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Optical Properties of Natural Dye Leaf Extracts and Nanostructured TiO2 Particles as Photosensitizers for Dye-Sensitized Solar Cells

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Abstract: A threat to the energy production in the world is emerging mainly because of the shortage of energy resources and world industrialization. Although the cost factor is also a problem here, the future of solar energy is now growing and its conversion efficiency is also increasing. An important realization that can be made is that a dye-sensitized solar cell is a means of refining solar energy conversion technology, in which the use of wide bandgap semiconductors is based on photocurrent. Among the elements of the dye –sensitized solar cell, the dye as a sensitizer determines the performance of the cell. Common natural dyes are obtained from leaves, flower petals, and roots for instance. Considering the aspect of simplicity and cost of natural dyes, less complex extraction process than synthetic dyes and being friendly to the environment, researchers are striving to find ways of replacing the synthetic dyes with natural dyes. Here, TiO2 was prepared with the Sol-gel spin coating method with titanium tetraisopropoxide, isopropanol, acetic acid, and deionized water as precursors. The results showed that there was changes in the optical properties like transmittance, reflectance, and bandgape energy when the dye leave extract of Mangifera Indica, Manihot Esculenta, and Hibiscus Sabdariffa was examined. Morphological and compositional properties of the nanostructured TiO2 are also ascertained.

Keywords: Characteristics, Optical, Dye-Sensitized, Photosensitizers, Nanostructure.

1. INTRODUCTION

Since creating the silicon solar cell, people have accepted, that photovoltaic systems can be an ideal solution for the mass production of electricity (kumara et al, 2006). Dye sensitive solar cell (DSSC) is photovoltaic system which can produce electrical energy from the irradiation of sun light (Sanchez et al, 2018). It is a device on the principle of conversion of visible light directly into electricity with help of wards wide band gap semi-conductors. The dye-sensitized solar cells which are also known as Gratzel cells were discovered in the year 1991 by Michael

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Gratzel and Brian O' Regan reporting a new in a chemical solar cell by the successful combination of nano structured electrodes and efficient charge injection dyes with a photo electric conversion of 7% using simulated sunlight (O' Regan & Gratzel, 1991).
However, the cost factor has not severed the growing trend of solar energy because of its long-term resource endowment besides the increasing conversion efficiency (Rawal et al., 2015).
A dye-sensitized solar cell is a solar cell aimed to transform visible light into electric current. Therefore, the process of using dye for its operation as a sensitizer is very important leading to the efficiency of the dye-sensitized solar cell (Cherry & Pardeep, 2024). Concerning the above, it has been established and proved that DSSCs are a promising class of the low cost and moderately efficient solar cell based on the organic materials Hagfeldt & Gratzel; 1995, Haruna et al. , (2015). Natural dyes are available in variety such as leaves and flowers petals, roots and many more resources available in nature. Hence, in light of these natural dyes insights including cost efficiency, easy extraction procedure, non-toxic (eco-efficient), availability, heat compatible and the use of low-cost materials like TiO2, researchers are currently devoting their effort for the development of natural dyes in place of synthetic dyes.
This research paper expounds the features of some optical properties (transmittance, reflectance and energy bandgap) of natural dyes extract from Mangifera indica, Manihot Ecsulenta and Hibiscus Sabdariffa and nanostructured TiO2 particles that can be employed for the fabrication of dye sensitized solar cells.

2. RELATED WORKS

Investigations on the possibility of natural dyes sourced from plants to be used in place of a photosensitizer in dye-sensitized solar cells (DSSCs) have been a very active area. Aziza, et al (2023) for instance in a study done on the effectiveness of natural dyes, the following were considered as potential enhancers to DSSCs which included chlorophyll, tannin and cyanin which are sourced naturally from plants. It can be noted that some of the extracted natural dyes possess beneficial optical properties as well as enhance the performance of the developed DSSCs. In their work, Yuniati, et al (2021) conducted a study that was based on the extraction of dyes from rosella flowers as well as the blue pea flowers. The rationale for this work was to employ the mentioned dyes as sensitizers in DSSC devices. According to their work, extracts from some floral dyes used in making the dye-sensitized solar cells can act as efficient photosensitizers with a reasonable level of efficiency rated with the use of DSSCs. Pathak, et al. (2019) provided a systematic review on the use of natural colors originating from fruits, vegetables, leaves, and flowers in DSSC systems. The review examined the extraction techniques, optical characteristics, photovoltaic efficiency, and durability of natural dye-sensitized solar cells produced by different researchers. The study emphasized the capacity of natural dyes to serve as inexpensive and environmentally acceptable substitutes for synthetic dyes in DSSC technology.
Another work of Chakraborty, et al. (2016) describe materials for DSSCs however, they have prepared nanostructured TiO2 thin films by sol-gel spin coating and it is quite alike the technique used in this paper. The analysts also over ponder on the TiO2 Nano Structures structural, optical and electrical properties then evaluate them on the suitability as photo anode material DSSCs. These highlighted works indicate that research has been on a steady in

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analysing the natural dye extracts and nanostructured metal oxide's like TiO2 for their possible use in developing dye-sensitized solar cell technology. This research aligns closely with the main subject of the current study.

3. METHODOLOGY

Experimental Procedure Methodology

Preparation of the Dye

The Manjifera Indica, Manihot Esculenta and Hibiscus Sabdariffa leaves were individually procured directly from their trees in Agbor, Delta State; then, washed and sun dried. These leaves were air dried in a shade to avoid the bleaching of the pigments (Eli, et al., 2016). Each of the Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa leaves samples was weighed using an electronic weighing balance; 10 g each. Each was ground with porcelain mortal and pestle and then 25ml absolute ethanol (99 %) at room temperature was added. The filtrate obtained from the mixtures were used to retain the dye. Filtrate is the sensitizer solution.

Synthesis of TiO_2 Nanostructure

Initially, 15 ml of the aqueous solutions of titanium tetraisopropoxide (Ti[OCH(CH3)2]4, was gradually added into 30 ml of the acetic acid (HCOOH) within a three neck flask and the solution was stirred for 5 minutes to prevent agglomeration (Simon et al. , 2019). The deionized water (4.0 mL) and isopropanol CH2CH(OH)CH3 was also added drop wise into the solution before the mixture was stirred vigorously for a further 10 minutes. After the complete mixing of the solution, 4 mL of concentrated nitric acid [(HNO3)] was added into the solution as a stabilizer, and the solution was mixed again in the same manner for another 20 minutes. Spherical anatase TiO2 colloid in the nanometer range was prepared by hydrolytic as well as condensation reactions among titanium alkoxide precursors (Mohsen Azizi, P. et al. , 2009). Formerly, on the well-cleaned borosilicate glass substrates, the titanium alkoxide was hydrolzed and undergone polymerization process to build up a 3-dimensional network of TiO2 which was dispersed on the borosilicate glass substrates and spun at 4000 rpm for 30 sec at RT (Simeon et al. , 2019). In the case of preparing the thin films, following the spin-coating step, another post thermal treatment was carried out on the films which included heating them at 500 0C in air for one hour and then leaving them to cool down to room temperature.

$TTIP + isoPrOH + AcOH \rightarrow Ti(OR)_4 + 4H_2O + 2Ti(OH)_4 + 4ROH$ (Hydrolysis)

$2\,Ti(OH)_4 \rightarrow TiO_2 + TiO_2\,2H_2O + 2H_2O$ (Condensation)

Characterization Technique

Finally, upon the preparation of the sample, a number of characterization technqiues were employed for the study of the optical properties of the sample and nanostructured TiO2 particle of the sample.

Particularly the transmission, reflection and energy band features which formed the core of the research as earlier indicated were analyzed. The spectra characteristics of the dye extract were analyzed using UV-Visible spectrophotometer of brand Avalon, model no: Ava-spec-uls 2048CL-2EVo. In this survey the measured wavelength range was from 300 nm to 1100 nm.

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The UV range is between (300-400) nm, VIS band is in between (400-700) nm and the NIR band is (700-1100) nm band.

The X-ray microanalysis was done using a sophisticated X-ray diffractometer which is new model ALR

(EQUINOX) 100 analyzer. The two theta gross angles were determined from the diffractogram, while the FWHM, miller indices, and the d-spacing were as well assessed. The crystalline size (D) was calculated using the Debye-Scherrers's equation of the form: (1) as adapted below; (Egwunyenga et al . , 2021).

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

$$2d \sin \theta = n\lambda \quad (2)$$

The inter-planner spacing between atoms (d-spacing) was calculated using Bragg's law equation (2) above as utilized by Daniele et al., (2010)

The energy dispersive X-ray (EDX) characterization was carried out with Phenom Pro X Model, Eindhoven de Netherlands machine.

The band gap Eg was determined by using the Tauc relation between the absorption (α) and the incident photon energy (hν), given by the equation 3 as described by (Ekwealor et al., 2015)

$$Ah\nu = A\,(h\nu - Eg)^n \quad (3)$$

Where A is a constant, Eg is the band gap energy and n depends on the nature of the transition. In this study, the possible transition was estimated from the plot of absorption coefficient squared $(\alpha h\nu)^2$ versus photon energy hν.

4. RESULTS AND DISCUSSION

4.1 Optical Studies

FTS of Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa leaves extract are illustrated in Figure 1.

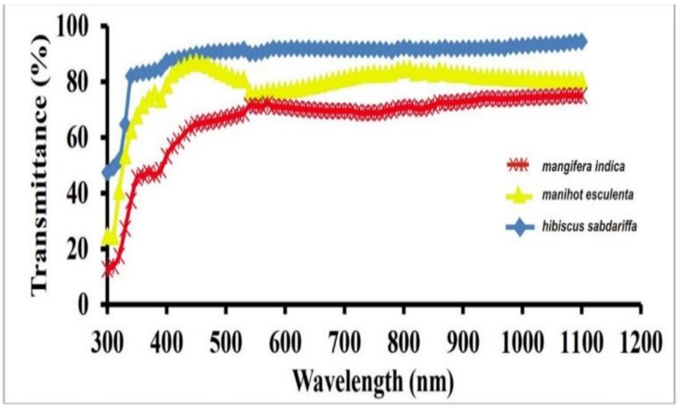

Figure 1: The representations of transmittance spectra and wavelength of the extract made from Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa fresh leaves.

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The resulting graph demonstrates that the amount of light transmittance is lowest for the dye leaves extracted from Mangifera Indica, which equaled to 48 percent at 350 nm. Analyzing the percentage value of the sample, the hibiscus sabdariffa leaves dye extract contains has the highest percentage value of eighty four percent at thirty five zero nM. Using the percentage transmittance value obtained, it can be seen that at_the wavelength 350 nm, the dye extracted from Manihot Esculenta was found to be 72%. The graph also revealed that the transmittance of water also increased as the wavelength was increased throughout the VIS and NIR EMS. The high transmittance displayed by the three dye leaves extract in the NIR region crown them for coating of glass window which is able to absorb the sun's heat near-infrared rays in winter and reflect in summer with the glass being transparent. (ACS Photonics, 2021).

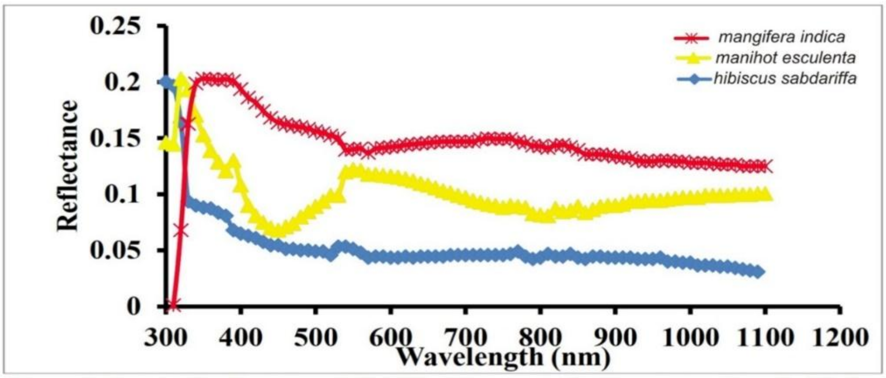

Figure 2: Reflectance spectrums of Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa leaves extract against the wavelength.

From the observation made on figure 2 it was observed that the reflectance value which was highest was 0. Possible reason this absorption may be attributed to specific chemical groups in the Mangifera Indica that has an ability to bond with the dye leaves extracted and obtain this unit of 20 abr in the UV area. This is followed by the reflectance value of 0. 14 Apri unit was also produced with Manihot Esculenta in the UV area. The minimum reflectance of 0 was observed in the streak of color red. 07 apr unit was observed for the dye leaves in the VIS region extracted from Hibiscus sabdariffa while the reflects of Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa extracted leaves exhibited maximum reflectance values of 0. 15 arb unit, 0. 12 abr unit and 0. 12 abr allow the institution to penetrate deeper into its strategic objectives by enabling employees to implement them gradually and consistently at the workplace. 05 arb unit respectively. Comparing the data of reflectance the following trends were observed: in general, reflectance was less with the increasing wavelength in the VIS and NIR regions. This decrease in the reflectance can be linked with enhanced transmittance having small values of reflectance in the VIS-NIR region; the sampled leaves extract can be applied in other glass reflective coating as used during the float process to increase amounts of heat reflected in the glass. It can block and deflect the dangerous UV and NIR light from the sun but let all other forms of natural light to filter through. It also minimised high intensity of solar glazing (Haruna et al, 2015).

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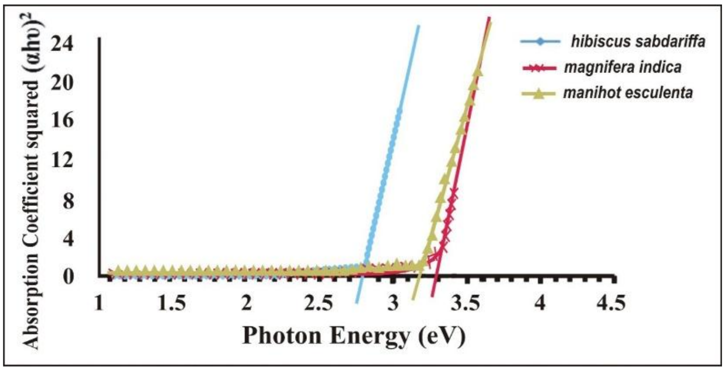

Figure 3: Optical band gap spectra of Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa leaves extract.

Diagrams represented in Figure 3 were the plot of $(\alpha hv)^2$ on the y-axis and photon energy on the x-axis for Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa leaves extract. The value of optical energy band gap was calculated by drawing a tangent line on the plot in the region of the straight line with the help of interactive facility and calculated the intersections with the y-axis at photo energy 'h'. The values of bandgap energy for the leaves extracted with Mangifera Indica, Manihot Esculenta and Hibiscus Sabdariffa leaves extracts were between 3. 30eV, 3. 20eV and 2. 80eV respectively. It was noted from the Figure 3 that the bandgap energy was wide and ranged from 2. 80eV to 3. 30eV. Shown values of the bandgap energy are consistent with the one found in literature presented by Kokkonen et al. 2021.

The wide bandgap obtained in this study placed the leaves extract useful in the coating of absorber layers of solar panels (Bart et al. , 2019). The layer is a semiconducting material commonly known as the core of all thin film solar cells. And quite fittingly, it is the layer that captures the most photons and in turn is responsible for exciting the appropriate number of electrons to the conduction band for photocurrent generation (Mazunder, 2022).

4.2 Morphological and Compositional Studies

XRD pattern of the nanostructured TiO2 particles is depicted in the following figure 4. Especially the peak which is represented by miller indices of (101) has the highest intensity which indicates it has the most preferential orientation. The x-ray pattern in this study presented an experimental pattern of the anatase TiO2 crystal which belongs to the space group- 141/amd with the density of 3. 874 g/cm3, lattice constants, a = 3. 7892 A = 5 and c = 9. 5370 A.

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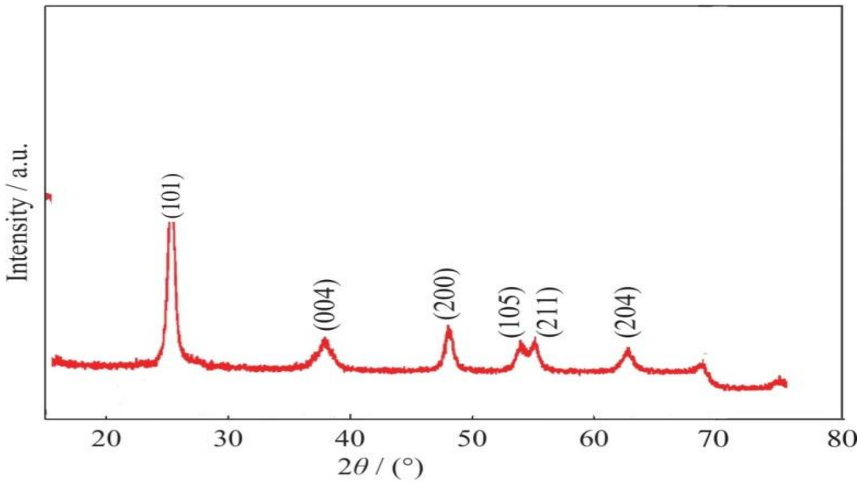

Figure 4: XRD pattern used to confirm the formation of nanostructured TiO_2 particles.

Atanse phase is identified as a metastable phase (Yang et al.2021). Lupan et al,have revealed that Anatase is the most effective photocatalytic material available. With reference to the outcome of the X-ray in this study, the results can be useful in the inspection of electronics. X-ray sources are present in essentially all large production facilities and the use of carbon nano materials can supplement the existing market leader of traditional thermionic devices (Zang et al.2009). The EDX spectra of the particles revealing the components existing in the synthesized TiO2 nanostructures is depicted in the Figure 5. EDX analysis gave the quantitative composition and the weight present of Titanium, Oxygen, Nitrogen and Carbon as 70. 33 %, 15. 30 %, 10. 4 % and 4. 13 % respectively.

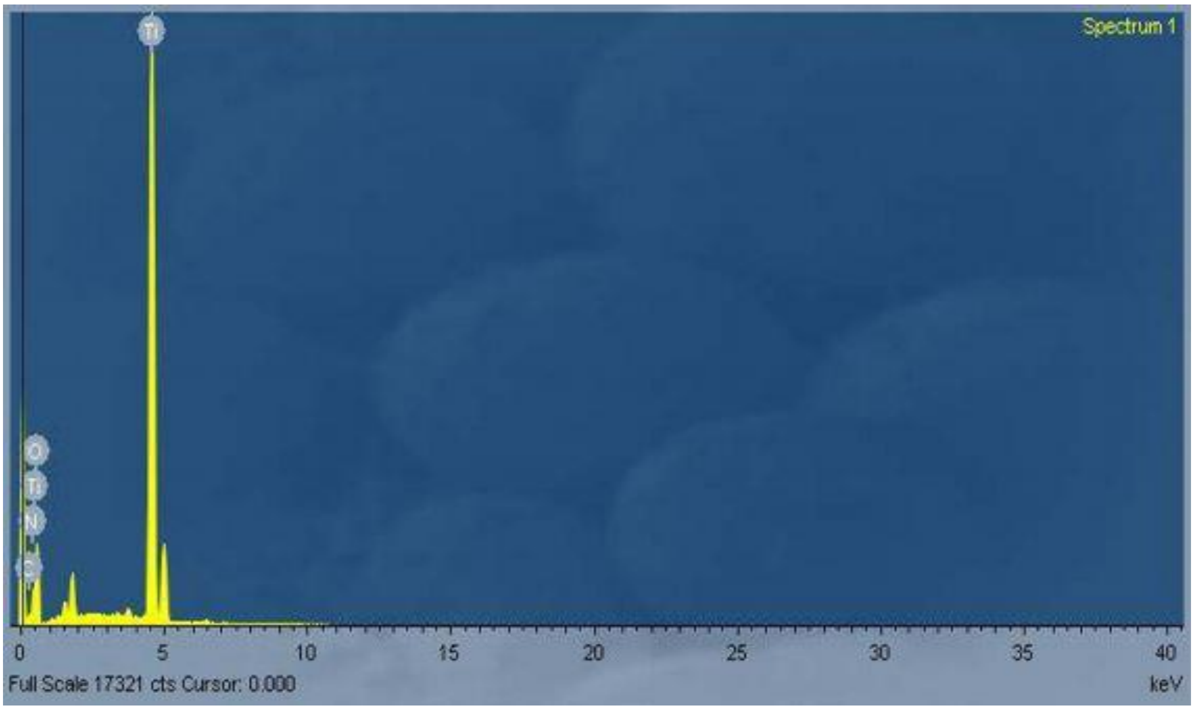

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Figure 5: This is EDX image showing the elements present in the TiO2 nanostructured particles.It is worth noting that by the help of the Figure, the peak of Titanium is very high. This is in concordance to studies conducted by (Danladi et al., 2016). The quantitative result for TiO2 compound thus depicted in figure 6 of this study was relatively close and almost equal to standard recorded values of 73. For Titanium, the figure was only 5 % while for Nickel it was only 16. 00 % for Oxygen and 12. I could not determine the concentration of the other gases in the air because the percentage of each element dropped to a decimal point in the following sequence: Nitrogen 75, Hydrogen 0. Respective of 1.17% for phosphorus, 0.84% for potassium and 10% for Nitrogen respectively (Jabir et al, 2012).

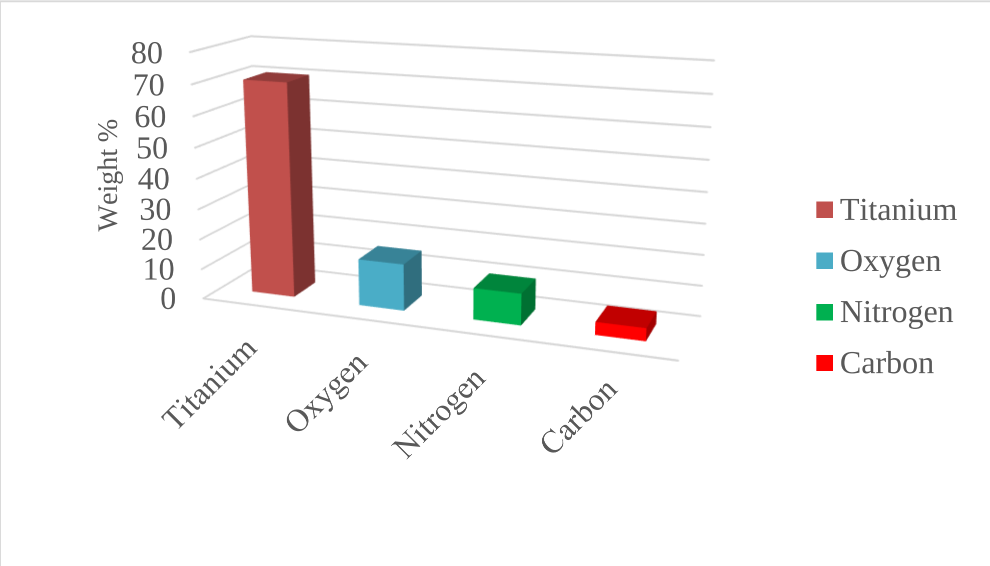

Figure 6: Quantitative result present in the TiO_2 nanostructured particles

5. CONCLUSION

A TiO2 nanostructure film has been prepared using Sol-gel spin coating technique. There are reports from the present analysis with EDX and XRD of the morphological as well as the compositional properties of the nanostructured TiO2. The specifics of the behaviour, the character and the implications of the dye leaves extract of Mangifera Indica Manihot Esculenta and Hibiscus Sabdariffa in the spectra of electromagnetic wave spectrum are also presented. The findings of this research will help researchers in the ascertainmenTs and fabrication of dye-sensitized solar cells so as to enhance the cells conservation efficiency.

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