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Natural dye sensitization of TiO_2 Thin Films using Lawsone dye extracted from *Lawsonia Inermis* for Solar Cell Applications

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ABSTRACT

The TiO_2 thin films were successfully coated by spin coating technique using $Ti(OH)_2$ as a precursor. The precursor was prepared by sol-gel synthesis. The TiO_2 thin films were dye-sensitized with Lawsone dye extracted from Lawsonia Inermis. The as-synthesized TiO_2 thin films were subjected to X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), UV-Vis spectrophotometer, Scanning Electron Microscope (SEM), Field dependent dark and photo conductivity and temperature dependent conductivity studies. From XRD, it was confirmed that the compound synthesized is TiO_2. Fourier Transform Infrared Spectroscopy (FTIR) confirms that a TiO_2 phase has been formed. The field dependent conductivity showed an insignificant rise in photocurrent for TiO_2 which was in conformity with its wide band gap nature. The temperature dependent conductivity studies confirmed the semiconducting nature of the film. The surface properties of the thin films were analyzed using Scanning Electron Microscopy. The Lawsone dye-sensitized TiO_2 thin film showed a significant rise of photocurrent over the dark current.

Keywords: Thin films, sol gel, TiO_2, dye sensitization, photoconductivity

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INTRODUCTION

The conversion of solar radiation to electrical energy (photovoltaic) has become more and more important because sunlight is a clean and limitless energy source compared to the traditional fossil energy sources. Up to now, solid state junction devices based on crystalline silicon (so called the first generation solar cell with market share more than 80%) needs high purity (i.e., impurity level in parts per million or billion range); required in a form of a thin wafer (200 micron thick or lower); and hence a large amount of energy is required for purification and crystal growth. Dye sensitized Solar Cell (DSSC) based on mesoporous TiO_2/organometallic dye molecule junction appears to be very promising due to its low cost fabrication (solution based printing) together with other attractive features like flexibility [1-5]. Nanostructured TiO_2 has attracted greater interest because it is widely used for various applications like dye sensitized solar cells, catalysts, fuel cells, optical coatings etc. The properties are influenced by many factors such as crystallinity, particle size, surface area and preparation [6-8]. TiO_2 is the most extensively studied oxide because of its optical and electrical properties. Dye-sensitization has provided a successful solution to extending the absorption range of the cell to low-energy light with effective result. This approach presents advantages over the direct band to band excitation in conventional solar cells, since the attached dye rather than the semiconductor itself are the absorbing species and the processes of the light absorption and charge separation are separated by the semiconductor/sensitizer interface preventing electron hole recombination [9, 10]. Henna, *Lawsonia inermis* produces a red orange dye molecule, “lawsone”, also known as “hennotannic acid”. This molecule has an affinity for bonding with protein and has been used to dye skin, fingernails, hair, leather, silk and wool [11].
In this present work, TiO_2 thin films were coated on glass substrate by spin coating technique with $Ti(OH)_2$ as precursor and their structural, optical, electrical and surface properties were studied. The as-synthesized TiO_2 thin films were sensitized with Natural dye Lawsone extracted from *Lawsonia Inermis* and its photo response was studied.

MATERIALS AND METHODS

2.1 Synthesis of TiO_2 Thin films

Titanium dioxide (TiO_2) powder and thin films were synthesized by sol-gel method using $Ti(OH)_2$ as precursors. 1: 10 ratio of Titanium tetrachloride ($TiCl_4$) is added drop wise at room temperature. A light yellow solution is evolved with the evolution of HCl gas. The resultant solution was allowed to gelatinize for four days. During gelatinizing process, $TiCl_x(OCH_2CH_3)_{4-x}$ species absorbed water from atmosphere to form $Ti(OH)_4$ precursor. The precursor gel was coated onto glass slides which were cleaned by acetone using spin coating with a spinning speed of 3000 rpm for 30 sec. Then the film was dried naturally in air for 24 hours. It was then heated in a muffle furnace to 450^{o}C at the heating rate of 5^{o}C/min and maintained at the maximum temperature for 30 minutes to form anatase phase. The TiO_2 powders were also obtained by heating the precursor solution in muffle furnace by similar procedure.

2.2 Extraction of Lawsone dye from *Lawsonia Inermis* leaves

The leaves of plant *Lawsonia Inermis* (commonly known as Marudhani or Mehendi) were collected from Loyola College campus, Chennai. The collected leaves were thoroughly washed with water to remove the adhering particles and dust from the surface. The leaves were then dried in an oven at 40^{o}C for 24 hours and finely powdered. 100g of dried powder sample was soaked in 100 ml distilled water, shaken well and left undisturbed for 24 hours. The solution turns reddish orange colour [11, 12]. This solution was then filtered and used as dye solution. The sol-gel synthesized TiO_2 thin films were soaked in the dye solution for one day. The resultant dye-sensitized thin films were dried naturally and used for studies.

1. Characterization

The phase evolution of the as-synthesized samples were examined by the Rigaku II Cu K(α) X-ray Diffractometer using a Cu Kα radiation (λ = 0.154nm). The mean crystallite size of TiO_2 was calculated by Scherrer's formula $D = 0.9\lambda/\beta\cos\theta$. Where D is the particle size, λ be the wave length, θ be the angle of diffraction, β is the FWHM [13, 14]. The Fourier transform infrared spectra of the samples were studied using Perkin – Elmer infrared spectrophotometer. The spectrum was recorded in the range of wavenumber 400 – 4000 cm^{-1}.The absorbing wavelength of the dye was found by UV- Vis spectrum. The UV-Vis spectra were obtained using UV-Vis-NIR spectrophotometer. The spectra were recorded at room temperature in the range 200-1000 nm. The Field dependent dark and photoconductivity studies were studied using Keithley Picoammeter to study the increase of photocurrent over the dark current [15]. The experimental setup for the field dependent conductivity study is shown in Fig. 1. Temperature dependent conductivity studies were performed using Keithley Picoammeter to find the activation energy of the as-synthesized samples [15]. The circuit diagram for temperature dependent conductivity study is shown in Fig. 2. The activation energies of the as-synthesized samples were calculated using the relation

$$I = I_o \exp(-E_a/kT) + C$$

where I is the resultant current, I_o the current at initial thermal equilibrium, k the Boltzmann constant, E_a the activation Energy and C the constant due to leakage current [16]. The microstructures of the as-synthesized samples were analyzed by JEOL JSM 6360 scanning electron microscope (SEM).

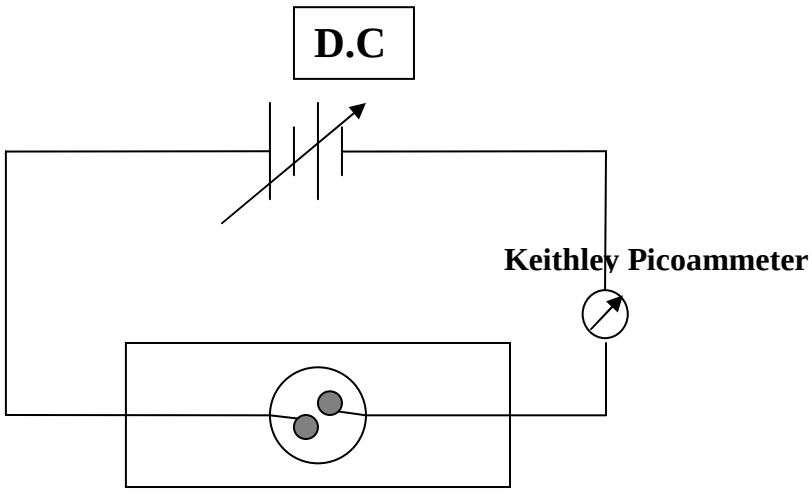

Fig. 1: Experimental setup for field dependent conductivity

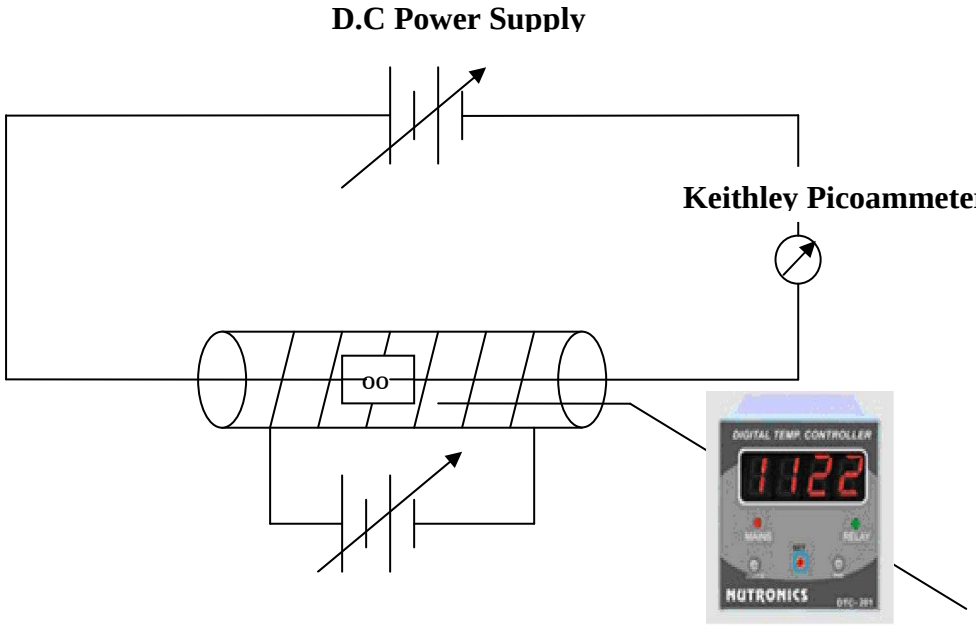

Fig. 2: Experimental setup for Temperature dependent conductivity

RESULTS AND DISCUSSION

The XRD patterns of as-synthesized TiO_2 thin film and powder sintered at 450°C are shown in Fig. 3 and Fig. 4 respectively. Both the patterns confirm the formation of anatase phase of TiO_2 and are in good agreement with the reference pattern (JCPDS no. 21-1272). It should be noted that only anatase phase could be detected and the rutile or brookite phase could not be observed, which can be attributed to the contribution of the low concentration of oxygen vacancies due to the presence of high concentration of atmospheric oxygen during particle growth [17]. The diffraction peaks of as-synthesized TiO_2 nanoparticles were found to be very sharp, indicating high crystallinity. The crystallite size of TiO_2 nanoparticle was calculated from line broadening of anatase (101) diffraction peak using Scherrer's formula [13, 14] and the results are tabulated in Table 1. The peak positions around 25°, 38°, 48°, and 55° corresponds to the h k l values (1 0 1), (1 1 2), (2 0 0) & (2 1 1) of standard anatase TiO_2 crystal and hence it could be concluded the synthesized sample is TiO_2.

Table 1: Crystallite size of TiO_2

Sample (TiO_2)	Crystallite Size (nm)
Thin Film	17.41
Powder	17.99

Fig. 5 shows the Fourier Transform Infrared (FT-IR) spectrum of as-synthesized TiO_2 powder. It indicates the occurrence of strong Ti=O vibrations around 687 cm^{-1} [17]. The absorption peaks around 3640 cm^{-1} to 2500 cm^{-1} may be related to the presence of O-H stretching vibration (monomer, intermolecular, intramolecular and polymeric) [18]. The absorption band at 1629 cm^{-1} indicates the presence of O-H bending vibration. Fig. 6 shows the Fourier Transform Infrared (FT-IR) spectrum of as-synthesized TiO_2 thin films. In the case of film, the peak centered around 650 cm-1 is attributed to the Ti=O stretching vibrations [17]. The FT-IR spectra confirm the presence of Ti=O vibrations in both cases.

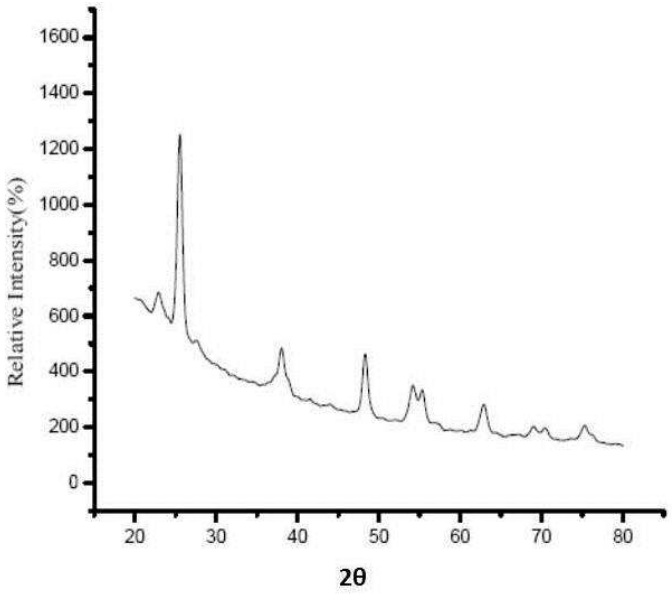

Fig. 3: XRD pattern of as-synthesized TiO_2 thin films sintered at 450°C

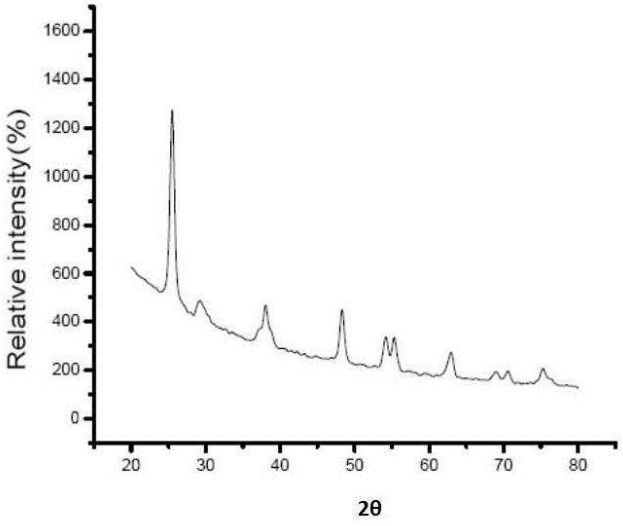

Fig. 4: XRD pattern of as-synthesized TiO_2 powder sintered at 450°C

The UV-Vis spectra of as-synthesized TiO_2 powder, Lawsone dye powder, TiO_2 - Lawsone composite powder, as-synthesized TiO_2 film and Lawsone dye-sensitized film are shown in Figs. 7, 8, 9, 10 and 11 respectively. The absence of any absorption peak in the spectra of as-synthesized TiO_2 powder and as-synthesized TiO_2 film is in good agreement with the wide band gap nature of the material and its inability to absorb in the visible range.

The electronic spectrum of Lawsone dye exhibited two prominent peaks one around 400 nm and another around 660 nm which could be attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively [19]. Thus the absorption wavelength maximum of the dye Lawsone in the visible range was observed to be 650nm. The TiO_2-Lawsone composite shows a boarder absorption peak in the range 500 to 700 nm and similarly the dye-sensitized film also exhibits a broad peak within the same range. This is a characteristic feature of charge transfer transitions due to the transfer of electrons between the dye and TiO_2 molecules. This behavior could be correlated to the enhanced photo response to visible light, exhibited by the dye-sensitized TiO_2 film.

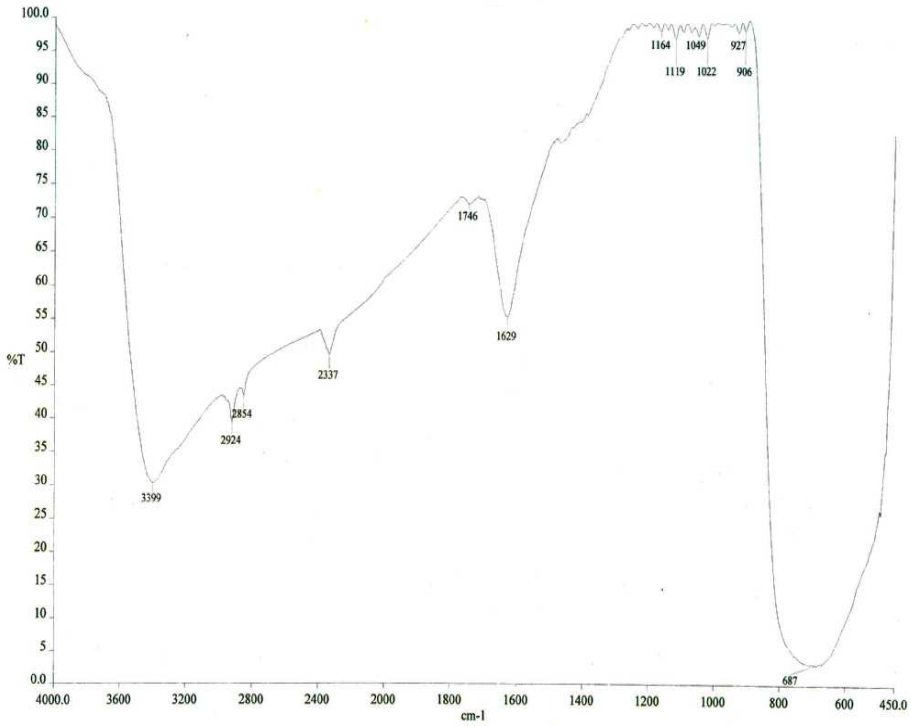

Fig. 5: FTIR pattern of as-synthesized TiO_2 powder

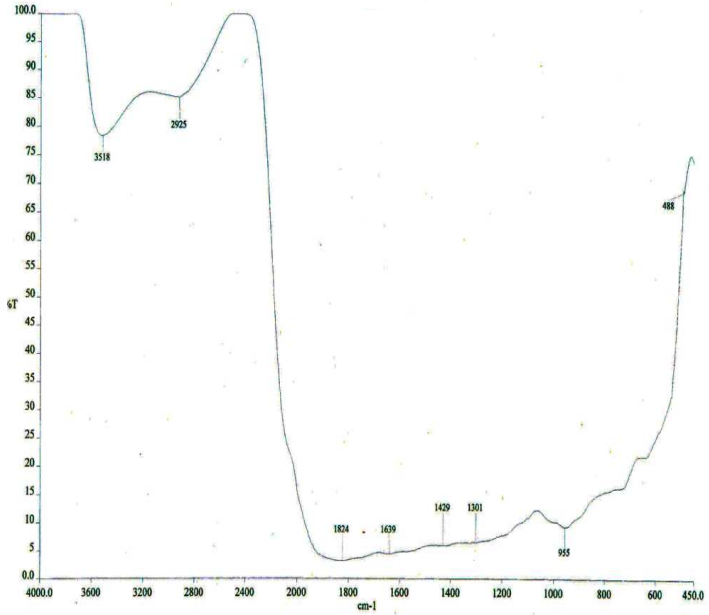

Fig. 6: FT-IR pattern of as-synthesized TiO_2 Thin film

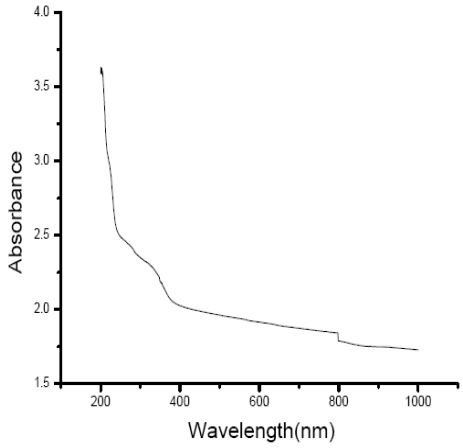

Fig. 7: UV-Visible spectrum of as-synthesized TiO_2 powder

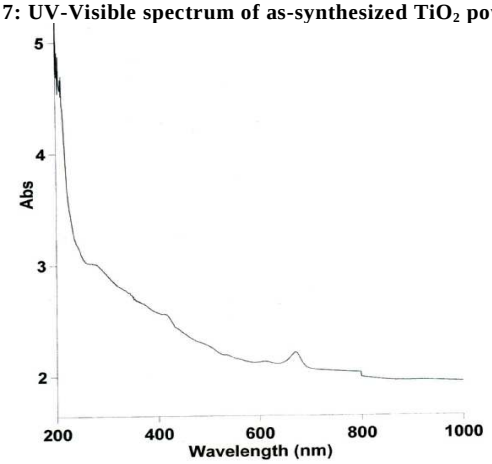

Fig. 8: UV-Visible spectrum of Lawsone dye powder

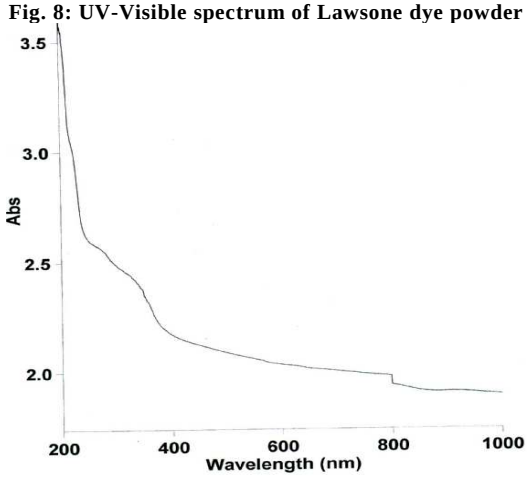

Fig. 9: UV-Visible spectrum of Lawsone dye-sensitized TiO_2 powder

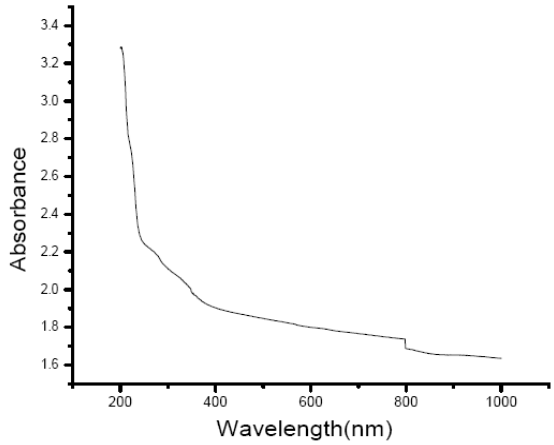

Fig. 10: UV-Visible spectrum of as-synthesized TiO_2 thin films

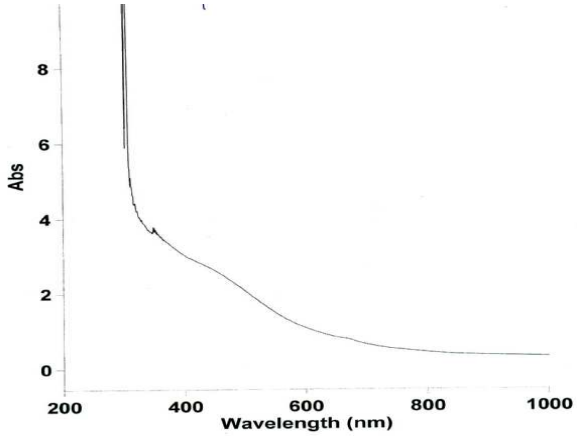

Fig. 11: UV-Visible spectrum of Lawsone dye-sensitized TiO_2 thin films

The variation of dark and photo (UV and Vis) conductivity of as-synthesized TiO_2 thin film with applied electric field is shown in Fig. 12. The plots indicate linear increase of current with increase in applied field in the dark, visible light illuminated and UV light illuminated samples, depicting the ohmic nature of the contacts [18, 20]. The low values of dark current and an insignificant rise in photo current upon visible light illumination are as expected. Owing to the wide band gap of TiO_2, it is capable of absorbing light below wavelengths of 400 nm only. This is the reason for the insignificant rise in photocurrent upon illumination with visible light using 100V Halogen lamp [19, 21]. However it is observed that when the sample is illuminated with UV lamp whose wavelength is below 400 nm, there is considerable increase in the photocurrent. This is the direct consequence of the capability of TiO_2 sample to absorb UV light.

The Fig. 13 exhibits the field dependent dark and photocurrent plots for Lawsone dye-sensitized TiO_2 thin films. The plots indicate linear increase of current in the dark and visible light illuminated samples. There is a significant rise of photocurrent over the dark current when the sample is illuminated with visible light. The enhancement of photocurrent is attributed to the presence of Lawsone dye which improves the spectral response of TiO_2 in the visible region. For example, for a fixed applied field of 1500 V/cm, the photo current value of as-synthesized TiO_2 is 0.1517 μA whereas the photo current of Lawsone dye-sensitized TiO_2 is 1.2245 μA. The onset of a charge transfer process where in the photon absorbed by a dye molecule gives rise to electron injection into the conduction band of the TiO_2 semiconductor is responsible for the increase in photocurrent. The Lawsone dye has thus made the TiO_2 photosensitive to visible range of light.

Temperature dependent conductivity studies performed on the samples reveal the variation in activation energy upon dye sensitization. The temperature was varied in the range 303 K to 423 K for a constant applied field of 600 V/cm. The variation of current with temperature for as-synthesized TiO_2 and Lawsone dye-sensitized TiO_2 are shown in Fig. 14 and Fig. 15 respectively. The plots indicate the exponential behavior of temperature dependent current confirming the semi conducting nature of the samples. Traps which are present in the samples may be filled by

excitation at low temperature and may be emptied by raising the temperature upon thermal activation [22]. Upon thermal activation the mobility of charge carriers increases, it is possible that they adopt a hopping mechanism to cross the potential barrier and hence produce enhanced current [15, 19].

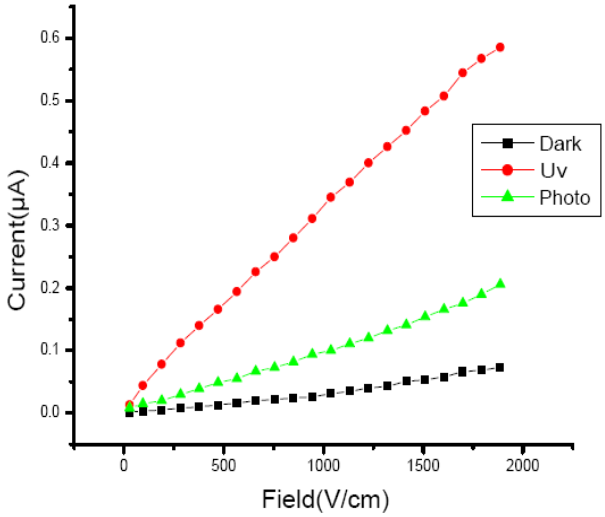

Fig. 12: Field dependent conductivity of as-synthesized TiO_2 thin films

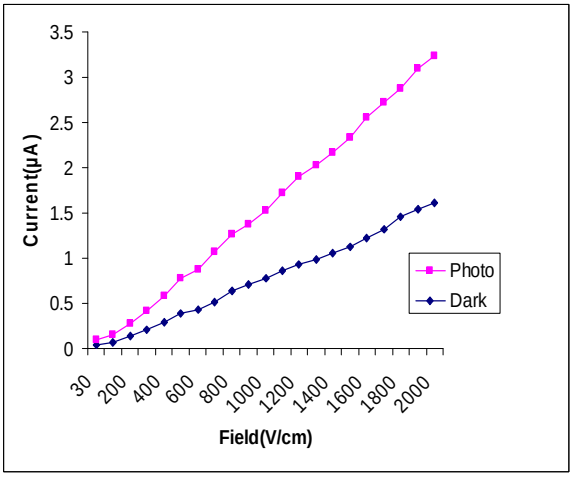

Fig. 13: Field dependent conductivity of Lawsone dye-sensitized TiO_2 thin films

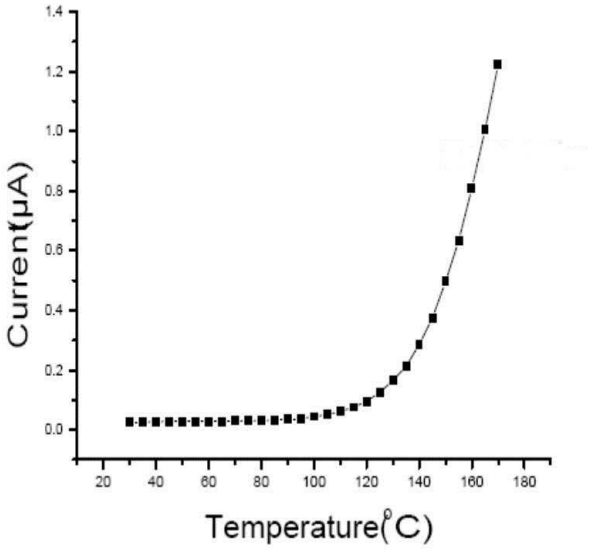

Fig. 14: Temperature dependent dark conductivity of as-synthesized TiO_2 thin films at constant E = 600 V/cm

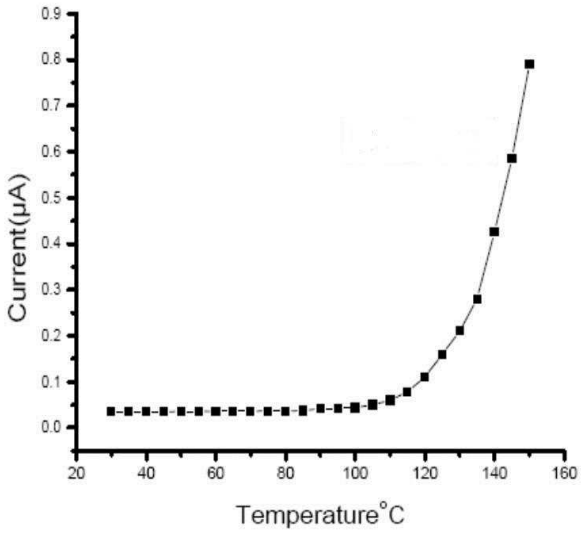

Fig. 15: Temperature dependent dark conductivity of Lawsone dye-sensitized TiO_2 thin film at constant E = 600 V/cm

The ln (I) versus 1/kT plots for as-synthesized TiO_2 and Lawsone dye-sensitized TiO_2 are shown in Fig. 16 and Fig. 17 respectively. The activation energy of as-synthesized TiO_2 and Lawsone dye-sensitized TiO_2 thin films was calculated and tabulated in Table 2. On analysis, it was found that the activation energy was decreases upon dye-sensitization of TiO_2. The decrease in activation energy could be correlated to the observed increase in current with increasing dye concentration [23].

Table 2: Activation energy of as-synthesized TiO_2 and Lawsone dye-sensitized TiO_2 thin films

Sample	Activation Energy (eV)
As-synthesized TiO_2	0.843
Dye-sensitized TiO_2	0.801

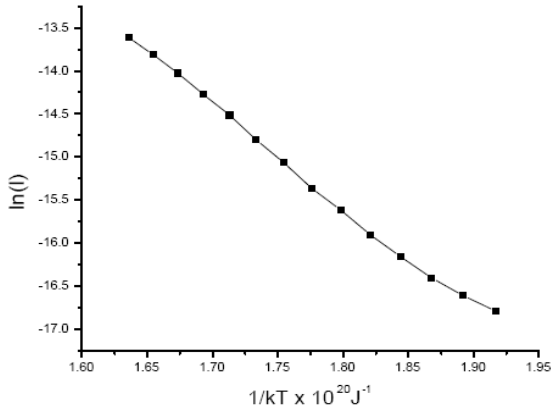

Fig. 16 ln (I) vs 1/kT of as-synthesized TiO_2 thin films at constant E = 600 V/cm

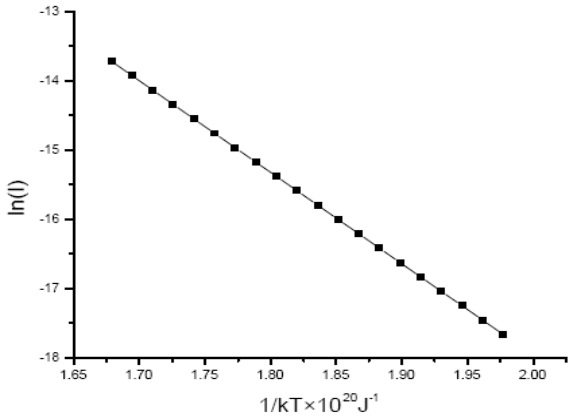

Fig. 17: ln (I) vs 1/kT of Lawsone dye-sensitized TiO_2 at constant E=600V/cm

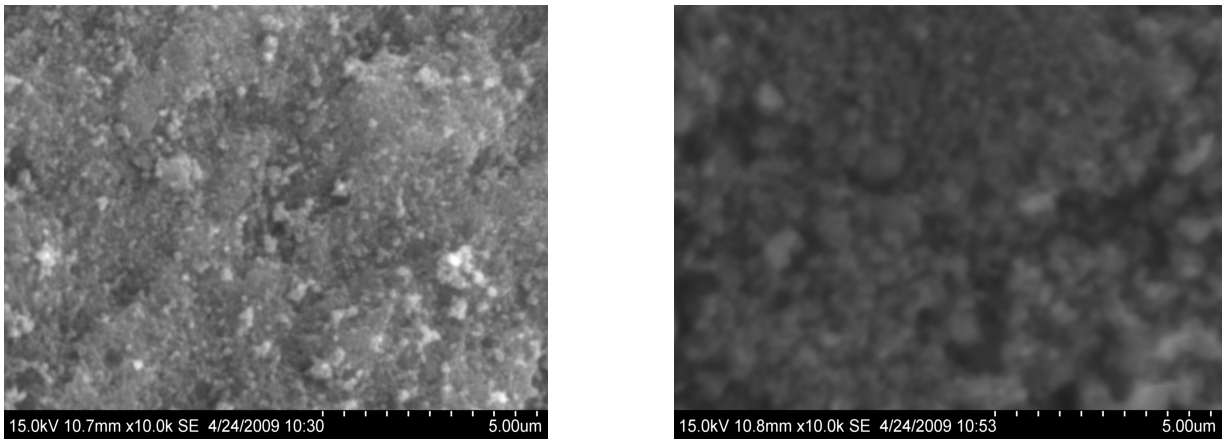

Fig. 18: SEM images of as-synthesized TiO_2 thin films sintered at 450°C

Surface morphology of as-synthesized TiO_2 thin films was investigated using Scanning Electron Microscope (SEM). Fig. 18 shows the SEM images of as-synthesized TiO_2 thin films. It could be observed from the micrographs that the film was highly mesoporous in nature and contained particles of uniform size in aggregated clusters consisting of many nanoparticles. The mesopores that are present on the sample surface would increase the dye absorption onto it, which in turn would enhance its photosensitivity to solar radiation [18].

CONCLUSION

TiO_2 thin films were coated by spin coating method using $Ti(OH)_2$ as precursor. The precursor was prepared by sol-gel synthesis. TiO_2 thin films thus prepared were dye- sensitized using Lawsone dye extracted from the plant *Lawsonia Inermis*. The UV-Vis spectrum of TiO_2-Lawsone composite showed a boarder absorption peak in the range 500 to 700 nm. Similarly the Lawsone dye-sensitized films also exhibited a broad peak within the same range. The XRD studies confirmed that the compound synthesized was TiO_2. It also confirmed the formation of anatase phase of TiO_2. The FT-IR spectra of as-synthesized TiO_2 powder and as-synthesized TiO_2 thin films indicate the occurrence of strong Ti=O vibrations around 687 cm^{-1}. The field dependent conductivity of Lawsone dye-sensitized TiO_2 showed a significant rise of photocurrent over the dark current when the sample was illuminated with visible light which could be attributed to the enhanced photo-response of TiO_2 thin film upon dye-sensitization. The temperature dependent conductivity of as-synthesized TiO_2 thin film and Lawsone dye-sensitized TiO_2 indicated the exponential behavior of temperature dependent current confirming the semi conducting nature of the samples. From in (I) vs. 1/kit plots for as-synthesized TiO_2 and Lawsone dye-sensitized TiO_2 thin films, it was found that the activation energy decreases upon dye sensitization of TiO_2 which could be further correlated to the increased conductivity in the case of dye-sensitized TiO_2. It is found that the mesoporous nature of the thin films could enhance dye-absorption onto its surface. Thus, the present investigation suggests that Lawsone dye-sensitized TiO_2 thin film emerges as a photoconductor as well as a good candidate for harvesting solar light for construction of solar cell.

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