Performance Analysis of Mixed Natural Dye and Nanostructured TiO₂ based DSSC

A. Ayaz, D. Sinha, D. De

Abstract: The performance of the mixed natural dye based DSSC has been evaluated in this paper. The mixture of beet root, spinach and turmeric are used with nanostructured TiO₂ are used for the fabrication of DSSC. TiO₂ is synthesized by sol-gel technique and considered as semiconductor metal oxide (SMO) to act as photo anode here. Nano wire type of morphology of TiO₂ is found from the FESEM image which exhibits unidirectional and uniform electron flow. The XRD study reveals anatase and rutile phases of TiO₂ that ensure the stability of synthesized TiO₂. The mixed dye made of beet root, spinach and turmeric shows their congruent characteristics with the broad light absorption spectra, lower diffused reflectance spectra after anchoring with SMO and better I-V characteristics in comparison with the individual one. The mixed dye-based DSSC provides the open-circuit voltage of 0.755V, short circuit current of 2.05mA, voltage and current at maximum power equal to 0.51V and 1.7mA, respectively with the efficiency of 0.867%, in comparison to the efficiency of the individual dyes 0.305%, 0.266% and 0.473% with beet root, spinach and turmeric, respectively.

Keywords: DSSC, Sol gel method; Tau’s plot; Photo sensitizing properties; Diffused reflectance spectra (DRS)

I. INTRODUCTION

The dye sensitized solar cell (DSSC) known as Gratzel’s cell, is operating according to the process of photosynthesis. As a renewable energy source DSSC has a remarkable impact in recent time due to its low cost and simple fabrication process. Its structure comprises 4 vital parts. The semiconductor metal oxide (SMO), which is coated on a transparent conductive glass (TCO) substrate and formed the photo anode. It acquires and conveys the excited photo electrons from dye to TCO. In this paper nano-structured TiO₂ is used as a SMO, which is well known and more efficient photo anode for photon to electron conversion [1-5] although its morphology and phase composition have great impact on the performance of DSSC. TiO₂ is considered as ideal semiconductor for photo-catalysis still it has certain limitations, such as poor absorption of visible radiation and rapid recombination of photo generated electron/hole pairs. These limitations can be improved by using efficient dye, another vital part of DSSC. At sunlight, the electrons of the dye molecules are energized, and these electrons are transferred to the conduction band of SMO. Here a mixed natural dye is used as a photo-sensitizer. The natural dyes are abundant in nature, economic, biodegradable, non-toxic materials and they can extract easily in compare with other synthetic dye [6]. A mixed of beet root, (contains betalain pigment), spinach (contains chlorophyll pigment) and turmeric (contains betaxanthin pigment) is used here. These dyes are compatible to each other and their mixed one has the advantages of these dyes. Electrolyte is another essential part of DSSC. Regeneration of dye takes places through the electrolyte reduction process, where electrolyte supplies the electrons from the conduction band of SMO in a closed circuit among the FTOs [7]. The performance of the mixed dye based DSSC is analyzed over the individual dye. Not all the dyes available in nature are compatible. Some dyes are compatible and didn't exhibit better performance. Some are not compatible with each other. We have tested lots of combinations of dyes and found these dyes are consistent and provide better performance than their individual performance. The dyes are chosen, such as their UV-Vis light absorption ranges are different. Turmeric has an absorption in lower wavelength, beet root has lower to middle range and spinach has absorption at lower, middle as well as higher wavelength. For the mixed one, it has the absorbance in all the region of all these three and has lower diffused reflectance spectra (DRS). The paper is structured as: in section 2, the methodology is discussed. In section 3 results and performance of the mixed dye is analyzed and at last, some conclusion has been made.

II. METHODOLOGY

A. Fabrication of Photo anode

In this present work, we have used nanostructured Titanium dioxide (TiO₂) as a photo anode. TiO₂ is synthesized from Titanium isopropoxide. In a cleaned beaker 60ml of Ethanol (99.9%) is mixed with 9ml of Titanium isopropoxide and 18ml of acetic acid. After 20days the mixture formed in white gel and then the gel is heated in 70°C in air for drying. It then becomes white powder form of mesoporous TiO₂. Again it is heated in a furnace at 650°C for 2 h. Now, the synthesized TiO₂ is mixed properly with acetone and using spin coating method at 3000 rpm it is coated over FTO at room temperature. Again the TiO₂ coated FTO is heated in 70ºC in air for drying. It then becomes white powder form of mesoporous TiO₂. After 20 days the mixture formed in white gel and then the gel is heated in 70°C in air for drying. It then becomes white power form of mesoporous TiO₂. Again it is heated in a furnace at 650°C for 2 h. Now, the synthesized TiO₂ is mixed properly with acetone and using spin coating method at 3000 rpm it is coated over FTO at room temperature. Again the TiO₂ coated FTO is heated in a furnace at 450°C to make firm anchor between FTO and TiO₂. A flow chart in this process is shown in Fig.1.
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B. Synthesis of dyes
Chlorophyll is extracted from fresh spinach leaves. Betaxanthin is extracted from fresh turmaric and betalain is extracted from fresh beet root. Individually the dyes are extracted as reported in the papers [8-10]. Then the extracted juice of the mentioned dyes are mixed in 1:1:1 ratio and the total mixed dye is mixed with ethanol at a ratio of 1:1.

C. Fabrication of DSSC
The synthesized TiO₂ coated FTOs are dipped with prepared dyes individually for 24 hrs and DSSCs are fabricated with different dyes following the process as illustrated in [9]. The performances of the fabricated DSSCs are analyzed by a solar simulator with a constant light source of 100 mW/cm².

III. RESULTS AND DISCUSSIONS

A. Morphology of photo anode
The FESEM image of surface layer of synthesized TiO₂ on FTO glass reveals the nano wire of circular shaped morphology as shown in Fig. 2. The nano wires are oriented in different direction but the thicker sides are connected in one point with each other. It depicts the unidirectional and uniform electron flow through the photo anode. The average length of the nano wire is 2 μm and diameter is 300 nm. Diameter of the nano wire reduces while approaching from bottom to top. Fig. 3 shows the X ray diffraction pattern. The XRD shows the most stable phases of TiO₂ i.e., anatase and rutile both phases are present. The diffraction peaks at 25.95°, 36.81°, 38.27°, 48.48° and 55.41° show the anatase phase and 28.11°, 41.61°, 44.45°, 54.63° and 57.13° show the rutile phase of TiO₂. Rutile has high absorbance property than anatase, and it is more stable. Anatase is metastable but more active than rutile. Both the phases are tetragonal. With the heat treatment anatase phase can be converted to rutile phase.

B. Photo-sensitizing properties of extracted and prepared dyes
The UV and visible light absorption characteristics of the extracted dyes are shown in Fig. 4. The spinach consisting chlorophyll dye has peaks at 412nm, 666nm and 735nm with a broad spectrum of light absorption at 516nm to 600nm. The turmeric consisting betaxantin pigment has light absorbption at 397nm to 424 nm with a peak of 415nm and 509nm to 568nm with a peak of 528nm. The beet root consisting betalain pigment has light absorption at 438nm to 461nm with a peak of 452nm and other peaks are at 474nm and 490nm. The mixed dye is compatible with all these dyes and shows a broad spectrum of light absorption characteristics with a combination of all these dyes. At lower wavelength, it has absorption at 410nm to 431nm with a peak of 418nm, at the middle wavelength of 506nm to 600nm with a peak at 515nm and at higher wavelength, it has same absorption that of spinach, i.e., at 666nm and 735nm. Fig. 5 shows the diffused reflectance spectra (DRS) of dye and TiO₂ before and after dye loading. It shows that after 370nm TiO₂ has reflectance and gradually it increases upto 80% at a higher wavelength. After mixed dye loaded with TiO₂, its DRS reduced. At 700 nm it has full reflectance of 43% only. Lower DRS proves light-harvesting ability of the dye and the mixed dye shows better light-harvesting ability in comparison with the individual dyes as reported in [11, 12].
Fig. 6 shows the bandgap energy of the synthesized TiO$_2$ and the extracted and prepared mixed dye through Tauc’s plot. In the Tauc’s plot photon energy is plotted in absentia and the quantity $(a_0h)^{1/n}$ is plotted in ordinate. By extrapolation of the linear region to zero absorbance, the bandgap energies are calculated. For direct bandgap “n” is considered as 2 [9]. For TiO$_2$ as two types of phases are present, anatase has a little higher bandgap energy approx 3.2 eV and rutile has 3.0 eV. Here the Tauc’s plot provided average bandgap energy of 3.18 eV, which ensures the stable form of TiO$_2$.

C. Performance analysis of fabricated DSSCs

The performances of the DSSCs are evaluated through I-V and P-V characteristics of individual and the mixed dyes, as shown in Fig. 7 and Fig. 8, respectively and are summarized in Table.1.

![I-V characteristics of DSSCs fabricated by individual dyes and their mixture](image_url)

**Table I: Performance parameters of fabricated DSSCs**

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$V_{mp}$ (V)</th>
<th>$I_{mp}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beet</td>
<td>0.45</td>
<td>0.69</td>
<td>0.56</td>
<td>0.83</td>
<td>66%</td>
<td>0.306</td>
</tr>
<tr>
<td>Spinach</td>
<td>0.38vi</td>
<td>0.7</td>
<td>0.74</td>
<td>1.02</td>
<td>35%</td>
<td>0.266</td>
</tr>
<tr>
<td>Turmeric</td>
<td>0.43</td>
<td>1.1</td>
<td>0.63</td>
<td>1.48</td>
<td>50.7%</td>
<td>0.473</td>
</tr>
<tr>
<td>Mixed</td>
<td>0.51</td>
<td>1.7</td>
<td>0.755</td>
<td>2.05</td>
<td>56%</td>
<td>0.867</td>
</tr>
</tbody>
</table>

The efficiencies of DSSC fabricated by beet root, spinach and turmeric are 0.306%, 0.266% and 0.473% respectively, whereas the mixed dye shows
better performance of 0.867%. The mixed dye-based DSSC shows the maximum current density of 2.05mA/cm² and an open-circuit voltage of 0.755 V whereas voltage and current density at maximum power is 0.51V and 1.7 mA/cm² and a fill factor of 56%.

IV. CONCLUSION

In this paper the performance of DSSC fabricated by mixed natural dye and nanostructured TiO₂ has been explored. The natural dyes of beet root, spinach and turmeric are compatible to each other and absorbs light in three different regions of wavelength. Hence the mixed one provides a broad range of light absorption, and comparatively low diffused reflectance spectra when anchored with TiO₂. TiO₂ is synthesized by the sol-gel method, which exhibits the presence of both anatase and rutile phase of TiO₂. FESEM shows nano wire structure which provides unidirectional electron flow. The Tauc’s plot provides the approx bandgap of 2.66 eV and 3.18 eV for mixed dye and TiO₂ respectively. The efficiency of the individual dyes are 0.305%, 0.266% and 0.473% for beet root, spinach and turmeric respectively, and the mixed dye-based DSSC provides 0.867% efficiency. In this paper, no efficiency enhancement technology is used, but the effectiveness of the mixed dye is established. Using other composite materials as SMO with this mixed dye, the efficiency of the fabricated DSSC will be higher.

REFERENCES


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