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Extraction and Absorption Study of Natural Plant Dyes for DSSC

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Abstract: The absorption spectrum of sensitizer plays an important role in the conversion efficiency of DSSC. It is noted that a minimum gap of 0.2eV from the HOMO level of TiO₂ is necessary to provide the electron injection from the dye to TiO₂ layer conduction band. One of the basic requirements is the dye absorption on the nonporous TiO₂ layer which is indicated by VU absorption spectrum. In the present work dyes extracted from beetroot, pomegranate using water and yellow bell flower (Thanga arali) using hot water and the wavelength of light absorption is found out with UV-Vis spectrophotometer. The absorption peak was found to be 516 to 528 nm, for beetroot dye with pH ranges from 7.43 to 8.28 and 322nm for pomegranate with pH 6.99 and for yellow bell flower the peak position was found to be at 308 and 205nm. From the absorption spectrum the band gap of the dye and the extinction coefficient is also calculated.

Introduction

Among the different types of solar cells, DSSC falls under the category of solid/liquid type. These types of solar cells belong to a new generation of solar cells which emerged in the early 1990's targeting to achieve moderate efficiencies at a low cost. The efficiency of the cell depends not only on the grain size of TiO₂, nature of the electrolyte and electrode but also on the light harvesting capacity of the sensitizer (dyes). The performance of the sensitizer mainly depends on the type of functional groups available, its ability to absorb light in the visible region, energy band gap of the dye molecules and its bonding with TiO₂ substrate. Although there are numerous inorganic dyes such as ruthenium polypyridyl complexes are available which are capable of achieving high efficiencies, their synthesis is much more complex, difficult and less environmental friendly when compared to organic dyes. The organic dyes can replace them due to certain advantages such as large absorption coefficients and wide variety of molecular structures. They are also cheap and abundant in nature and are available in pure form. But, the organic dyes suffer few drawbacks such as poor electrochemical stability (only 1% of the incident light is absorbed) which leads to low current conversion efficiency.

Experimental:

In the present work, the dyes of Beet root (Beta Vulgaris), Thanga Arali – Yellow bells (Tecoma Stans) and Pomegranate (Punica granatum) were analyzed for their light absorbing capacity in the UV-Visible region.

(1) Beetroot:

Qualifies as a good sensitizer because of the precense of COOH group in betalin which is capable of binding well with the TiO_2 substrate. Beetroot was made to a paste (without the skin). 2, 3 and 5 grams by weight of the paste is dissolved in 100 ml of water.

(2) Pomegranate:

Presence of Anthocyanins (with Carboxyl and Hydroxyl groups) in pomegrante dye makeit suitable to bind to TiO_2 susbtrate and allow electrons to reach the conduction band of the substrate. It was made to a paste along with the seeds using a crusher. 2, 3 and 5 grams by weight of the paste was dissolved in 100 ml of water.

(3) Thangarali(Yellowbells- Tecoma Stans):

5grams of the flower by weight was taken and was put in 200 ml of hot water. The filtered extract of above samples were taken for analysis and the pH value is noted using pH meter.

Results and discussion.

Optical Absorption study:

Sensitizer should have wide and intense absorption spectrum as the absorbed photons correlates with the number of injected electron and affects the accumulation in the conduction band of TiO_2 [1]. For an electron to be injected, the sensitizer must have a Lowest Unoccupied Molecular Orbital (LUMO) of sufficient energy located in the proximity of the semiconductor [2]. UV- Visible spectroscopy is used to analyze the optical properties of prepared dyes with and without dilution. UV- Visible Spectroscopy studies were taken in the wavelength range of 200-800nm and the maximum absorption of the dye solutions were noted. Fig (1) and (2) shows the optical absorption of all the samples with and without dilution. As a general rule, dyes that absorb strongly do not typically exhibit broad absorption and in the present case it shows broad obsorption. The maximum absorption peaks and the corresponding pH values are listed in the Table1. The absorption peak was found to be 516 to 528nm, for beetroot dye with pH ranges from 7.43 to 8.28 and 322nm for pomegranate with pH 6.99 and for yellow flower the peak position was found to be at 308 and 205nm.



Fig 1 Optical absorption of samples without dilution (R1) Beta vulgaris (R2) Punica granatum (R7) Tecoma Stans samples without dilution

| Sample | Sample | Botanical Name | Amt. of water | Amt. of paste | рН |
|--------|-------------|---------------------|---------------|----------------|----------|
| No. | Name | | used (ml) | by wt. (grams) | measured |
| 1 | Beetroot | Beta vulgaris | 100 | 2 | 7.78 |
| 2 | Beetroot | Beta vulgaris | 100 | 3 | 8.28 |
| 3 | Beetroot | Beta vulgaris(R1) | 100 | 5 | 7.43 |
| 4 | Pomegranate | Punica granatum(R2) | 100 | 5 | 6.99 |
| 5 | Yellow bell | Tecoma Stans(R7) | 200 | 5 | 2.6 |
| | flower | | | | |

Table 1- Samples data for the optical analysis



Fig 2 Optical absorption of samples with dilution (D2) Beta vulgaris (D3) Punica granatum (D7) Tecoma Stans samples with dilution

Molar extinction co-efficient:



Fig 3 Extinction coefficient Vs wavelength of (EC1) Beta vulgaris (EC2) Punica granatum (EC7) Tecoma Stans without dilution

The light absorption in DSSC depends on the molar extinction coefficient of the sensitizing dye, the surface coverage of the dye and the total surface area of the oxide film [3]. The chemical species, how strongly it

absorbs the light radiations at a particular wavelength is measured by the molar absorption coefficient, molar extinction coefficient, or molar absorptivity (ϵ). The optical absorption is quantified by the molar extinction coefficient which involves the actual absorbance A, path length l and the concentration c of the solution (Beer–Lambert law[4]). For the efficient functioning of the dye, it should have higher extinction coefficient [5]. The Fig 3 shows the molar extinction coefficient for the concentrated samples. In the present work, the prepared samples show higher absorption coefficient.

Band gap analysis:

The energy band gap of the dye decides the amt of ejection of electron into the conduction band of TiO₂ layer. The optimum band gap of the dye should be in such a way that, it should reduces the recombination loses. So the energy gap of the dye should be suitable to enhance the injection. Also, the maximum conversion efficiency can be achieved with absorbers having a band gap between 1.1 and 1.4 eV, which corresponds to a wavelength between 900 nm and 1100 nm. A graph is plotted between $(\alpha hv)^{1/r}$ Vs hv and r = 1/2,3/2 for direct allowed and forbidden and r = 2,3 for indirect allowed and forbidden. In the present case the band gap was calculated for the concentrated samples and given in Table 2. The graph between $(\alpha hv)^2$ Vs energy gap was plotted for all the concentrated samples are shown in Fig 4(a-c). Bandgap analysis shows that they follow indirect allowed transitions. Ban Rasheed Ali et al observed direct allowed transition for the organic dye [6].



Fig 4 (a-b) photon energy Vs (ahu)^{1/2} graph for (a) Beta vulgaris (b) Punica granatum (c) Tecoma Stans

| Sample No. | Botanical Name | Energy gap(eV) |
|---------------|---------------------|----------------|
| 1 | Beta vulgaris(R1) | 1.88 |
| 2 | Punica granatum(R2) | 2.13 |
| 3 | Tecoma Stans(R7) | 2.43 |

 Table 2: Energy gap for the concentrated samples

Conclusion

The natural dyes from beetroot (*Beta vulgaris*), pomegranate (*Punica Grantum*) and yellow bell flowers (*Tecoma Stans*) have been extracted and absorption studies have been carried out to measure the various properties of dye solutions. From the optical absorption analysis, it is noted that beetroot shows optical absorption in the region around 500nm. Pomegranate show optical absorption in the lower wavelength region i.e. 322nm. Thangarali shows optical absorption around 308 and 205nm. From the results it is concluded that by mixing these dyes at a suitable proportion, it is possible by the dyes to absorb the light in the visible region. The molar extinction coefficients and the band gap energy values for the dye solutions have been calculated and it is found that the dye from Tecoma Stans (R7) has a higher band gap value of 2.5 eV indicating that it can be used effectively as a sensitizer that can absorb light in the shorter wavelength region.

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