Application of Natural Betalain Dye from Beetroot for Improved Efficiency in Dye Sensitized Solar Cell

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Abstract. C, N, S co-doped TiO₂ (TU-TiO₂) synthesized through solid state method using high energy ball milling was applied onto fluorine doped tin oxide (FTO) glass substrate and sintered at 450°C for half hour for use as a photoanode of dye-sensitized solar cells (DSSCs). Natural Betalain containing dye extracted from beetroot was used as sensitizer, Iodide triiodide was used as electrolyte and graphite as counter electrode to obtain FTO/C, N, S-TiO₂/Dye/Electrolyte/Graphite/FTO DSSC. X-ray Diffraction analysis established the formation of single phased materials retaining the basic TiO₂ structure. Optical properties were enhanced with increase in molar concentration of thiourea in TiO₂. Fourier Transform Infrared spectroscopy confirmed the incorporation of sulphur into TiO₂. The highest of 94% relative increase is observed in solar to electric conversion efficiency for C, N, S co-doped TiO₂ compared to un-doped TiO₂. Along with decrease in the band gap making the cell more sensitive to visible light, the improved performance is also due to the rise in charge injection from betalain dye to the C, N, S co-doped TiO₂.

1. Introduction

Dye-sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity, based on the sensitization of wide band gap semiconductors [1] and have become an attractive alternative to conventional solid state solar cells due to their remarkably low cost, ease in manufacturing and fairly good energy conversion efficiency [2-5]. For example, the photoelectric conversion efficiency of the DSSC TiO₂/2 organic dye/Co(II/III) tris(phenanthroline)-based redox electrolyte /Pt has reached 14.30% [6]. Some of the popular materials used as photoanodes are TiO₂, ZnO, SnO₂ etc. However, since these materials have large band gaps of the order of 3 eV, they do not respond to visible light and become active only under ultra violet (UV) light [7]. Due to this limitation, solar energy cannot be utilized extensively in these materials and it is necessary that the band gap be decreased so that the visible light, which is majorly emitted by the Sun, can be absorbed. One method of doing this is by doping with anions leading to narrowing of band gap [8].

Among the popular photoanode materials, TiO₂ has a relatively smaller band gap along with fairly good conversion efficiency. Studies showing the shifting of the optical absorption edge of TiO₂ towards lower energy i.e., from UV to visible, by doping it with anions such as C [9-10], N [11-12] and S [13-16] have been reported. Recent studies have also revealed that TiO₂ nanofibers enhanced the optoelectrical properties of DSSCs. For instance, Mahmoud et al [17] have synthesized sulphur doped TiO₂ nanofibers and have reported solar to electrical conversion efficiency of 4.27% as compared to...
the 1.54% efficiency of untreated TiO$_2$ nanofibers. The choice of sensitizer in DSSCs also plays an important role in the working efficiency and also their stability, cost and visible light absorption characteristics. Most of the dyes used as sensitizers for DSSCs are Ruthenium (Ru) based and are costly [18]. There is thus a need to explore low cost, Ruthenium metal-free dyes for developing cost effective DSSCs. Recently, organic dyes have attracted interest due to their low cost and environmentally friendly nature [19-21]. As compared to synthetic organic and inorganic dyes, extraction of dyes from natural biological resources is an effective way of reducing the overall cost of solar cells. Studies of natural dyes extracted from various plants and fruits containing anthocyanin, betalain, chlorophyll, indigo etc. [22-25] show that these serve as effective sensitizers and have proved to bind easily with the surface of the photocatalyst [26].

To the best of the authors’ knowledge, DSSCs prepared by C, N, S co-doped TiO$_2$ and betalain containing natural dye together have not been reported yet. In this work, our aim is to combine the enhancement of optoelectronic properties of TiO$_2$ on doping with anions C, N, S along with the use of a natural sensitizer, namely, betalain, present in the juice of beetroots, to prepare a low cost DSSC. The results show that the photovoltaic efficiency of the resulting DSSC is enhanced and is promising especially considering the ease of fabrication, environmentally friendly nature of the dyes and low cost of materials used.

Figure 1. Schematic representation of the DSSC.

2. Experimental

2.1. Main Materials
The following materials have been used without any further purification. TiO$_2$ particles (Merck India), Thiourea (S.D Fine Chem. Ltd.), I$_2$ (Aldrich, USA, 99.99% pure), Potassium iodide (S.D Fine Chem. Ltd., 99.8% pure), Ethylene glycol anhydrous (Sigma Aldrich, USA, 99.8% pure), Acetonitrile (Merck, India, 99.5% pure), Ethanol (Jebsen & Jessen GmbH & Co., Germany, 99.9% pure), Acetic acid (Sigma Aldrich, USA, 99% pure), Ethyl Cellulose (Aldrich, USA), Terpinol (Aldrich, USA), Acetone (Merck, India) and FTO glass (USA, Aldrich, 2.2 mm thickness, surface resistivity 8Ω/cm$^2$).

2.2. Synthesis of C, N, S sulphur-doped TiO$_2$
Using TiO$_2$ and thiourea as a precursor, a series of un-doped and C, N, S co-doped TiO$_2$ samples were prepared by high energy ball milling. Three samples were prepared with a change in molar ratio of 0.25 in thiourea (0.25:4, 0.50:4 and 0.75:4) in order to dope carbon, nitrogen, sulphur into TiO$_2$. Pure
TiO$_2$ and thiourea mixed TiO$_2$ powders were ball milled in a high energy SPEX8000M mixer mill with a milling speed of 1080 rpm for 20 minutes. Tungsten carbide (WC) balls and vials were used fixing the ball to sample weight ratio to be 10:1. For purposes of discussion in the rest of this paper, the samples after milling are designated as TU-x, where, x represents the molar ratio of thiourea.

2.3. Extraction of natural dye

For the extraction of betalain dye, fresh beetroots were peeled, sliced to small pieces and ground to juice using a grinder machine. The juice was sonicated with 75% ethanol acidified with 10 mM HCl for 30 minutes and the solution was then filtered using a filter paper.

2.4. Preparation of DSSCs

Fluorine doped Tin Oxide (FTO) slides were successively cleaned in surfactant dissolved distilled water, distilled water and acetone for cycles of 30 minutes each respectively in an ultrasonic bath. The C, N, S co-doped and un-doped TiO$_2$ powders obtained after ball milling were mixed with acetic acid, ethyl cellulose and terpinol as surfactant and kept suspended for half an hour after which it was sonicated using probe sonicator. The prepared slurries were doctor bladed on the conducting side of the FTO glass, followed by sintering at 450ºC for 30 minutes in a furnace and then cooled to room temperature. The films were then kept dipped in 0.5 mM ethanol solution of the natural dye prepared from beetroot for 24 hours for complete dye loading. Graphite, which served as counter electrode, was prepared by rubbing high carbon pencil on FTO glass and sintering at 100 ºC for 30 min. The electrodes (dye sensitized TiO$_2$ photo-anode) and counter electrodes were sandwiched together to make a solar cell with an active cell area of 0.25 cm$^2$. The two electrodes were held together by binder clips. An electrolyte consisting of 0.5 M I$_2$ and 0.05 M KI in 10 mL ethylene glycol was injected into the gap of the two electrodes. The schematic diagram for DSSC is shown in Figure 1.

2.5. Characterizations

The X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer at 40 kV and 40 mA over a range of 20 from 15º to 80º using Cu K$_\alpha$ radiation. Images were obtained using a multimode NT-MDT Solver NEXT Atomic Force Microscope (AFM) by scanning over an area of 10 μm x 10 μm. Field Emission Scanning electron microscope image of the TU-0.75 sample were taken in NOVA NanoSEM 450. The voltage and pressure were maintained at 15 kV and 2.44 x 10$^{-5}$ torr, respectively. Optical properties of the C, N, S co-doped TiO$_2$ were determined using a UV-Vis spectrophotometer (ELICO SL 159) in the range of 250 – 800 nm. Fourier transform infrared (FT-IR) spectra were obtained using Bruker model Alpha IR spectrometer in the range of 4000-420 cm$^{-1}$. The photovoltaic test of the DSSC was carried out by measuring the I-V characteristics curves using Keithley 2400 source meter under white light irradiation from a 200 W lamp. An irradiation intensity of 100 mW/cm$^2$ was used for measurement of I-V curves.

3. Results and Discussion

3.1. X-ray Diffraction analysis

The best fitted XRD patterns of the un-doped and C, N, S co-doped TiO$_2$ powders calcined at 400ºC for 1 hour are shown in Figure 2(a) which show well resolved diffraction peaks corresponding to the reflections of anatase phase of TiO$_2$. The diffraction patterns match well with the JCPDS data 894921[ICSD # 076173] and corresponds to a tetragonal structure with spacegroup l41/amd [27]. From the good fitted graphs, it is evident that mixing of thiourea and TiO$_2$ for the compositions studied results in a single phased material with the basic crystal structure of TiO$_2$. The average particle size, observed to be about 40 nm for all samples, and strain have been estimated by the Williamson Hall method and are tabulated in Table 1. Also, the refined parameters such as lattice parameters, volume, R$_{Bragg}$, R$_{f}$ and $\chi^2$ are given in Table 1. The variation of strain with change in the dopant molar concentration is shown in Figure 2(b) and is observed to range from 11.2 x 10$^{-4}$ to 22 x 10$^{-4}$. From the figure it is clear that an increase in the thiourea molar concentration leads to an increase in strain with the relative strain of TU-0.75 sample being double than that of pristine TiO$_2$. This is because the
sulphur atom has a much larger size than oxygen atom and on being incorporated into the TiO$_2$ lattice without changing the crystal structure, the lattice becomes increasingly strained with an increase in the content of sulphur.

Table 1. Average particle size, strain and refined parameter of undoped and C, N, S co-doped TiO$_2$.

| Sr. No. | Sample Name | Particle Size (nm) | Strain ($10^{-4}$) | (x) Lattice parameter | Volume ($\text{Å}^3$) | $R_{\text{Bragg}}$ | $R_{f}$ | $\chi^2$ |
|--------|-------------|-------------------|-------------------|-----------------------|------------------------|----------------|--------|--------|
| 1      | TU-0        | 43                | 11.5              | 3.7840                | 9.5104                 | 136.180       | 9.73   | 6.64   | 3.79   |
| 2      | TU-0.25     | 40                | 9.3               | 3.7841                | 9.5099                 | 136.178       | 8.83   | 6.57   | 3.99   |
| 3      | TU-0.50     | 44                | 9.8               | 3.7843                | 9.5099                 | 136.197       | 7.61   | 6.70   | 3.90   |
| 4      | TU-0.75     | 40                | 22.4              | 3.7840                | 9.5093                 | 136.167       | 6.55   | 5.27   | 3.70   |

Figure 2. (a) XRD of undoped and C,N,S co-doped TiO$_2$; (b) variation of strain with change in molar concentration of thiourea in TiO$_2$.

3.2. Field Emission Scanning Electron Microscopy
Field Emission Scanning Electron Microscopy (FE-SEM) micrograph of C, N, S co-doped TiO$_2$ (TU-0.75) is reported in Figure 3(a). The surface morphology of TU-0.75 exhibits spherical shape, uniform distribution of grains and slight agglomeration. From the histogram plots in Figure 3(b), the average particle size obtained was 75 nm. Energy dispersive X-ray analysis (EDX) confirms the presence of carbon, nitrogen, sulphur, titanium and oxygen as observed by Figure 3(c). The quantitative results of EDX of C, N, S co-doped TiO$_2$ sample clearly show that the wt. % of C, N, S, Ti and O are 24.09, 0.45, 0.09, 41.01 and 34.36, respectively.
Figure 3. (a) FESEM image of TU-0.75; (b) histogram for particle size determination and (c) EDX of TU-0.75.

3.3. Atomic Force Microscopy
Analysis of the AFM images have been done by 3D and 2D profile analysis and the 3D AFM images are presented in Figure 4. The artefacts obtained in the AFM images were removed using the Gwyddion software and value of parameters such as average roughness, skewness, kurtosis and entropy are given in Table 2. Average roughness is calculated by the arithmetic average of height of the surface above a hypothetical smooth plane. It can be seen from the table that roughness of undoped TiO$_2$ is the least and increases with an increase in the content of thiourea doping. This can be related to the increase in strain induced in the lattice due to the larger size of sulphur, as also observed from XRD studies. The Skewness ($R_{sk}$) shows the degree of symmetry of rough surface profile and can be used as a measure of balance between the peaks and valley of the asperites and describes the profile symmetry about a mean line. Accordingly, $R_{sk}$ would be zero for symmetrical profile, negative for a surface with predominantly planar and valleys morphologies and positive for a surface which has more peaks than valleys [28]. The values obtained for the skew from the curve have positive value indicating that all the samples have more peaks than valleys. Kurtosis ($R_{ku}$) measures surface sharpness and show the degree of pointedness or bluntness of asperities on surface ($R_{ku}$ is less than 3 for a platykurtic or flat surface). $R_{ku}$ for all samples in the present study have values less than 3 (table 2) implying that the surface is platykurtic. Figure 5 gives the linear fits of skew and kurtosis for
varying molar concentration of dopant in TiO$_2$ from which it is apparent that there is nearly a linear rise in these statistical or functional parameters with an increase in the molar concentration of thiourea. Entropy generally describes the morphology connected to the degree of order or disorder in grain structure distribution and the values obtained, given in table 2, are nearly the same for all four samples.

**Table 2.** AFM parameters of pure and C, N, S co-doped TiO$_2$.

| Sr. No. | Sample No. | Mean Roughness | Skew | Kurtosis | Entropy |
|---------|------------|----------------|------|----------|---------|
| 1       | TU-0       | 208 nm         | 0.677| 1.710    | -14.58  |
| 2       | TU-0.25    | 158 nm         | 0.305| 1.634    | -14.66  |
| 3       | TU-0.50    | 220 nm         | 0.772| 1.780    | -14.62  |
| 4       | TU-0.75    | 211 nm         | 0.786| 1.795    | -14.80  |

**Figure 4.** AFM 3D Images of (a) TU-0; (b) TU-0.25 doped TiO$_2$ ;(c) TU -0.5 doped TiO$_2$ and (d) TU -0.75 doped TiO$_2$. 


Figure 5. Trends of skew and kurtosis with varying molar concentration of thiourea in TiO$_2$.

3.4. UV-Visible Spectroscopy

Optical properties of the samples have been measured using UV-visible spectrophotometer and are based on the Beer - Lambert Law which relates the absorption of light with the physical property of the material. The optical absorption measurements of the samples were carried out in the wavelength range of 230-800 nm. In general, although the absorbance was observed to be high in the UV and lower visible regions with decrease at higher wavelengths, the absorption edge of TiO$_2$ shifts towards higher wavelengths with increase in the molar concentration of thiourea indicating that doping with carbon, nitrogen, sulphur leads to a higher response of TiO$_2$ to visible radiation. The shifting of the absorption edge towards higher wavelength results in the reduction of band gap energy with an accompanying enhancement in the optoelectronic properties.

The absorption coefficient was calculated using the following equation

$$\alpha = \frac{A(E_g - h\nu)^{1/2}}{h\nu}$$

Where, $\alpha$ represents absorption coefficient, $E_g$ the band gap, $h$ Planck constant and $\nu$ the frequency of the radiation. For determining the band gap of the C, N, S co-doped and undoped TiO$_2$, Tauc plots are plotted as shown in Figure 6. The linear behaviour of the graph indicates direct nature of optical
bandgap. Direct bandgap values were evaluated from the intercepts obtained from straight line extrapolation towards the energy axes. The band gap obtained was 3.94 eV, 3.86 eV, 3.84 eV and 3.8 eV for TiO$_2$, TU-0.25, TU-0.50 and TU-0.75 respectively. A linear variation of the band gap as a function of the molar concentration of thiourea is obtained (Figure 7) from which it is observed that band gap decreases by 0.18 eV with an increase of every 25% in the doping molar concentration of thiourea into TiO$_2$.

![Figure 7. Variation in band gap as a function of change in molar concentration of thiourea in TiO$_2$.](image)

3.5. Fourier Infrared Spectroscopy

![Figure 8. Infrared spectrum of undoped and C, N, S co-doped TiO$_2$.](image)

Fourier transform infrared (FTIR) spectroscopy is a useful tool in recognizing the chemical bond structure and provides an insight into the essential chemistry of the material such as the existence of interactions present in samples, material phase composition etc. FTIR spectra of pristine TiO$_2$ and C, N, S co-doped TiO$_2$ in the range of 420-4000 cm$^{-1}$ are shown in Figure 8. The peaks in the range of 3400-3100 cm$^{-1}$ and 1700-1600 cm$^{-1}$ are attributed to surface absorbed H$_2$O and hydroxyl groups respectively [29, 30]. From the figure, a strong band at 1630 cm$^{-1}$ for all the samples is observed which is attributed to the O-H bending vibration of adsorbed water molecule on the surface of material [31]. The intensity of 1630 peak is stronger for TU-0.75 doped TiO$_2$ as compared to undoped TiO$_2$. This is due to the of imbalance of extra positive charge created locally due to the introduction of S$^{6+}$ into the
TiO₂ lattice since Ti is present as Ti⁴⁺ in the TiO₂ crystal structure resulting in attraction of more hydroxide ions on the crystal surface. Devi et al. [29] have also obtained similar results in their study of S doped TiO₂ for enhancement of photocatalytic activity. For all C, N, S co-doped TiO₂ samples, a band in the range of 1150 – 1130 cm⁻¹ is seen, which is indicative of S-O vibration and confirms the incorporation of sulphur in the TiO₂ crystal structure [32]. Various peaks are observed in the range of 800 – 420 cm⁻¹ which can be attributed to the Ti-O-Ti stretching vibrations [33, 34].

3.6. Device performance
Current density (J) versus voltage (V) plot of DSSCs of undoped and C, N, S co-doped TiO₂ are given in Figure 9 and the short circuit current density (J_sc), open circuit voltage (V_oc), fill factor and efficiency are summarized in Table 3. The plot comparing the efficiency and fill factor as a function of the doping molar concentration of thiourea in TiO₂ is shown in Figure 10 from which it can be seen that the DSSCs with carbon, nitrogen and sulphur doping show improved performance as compared to the undoped TiO₂. From Table 3, it can be seen that maximum V_oc and J_sc is observed for TU-0.75 doped TiO₂ due to which the efficiency of TU-0.75 is 94% more than that of undoped TiO₂. Our obtained efficiency is higher than that of reported value by García-Salinas et al. and Sengupta et al. [33, 34]. This is due to the higher obtained maximum point current and maximum point voltage leading to increased fill factor. However, for these solar cells, the observed J_sc and V_oc are less compared to the DSSCs prepared using commercial dyes (e.g. N719, N3). The lower value of open circuit voltage (V_oc) may be due to the molecular structure of the natural dye (betalain) used in these samples. The obtained efficiencies are also lower than the commercial dye based DSSCs and is due to the comparatively weaker binding of natural dyes with metal oxides (e.g. TiO₂, ZnO, SnO₂) along with a lower charge transfer spectra of these dyes under solar spectrum [35].

Figure 9. J-V plots of prepared DSSCs (Lines are Sigmoidal fitted).
Figure 10. Efficiency and fill factor vs. doping concentration of thiourea of fabricated DSSCs.

Table 3. Photovoltaic parameters of DSSCs sensitized by betalain dyes.

| Configuration                                      | Sample name | J_{sc} (mA/cm²) | V_{oc} (V) | Fill factor | Efficiency (%) |
|----------------------------------------------------|-------------|-----------------|------------|-------------|----------------|
| FTO/TU-0/Dye/Electrolyte/Graphite/FTO (our work)   | TU0         | 0.04            | 0.28       | 0.49        | 0.02           |
| FTO/TU0.25/Dye/Electrolyte/Graphite/FTO (our work) | TU 0.25     | 0.16            | 0.24       | 0.55        | 0.08           |
| FTO/TU0.50/Dye/Electrolyte/Graphite/FTO (our work) | TU 0.5      | 0.11            | 0.32       | 0.38        | 0.05           |
| FTO/TU0.75/Dye/Electrolyte/Graphite/FTO (our work) | TU 0.75     | 0.42            | 0.35       | 0.61        | 0.36           |
| FTO/ZnO/Dye/Electrolyte/carbon/FTO (others work)   |             |                 |            |             |                |
| FTO/ZnO/Dye/Electrolyte/Platinum/FTO (others work) |             |                 |            |             |                |

4. Conclusions

Different molar concentrations of thiourea i.e C, N, S co-doped TiO₂ were prepared by high energy ball milling to device a DSSCs. Investigations using X-ray diffraction have ruled out formation of other phases and average particle sizes and strain have also been estimated from the spectra. Dye sensitized solar cells have been fabricated using C, N, S co-doped TiO₂ as photoanode and betalain containing natural dye, extracted from beetroot, as sensitizer. AFM measurements show increased roughness on doping with thiourea. FT-IR results confirm the incorporation of sulphur in TiO₂. Analysis of the optical parameters shows that thiourea doping has enhanced the optical properties. Doping TiO₂ with carbon, nitrogen and sulphur has led to a systematic decrease in the band gap. Results show that C, N, S doping has increased the efficiency of the solar cell with respect to un-doped TiO₂. This study thus shows the promising nature of using the chosen methods/sensitizer with
advantages such as the ease of fabrication and cost effectiveness of the overall fabrication process of DSSCs. More importantly, the use of natural dye as sensitizer makes it environmentally friendly and with this simple process a relative increase of highest of 94% in the efficiency is obtained for 75% molar concentration of thiourea doped into TiO$_2$. Extensive availability of beetroot and ease of extraction of betalain dye from it makes this technique novel and inexpensive one for solar cells applications.

Acknowledgement
We acknowledge support from DST-FIST and UGC-DSA schemes of the Department of Physics, MLSU. Kumavat Soni acknowledges UGC NET-JRF. The authors are grateful to K.D. Patel, Professor, Department of Physics, Sardar Patel University, Gujarat, India for his useful discussion and guidance in electrical properties measurement. FT-IR and UV-Vis optical measurements were performed respectively in the Department of Industrial Chemistry and Department of Botany, MLSU.

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