo-sensitizer for wide band gap semiconductors such as TiO_2 which alone cannot absorb visible light. The photo-conversion efficiency of dye sensitized solar cell developed with the doped nanocrystalline titanium (iv) oxide was 0.492%.

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SUGGESTED CITATION

Okoye, I.F. and A.O.C. Nwokoye. 2020. “The Optical Properties of Cassiasiamea (Kassod) Plant Natural Dye-Doped Nanocrystalline -TiO2 and the Photovoltaic Efficiency On DSSC”. *Pacific Journal of Science and Technology*. 21(2):128-134.

Pacific Journal of Science and Technology