A New Organic Dye *Cordia sebestena* Sensitized Solar Cell with Current-Voltage Characteristics

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Titanium dioxide nanoparticles have been synthesized by a novel modified sol-gel for the fabrication of natural dye sensitized solar cells. The natural photo sensitizer extracted from *Cordia sebestena* flower was mixed with the precursor solution. The flower dye has put the effort of a surfactant which has resulted colourized TiO_2 instead of white TiO_2. When compared to the conventional sol-gel method, this modified process has enhanced the properties of TiO_2 like, morphology, uniformity in dye absorption. It has reduced the agglomeration of TiO_2 and dye aggregation significantly. The optimized molecular geometry of sebestenoid D, the major pigment of *Cordia sebestena* and HOMO-LUMO plot are found using density functional theory. The TiO_2 nanoparticles were subjected to structural, optical, spectral and morphological studies which showed improved properties in modified sol-gel process. Ecofriendly and low-cost natural dye sensitized solar cells (DSSC) were fabricated using conventional and pre-dye treated TiO_2 sensitized by *Cordia sebestena* flower extract. The I-V studies showed the solar light photon to electron conversion efficiencies of 0.87 and 1.28 % for sol-gel and modified sol-gel methods, respectively. There has been an enhancement in efficiency by 47 % in modified sol-gel method which is very much promising in terms of efficiency for natural dye sensitized solar cells.

Keywords: Natural dye sensitized solar cell, Modified sol-gel preparation, *Cordia sebestena*, Titanium dioxide nanoparticles.

INTRODUCTION

Dye sensitized solar cell (DSSC) has the potential to solve the present-day energy crisis owing to its prominent features, like eco-friendly, less expensive, simple fabrication, compatibility, less reliance on high cost equipments and high quality of starting materials providing a way for many applications including optoelectronic devices, solar cells, electro-chromic devices, gas sensors and at-panel displays. DSSCs components are a semiconductor, a dye sensitizer, a counter electrode and an electrolyte solution. When exposed to solar light radiation, electrons are injected from the photo excited photo sensitizer molecule onto the conduction band of semiconductor and the holes moves towards the counter electrode through the electrolyte. In silicon based solar cells, the semiconductor performs both the task of light absorption and charge separation. Most importantly, the DSSC produces efficiency over 10 % easily without the advanced fabrication requirements unlike silicon solar cells [1-4]. Hence, harvesting green energy from abun-

dantly available sunlight can be made possible at a very low cost per unit watt. The efficiency of DSSC depends on its major components, design and fabrication processes [5]. Consequently, optimizing each component is very much essential in order to achieve optimum efficiency. In present work, the metal oxide semiconductor and natural photo sensitizer are investigated to fabricate an efficient DSSC. TiO_2 is the metal oxide semiconductor used due to its strong oxidizing power, low cost, biocompatibility *etc*. [6,7]. The crystalline nature, surface defects, particle size *etc*., will affect the photo catalytic activity of TiO_2 [8]. It is essential to improve these essential properties of TiO_2 in order to harvest fair amount solar energy. Hence, the sol-gel method, a versatile technique is engaged to produce TiO_2. Since, it is having certain drawbacks, like development of nano cluster, uneven particle size, shape and dye aggregation *etc*., [9], it was modified by incorporating the natural dye sensitizer during the synthesis. Hence, the photo anode material for DSSC is ready in a one pot modified sol-gel process [10]. This superior behaviour namely,

reduced agglomeration, improved morphology, uniform dye absorption and less dye aggregation *etc.*, will influence the efficiency of DSSC. The photo sensitizer serves an important role in creating electron-hole pairs and it should absorb maximum incident energy to achieve better efficiency [11,12]. The dye aggregation and non-uniform adsorption of dye sensitizer into the metal oxide semiconductor surface are the other important issues to be solved [13]. The most successful ruthenium based chemical dyes have high solar light to electron conversion efficiency and better life time *etc*. But, due to their high cost, toxic heavy metal presence *etc.*, the natural dyes have gained enormous interest. The natural photo sensitizers are easily extractable, very cheap and eco safe materials [14]. A natural dye sensitizer was extracted from *Cordia sebestena* flower. This natural dye and modified sol-gel method derived TiO$_2$ are used to fabricate efficient natural dye sensitized solar cells in the present work. From I-V studies, the photoelectric conversion efficiency of conventionally prepared and modified sol-gel derived TiO$_2$ photo anode based DSSC are 0.87 and 1.28 %, respectively. The modified sol-gel technique has enhanced the efficiency by 47 % which is the novelty and significance of this work. Hence, the modified sol-gel method of yielding coloured TiO$_2$ nanoparticles can be adopted for harvesting more green energy efficiently in natural dye sensitized solar cells.

EXPERIMENTAL

Dye extraction: *Cordia sebestena* belongs to Boraginaceae family and the flowers blooms in clusters at branch tips all through the year. They are dark orange in colour, tubular and flaring to a width of two inches. Sebestenoid, a flavonoid, is the major pigment included in organic dyes. Fresh *Cordia sebestena* flower were gathered, thoroughly cleaned, dried and sliced into small pieces without crushing. The dye was extracted by soaking 200 g of small pieces of *Cordia sebestena* flower in double distilled water, ethanol (1:3 ratios) blended solvent for 12 h. The extract was procured by delicate heating in a similar solvent then allowed to cool over-night. The mixture was filtered and a dark blackish brown filtrate was amassed. It was stored in an airtight container which is placed away from the sun light. This dark orangish red extract was used as organic dye sensitizer without further purification to sensitize TiO$_2$ nanoparticles.

Synthesis of pure TiO$_2$: The conventional sol-gel procedure was adopted to synthesize pure TiO$_2$. Titanium isopropoxide (97 % sigma Aldrich) is taken as titanium precursor in addition to a blend of isopropyl alcohol and double distilled water as the hydrolysis medium. The isopropyl alcohol (15 mL) was combined properly with double distilled water (250 mL). The preliminary pH on this hydrolysis medium is observed as 8.75. It is given that the pH carries intense control on the formation and dimensions of TiO$_2$, the optimization of suitable pH value is significant. Whenever the pH is maintained above 2, a white-coloured rough precipitation was formed. And even, for a pH value less than 2, minimal quantity white-coloured precipitation was formed. Conversely, for pH 2, a consistent suspension of white-coloured precipitation was produced with good quantity as well. Henceforward, the pH was optimized

as 2, in order to retain that pH, nitric acid is added drop-wise. Then, this precursor was emphatically stirred and the other precursor titanium isopropoxide (5 mL) was supplied in drop-wise manner to result in a milky white-coloured precipitation. Once this hydrolysis process was completed, a turbid white-coloured viscous solution of TiO$_2$ was acquired. And then, this combination was heated to 80 °C for 3 h and set aside for aging at room temperature. The dried white-coloured suspension was rinsed in double distilled water and in ethanol to eradicate the byproduct impurities. At this point, this white-coloured precipitate was dehydrated at 100 °C for 5 h to obtain fine particles of absolute TiO$_2$.

Synthesis of modified sol-gel based TiO$_2$: The conventional sol-gel procedure of synthesizing pure TiO$_2$ was modified in order to eliminate certain downsides including, non-uniform particle size, agglomeration *etc*. In modified sol-gel process, a natural surfactant was introduced in the course of synthesis on its own to produce superior TiO$_2$. The organic dye, *Cordia sebestena* flower extract, was blended with the primary precursor solution (distilled water and isopropanol). At this point, the precursor solution contains the colour of the organic dye as well as the pH is adjusted to 2, making use of nitric acid. Once the hydrolysis process commences by the dropwise inclusion of titanium isopropoxide, a dark reddish orange precipitation begins to form as opposed to white-coloured precipitation just like the previous case. This is attributed to the strong adsorption of *Cordia sebestena* organic dye molecules onto the surface of TiO$_2$ as a surfactant and a photo sensitizer. After following the post synthesis procedures alike synthesizing of absolute TiO$_2$, tinted TiO$_2$ nanoparticles were obtained.

Fabrication of DSSCs: The absolute TiO$_2$ obtained by conventional sol-gel procedure was grinded well and made into a fine paste by thoroughly blending with titanium isopropoxide solution. By employing the doctor-blade procedure, a thin film of absolute TiO$_2$ was coated on the precleaned FTO glass plate. The doctor-blade coating procedure was carried out twice to develop a sufficiently thick layer. This has been accomplished very diligently on the FTO glass plate as the possibility for generating cracks on TiO$_2$ film is high. Then, the thin film was dried in air and is sintered at 250 °C for 0.5 h. This will strengthen the electrical contact between the TiO$_2$ nanoparticles also to eliminate internal gas and voids in the TiO$_2$ coated FTO glass plate. Soon after, this photo anode was soaked in the *Cordia sebestena* flower extract for 10 h for organic dye adsorption on the surface of TiO$_2$. Then, it is cleaned out in ethanol and dried in dark. A platinum coated FTO glass plate was used as counter electrode and joined to TiO$_2$ photo anode without air bubbles. The liquid electrolyte (I$^-$/I$_3^-$) was poured through the fine holes in the two electrodes meticulously and sealed to prepare TiO$_2$ based conventional DSSC. In the tinted TiO$_2$ based DSSC fabrication, the modified sol-gel procedure derived tinted TiO$_2$ was used to prepare the photo anode by repeating the above process of conventional DSSC. Unlike in the previous case, the photo anode is already tinted since it contains *Cordia sebestena* organic dye molecules. This is attained by the modified sol-gel procedure and the dye loading time is minimized considerably. Whenever

the sintering processes were over, the photo anode was once again soaked in *Cordia sebestena* flower extract for 3 h. This will assist the photo anode film to adsorb more photo sensitizer when compared with the conventional TiO₂ based electrode. By following the same fabrication methods, the modified sol-gel procedure derived tinted TiO₂ based DSSC was fabricated.

Characterization studies: The powder X-ray diffraction (PXRD) pattern was evaluated using ISO DEBYEFLEX 2000 diffractometer employing CuKα ($\lambda = 1.5418$ Å) radiation. The UV-visible absorption spectrum was analyzed operating Shimadzu Model 1601 spectrophotometer. The Perkin Elmer Spectrum 1 FT-IR instrument with a resolution of 1.0 cm^{-1} was utilized to acknowledge the functional groups available in the absolute and tinted TiO₂. TECNAI–T20 Transmission Electron Microscope was used to observe the morphological behaviour. The I-V characteristics of the organic dye sensitized solar cells were calculated through Keithley 2400 source meter with Xenon lamp of 100 mW cm^{-2} as solar simulator.

RESULTS AND DISCUSSION

Power XRD studies: The PXRD pattern of the tinted TiO₂ nanoparticles calcined at 250 °C for 2 h is shown in Fig. 1. The existence of prominent diffraction peaks including, (101), (004), (200), (211), (204), (116) and (215) ensures the nano crystalline anatase structure of TiO₂. It is worth to specify that the anatase is the most suitable form of TiO₂ for the fabrication of DSSCs. As well as, the particle size of TiO₂ was acquired by using Scherrer's equation,

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where, D is the particle size, λ is the wavelength of the CuKα X-ray radiation ($\lambda = 0.15418$ nm), K is shape factor, a dimensionless constant (0.94 in case of spherical shaped particles) and β is the full width at half the peak height (FWHM) of the respective diffraction peaks [15]. The coloured TiO₂ nanoparticle possesses an average crystalline scale of 40 nm.
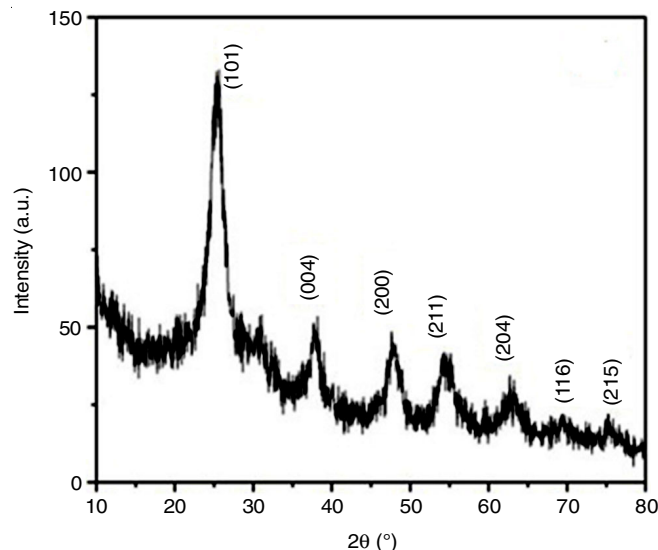

Fig. 1. PXRD pattern of coloured TiO₂ after calcination at 250 °C

Transmission electron microscope analysis: The transmission electron microscope (TEM) image of absolute TiO₂ nanoparticles outfitted by typical sol-gel process is portrayed in Fig. 2a. The TEM uncovers that the absolute TiO₂ possess non-uniform morphology with agglomerated tendency which forms nanoclusters. Such nanoclusters will certainly influence the photo electric behaviour of TiO₂ unconstructively. In general, a surfactant or perhaps a capping agent will probably be utilized to diminish this agglomeration. In present study, the modified sol-gel procedure eliminates this incongruity by adding the organic dye. Due to this fact, the *Cordia sebestena* organic dye used here normally takes function of photo sensitizer and even surfactant. The TEM image of tinted TiO₂ nanoparticles synthesized through modified sol-gel method (Fig. 2b), reveals the betterment in morphology being individual spherical particles as compared to that of absolute TiO₂ by sol-gel method. Most significantly, the nano cluster arrangement was abridged to a remarkable extent in modified sol-gel procedure. This is
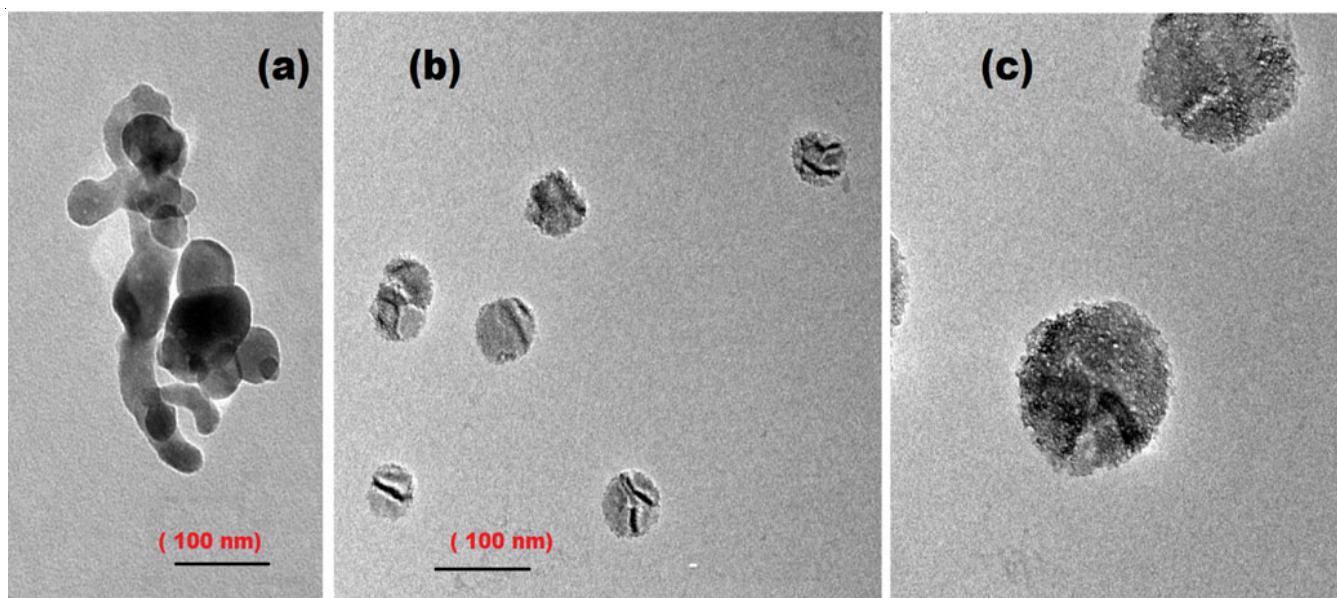

Fig. 2. TEM images of (a) pure TiO₂ (b) coloured TiO₂

attributed to the sturdy adsorption of *Cordia sebestena* organic dye molecules on the TiO₂ surface.

This prevents the merging of TiO₂ particles together as the *Cordia sebestena* flower extract acts as a capping agent. The roughness and surface to volume ratio are also enhanced as shown in Fig. 2c. And, dye aggregation on nano crystalline film may block the physical contact between the electrolyte and TiO₂ and results, reduction in efficiency will occur [16]. This uniform adsorption of organic dye on TiO₂ surface lessens the possibility of dye aggregation and then enhances the efficiency of DSSC. The average crystalline size of tinted TiO₂ nanoparticles by TEM examination is 48 nm.

Energy dispersive X-ray spectrum studies: The energy dispersive X-ray (EDAX) spectrum of natural TiO₂ nanoparticles is proven in Fig. 3a. The spectrum has prominent peaks of Ti and O. From the peaks, it is affirmed that the nanoparticles synthesized by sol-gel technique is pure TiO₂. The weight contributions are 33.83 and 61.45 % for oxygen and titanium, respectively which is in perfect agreement with 2:1 stoichiometry of TiO₂. Both the elements collectively contribute 95.28 % of the total weight of absolute TiO₂. The EDAX spectrum of *Cordia sebestena* natural dye sensitized tinted TiO₂ is displayed in Fig. 3b. The weight contributions are 36. 01, 33. 13 and 30.85 % for oxygen, titanium and carbonyl group found in *Cordia sebestena* organic dye, respectively. Overall, they contribute 90.85 % of the total weight and confirm the adsorption of natural dye on TiO₂. The change in weight contributions of *Cordia sebestena* natural dye sensitized TiO₂ is attributed to O–Ti–O bond changed into O–Ti–OOC due to the adsorption of organic dye on TiO₂.

UV-visible absorption spectral studies: The UV-visible absorption spectrum of absolute TiO₂ nanoparticles is depicted in Fig. 4a shows that organic TiO₂ absorbs light photons in UV and nearby regions only. Therefore, a separate dye sensitizer must be attached with TiO₂ surface for absorbing more light in the solar spectrum. This makes TiO₂ suitable material for the fabrication of DSSCs. From the absorption spectrum of absolute TiO₂, the cutoff wavelength (λ) is found to occur at 356 nm. And, the band gap energy calculated using the relation $E_g = 1239. 8/\lambda$ eV (λ, nm) [17] was 3.48 eV. The band gap of normal or bulk TiO₂ is 3.2 eV and this variation is due to the change in particle size, quantum confinement effect [18]. The absorption spectrum of *Cordia sebestena* natural dye sensitized TiO₂ (Fig. 4b) shows enhanced light photon absorption and extension of absorption region up to 450 nm. In addition, this UV-visible spectrum shows absorption peaks at 568 and 621 nm. This improvement in photo sensitization of coloured TiO₂ is attributed to the strong adsorption of photo sensitizer molecules on TiO₂ surface. The charge injected into the conduction band of the TiO₂ is also affected by the type of attraction between photo sensitizer and its anchoring group with TiO₂ [19]. The *Cordia sebestena* organic dye possesses several C=O and –OH groups capable of anchoring the Ti sites on TiO₂. This creates a strong electronic coupling between the natural dye and conduction band of TiO₂ which results efficient charge transfer [20]. The cutoff wavelength of organic dye sensitized TiO₂ is 541 nm as well as the band gap is calculated as 2.29 eV. The decrease in band gap and improvement in absorption patterns were observed in tinted TiO₂ synthesized through modified sol-gel procedure. Thus, the *Cordia sebestena* organic sensitizer strengthens the photo sensitization behaviour of TiO₂ and can influence the photocurrent and total conversion efficiency constructively.
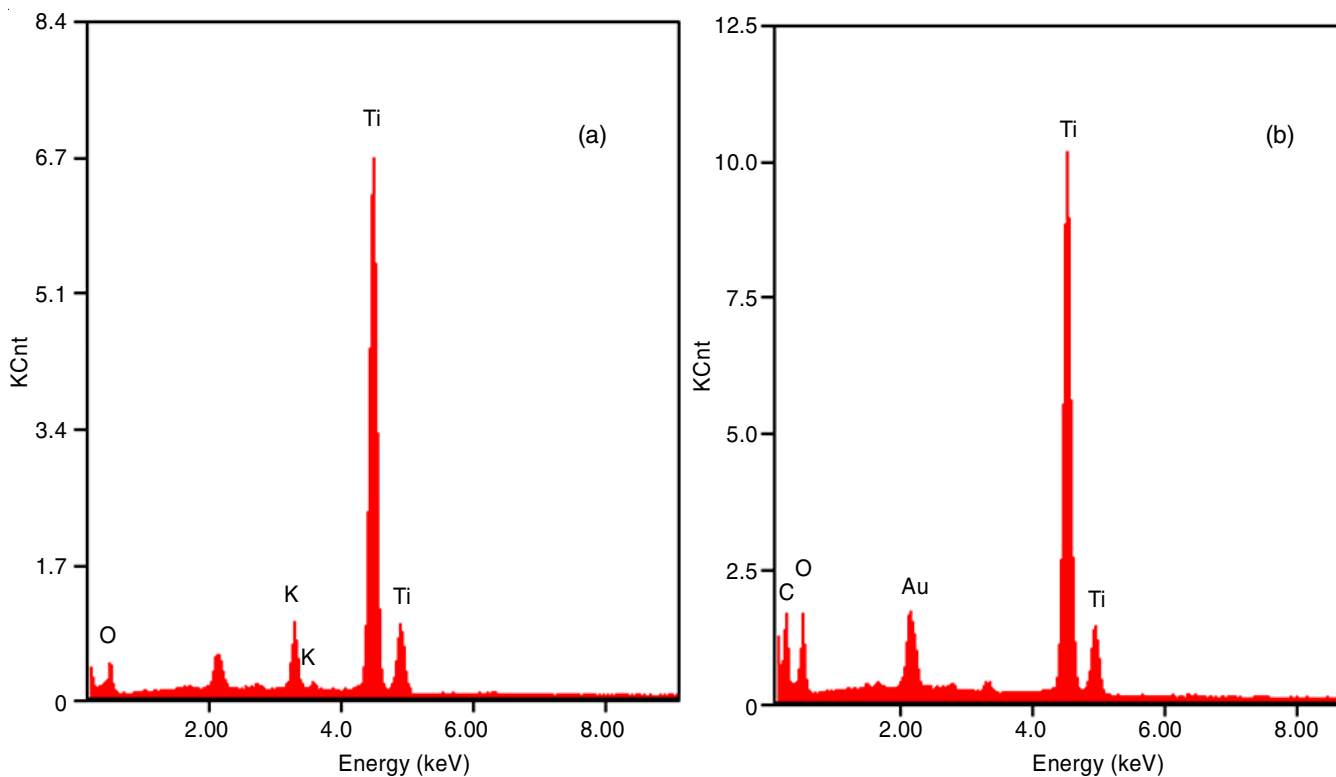

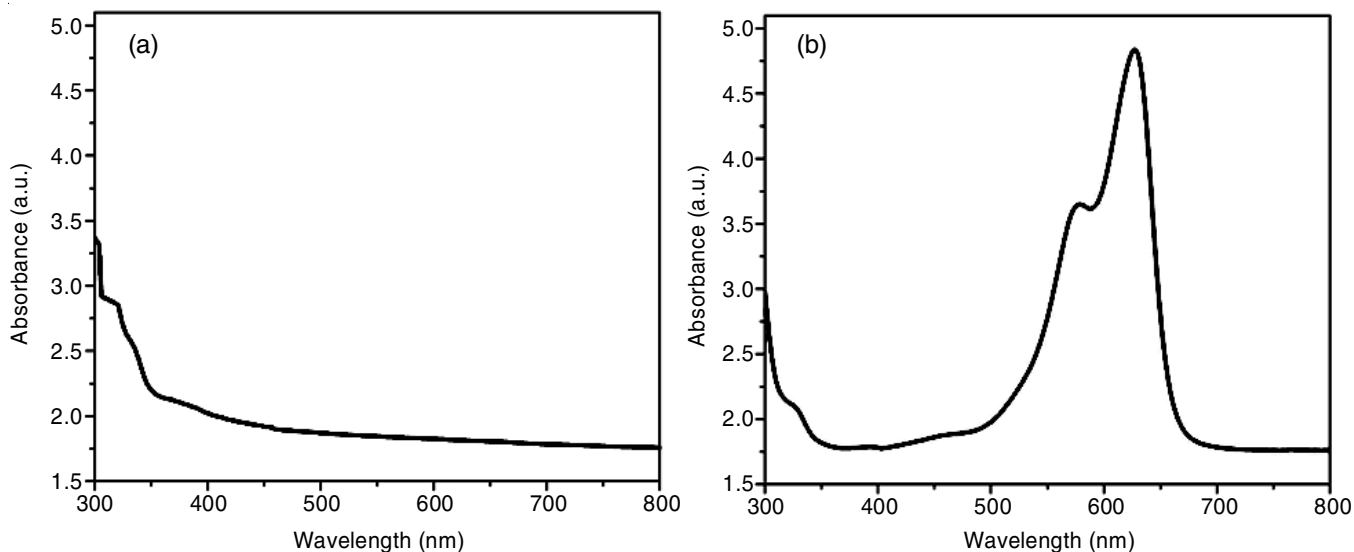Fig. 3. EDAX spectra of (a) pure TiO₂ (b) coloured TiO₂

Fig. 4. Absorption spectra of (a) pure TiO₂ (b) coloured TiO₂

Frontier molecular orbitals: The molecular structure of sebestenoid D, a pigment present in *Cordia sebestena*, was optimized by DFT method using B3LYP, hybrid function consisting three parameters of Becke's non-local exchange function with the correlation function of Lee, Yang and Parr [21]. DFT calculations were carried out using Gaussian 03, B3LYP/6-31G (d) basis set [22].

The optimized molecular geometry of sebestenoid D is shown in Fig. 5. The HOMO–LUMO energy gap for the isolated gas period of sebestenoid D seems to be 7.2 eV. The obtained energy orbitals are shown in Fig. 6. The HOMO plot presents the charge densities of the entire benzene ring attached on the right-side chain of the sebestenoid D molecule with a hydroxyl group attached to it. Furthermore, the LUMO contributes to the intermediate chain with C-H atoms linking the left side chain benzene ring and right-side chain benzene ring. The LUMO plot does not have contributions in the right-side chain of the benzene ring.

FTIR spectral studies: Fourier transform infrared (FTIR) spectra of absolute TiO₂ and tinted TiO₂ with *Cordia sebestena* natural dye are shown in Fig. 7a and b, respectively. Both spectra have characteristic peak of Ti–O bond at 646 cm⁻¹ in pure and at 710 and 753 cm⁻¹ in tinted TiO₂ whose standard
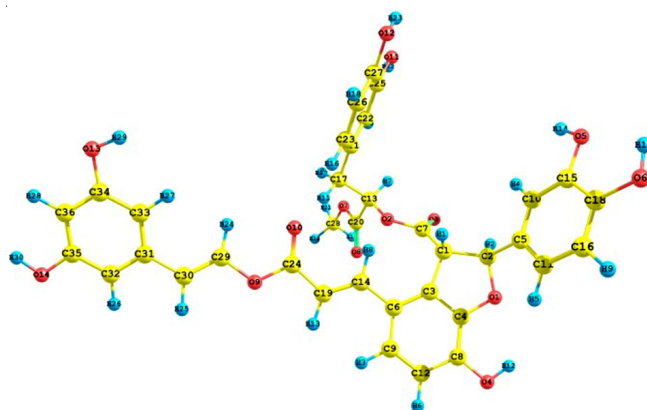

Fig. 5. Optimized molecular geometry of sebestenoid D molecule

range is 1000-450 cm⁻¹ [23]. This confirms the formation of TiO₂ in both conventional and modified sol-gel procedures. The absorption peak at 1050 cm⁻¹ is assigned to C–O stretching mode of natural dye. The peak present at 1157 cm⁻¹ is assigned to C–H bending mode. The peak present at 1239 cm⁻¹ in coloured TiO₂ is assigned to C–C stretching vibration [24]. The absorption peak at 1647 cm⁻¹ is assigned to N–H bending vibration of nitric acid which is added to modify the pH of the precursor
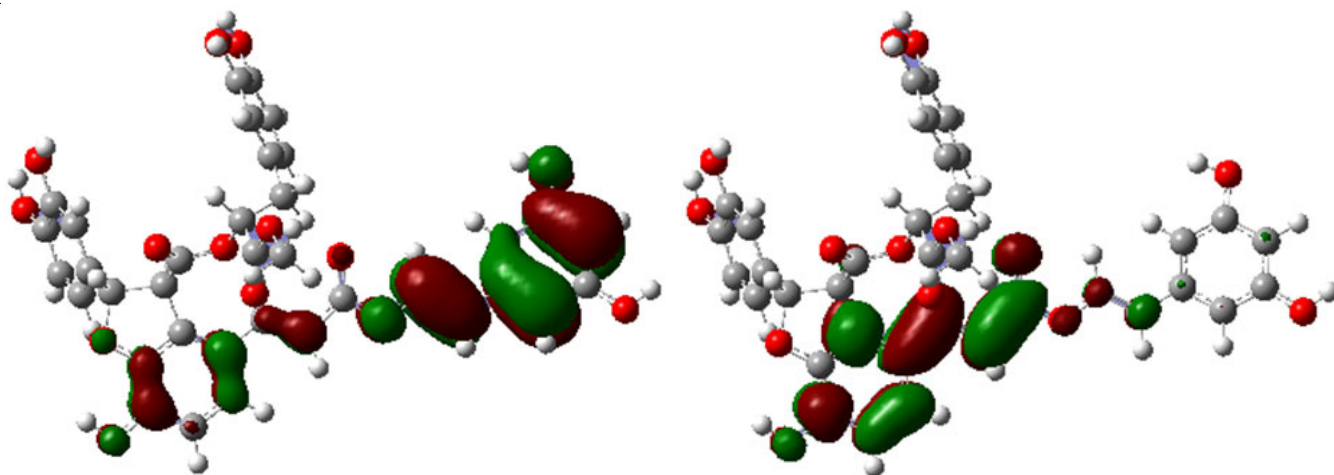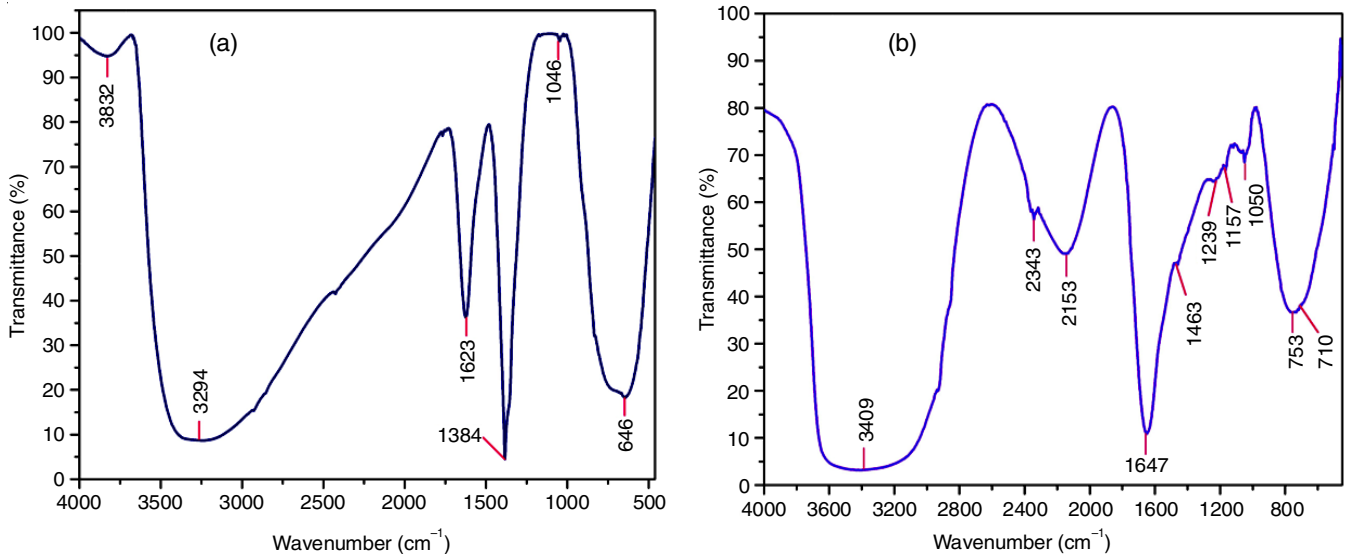

Fig. 6. HOMO-LUMO plot of sebestenoid D

Fig. 7. FTIR spectra of (a) pure TiO_2 (b) coloured TiO_2

solution. The peaks present at 2153 and 2343 cm^{-1} are assigned to N–H stretching mode [25]. The absorption peak at 3409 cm^{-1} is assigned to O–H stretching of water molecules.

Efficiency studies of *Cordia sebestena* flower extract sensitized DSSCs: The current-voltage (I-V) characteristics of *Cordia sebestena* flower extract sensitized pure and coloured TiO_2 based natural DSSCs are measured by using Keithley 2400 source meter and given in Fig. 8. The solar light photon to electron conversion efficiency of both the solar cells are examined under the AM 1.5 G illumination at 100 mW/cm^2. The fill factor (FF) was found using the relation [26]:

$$\text{Fill factor} = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}}$$

where I_{max} and V_{max} denote the maximum output value of current and voltage, respectively and I_{sc} and V_{oc} denote the short-circuit current and open-circuit voltage, respectively. The conventionally prepared TiO_2 based DSSC exhibits the observed values of $I_{sc} = 2.8$ mA cm^{-2}, $V_{oc} = 0.49$ V and the calculated value of fill factor is 63.39 %. Similarly, for tinted TiO_2 based DSSC, the observed values of $I_{sc} = 3.6$ mA cm^{-2}, $V_{oc} = 0.59$ V

Fig. 8. I-V characteristics of pure and coloured TiO_2 based natural DSSCs sensitized by *Cordia sebestena* natural dye

and the calculated value of fill factor is 66.09 %. The solar light energy conversion efficiency was found using the relation:

$$\eta = \frac{I_{sc} \times V_{oc} \times FF}{P_{in}}$$

where, P_{in} denotes the energy of incident photon and FF is fill factor.

The efficiency of absolute TiO_2 based DSSC was calculated as 0.87 % and the efficiency of tinted TiO_2 based DSSC is 1. 28 %. The I_{sc} and η were discovered to be higher for the DSSC fabricated implementing the tinted TiO_2 based electrodes than that of conventionally prepared TiO_2 based DSSC. The tinted TiO_2 based DSSC showed 47 % improvement in solar light photon to electron conversion efficiency. This is the outcome of direct mixing up of *Cordia sebestena* flower extract during synthesis of tinted TiO_2 by modified sol-gel procedure. The I-V studies concludes that the tinted TiO_2 nanoparticles absorbs more light, transfers more charges and enhances the efficiency in organic dye sensitized solar cells.

Conclusion

Pure and coloured TiO_2 nanoparticles were successfully synthesized *via* conventional and modified sol-gel procedure. The *Cordia sebestena* flower extract was successfully used as natural dye sensitizer and natural surfactant. The anatase phase of TiO_2 sintered at 250 °C was confirmed by PXRD analysis. The UV-visible spectra revealed the cutoff wavelength band gap of pre-dye treated TiO_2 is reduced to 2.29 eV compared to 3.48 eV of pure TiO_2. The FTIR spectra confirm the formation of TiO_2 in both sol-gel procedures by means of their functional groups. The TEM images confirm the improvement in morphology and reduction in agglomeration due to pre-dye treatment. Natural DSSCs were fabricated using conventionally prepared and modified sol-gel procedure based TiO_2. *Cordia sebestena* flower extract is a potential natural dye sensitizer and surfactant for environmentally friendly DSSCs. The efficiency of conventionally prepared natural DSSC is 0.87 % and that of coloured TiO_2 based natural DSSC is 1.28 % with a remarkable enhancement of 47 %. Thus, the modified sol-gel procedure producing
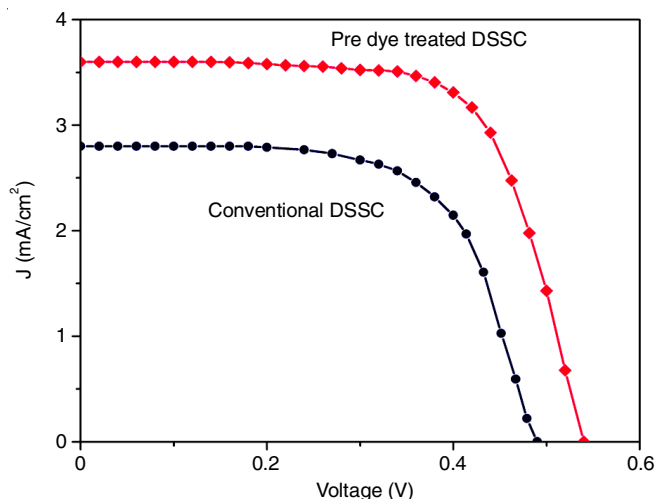
coloured TiO_2 is a promising methodology in terms of more dye adsorption, less dye aggregation and improved efficiency. Therefore, this can be adopted for efficient natural DSSC fabrication successfully.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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