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The Fabrication of Natural Dye Sensitized Solar Cell (Dssc) based on TiO_2 Using Henna And Beetroot Dye Extracts

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Abstract

In this work, a general approach for the preparation of natural dye sensitized solar cells (DSSC) and its efficiency is calculated . DSSCs are a promising class of photovoltaic cells with the capability of generating green energy at low production cost since no vacuum systems or expensive equipment are required in their fabrication. The TiO2 Nano powder were successfully synthesized by sol-gel method and using Titanium butaoxide (TBT) as a precursor. Dye-sensitized solar cells (DSSCs) were constructed by using the Henna (Lawsonia inermis) leaves and Beetroot as natural sensitizers of anatase-based nanostructure TiO2 thin film Paint-coated on FTO conducting glass. The orange-red Lawsone, dark red color Beetroot are the main components in the natural dyes obtained from these natural products. A blend of KI, acetonitrile and iodine was used as a solid state thin film electrolyte. Structural and optical properties of the semiconductor thin films were characterized by X-ray diffractometer and UV-VIS spectrophotometer respectively. The XRD result exhibit the structure of anatase phase of TiO2 and UV exhibit TiO2 which was in conformity with its wide band gap nature. And then TiO2 was subjected or treated to Scanning Electron Microscopy (SEM), Thermogravimrtric/Differential Thermal Analysis (TG/DTA), and Efficiency of DSSC was calculated. In this paper two natural dyes are selected and based on this, DSSC are fabricated and the efficiencies were measured. The efficiency of the DSSC with beetroot dye is 1.3 % and that of henna dye is 1.08 % .

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Keywords: Synthesis;XRD; UV; SEM;TG/DTA;Efficiency

1. Introduction

Solar cells are the important applications of solar energy. It is an alternative energy source to produce energy from freely available solar radiation. Dye sensitized solar cells are one of the important alternative technology for solar energy conservation. Dye-Sensitized Solar Cells (DSSCs) have been developed, which are receiving increasing attention from researchers because of their low-cost materials.

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DSSCs are devices that convert visible light into electricity through the sensitization of wide-band-gap semiconductors. The operational principle of DSSCs is very simple: Photons interact with dye molecules to create excitons, which rapidly split to form electrons and holes. Electrons are attracted toward the photoelectrode and holes are transported by redox species at the nanoparticle surface in the electrolytes used in the DSSC. DSSC have the advantages of simple fabrication, low cost and large area. Recent research has indicated that the photoelectric conversion efficiency of DSSC can exceed previous solar cells by 10-11% [1-2]. Gratzel et al. indicated that, solar cell system we developed in this work is Dye-Sensitized Solar Cell, composed of the TiO2 layer acting as the electron carrier and the organic dye layer acting as the electron generator, which will recover to its original state by electron donated by the electrolyte solution. The efficiency of solar cells is one of the greatest limiting factors for solar cells. In order to become an efficient solar cell, the photo sensitizer, which is the organic dye layer mentioned above must have characteristics corresponding to the spectrum of available light. Different photo sensitizers will have different absorption of available light, thus a different efficiency and cost. Based on the efficiency and cost information given, we chose the dye sensitized solar cell, which has good quantum efficiency reported [3].

TiO2 material also bears tremendous hope in helping ease the energy crisis through effective utilization of solar energy based on photovoltaic and water-splitting devices [4]. India is rich in natural plant resources. Many plants possess the dye products. These dyes can be utilized for various applications [5]. Dyes are one of the most important uses of the plants, as they are related with cultural practices, rituals, arts and crafts, fabrics and to satisfy personal embodiment, however, dye yielding plants have not received significant attention. A few publications on the vegetable dyes from India and some state specific reports from West Bengal, Manipur, Arunachal Pradesh, Uttarakhand and others have generated a fresh interest on this aspect [6-11]. The dye pigments are present in the different part of the plant including flowers petals, fruits, leaves, stems and roots. We report here the results of a series of experiments carried out on raw extracts of the following species: two types of natural dyes were extracted from leafs and root, one is Lawsoniainermis (Henna leafs) and other is beetroot (Betanine). Fig.1 shows a schematic chemical structure of lawsone pigment in henna leafs. Henna (Lawsoniainermis, also called henna tree) [12] is a flowering plant used since antiquity to dye skin, hair, fingernails, leather and wool. The name is also used for dye preparations derived from the plant. Henna's coloring properties are due to lawsone, (2-hydroxy-1,4-naphthoquinone), also known as hennotannic acid, C10H6O3, a burgundy organic compound that has an affinity for bonding with protein.

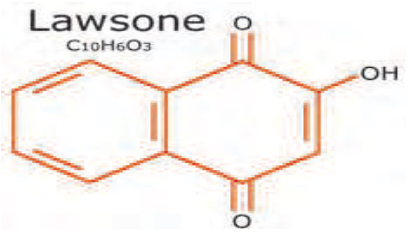

Fig. 1.Schematic Chemical Structure of Lawsone pigment in Henna leafs

Lawsone is primarily concentrated in the leaves. Fresh henna leaves will not stain color until the lawsone molecules are made available (released) from the leaves and they are smashed with a mildly acidic liquid. The lawsone will gradually migrate from the henna paste/solution into the outer layer of the skin and bind to the proteins in it known as keratin, creating a fast stain. Lawsone is skin protective since it strongly absorbs UV light [13].

Beetroot (Beta vulgaris) is botanically classified as an herbaceous biennial from Chenopodiaceae family and has several varieties with bulb colors ranging from yellow to red. Deep red-colored beet roots are the most popular for human consumption, both cooked and raw as salad or juice. There is growing interest in the use of natural food colors, because synthetic dyes are becoming more and more critically assessed by the consumer. But in food processing, as compared with anthocyanins and carotenoids, betalains are less commonly used, although these water-soluble pigments are stable between pH 3 and 7 [14-15].

The Chemical and structural formula of Betanine is shown in figure 2:
Chemical formula : C24H26N2O13
Structural formula:

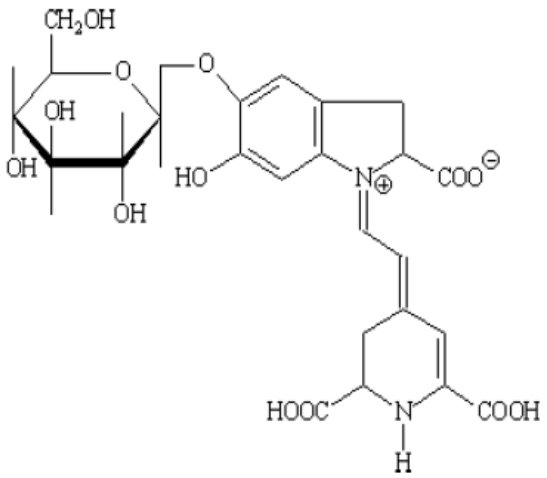

Fig. 2.Schematic Chemical Structure of Betanine from Beetroot.

2. Experimental Procedure

2.1 Preparation of TiO_2 nanoparticles by sol-gel method

All the reagents used were of analytical grade and no further purification was done before use. The sol-gel synthesized TiO_2 was obtained from 10 ml Titanium (IV) butoxide (TBT) was dissolved in absolute 10 ml ethanol and it was stirrer for 1 hr. Then 5 ml of distilled water was added to the solution in drop wise. Immediately the resultant gel was formed and it was stirred to few minutes. Then 1 mole of NaOH was used to adjust the pH and the solution was vigorously stirred for 1 hr in order to form white colloidal precipitate. After aging for 24 hrs, the solution was filtered and it was washed three times with distilled water and three times with ethanol. Finally it was transferred into oven under 100ºC for 12 hrs to evaporate water and organic material to the maximum extent. Then the material was grain fine powdered, and then dried. Resultant precipitate was sintered at 500ºC for 2hrs to obtain desired TiO_2 nanoparticles.

2.2 Preparation of dye sensitized solar cell (DSSC)

2.2 .1. Preparation of TiO_2 electrode (photoanode)

The photoanode is prepared by adsorbing a dye(s) on a porous titanium dioxide, TiO_2 layer is deposited on Fluorine-Doped tin oxide (FTO). FTO conducting glass plate sheet resistance is 7Ω/cm^2. By this approach, the dye extends the spectral sensitivity of the photoanode, enabling the collection of lower energy photons. The titanium dioxide (TiO_2) nanopowder was prepared by sol-gel method. The semiconductor paste was prepared by blending 3.5g of commercial TiO_2 nanopowder of anatase structure, 3ml of 0.1M Nitric acid, and 15ml of ethanol. The resulting suspension was stirred for 1h. Two edges of the FTO glass plate were covered with a layer of adhesive tape to control the thickness of the film and to mask electric contact strips. Successively the TiO_2 paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer. The FTO glass spreaded TiO_2 nanoparticle was sintered at 100°C for about half an hour. After the sintering process was completed, the TiO_2 deposited-electrode was cooled down from 100°C to 60°C at cooling rate of 3°C/min to avoid cracking of the glass.

2.2 .2. Graphite coated counter electrode

To prepare the counter (positive) electrodes, uncoated FTO plates were coated with carbon on the conducting side using a graphite rod or soft pencil to apply a light carbon film to the entire conductive side of the plate. Any loose graphite particles should be gently removed. This thin carbon layer serves as a catalyst for the tri iodide-to-iodide regeneration reaction. For long-lasting, the carbon-coated counter electrode was annealed at 450°C for a few minutes and washed with ethanol and gently blotted dry before the device is assembled.

2.2 .3 Preparation of solid state polymer electrolyte

Meanwhile, electrolyte solution was prepared by mixing 0.8 g KI, 10 ml acetonitrile and added by 0.127 g I_2. The Solution was stirred for 30 minutes and then stored in a sealed bottle.

2.2 .4 Preparation of natural dye sensitizers

The fresh Henna (Lawsoniainermis) leaves and Beetroot extracts were prepared by crushing the leaves and vegetables and it was filtered by using pure white cotton cloth respectively. Then take 60 ml of extracts and 30 ml of ethanol was added to the pastes and bring to boil for 30 minutes. The as prepared extract solutions were filtered to remove solid fragments and stabilized at pH = 2.5, 3.0, and 3.5 by addition of aqueous (0.1 M) HCl. Extracts further purification was avoided to check whether an efficient sensitization could be achieved with minimal chemical procedures. If properly stored, protected from direct sunlight and refrigerated at about +4°C, the acidic natural dye solutions (pH = 5.0) are usually stable, with a deactivation half-time of more than 12 months.

2.2 .5 Assembly of DSSC

To sensitize the semiconductor material, dye solution was placed in a petri dish and the TiO_2-coated FTO was immersed into dye solution for 1 hour, so that dye was absorbed inside TiO_2 active areas. The TiO_2-coated FTO was then rinsed in distilled water and ethanol and dried in open air. The dye-sensitized solar cells were assembled by fixing a TiO_2 electrode casted with polymer electrolyte and a graphite counter electrode so that the dyed TiO_2 plates facing down onto the coated graphite anode. They should be placed so that they are slightly offset to allow connections (for the crocodile clips). The two electrodes were pressed against the electrolyte and clamped firmly in a sandwich configuration. By illuminating the cells with a light source/sun light, the voltage across each individual cell can be measured.

3. Results And Discussion

3.1 XRD analysis of TiO_2

The XRD patterns of the TiO_2 nanoparticles obtained by sol-gel method are shown in Fig.3.1(a) . The peak positions and their relative intensities are consistent with the standard powder diffraction patterns of anatase-TiO_2 and anatase phases of TiO_2 were in good agreement with JCPDS card # 21-1272. It has a main peak at 25.5° corresponding to the (101) plane. The other peaks position at 38.3º (004), 48.4º (200), 54.8º (105), 63.2º (204), 69.9º (215), and 76.2º (224) are in accordance with the TiO_2 anatase phase. For the TiO_2 particles prepared by sol gel method the peak intensity of anatase phase increases with the calcined temperature of 500ºC compared with as-prepared TiO_2 material. This pure anatase structure of TiO_2 is extremely important to achieve high performance for electrons transport and dye adsorption in TiO_2-based dye-sensitized solar cells. The crystalline size was calculated by using Debye-Scherrer's formula given by equation

$$D=K\lambda/(\beta\cos\theta) \text{ ------ } (1)$$

Where, D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm); K is usually taken as 0.89; and β is the line width at half-maximum height. The crystallite size obtained using this formula is 13 nm.

Fig 3.1(b) shows the XRD patterns of TiO_2 nanomaterial which has been coated on top of FTO glass. The obtaining peaks are all most same as fig 3.1(a). Tthe peaks are obtained at 25.5º (101), 38.3º (004) and 48.4º (200). The resulting patterns are in good agreement with JCPDS card # 21-1272. The main peak of FTO glass was reflected at 52.3º and 65.8º.

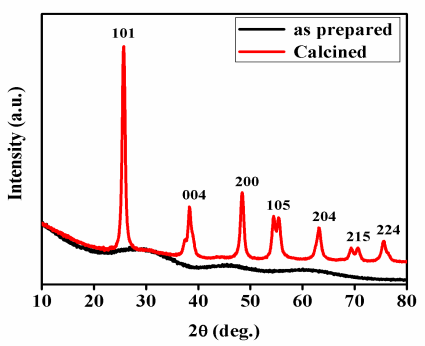

Fig 3.1 (a) XRD pattern of TiO_2nanoparticles

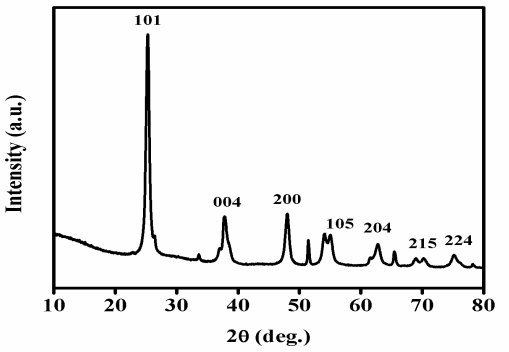

Fig 3.1(b) XRD pattern of TiO_2nanoparticles coated by FTO conductive glass substrate.

3.2 UV-VIS Spectroscopy

The optical absorption behavior and band gap energy of TiO_2 was studied by means of UV-visible spectroscopy. For the recording of UV-Visible absorption spectrum, TiO_2 nanopowder were dispersed well in 10 ml distilled water. Fig 3.2(a) shows the UV absorption of the TiO_2 nanoparticles. The optical absorption spectrum of TiO_2 was found to be 388 nm. The band gap of the TiO_2 nanoparticles calculated using the formula,

$$Eg = hc / \lambda \text{ ---------- (2)}$$

Where E_g- Band gap energy, h - Plancks constant (6.626 x 10^{-34} Joules/sec), C - Velocity of the light (3 x 10^8 meter/sec), λ - Absorbance of the sample, 1 eV- 1.6 x 10^{-19} Joules (Conversion factor). The calculated band gap of the TiO_2 is 3.2 eV.

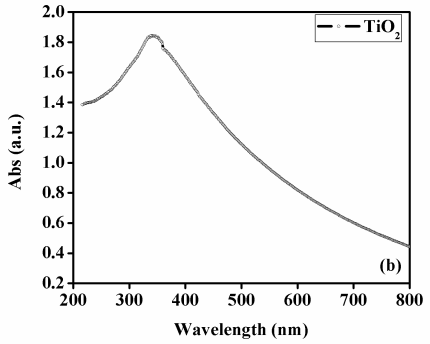

Fig 3.2 (a) UV-vis absorption spectra of TiO2 nanoparticles

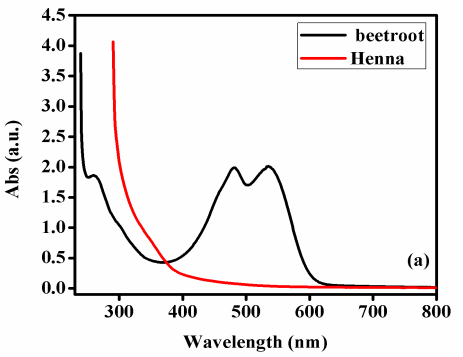

Fig 3.2 (b)UV-visabsorption spectra of Henna and Beetroot dye.

3.3 Scanning Electron Microscopy (SEM) analysis of TiO_2:

The particle morphology was investigated by means of Scanning Electron Microscope (SEM). The microstructure of the TiO_2 nanoparticles synthesized by sol gel method in the present study was observed by shown in Fig.3.3. Typical SEM micrograph of the anatase TiO_2 is calcined at 500ºC for 1 h, show morphologies clearly different from each other and different magnifications. From the SEM image it could be observed that the shape of pure TiO_2 is not uniform and it looks like spherical in shape. Nanoparticles have aggregated and also the size of the TiO_2 nanoparticle is found to be 72 nm.

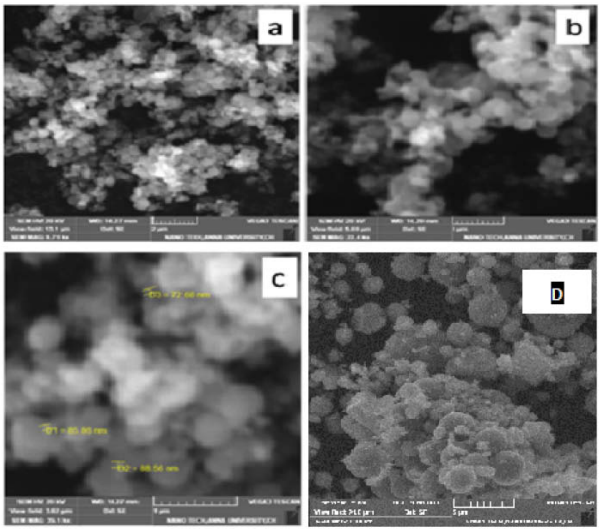

Fig 3.3 .SEM image of TiO_2 at different magnifications

3.4 Thermo gravimetric / Differential Thermal Analysis (TG / DTA)of TiO_2:

The TGA analysis curve of TiO_2 is shown in fig.3.4 and weight loss (~23%) at about 200ºC is associated with decomposition of absorbed water, alkane groups and organic, inorganic compounds respectively. Then the curve was maintaining the stability about the temperature range 200ºC- 1000ºC. From DTA curve four peaks are observed in the as-precipitated gel and is curve around 100, 300, and 450ºC. The first endotherm peak at 100ºC is attributed to the desorption of water molecules. This peak occurs concurrently with a moderate TG weight loss of 3%. The second exothermic peak at 300ºC may correspond to the decomposition of the organic species. The third exothermic peak at 440ºC is attributed to the crystallization of anatase phase. With increasing aging time, the amount of anatase phase and crystallite sizes increased and correspondingly, the intensity of exotherms due to the decomposition of organics and crystallization of anatase decreased.

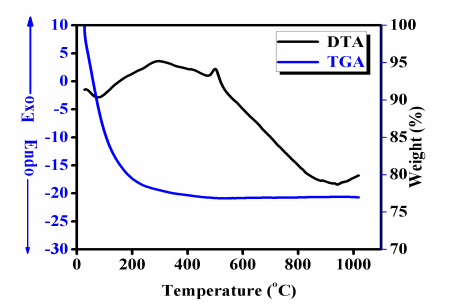

Fig 3.4 TG/DTA Curve of Titanium dioxide Nanoparticle.

3.5 Efficiency Measurements of DSSC:

The (η) of DSSC is calculated using the formula,

$$\eta = P_o/P_{in} \text{ ---------- (3)}$$

Where P_O= output power from the solar cell, P_{IN} = input power given to the solar cell, v = open circuit voltage, I = short circuit voltage, A = Effective area of cell.

Power per unit area (p_o) is calculated from the formula is given by below from [11].

$$P_0 = VI/A \text{ ---------- (4)}$$

The efficiency of the DSSC for Henna and beetroot dye is given in Table 1.

Table 1: Efficiency of DSSC for Henna and beetroot

Dyes	V(mV)	I(mA)	A (cm^2)	P_{IN} (mW/cm^2)	η (%)
Henna	0.40	4.9	3	60	1.08
Beetroot	0.46	5.1	3	60	1.3

3.6 Current- Voltage (I-V) curve of DSSC

The I-V characteristics of the DSSC were measured. The current flow was maximum when the intensity of sunlight is maximum (598 W/m^2) at noon. Table.2 show the variation of current and voltage measurements for DSSC with Henna dye.

Table 2: I-V Measurement of DSSC with Henna dye

Intensity (w/m^2)	V(mV)	I(mA)	Time
473	22	2.19	10.00
571	30	2.70	11.00
590	35	3.34	12.00
598	43	4.17	13.00
510	46	4.90	14.00
430	39	3.96	15.00
284	37	3.70	16.00
180	8	0.27	17.00

Table.3 shows the variation of current and voltage measurements for DSSC with Beetroot dye. Fig 3.5 shows the Time vs Voltage curve for both the dyes. Fig 3.6 shows the time vs current for DSSC with Henna and beetroot dyes and it is found that current and voltage flow is higher for DSSC with Beetroot dye then Henna dye.

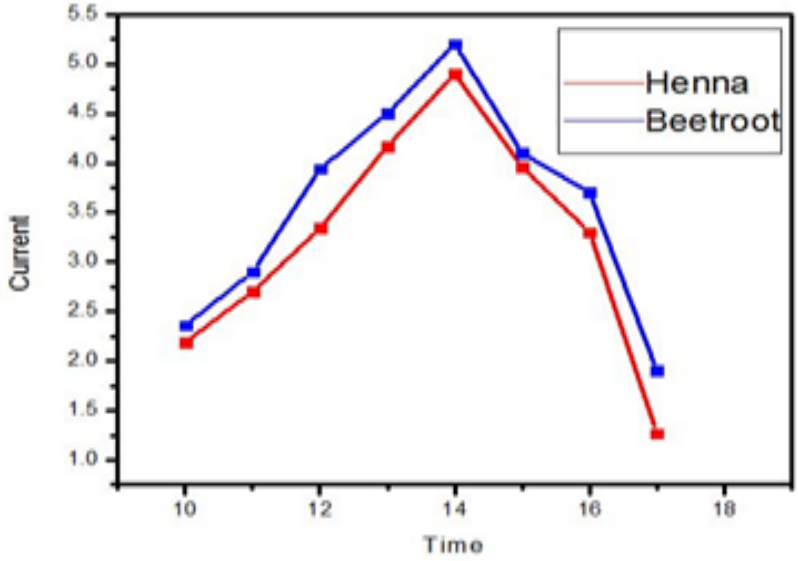

Fig 3.5 time vs current curve of DSSC

Table 3: I-V Measurement of DSSC with Beetroot dye

Intensity ($w/m^{2)}$	V(mV)	I(mA)	Time
473	24	2.36	10.00
571	33	2.90	11.00
590	39	3.94	12.00
598	47	4.50	13.00
510	53	5.20	14.00
430	42	4.10	15.00
284	34	3.36	16.00
180	20	1.90	17.00

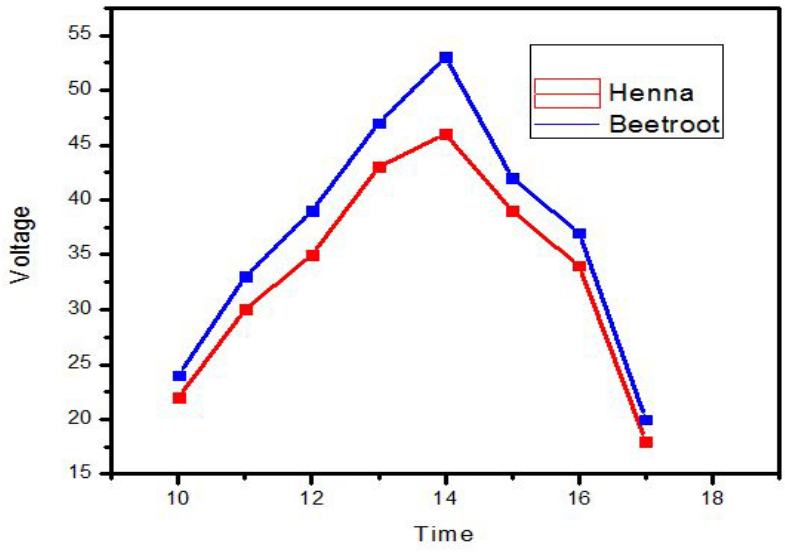

Fig 3.6 time vs voltage curve of DSSC

4. Conclusion

DSSC have been successfully prepared from TiO_2 nanomaterial of anatase structure. In this work we have reported an investigation on two types of pigments as natural photosensitizers, describing and comparing their sensitization as well as how it differ from various time respectively to one another. It was found that DSSC prepared with Beetroot dye is more efficient then that prepared with Henna dye. The result of this work is motivated to the search of new natural sensitizers and to the optimization of solar cell components compatible with such dyes.

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