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Natural dye-sensitized solar cells using Lawsone pigment of Lawsonia inermis (henna leaves) as sensitizers

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ABSTRACT
The need for the alternative source of green energy is very high in the current developing world and one of the promising sources is Dye-Sensitized Solar Cells (DSSCs). DSSCs working principle is a mimic of photosynthesis taking place in plants. During photosynthesis, chlorophyll (coloring pigment) absorbs the incident light energy and converts it to chemical energy. Similarly, in DSSCs dye absorbs the incident light and converts it to electrons (electrical energy). Hence by replacing the dye with a natural dye, a more eco-friendly and cost-effective solar cell technology can be developed. In the present work, Lawsone pigment exacted from Lawsonia inermis (henna leaves) is used as a natural dye, to sensitize TiO_2 thin films. The TiO_2 layers were prepared on FTO slides by doctor blade method using double surfactant to increases the porosity of the TiO_2 layers. Henna leaves dye was extracted in methanol and was used as a sensitizer. The potassium iodide and iodine electrolyte were prepared and the counter electrode of carbon/graphite was used in cell fabrication. The optical properties of the henna dye were studied using UV-Vis-NIR spectrometer and it was found that the henna dye as a strong absorbance from 200nm to 550nm and reduced absorbance up to 700nm wavelength region. This was further confirmed from absorption and extinction coefficient spectrum. The fabricated solar cells were characterized for the fill factor and efficiency.
KEYWORDS: 1. DSSCs, 2. Lawsone, 3. Henna, 4. Lawsonia inermis, 5. Natural dye.

I. INTRODUCTION

Sunlight is an abundant source of energy which dwarfs all other renewable and fossil fuel resources combined [1]. About $3x10^{24}$ joule/year energy is received in the form of sunlight on the earth surface, which is 10^4 times more than the world's energy consumption [2]. With increasing demand for environmentally-friendly, carbon-neutral energy production, photovoltaic (PV) technology is receiving immense attention as a potential alternative to develop sustainable energy infrastructure [3, 4]. Harvesting solar energy using DSSCs is a unique way of capturing sunlight which is derived by mimicking nature's photosynthesis.

DSSCs are promising low-cost third-generation device concept based on sensitization of wide band-gap semiconductors using spectral sensitive dyes of herbal origin [5]. Later, this concept was extended to utilize many inorganic metal complexes like Ruthenium (Ru) based sensitizers [6] because of their efficient absorption and charge transfer over the entire visible spectral range. But, this idea of utilizing synthetic materials is still a challenge for many researchers as they are held back by high cost and the complicated synthesis process. Accordingly, research has been focused on alternative, easily available photosensitizers extracted from natural sources because of its inexpensive, easy extraction, higher efficiency, large absorption coefficients and environment friendliness [7]. To date, several photo excitable natural pigments that can cede electrons are found such as anthocyanins, carotenoids, betalains and chlorophylls extracted from Cyanococcus (blueberry) [8], Rubus idaeus (raspberry) [9], Hibiscus rosa-Sinensis [10], Beta vulgaris (beetroot) [11], Fragaria × ananassa (strawberry) [12], Rosa, Capsicum annuum [13] etc., have been used as sensitizers in DSSCs. In this context, '*lawsone'* is one such flavanoid compound present in leaves of the *'Lawsonia inermis'* (henna plant) which is responsible for the orange-red color and known to mankind for more than 5000 years. The preparation of TiO_2 films functionalized with lawsone pigment extracted from lawsonia inermis (henna dye hereafter) has been studied for application as a sensitizer in DSSCs and the results are discussed in detail.

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II. EXPERIMENTAL DETAILS

2.1 Chemicals and Materials used for Natural DSSCs.

FTO-coated glass slides (Sigma-Aldrich), Ethylene glycol (99%, Thomson baker), Titanium dioxide powder (98%), Iodine (99%), Potassium iodide (99%) from SD Fine Chemicals, Ethanol absolute (99%, Jebsen & Jessen chemicals Germany) are used. Fresh Henna leaves were obtained and dye was extracted.

2.2 Structure and working principle of DSSCs.

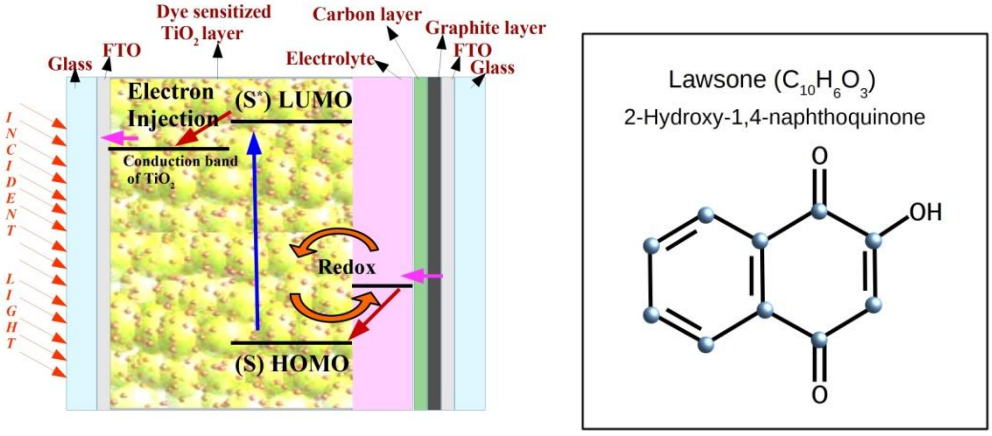

Figure 1. (a) Structure and working principle of DSSCs. (b) The chemical structure of Lowsone pigment.

The structure of DSSCs (Figure 1(a)) consists of a transparent conductive FTO-coated glass, TiO_2 as a photo-anode, natural sensitizer, the electrolyte used as a mediator between electrodes, a counter electrode made up of FTO-coated thin films with graphite and carbon used as a catalyst, figure 1(b) shows the chemical structure of Lowsone pigment. When the light is incident on the TiO_2 layer, it penetrates through it and gets incident on the sensitizer and photons are absorbed. The absorbed photons excite electrons from HUMO to LUMO (equation 1), these electrons are injected into the conduction band of the TiO_2 electrode, resulting in the oxidation of the photosensitizer (S^+) [14] which is given by equation 2.

$S + h\nu \rightarrow S^*$ (1)

$S^* \rightarrow S^+ + e^-$ (TiO_2) (2)

The electron from the conduction band of TiO_2 layer diffuses to front contact and thereby to an external circuit. On the other end, oxidized photo-sensitizer (S^+) accepts electrons from the I^- ion redox mediator, leading to restoration of dye electron to the ground state (S) (equation 3), and the I^- is oxidized to the oxidized state I_3^-. The oxidized redox mediator I_3^- diffuses toward the counter electrode and then it is reduced to I^- ions (equation 4) [14] completing current flow in the circuit.

$S^+ + e^- \rightarrow S$ (3)

$I_3^- + 2\ e^- \rightarrow 3\ I^-$ (4)

However, DSSCs efficiency depends on many parameters especially on the band energy alignment of the photo-anode, photosensitizer and counter electrode, stability of electrolyte, preventing leakage current, adsorption of dye on the TiO_2 layer and absorption range of dye. In this work, dye extraction and adsorption of dye on the TiO_2 layer and detailed optical properties of the lawsone pigment were studied.

2.3 Preparation of TiO_2 Photoanode.

To start with, glass and FTO-coated glass slides were thoroughly washed with soapy water and then with distilled water and repeated sonication using distilled water till complete removal of soap. The cleaned substrate was dried and further repeatedly sonicated for 10 minutes in acetone, distilled water, methanol and finally in distilled water respectively with consecutive drying the slides. Finally, cleaned glass and FTO substrate were annealed at 100°C for 30 minutes.

Preparation of TiO_2 thin films is one of the key factors of the DSSCs. Initially, TiO_2 paste is prepared by adding 3g of Titanium dioxide (TiO_2) powder to 0.357ml of polyethylene glycol. To this 1.5ml of ethanol and a few drops of surfactants is added and mixed. This mixture is grinded for 30 minutes to produce an adhesive homogeneous paste. Further, the paste is aged for one day and coated on a substrate coated with transparent conducting oxide using the doctor-blade method. The conducting side of FTO coated slides was masked with tape leaving a required active area (less than $1cm^2$). The gap between tapes was

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covered with titanium dioxide paste using glass rod and desired thickness thin films were obtained. The tape was removed and allowed to dry in ambient for half an hour and then sintered at 400°C for 1 hour to get the final TiO_2 thin films. The schematic of each step in the preparation of TiO_2 thin films is shown in figure 2.

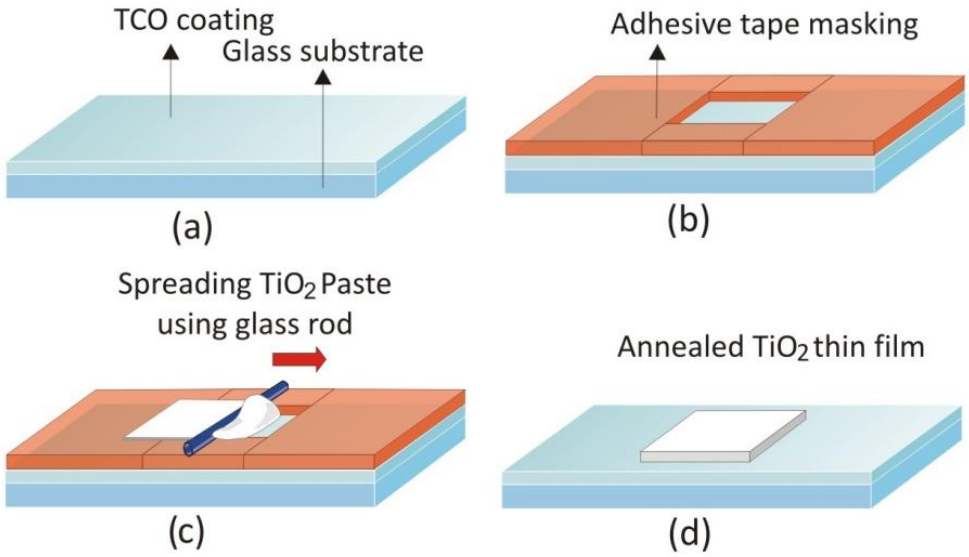

Figure 2. Schematic of TiO_2 thin films preparation. (a) Transparent conducting oxide thin film coated on a glass substrate. (b) Masking the TCO coated glass with adhesive tape leaving active area less than 1cm. (c) Filling the active area with TiO_2 paste using doctor blade method. (d) Final annealed TiO_2 thin film ready to use in DSSCs.

2.4 Dye Extraction and Preparation of electrolyte.

Henna leaves were washed thoroughly with water followed by distilled water, grinded using mortar and pestle to obtain a paste. 50ml of methanol was added to the extracted paste and refluxed at 60°C for a few hours to obtain liquid dye. The refluxed solution was filtered and dye was extracted and stored in a container at room temperature.

Electrolyte plays as the bridge between the TiO_2 electrode and the counter electrode for electrical conductivity in a liquid medium. The electrolyte is electrically neutral without external potential applied. The standard electrolyte solution was prepared by taking 0.5M of (0.1042g) potassium iodide (KI) and 0.5M of (0.0063g) iodine (I_2), to this 1ml ethylene glycol was added and sonicated for 5 minutes. The prepared electrolyte was stored in a dark bottle at room temperature.

2.5 Fabrication of counter electrode.

The need of counter electrode is to recover the electrolyte to its original state; here carbon/graphite coated FTO glass is used as the counter electrode. The counter electrode is prepared by coating a thin layer of graphite (using pencil) and carbon film from the candle flame on the conducting side of FTO-coated glass slides. Here graphite and carbon are used as a catalyst.

2.6 Construction of Natural dye-sensitized solar cells.

After photoanode (TiO_2 paste coated on FTO glass), a counter electrode (graphite /carbon coated on FTO slides), liquid electrolyte and henna dye extracted DSSCs were assembled as follows, 1. Photo-anode (TiO_2 thin films) were sensitized with henna dye, The TiO_2 thin films were heated to 60°C and at this temperature TiO_2 thin films were brought in contact with dye molecules (liquid form) and allowed to adsorb dye on TiO_2 surface (for about 24 hours). 2. This sensitized TiO_2 layer is dried in vacuum and the counter electrode are bound such that a small air gap is created between them; while assembling, these electrodes aligned little offset to expose FTO layers for external connection. 3. The air gap is filled with liquid electrolyte by injecting it through a microsyringe, this completes the cell fabrication. These cells were characterized for solar cell efficiency using Keithley source meter.

2.7 Characterization.

Prepared DSSC were characterized for their optical (absorbance, transmittance, band gap,

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absorption, and extinction coefficient) and electrical properties (of FTO, cell behavior in light and dark) using UV-Visible-NIR spectrophotometer (Ocean optics USB 4000XR) in the 200-1000nm wavelength range and Keithley 2602A source meter respectively. The cell efficiency of DSSCs was studied under constant illumination of 1 sun (1000W/m^2) optical irradiation at A.M. 1.5.

III. RESULTS AND DISCUSSIONS

3.1 Optical Properties.

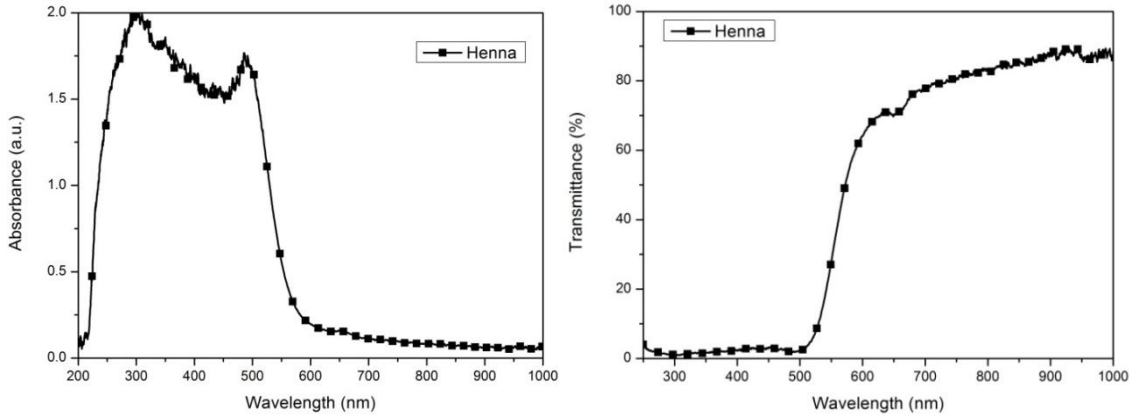

Figure 3. (a) Absorbance spectrum of henna dye. (b) Transmittance spectrum of henna dye.

Optical properties play a major role in understanding the absorption properties of the dye and depending on absorbance of dye; the performance of solar cells varies. If the dye absorbs a wide range of wavelength of the visible region, it results in a higher photoinduced electron-hole pairs generation implies higher photoconversion efficiency. Figure 3.(a) and 3.(b) shows the absorbance and transmittance spectrum of henna leaves extract. The absorbance spectrum shows a wide band of strong and steady absorbance from 200nm up to 550nm and reduced absorbance up to 700nm, due to lawsone pigment present in henna leaves. Also, 550nm corresponds to greenish-yellow and 700nm corresponds to the red color of the visible spectrum. Figure 3.(b) shows two transmittance edges, a sharp edge at 550nm with a transmittance of 70% above this wavelength, the second transmittance edge occurs at 700nm, above which transmittance as increased to 90%, 550nm corresponds to 2.26eV and 700nm corresponds to 1.77eV. This energy band is best suitable for energy harvesting as earth receives maximum radiation in this region of the solar spectrum.

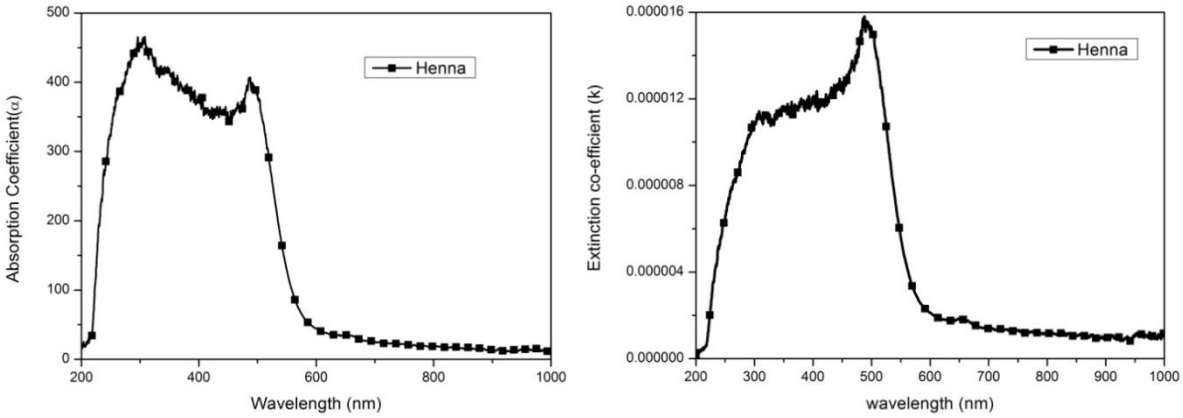

Figure 4. (a) Absorption coefficient of henna dye. (b) The extinction coefficient of henna dye.

Figure 4 (a) and 4 (b) shows the absorption and extinction coefficient spectrum respectively. The absorption coefficient of the material determines how fast a particular wavelength of light can penetrate before it is completely absorbed. Higher the absorption coefficient of the material, faster is the absorption. Absorption coefficient (α) of the material is given by $\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right)$ where, T is transmittance data and'd' is path length of light in

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the medium [15]. Figure 4(a) shows a strong absorption from 200nm to 550nm and further the absorption is decreased, however, it has not reached zero showing that dye absorb completely in range 200nm to 550nm and the absorbance was found to be minimal thereafter. The extinction coefficient (k) of the material is a measure of the damping factor i.e. how fast the incident light is damped completely through absorption or scattering. k is given by $k = \frac{\alpha\lambda}{4\pi}$ where α is the absorption coefficient of material and λ is the wavelength of incident light [15]. Figure 4(b) shows the extinction coefficient of henna dye, it clearly depicts a strong extinction coefficient from 200nm to 550nm and weak extinction coefficient up to 700nm wavelength. This clearly implies that the incident light is rapidly absorbed in 200nm to 550nm, gradually decreases up to 700nm, and above 700nm damping is minimal. These results clearly demonstrate that the dye is best suitable for DSSCs.

3.2 Electrical Properties

The solar cells were fabricated with TiO_2 thin film layers on FTO glass and sensitized with a dye. The cells were characterized for their electrical properties under dark and with the illumination of 1000W/m^2 and their efficiencies were studied. FTO-coated glass slides, optical properties has been discussed in detail in our previous paper [12] and it clearly shows that the selected FTO is completely transparent in visible and above wavelength region, which is the desired properties for the efficient solar cells. Figure 5 shows the IV characteristics of FTO-coated glass slides, a slope of 0.174 is obtained, which yields a sheet resistance of 5.7 ohm/cm. Also, the I-V characteristic is completely linear implying FTO exhibits an ohmic behavior. This is one of the key factors to transport charge carriers in solar cells without any additional loss.

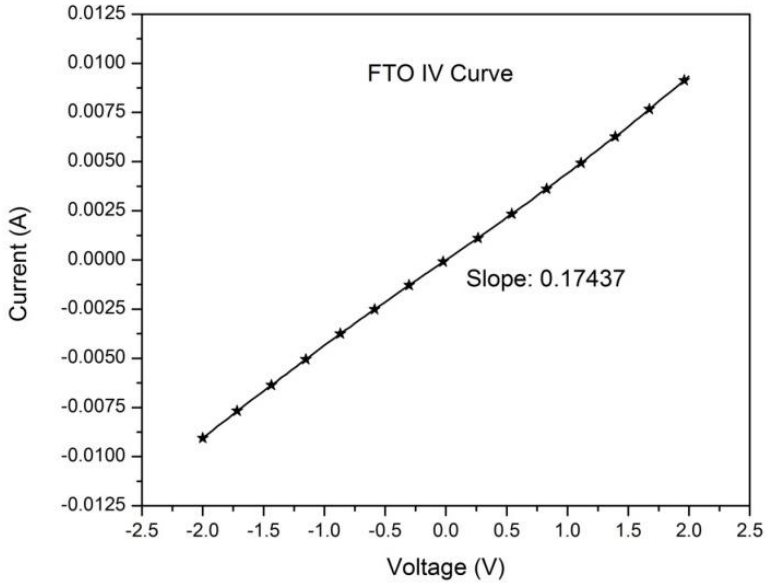

Figure 5. I-V characteristics of FTO.

Figure 6 (a) and (b) shows the IV curve of the DSSCs in dark and with illumination respectively, show perfect diode behavior, implying the working of the cell and the formation of junctions. Figure 6 (b), also shows that there is an increase in current with respect to dark current, indicating the generation of photocurrent. This infers that when the light is absorbed by the henna dye, it generates electron-hole pairs and hence voltage. Figure 5 (b) also shows the current in the fourth quadrant, the enlarged plot of the same is given in figure 5(c).

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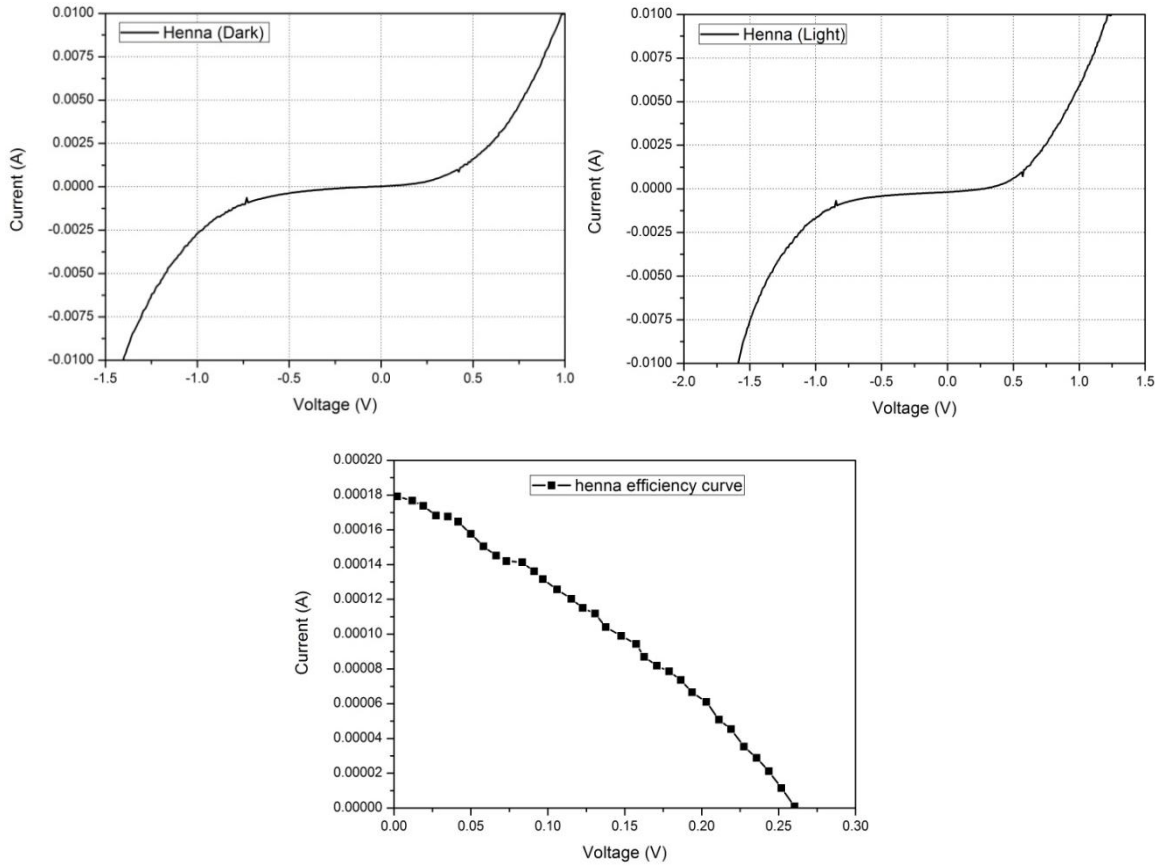

Figure 6. (a) I-V curve for Henna dye-sensitized solar cell in dark. (b) I-V curve for Henna dye-sensitized solar cell with illumination. (c) Henna dye-sensitized solar cells efficiency curve.

Efficiency curve of Henna DSSC is shown in figure 6(c), the short circuit current (I_{SC}) and open circuit voltage (V_{OC}) is found to be 180µA and 261.2mV respectively. The fill factor of the cell is given by

$$ff = \frac{I_{max} \times V_{max}}{I_{SC} \times V_{OC}}$$

Where I_{max} and V_{max} are maximum achievable current and voltage output from the cell at a time or the maximum power output of the cell. Fill factor of the cell describes how close the cell matches to the ideal behavior of the cell, higher the fill factor better is the cell performance. For the current henna DSSCs the fill factor, achieved is 31.5%. Further, the efficiency (η) is calculated using equation.

$$\eta = \frac{I_{SC} \times V_{OC} \times ff}{A \times P_{in}} = \frac{P_{max}}{P_{in} \times A}$$

Where, P_{in} and P_{max} are the input power and maximum output power of the cell and here P_{in} was taken to be 1000W/m^2 and A is the active area of solar cell, in this case, its 0.7x0.7cm. The achieved efficiency is 0.03%. The possibilities of enhancing the efficiency of henna DSSCs is by changing fabrication steps and mainly TiO_2 layer to be more porous, TiO_2 layer improves the sensitization and further cell efficiency drastically. Also, by changing the counter electrode to platinum efficiency can be increased. However, the present work proves that the henna dye is a stable worthy sensitizer with the best optical properties, which can be used as an effective alternative to other dyes.

IV. CONCLUSIONS

Henna DSSCs were fabricated using TiO_2 photoanode sensitized with henna leaves extract. The optical properties of the henna dye revealed a strong absorbance from 200nm to 550nm and reduced absorption up to 700 nm, covers a wide range of visible region. The absorption and extinction coefficient showed that the henna dye absorbs complete incident light from 200nm to 550nm and above 550nm absorption decreases. These results confirm that henna dye is the best candidate, to replace metallic or organic dyes currently used in DSSCs. The fabricated cell with standard electrolyte and carbon /graphite counter electrode shows the short circuit current I_{sc} of 180µA, open circuit voltage V_{oc} of 261mV, fill factor of 31.5% and efficiency of 0.03%. Through

the achieved efficiency is very less there is a tremendous scope for the modification and development of environmental friendly high efficient natural solar cells.

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